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UNDER THE CARBON SPELL: DIBORANE'S PUZZLING STRUCTURE AND THE EMERGENGE OF BORON CHEMISTRY

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Resumo

Este trabalho apresenta o primeiro estudo sistemático da história da química dos boranos, compostos de boro e hidrogénio cujas estruturas e natureza das ligações químicas desafiaram de forma irredutível a teoria da ligação química até aos anos cinquenta do século XX.

Actualmente, a química do boro é um dos mais promissores ramos da química, com um vasto leque de aplicações às indústrias química e farmacéutica, à nano-tecnologia e à medicina. Neste último ramo, destacam-se as aplicações na luta contra o cancro e no desenvolvimento de medicamentos com um elevado grau de especificidade e inovação.

Num futuro próximo, espera-se que a química do boro seja capaz de operar uma verdadeira revolução social, posicionando-se como uma poderosa alternativa à química do carbono que será capaz de oferecer todo um novo mundo de aplicações inéditas. Estas são o resultado da fascinante capacidade do átomo de boro para se ligar de formas surpreendentes e formar complexas estruturas que se baseiam em compostos de boro e hidrogénio (boranos).

A grande apetência do boro para se ligar ao oxigénio impede que os boranos existam na natureza. A grande susceptibilidade destes à acção da humidade e do ar torna-os especialmente instáveis e difíceis de manusear e preservar.

Embora apresente pela primeira vez uma descrição detalhada das principais contribuições feitas pelos pioneiros desta química ao longo do século XIX, este trabalho foca-se na era moderna da história dos boranos, que pode considerar-se ter começado com o trabalho de Alfred Stock na Alemanha. A obra de Alfred Stock é aqui amplamente descrita e discutida. São descritos o carácter inovador e os detalhes técnicos das suas investigações, dando-se especial relevo àquelas que se viriam a revelar importantes na busca pela estrutura dos boranos. É também salientado o papel instrumental da analogia entre o carbono e o borano na obra de Stock.

Efectivamente, Stock dedicou-se ao estudo dos boranos porque a analogia entre carbono e boro o levou a acreditar que poderia vir a descobrir uma química do boro tão fértil quanto a do carbono. Recorrendo às suas inovações técnicas, Stock conseguiu isolar pela primeira vez vários boranos. Com efeito, entre 1912 e 1914, o tetraborano B_4H_{10}, o diborano B_2H_6 e decaborano $B_{10}H_{14}$ foram identificados e estudados. As suas fórmulas

puseram imediatamente em causa a ideia de que o átomo de boro era trivalente nas suas ligações e que tinha sido estabelecida ao longo do século XIX pelo estudo de outros compostos de boro. Pelo contrário, estavam mais de acordo com um boro tetravalente, o que se adequava à crença de Stock numa semelhança fundamental entre as químicas do boro e do carbono.

Em 1916, Gilbert Newton Lewis publicou a sua teoria, segundo a qual a ligação química entre dois átomos era estabelecida através de diferentes graus de partilha de pares de electrões. No entanto, os boranos não possuíam electrões suficientes para sustentar as suas ligações através da partilha de pares de electrões, quaisquer que fossem as suas estruturas. O fenómeno ficou conhecido como “insuficiência electrónica” (electron deficiency). Seguiram-se inúmeras tentativas para tentar lidar com este fenómeno, em especial no borano mais simples, o diborano B_2H_6. No entanto, este mostrou-se irredutível e todas as estruturas propostas implicavam, ou estruturas singulares no panorama químico, ou o abandono de princípios fundamentais da emergente teoria da ligação química, como a ligação por emparelhamento de electrões ou o octeto de electrões. Neste trabalho demonstra-se inequivocamente a grande relevância teórica atingida pelos boranos na época, com tentativas de resolução do problema por parte de todos os principais contribuidores para a teoria da ligação química.

No início dos anos vinte, Stock isolou os pentaboranos B_5H_9 e B_5H_{11} e o hexaborano B_6H_{10}, o que o obrigou a rever a tetravalência do boro nos boranos. No entanto, em 1925, Herman Mark e Erich Pohland (um dos colaboradores de Stock) tinham analisado uma amostra cristalizada de diborano (um gás à temperatura ambiente) por difracção de raios X e concluido que este apresentava uma grande semelhança com o etano C_2H_6. Este resultado levou Stock a manter a tetravalência do boro no diborano, mas foi obrigado a aceitar a coexistência da tetravalência e da trivalência do boro nos boranos.

Com o avançar do trabalho de Stock e do seu grupo, em especial com as suas investigações sobre os compostos de sódio e de amoníaco do diborano, pareceu ficar evidente que dois dos seis átomos de hidrogénio do diborano tinham um papel especial na sua estrutura. Esta interpretação levou a que apenas duas das muitas propostas para a estrutura do diborano fossem consideradas como concordantes com os factos empíricos: a estrutura semelhante ao etano $(BH_3) – (BH_3)$ proposta por Nevil Vincent Sidgwick em 1927 e apoiada e modificada por Linus Pauling em 1931, em que cada átomo de boro estaria ligado a um átomo de hidrogénio por um único electrão (one-electron bond), e a estrutura semelhante ao eteno $[H_2B^- = B^-H_2]2H^+$, em que os dois protões se encontravam inseridos dentro da nuvem electrónica dos dois átomos de boro, e que foi proposta em 1928 por Egon Wiberg, um dos alunos e colaboradores de Stock.

Em 1931, Stock, Wiberg, Hans Martini e August Nicklas publicaram um estudo sobre a electrólise do composto de amoníaco do diborano numa solução de amoníaco. Esta reacção foi explicada através de um mecanismo que apoiava fortemente a estrutura de Wiberg e contribuíu decisivamente para que esta ganhasse uma preponderância momentânea no debate sobre a estrutura do diborano.

Embora reconhecendo que a estrutura de Wiberg se adequava de forma notável aos resultados experimentais, incluindo resultados não publicados que haviam sido obtidos por Hausser sobre o espectro de absorção ultra-violeta do diborano, Stock preferiu manter-se de fora do debate, acreditando que a sua resolução não podia ser atingida através dos conceitos de uma teoria da ligação química que havia sido desenvolvida a partir da química enganadoramente simples do carbono.

Entretanto, a consciência de que os rendimentos extremamente baixos dos métodos de produção de Stock impediam uma investigação mais rápida e intensiva que pudesse levar à resolução do problema, levou a uma busca de novos métodos por volta de 1930. Quer Stock, quer Bertram Steele na Austrália conseguiram pequenos avanços no método de Stock, baseado na acção de ácido clorídrico (HCl) sobre um composto de magnésio e boro. No entanto, os novos métodos de ambos continuavam a usar soluções aquosas de ácidos, o que, dada a sensibilidade dos boranos à hidrólise, impedia um aumento significativo dos rendimentos das reacções de produção dos boranos.

A solução foi encontrada inadvertidamente por Hermann Irving Schlesinger e Anton Behme Burg em 1931, do departamento de química da Universidade de Chicago. A descoberta foi feita no contexto do trabalho doutoral de Burg, sob a orientação de Schlesinger, e a propósito de uma tentativa falhada de produzir boro puro em que foi detectada a presença de grandes quantidades de diborano. O novo método não envolvia a utilização de solucões ácidas mas sim a aplicação de uma corrente eléctrica e permitia obter rendimentos incomparavelmente maiores aos de Stock (55% contra os 3 a 5% de Stock). Schlesinger e Burg iniciaram então investigação que visava a produção dos restantes boranos a partir do diborano, agora mais acessível. Com muito poucas excepções inteiramente ocasionais, como a de Bertram Steele, os grupos de Stock e de Schlesinger foram até aos anos quarenta os únicos a sintetizar os boranos, tornando-se os centros difusores das amostras necessárias aos vários estudos que se fizeram sobre o diborano.

O problema estrutural constituíu a motivação de Schlesinger e Burg para se dedicarem a este tipo de química e o seu programa evidencia-se precisamente pela completa dedicação à sua resolução. Schlesinger e Burg acreditavam que o diborano tinha uma estrutura semelhante à do etano e que, portanto, consistia na ligação de dois radicais BH_3 entre si. Mas Stock havia falhado na decomposição do diborano em duas moléculas BH_3 e Schlesinger e Burg orientaram uma parte do seu programa de pesquisa para o estudo da estabilidade da ligação entre os dois átomos de boro. Também estudaram reacções que evidenciaram a incorporação de moléculas BH_3 que provinham do diborano, pretendendo assim estabelecer a molécula BH_3 como a unidade estrutural que permitia compreender as reacções do diborano com outros compostos e, indirectamente, estabelecer a realidade estrutural de dois grupos BH_3 no diborano.

As investigações de Schlesinger e Burg prosseguiam um pouco a contra-corrente, devido à vantagem de que usufruía o modelo de Wiberg por conseguir explicar a electrólise do composto de amoníaco do diborano. A situação agravou-se significativamente com a publicação por Wiberg de um extenso artigo de revisão em 1936. Wiberg admitia aí que a química por si só não podia resolver a questão e invocava como argumentos definitivos em favor da sua teoria uma série de medições de propriedades físicas do diborano, como o comportamento magnético ou o momento dipolar, que entretanto haviam sido realizadas por vários autores interessados em contribuir para esclarecer o problema estrutural do diborano.

No entanto, em 1936, Simon H. Bauer, do Instituto de Tecnologia da Califórnia, iniciou uma série notável de estudos de vários boranos através da recente técnica de difracção de electrões, que havia sido desenvolvida por Pauling a partir da técnica criada por Mark e Wierl em Berlim e que viria a ser usada num extenso programa de análise estrutural de centenas de moléculas. Ao contrário de outras técnicas, a difracção de electrões permitia colher informação directa sobre a estrutura de uma molécula, nomeadamente sobre as distâncias entre os vários núcleos da molécula. Assim, logo em 1937, Bauer publicou um artigo sobre a estrutura do diborano em que afirmou ter provado a veracidade de uma estrutura semelhante ao etano para o diborano e eliminado definitivamente a estrutura de Wiberg. Mais, usando o conceito de ressonância de Pauling, Bauer foi capaz de desenvolver uma estrutura electrónica para a molécula do diborano que lhe permitiu apropriar-se da maioria dos resultados experimentais que haviam sido invocados por Wiberg em 1936 e rejeitar os restantes. No entanto, ao fazê-lo, Bauer entrou em contradição com os resultados da química analítica que haviam sido obtidos por Stock e por Schlesinger e Burg e que indicavam um papel especial de dois átomos de hidrogénio na estrutura do diborano.

O resultado disto foi que se criou uma situação confusa em que os dois partidos oponentes se apropriaram dos mesmos resultados físicos e, pior ainda, foi criada uma separação entre os partidários da estrutura semelhante ao etano, que se viram obrigados a manterem-se fiéis às suas filiações disciplinares. Por um lado, Bauer e os seus resultados da difracção de electrões a que juntou uma teorização baseada na ressonância de Pauling e na teoria das orbitais moleculares de Robert S. Mulliken; por outro, Schlesinger e Burg, com as suas investigações de análise química que indicavam um papel especial para dois dos átomos de hidrogénio. Interessante foi o papel importante que a análise de difracção de raios X da estrutura cristalina do diborano, feita por Mark e Pohland em 1925, teve quer para Bauer, quer para Schlesinger e Burg. Interessante porque na verdade não podiam ser feitas inferências directas de uma estrutura cristalina para uma estrutura da mesma molécula na fase gasosa. Isto prova que, face à maior adequação experimental da estrutura de Wiberg quando Schlesinger e Burg iniciaram as suas investigações, a opção destes pela estrutura semelhante ao etano não se deveu a critérios objectivos mas sim a um princípio metafísico de uma analogia entre as químicas do carbono e do boro.

No meio disto tudo, os resultados da electrólise do composto de amoníaco do diborano persistiam como o grande trunfo que restava à teoria de Wiberg, para além da incompatibilidade entre os resultados de Bauer e de Schlesinger e Burg. Esta vantagem foi anulada por Schlesinger e Burg em 1938 quando estes apresentaram um novo mecanismo para a electrólise do composto de amoníaco do diborano. No entanto, a incompatibilidade entre os resultados da química e os de Bauer impedia o fecho do debate, que ameaçava eternizar-se.

Esta situação confusa viria a ser esclarecida com a emergência de uma terceira estrutura, denominada “em ponte” porque dois dos hidrogénios do diborano faziam a ponte entre os dois átomos de boro. Esta estrutura permitiu entender as diferentes posições no debate estrutural sobre o diborano como apropriações parciais de uma mesma realidade tornadas incompatíveis por diferentes filiações às duas alternativas disponíveis dentro do metaprincípio de uma analogia entre as químicas do carbono e do boro.

Entretanto, Schlesinger, Burg e Herbert C. Brown descobriram os metaloboranos, compostos de boro, hidrogénio e átomos metálicos (lítio, alumínio e berílio) e aplicações importantes dos diborano na química orgânica como agente redutor. Estas descobertas viriam a ter desenvolvimentos incríveis no contexto da participação de Schlesinger e Brown no Projecto Manhattan. Os resultados aí obtidos permitiram à química do boro abandonar o debate estrutural e fazer a transição para a produção em larga escala, prontamente apropriada pelas indústrias química e farmacêutica, bem como a busca pela utilização dos boranos como combustíveis de elevado rendimento (quase o dobro do dos combustíveis fósseis) em super bombardeiros, caças de combate, mísseis de longo alcance e foguetões espaciais, no contexto da Guerra Fria. Curiosamente, todas estas tentivas, e muitas outras desde então, de aplicações bélicas para os boranos apenas têm resultado numa destruição massiva de dinheiro, para além da perda de vidas humanas na sequência de acidentes na utilização industrial destes compostos perigosamente instáveis.

A história do diborano tem importantes implicações para uma série de temas proeminentes da história e filosofia das ciências. Contribui para a discussão sobre a plasticidade das ideias e o modo como estas são capazes de evoluir e serem apropriadas por diferentes contextos teóricos. Contribui também de forma muito esclarecedora para a resolução do eterno debate financiamento público *versus* financiamento privado da investigação científica.

A história do diborano pode contribuir de forma particularmente significativa para esclarecer a verdadeira natureza da química quântica e para o debate acerca da redutibilidade da química à física.

A história do diborano prova também o papel fundamental que princípios metafísicos, ainda que errados, como a analogia entre a química do boro e a do carbono, assumem na criação e manutenção de programas de investigação férteis, ainda que a comunidade científica envolvida não tenha consciência disso.

A nível historiográfico, a história do diborano prova a fecundidade da abordagem defendida por Jed Buchwald e Allan Franklin, nomeadamente em casos históricos relativamente recentes como o do diborano.[1]

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[1] Buchwald, J., Franklin, A., “Introduction: Beyond Disunity and Historicism”, in Buchwald and Franklin (eds.), *Wrong for the Right Reasons* (New York: Springer, 2005), pp. 1 – 17.

Abstract

Nowadays, boron chemistry is one of the most promising fields of chemistry, with pervading and exciting applications to chemical and pharmaceutical industry, to nanotechnology and medicine.

However, during their first three decades, the hydrides of boron had no application whatsoever and it was their puzzling structure that sustained all research on them. Since the isolation of the first hydride of boron in 1912 they had been considered one of the most puzzling phenomena in chemistry and they managed to keep their irreducibility until the 1950's. In the process, they forced bond theory to abandon one of its most fundamental paradigms: the atom-to-atom bond.

The present work offers the first systematic historical account of the borane's route to industrialization since their discovery, with a strong focus on the role played by the structural debate. The analysis is supported by a very thorough and comprehensive study of the technical questions involved in the dispute.

The historical investigation of any scientific field/discipline/specialty can be guided by numerous hopefully complementary approaches and plural methodological commitments. However, in any given area, no truly consistent historical account can exist without an initial systematic and comprehensive assessment of the evolution of its technical problems. It is my contention that this starting point should be the basis upon which social, cultural and intellectual approaches can later (or simultaneously) find their unquestionable grounding and utility. Thus, the present work is clearly assumed to provide such a groundbreaking point of departure.

The present work proves that the chemistry of the hydrides of boron was an integral and important part of theoretical chemistry in the twentieth century. No diachronic account of the history of chemistry in the twentieth century can ignore the history of the hydrides of boron. The history of these compounds is essential to put into a more inclusive perspective the history of chemical bond.

The history of diborane raises the question of how ideas are able to evolve and be appropriated by other participants in new theoretical contexts.

Ignoring the history of the hydrides of boron can only lead to a mistaken perception of their own identity. Such is the case with the presently prevailing idea that up until their use outside the academic environment, they had been laboratory curiosities. The present work demonstrates that during their laboratory phase they were rather seen as a pressing theoretical problem and this perception entirely guided all investigations.

An interesting historiographic issue raised by the history of the hydrides of boron is the dramatic role played by war in their mutation into industrial and commercial products.

Diborane's history also has important bearings on the debates over the reducibility of chemistry to physics and the true nature of quantum chemistry.

It is in complete agreement with the historiographic vision expressed a few years ago by Jed Buchwald and Allan Franklin and in fact it proves its fertility, at least on what concerns relatively recent historical processes.[2]

Keywords: diborane and theoretical chemistry, history of the chemical bond, puzzling structure, analogical reasoning, reductionism

Palavras-chave: diborano e química teórica, história da ligação química, estrutura surpreendente, raciocínio por analogia, reducionismo

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[2] J. Buchwald, A. Franklin, "Introduction: Beyond Disunity and Historicism", in Buchwald and Franklin (eds.), *Wrong for the Right Reasons* (New York: Springer, 2005), pp. 1 – 17.

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To Professor Simon H. Bauer I owe the singular honour of having met one of the most important contributors to the history of boron hydride's chemistry. His patience and kindness towards my insistence was truly remarkable. I feel especially sorry that the circumstances were not the ideal ones as to favour further learning from him. I do hope he finds this work to pay due tribute to him and all those who, through their heroic efforts, struggled to overcome the incredible intellectual and technical challenges that such an "insidious" molecule as diborane presented them.

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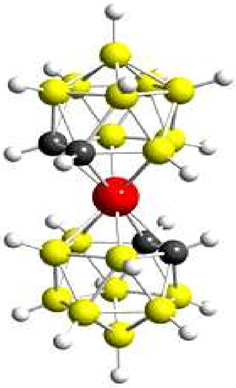
Introduction

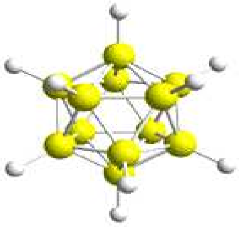
Nowadays, boron chemistry is one of the most promising fields of chemistry, with pervading and exciting applications to chemical and pharmaceutical industry, to nanotechnology and medicine. Amazing strategies to fight cancer, as Neutron Capture Therapy, are increasingly becoming implemented. They are based on peculiar nanostructures made possible by the unique physical and chemical properties of boron and its intriguing and beautiful compounds based on boron hydride structures: boron nano molecular devices designed to deliver medicine molecules to specific physiological structures; boron-10 inorganic copy structures of DNA, able to deceive cancer cells and enter their nuclei, waiting to be targeted by neutron cannons operated in gigantic high energy accelerators which will cause boron-10 isotope to disintegrate and liberate massive amounts of disruptive energy to the hosting cancer cell but not to its neighbours. None of these is science fiction anymore. In a near future they are expected to bring a profound revolution to society and to become a powerful alternative to organic chemistry, a whole new world of incredible applications which are made possible by boron's fascinating ability to bond in puzzling ways and form extremely complex structures that are not found in carbon structures. Because they can not be found in nature, live systems did not evolve to cope with boron compounds and therefore, these are not susceptible to enzymatic attack. This opens an entire field of unique opportunities that cannot be achieved with carbon compounds, such as designing medicines able to reach their objective absolutely unaltered.

One curious nice thing about the hydrides of boron is that, despite massive investment, no military applications have been possible. Every attempt ended up with a huge loss of money and a serious waste disposal problem (with further loss of money, naturally...).

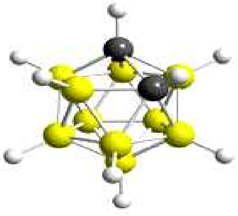
Boron hydrides (or boranes) were the first to be discovered, but since the late 1930's – early 1940's they have been combined with metallic atoms (metalloboranes) and carbon (carboranes) in beautiful and complex cage structures, such as those below:



$Co(C_2B_9H_{11})_2^-$



$B_{12}H_{12}^{2-}$



$C_2B_{10}H_{12}$

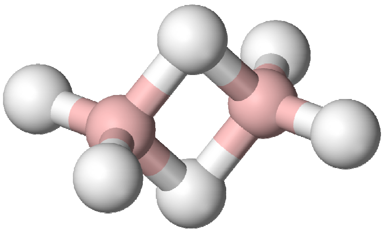
However, during their first three decades, the hydrides of boron had no application whatsoever and it was their puzzling structure that sustained all research on them. Since the isolation of the first hydride of boron in 1912 they had been considered one of the most puzzling phenomena in chemistry and they managed to keep their irreducibility until the 1950's. In the process, they forced bond theory to abandon one of its most fundamental paradigms: the atom-to-atom bond.

Although the first observation of a combination of boron and hydrogen was reported 200 years ago, its actual existence received generalized distrust for many decades. The modern age of the hydrides of boron began in 1912 and involved a crucial technical evolution specifically designed to establish and study these compounds. Most important, the decision to develop this field was sustained by the belief in an essential analogy between boron and carbon chemistry able to rule research for many decades.

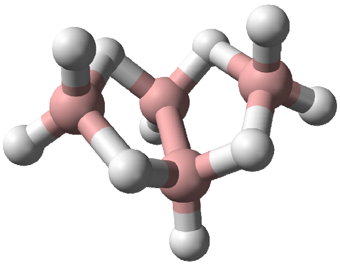
After their discovery in 1912, the peculiar empirical formulas of the hydrides of boron immediately put into question contemporaneous ideas on boron's trivalency. Nevertheless, they seemed to be in good agreement with a tetravalency similar to that of carbon. Just a few years latter, in 1916, they were found to be irreducible to Lewis' electron pair covalent bond. At this initial stage, little empirical information was available while bond theory was still struggling to achieve consistency. In this context a great deal of creativity and an incredible range of different structures for the simplest of the hydrides of boron, diborane (B_2H_6), were proposed by all key contributors to bond theory. However, diborane and the higher hydrides of boron kept defying the understanding of their chemical bond nature for over forty years.

Throughout this entire period, research was entirely guided by the belief in a wrong analogy between boron and carbon chemistries. This led to a vigorous debate between ethane-like and ethylene-like structures, each one implying unprecedented bond types. The dispute ran intertwined with the emerging physical methods of structure analysis, which were hungrily used to complement indirect chemical evidence. However, due to an unusually explosive combination of methodological and interpretation contingencies caused by the analogy with carbon chemistry, the debate led to a confusing state in which the same data were appropriated by both contending parties. Even more confusing, within the same party conflicting data and ensuing interpretations were put forward by advocates of different disciplinary cultures.

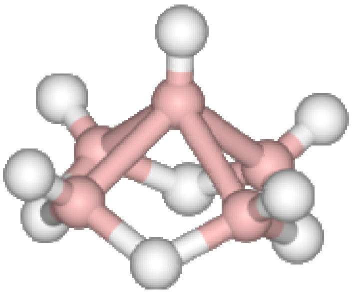
This authentic "Gordian Knot" was latter solved by the emergence of a third party which championed a non carbon-like bridge structure. Its rise began with the work of B.V. Nekrassov in 1940, which was followed by the work of Y. K. Syrkin and M. E. Diatkina in 1941. However it definitely became a serious candidate to the solution through the work of H. C. Longuet-Higgins and R. P. Bell in 1943. Finally, the blow fell in 1948, when an infra-red spectroscopic analysis by W. C. Price definitely ruled out the ethane-like structure. While diborane's structure was then reasonably established, such was not the case with the nature of its bonds. Its clarification was due to work of W. N. Lipscomb in 1956, with the abandonment of the atom-to-atom bond paradigm and the quantum explanation for the surprising bridge structures of the hydrides of boron. These structures revealed an entire new and complex structural world in chemistry, completely distinct from organic chemistry. The presently accepted structures for the most historically important hydrides of boron are presented below (boron atoms in pink and hydrogen atoms in white):



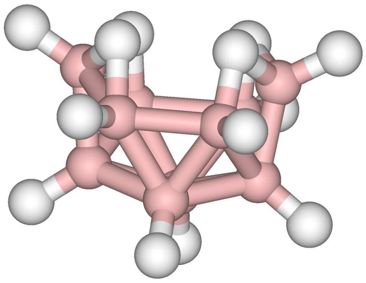
Diborane B_2H_6



Tetraborane B_4H_{10}



Pentaborane B_5H_9



Dekaborane $B_{10}H_{10}$

By this time, those engaged in analytical chemistry had already abandoned the structural debate and, with all the knowledge they had gathered while involved in the dispute, they were able to lead boron hydrides to their first applications in chemical and pharmaceutical industry. Their (frustrated) involvement in the Manhattan Project became crucial at this point.

The present work offers a systematic historical account of the borane's route to industrialization since their discovery, with a strong focus on the role played by the structural debate. The analysis is supported by a very thorough and comprehensive study of the technical questions involved in the dispute.

Curiously enough, despite being such a promising field, with an enthusiastic community that has grown from a very restricted number of pioneers to a fully globalized network of specialists, boron chemistry has been missing one major feature central to build the identity of any scientific community: its history.

To my knowledge, there is no comprehensive or systematic account of the history of the hydrides of boron, whatever the meaning one may ascribe to the words "comprehensive" or "systematic".

Typically, one can find very brief references to the pioneering character of Alfred Stock's work, invariably followed by a "quantum leap" of several decades to present-day research on boron chemistry.

The only independent biographical source on Stock seems to be Egon Wiberg's "Alfred Stock 1876-1946"[3]. Wiberg was a close friend and one of the most important Stock's co-workers. He was also one of the key players in the history of the hydrides of boron and a very famous inorganic chemist. In 1977, a much shorter English version of this

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[3] Egon Wiberg, "Alfred Stock 1876-1946", *Chemische Berichte*, 6 (Oktober 1950), XX – LXXVI.

work was published, containing just a few minor additions to the original article[4]. This publication in English was preceded in many years by Virginia Bartow's work "Pioneer Personalities in Borane Chemistry"[5], which, on what concerns Stock, can be considered a shorter free translation of the original biographical work on Stock by Wiberg. Bartow's work was found to be singularly informative on what concerns the "pre-Stock era".

Pierre Laszlo's work "Diborane story" must also be mentioned[6]. Although in a very different perspective and in a sketchy way, it refers for the first time, to my knowledge, to many key points in the search for the structure of diborane. It also contains a very interesting analysis of its philosophical and sociological implications.

A crucial contribution was made by one of the key players in this history, Herbert Charles Brown. His love for the history of chemistry led him to an unusual autobiographical approach in his book *Boranes in Organic Chemistry* that allowed privileged insight for the evolution of boron hydride chemistry from academic to industrial environment.[7] Several other publications by Brown followed the same historical approach.

Chemical Education and Chemical & Engineering News articles were also used as additional biographical sources. *The New York Times* articles were used in the history of the attempts to develop boron hydride super-fuels.

Apart from the aforementioned sources, the present work is entirely built on a historical analysis of contemporary research articles or books.

The few historical works on the history of diborane to which I have just referred were authored by participants, chemists or chemists involved in the history of chemistry. More surprising is the utter negligence of this topic by historians of science and specifically by historians of science, especially those who have delved in aspects of the history of the chemical bond, like Mary Jo Nye and William H. Brock. It is true that the

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[4] Egon Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977), 691-700. Translation from the German by H. Nöth and R. H. Walter.

[5] Virginia Bartow, "Pioneer Personalities in Borane Chemistry", in Robert F. Gould, (ed.), *Borax to Boranes*, Advances in Chemistry Series, 32, (Washington, D. C.: American Chemical Society Applied Publications, 1961), pp. 5 – 12.

[6] P. Laszlo, "Diborane Story". Available at http://www.pierrelaszlo.com/articles/angewandte-chemie/51-diborane-story. Last accessed on 16 November, 2011.

[7] H. C. Brown, *Boranes in Organic Chemistry* (New York: Cornell University Press, 1972)

history of the 20th century chemistry has deserved comparatively less attention from historians of chemistry than many other periodical periods. This is especially true for inorganic chemistry. One such example is an up to date *fin de siècle* survey such as William Brock's *History of Chemistry*[8] which offers a discouragingly brief and sketchy reference to the history of the chemical bond and an even sketchier discussion within the framework of quantum chemistry. Another such example is Aaron J. Ihde's *The Development of Modern Chemistry*[9]. Although including a section on the history of the hydrides of boron, a remarkable feature, it consists in a 3 pages sketchy account that contains some fundamental errors. Even authors such as Kostas Gavroglu and Ana Simões who have been consistently addressing various aspects of the history of quantum chemistry, have not addressed the history of the puzzling structure of diborane. Fortunately, Ana Simões has long been aware of its importance and presented me the theme, this way proceeding to correct the situation.

The pioneer character of this work dictated its nature in more than one way. Since the literature consulted has been devoted to complete oblivion, it was decided to include extensive citation of the most significant statements. This choice is due to the desirability to provide an argumentation truly open to survey. Furthermore, I hope that this decision will render relatively easy for others to use this investigation as a starting point for further work in this area, in such a way as to enable to offer a historical interpretation grounded on a sophisticated contextualization, able to pay heed to how different social and cultural contexts shaped in various ways different chemical communities and chemical cultures.

The historical investigation of any scientific field/discipline/specialty can be guided by numerous hopefully complementary approaches and plural methodological commitments. However, in any given area, no truly consistent historical account can exist without an initial systematic and comprehensive assessment of the evolution of its technical problems. It is my contention that this starting point should be the basis upon which social, cultural and intellectual approaches can later (or simultaneously) find their unquestionable grounding and utility. Thus, the present work is clearly assumed to provide such a groundbreaking point of departure. It was largely dictated by the circumstances under which it was written, deprived of any access to a less internalist

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[8] W. H. Brock, *The Fontana History of Chemistry* (London: Fontana Press, 1992).

[9] A. J. Ihde, *The Development of Modern Chemistry* (New York: Dover Publications, 1984).

type of sources allowing for a more appealing, but certainly no more fascinating, social or cultural approach. It must be said, however, that it is not clear that the latter will ever be possible in any considerable detail. The disturbing utter negligence to which the history of this field of chemistry has been devoted appears to have caused it irreparable damage and loss of precious eventual sources of documentation. With the fortunate exception of Simon H. Bauer, one of the key players in the history of the hydrides of boron, all the protagonists are already deceased. Their testimonies and recollections were never taken in any specifically oriented interview, in an appalling demonstration of inscrutable negligence by historians of science. There are no archive sources for most of them. Numerous attempts were made to locate eventual archive sources for the most important scientists involved in the development of this chemistry during the period covered but none of them succeeded. By the contrary, the inexistence of one of them was, unfortunately, definitely established with the kind help of specialists of the Special Collections Research Center of the University of Chicago. Repeated attempts to locate descendents of several scientists were also frustrated. Hans M. Mark, Herman Francis Mark’s son, was especially kind in his will to cooperate with this investigation, but unfortunately he could not help because the important participation of his father in the history of diborane has been completely overshadowed by his work as pioneer of structural and polymer science and founding father of polymer science in the United States. This is a paradigmatic example of how diborane’s history has been put aside, leading to irreparable loss of crucial historical sources.

The chapter on the numerous structures proposed for diborane aims at establishing diborane’s importance for the chemical bond theory and at illustrating the laborious ingenuity it required from researchers. Constrained by the sources used (mostly primary printed sources) a contextualized history of the various proposals for the structure of diborane remains largely to be done. Such work is clearly beyond the scope of the present work. I plan to contribute to it in the very near future.

In any case, and having in mind the type of sources and the historical choices behind this thesis, the history of diborane has proved extremely rich in enabling to understand the complexity of this discovery process, the role of analogy as a guide to discovery, the almost metaphysical assumptions behind it, and the resistance to discovery due to various methodological and cultural commitments. It also revealed itself as an important corroboration of the historiographic views put forward by Buchwald and Franklin[10] and an important contribution to the debate on the reducibility of chemistry to physics.

Due to a limited ability to translate the German literature, this account cannot avoid the risk of unbalanced evaluation of the argumentation from one of the parties. Even so, it is believed that all the important arguments and ideas were covered. The literature for the period studied in the MSc thesis was covered systematically.

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[10] J. Buchwald, A. Franklin, "Introduction: Beyond Disunity and Historicism", in Buchwald and Franklin (eds.), *Wrong for the Right Reasons* (New York: Springer, 2005), pp. 1 – 17.

1 - Pre-History

In a preliminary note written in 1879, Francis Jones traced back the history of the hydrides of boron to Humphrey Davy's announcement of a compound of boron and hydrogen.[11] Indeed, it has been unanimously attributed to Davy the first claim for such discovery. To be rigorous, at the time he made it, in 1809, Davy was still convinced that boron was a metal and named it *boracium*. It was only in 1812 that Davy changed his mind on the metal character of *boracium* and renamed it boron. "On ne connait pas de combinaison de bore avec l'hydrogène en proportion déterminée. Le gaz hydrogène qui se dégage de l'eau versée sur du bore réduit avec um excès de potassium contient des traces de ce metalloïde."[12] These statements clearly correspond to the following description made by Davy in his report on the identification of boracium:

> I heated the olive coloured substance with potassium, there was a combination, but without any luminous appearance, and a gray metallic mass was formed; but from the effect of this upon water, I could not affirm that any oxygene had been added to the metal, the gas given off had a peculiar smell, and took up more oxygene by detonation than pure hydrogene; from which it seems probable, that it held some of the combustible matter in solution.[13]

Davy's claim was also very clearly stated in a letter to Jacob Berzelius: "I have been much occupied by experiments upon combinations of hydrogen. [...] I have made a combination of boracium with hydrogen."[14]

According to Jones, Davy's claims met great scepticism; the inexistence of such a compound of boron was generally taken for granted, even though this would constitute an exception among non-metallic elements:

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[11] F. Jones, "On a Hydride of Boron", Journal of the Chemical Society, Transactions, 35 (1879), 41-42.

[12] J. Pelouze, E. Fremy, *Traité de Chimie Génerale, Analytique, Industrielle et Agricole,* Troisième Edition (Paris :1865). On 1004.

[13] H. Davy, "The Bakerian Lecture. An Account of Some New Analytical Researches On the Nature of Certain Bodies, Particularly the Alkalies, Phosphorous, Sulphur, Carbonaceous Matter, and the Acids Hitherto Undecomposed; With Some General Observations on Chemical Theory.", Philosophical Transactions of the Royal Society of London. For the Year MDCCCIX. Part I. London, MDCCCIX.

[14] H. G. Söderbaum, *Berzelius J Lettres publiées au nom de l'Académie Royale des sciences de Suède.* Tome 2. (Uppsala: 1912). On 17.

> In that year [1809] Davy stated that a gas, which he supposed to be a compound of boron and hydrogen, was evolved by the action of water on potassium boride; and he obtained a similar gas by the action of acids on a boride of iron prepared by heating a mixture of boracic acid and iron filings to a high temperature. These results have been attributed to impurities in the substances employed, and it is generally stated that boron is the only non-metallic element which forms no compound with hydrogen. [15]

Doubts on the existence of a hydride of boron and, consequently, on Davy's claims persisted for a long time: "Davy aurait-il vraiment réussi à isoler l´hydrure de bore? Cette assertion semble fort sujette à caution, car on sait que l'existence même de cette substance a été mise en doute et niée pendant très longtemps après cette date."

Nevertheless, the existence of Davy's compound was referred or defended by other illustrious chemists:

> Le borure de fer dissous dans l'acide chlorhydrique dégage un gaz don't l'odeur offre de l'analogie avec celle de *l'assa fœtida*, ce gaz se trouble au contact de l'eau de chlore, grâce à une petite quantité d'acide borique qui se dépose.[16] (M. Gmelin)

> Ces phénomènes prouvent que si le bore ne forme pas avec l´hydrogène des combinaisons semblables aus autres métalloïdes, il doit cependant être combiné avec l'hydrogène, car le bore ne peut être consideré comme contenu à l'etat de vapeur dans ce gaz.[17] (Berzelius)

In 1881, R. L. Taylor joined Jones and the two went beyond the latter's initial investigations, having developed three different methods to prepare what they assumed to be a single type of gaseous boron hydride. They characterized it and argued for the formula BH_3.[18]

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[15] F. Jones, "On a Hydride of Boron", Journal of the Chemical Society, Transactions, 35 (1879), 41-42.

[16] J. Pelouze, E. Fremy, *Traité de Chimie Génerale, Analytique, Industrielle et Agricole,* Troisième Edition (Paris :1865). On 1004.

[17] J. Pelouze, E. Fremy, *Traité de Chimie Génerale, Analytique, Industrielle et Agricole,* Troisième Edition (Paris :1865). On 1004.

[18] F. Jones, R. L. Taylor, "On Boron Hydride", Journal of the Chemical Society, Transactions, 39 (1881), 213-219.

According to Jones and Taylor there were three different reasons that substantiated their initial departure from the generalized scepticism toward the existence of such a compound. These can be characterized as involving inductive generalization, pure analogy and unification assumptions:

> That a hydride of boron might be prepared appeared highly probable from various considerations; first, the fact that all the other metalloids form compounds with hydrogen; second, the discovery by Buff and Wöhler in 1857 of the hydride of the closely analogous element silicon; and further, the discovery by Frankland of the compounds of boron with methyl and ethyl.[19]

Friedrich Wöhler and Heinrich Buff had obtained the silane hydride SiH_4 by pouring acid on magnesium silicide, and since boron ought to have a chemical behaviour similar to that of silicon, Jones and Taylor built on Wöhler's and Buff's method to synthesize their own hydride. Although Jones, in his preliminary note, stated he was not aware of any attempt to synthesize a hydride of boron since Davy, at least one such attempt was made. Ironically, it was done by Wöhler himself, in collaboration with Henri Sainte-Claire Deville. This was part of a comprehensive work on the chemical and physical properties of boron, in which Wöhler and Deville claimed the priority in establishing the very chemical similarity between boron and silicon invoked by Jones and Taylor:

> Il est digne d'observation que la plupart des corps simples, ceux du moins don't l'etude est faite complétement, se présentent à nous sous des formes intéressantes, soit à l'état gazeux ou à l'état liquide, soit à l´état solide avec des formes cristallines ou un éclat métallique remarquable. Le bore seul, placé entre le silicium et le carbone, qui cristallisent tout deux avec une grande perfection, échappait à cette règle. Des recherches sur cette matière, commencées par chacun de nous séparément à Göttingen et à Paris et terminées en commun, font cesser cette exception, et nous permettent aujourd'hui de montrer le bore comme un analogue du silicium et du carbone par toutes ses propriétés chimiques.[20]

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[19] F. Jones, R. L. Taylor, "On Boron Hydride", *Journal of the Chemical Society*, Transactions, 39 (1881), on 213.

[20] F. Wöhler, H. Sainte-Claire Deville, "Du Bore", *Annales de Chimie et de Physique*, Troisième Serie, Tome LII, Paris (1858). On 63.

Of course, having discovered the first hydride of silicon and established the chemical similarity between boron and silicon, it was only natural for Wöhler to search for a boron hydride. But Wöhler and Sainte-Claire Deville were faced with the pervasive contamination of silicon:

> Nous avons essayé également de produire un hydrogéne boré dans les conditions qui réussissent si bien pour le silicium. Du borure d'aluminium a éte attaqué par l'acide chlorhydrique liquide, et le gaz hydrogène séché a été chauffé à son passage par un tube étroit: il s'y est déposé du silicium brun sans trace de bore, et le gaz en brulant déposait sur la porcelaine un enduit blanc de silice entièrement insoluble dans l'eau, et ne contenant aucune trace d'acide borique. Ce silicium provenait manifestement des impuretés de l'acide borique ou de l'aluminium, et l'hydrogène boré ne se forme pas dans les conditions où l'on obtient l'hydrogène silicé.[21]

In their discovery of silane, Wöhler and Buff had used magnesium silicide, which they obtained from magnesium and potassium silicofluoride. In face of the chemical similarity between silicon and boron proven by Wöhler and Sainte-Claire Deville, it was only natural if they used magnesium boride to obtain a boron hydride.

However, from the above quotation, it is clear that they used aluminium boride instead. The reason is very simple: they tried to obtain magnesium boride from magnesium and potassium borofluoride, but failed.

Ignoring these failed attempts, Jones also tried Buff and Wöhler's procedures to use borofluoride, as described in his preliminary note in 1879. But he failed at it too. However, his endeavour ended differently as he was able to discover other method to produce magnesium boride. It relied on the action of magnesium on boric anhydride:[22]

> Boric anhydride recently ignited is finely powdered and intimately mixed with not less than twice its weight of magnesium dust. The mixture is placed in a hessian or iron crucible, the lid of which is firmly wired down, and heated in an ordinary fire. Repeated experiments showed that no better product was obtained by using more

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[21] F. Wöhler, H. Sainte-Claire Deville, "Du Bore", *Annales de Chimie et de Physique*, Troisième Serie, Tome LII, Paris (1858). On 88.

[22] B_2O_3, also known as boron trioxide or diboron trioxide.

> than the above proportion of magnesium, which corresponds nearly with that required by the equation $B_2O_3 + 6\ Mg = B_2Mg_3 + 3MgO$ [23]

In 1881, Jones and Taylor published two other methods. The first of these consisted in the direct union of boron with magnesium:

> Amorphous boron is thoroughly mixed with rather more than thrice its weight of magnesium dust, and heated in a current of hydrogen or in a closely covered crucible lined with magnesia. At a dull red heat combination takes place, the mixture glows and need not be further heated, but is allowed to cool in a current of hydrogen.[24]

Jones and Taylor's second method used magnesium to act on boron trichloride:

> Magnesium dust contained in a porcelain boat is placed in a combustion tube connected with a small retort containing boron trichloride. After the air has been expelled from the apparatus by a current of hydrogen, the boron trichloride is gently heated, and its vapour led over the magnesium, which is also heated.[25]

This evolved according to the equation

$$6\ Mg + 2\ BCl_3 = B_2Mg_3 + 3\ MgCl_2$$

Although these last two methods resulted in slightly better products than the first one, the latter was always preferred because it allowed greater yields.

Strong hydrochloric acid would then be gradually dropped on magnesium boride mixed "with a little water". The resultant gas, despite being slightly soluble, could be collected over water or might be dried over calcium chloride and collected over mercury.

Jones and Taylor were perfectly aware that the gas they were able to collect was far from purity, but all their efforts to improve this situation failed:

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[23] F. Jones, R. L. Taylor, "On Boron Hydride", *Journal of the Chemical Society*, Transactions, 39 (1881), on 213.

[24] F. Jones, R. L. Taylor, "On Boron Hydride", *Journal of the Chemical Society*, Transactions, 39 (1881), on 214.

[25] F. Jones, R. L. Taylor, "On Boron Hydride", *Journal of the Chemical Society*, Transactions, 39 (1881), on 214.

> The gas obtained in this way contains boron hydride mixed with a very large excess of hydrogen, and we have unfortunately not yet discovered any process which will yield the hydride in anything like a state of purity.[26]

Since they were announcing a novel compound whose inexistence had been long denied, they knew they were bound to face scepticism and so, they were extremely careful in their efforts to establish its empirical reality. Their boron hydride was submitted to a series of physical and chemical observations and analyses to assert its distinctive properties, the most conspicuous of those being the characteristic odour and colour of its flame:

> The gas obtained as above is colourless, and has an extremely disagreeable and very characteristic odour, producing nausea and headache even when inhaled in moderate quantity. The gas burns with a splendid green flame, producing boric acid by its combustion. This is well shown by the green tinge imparted to a Bunsen lamp flame held above a burning jet of the gas.[27]

The confirmation of the presence of boron in the hydride was an extremely important argument against any attempt to dismiss Jones and Taylor's claims. It was provided by spectroscopy and chemical analysis:

> When observed through the spectroscope, the flame of boron hydride exhibits the characteristic green boron lines. [...]
>
> Like the hydrides of arsenic and antimony, the gas is decomposed by passing through a red-hot tube, boron being deposited as a brown film, and if the gas at the extremity of the tube be kindled, it no longer burns with a green flame.[28]

The reference to the hydrides of arsenic and antimony leaves no doubt on the importance of analogical reasoning in Jones and Taylor's pioneering effort to devise fruitful empirical procedures to study their new hydride.

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[26] F. Jones, R. L. Taylor, "On Boron Hydride", *Journal of the Chemical Society*, Transactions, 39 (1881), on 215.

[27] F. Jones, R. L. Taylor, "On Boron Hydride", *Journal of the Chemical Society*, Transactions, 39 (1881), on 215.

[28] F. Jones, R. L. Taylor, "On Boron Hydride", *Journal of the Chemical Society*, Transactions, 39 (1881), on 215.

The two researchers also reported the great stability of their hydride when submitted to the action of water, even for extended periods of time: “It is sparingly soluble in water, to which it imparts its peculiar odour; the solution is apparently unaltered by keeping, some of it having been kept for two years without any appreciable alteration.”[29]

Although explicitly aware that the minute quantities of the hydride with which they had to work precluded any serious attempt to deduce its formula, Jones and Taylor devised an ingenious experimental method to do it anyway. Their experimental apparatus and procedure were designed to analyse a mixture of hydrogen and the hydride, due to their failure at isolating a pure form of the hydride. They also had to deal with a greater than normal amount of that mixture, since only extremely minute amounts of the hydride were present. This forced them to develop a modified version of Edward Frankland’s gas analysis apparatus, “differing from it chiefly in the greater capacity of the gas-measuring vessel”[30]. A detailed description of this apparatus and the experimental procedure used can be found in Jones and Taylor’s paper. Briefly, their procedure consisted in injecting and measuring a certain volume of gas in the apparatus, after mercury had been used to assure that all the air had been expelled from its interior. Afterwards, the gas was burned over copper oxide and the water resulting from the combustion was measured. The combustion tube was weighed before and after the combustion and from these measurements the amount of oxygen lost in the combustion determined. Because the gas used was a mixture vastly composed of hydrogen, the authors used the differences between the results found for a sample of pure hydrogen and the ones found for a sample of the mixture to determine the used quantity and formula of their hydride.

Since, in the case of the mixture sample, the amount of collected water was consistently greater than the expected one for the same exact volume of pure H_2, the authors were immediately able to deduce that the hydride molecule had to include more than two hydrogen atoms. They were also able to demonstrate the minute amount of hydride present in the mixture, since the amounts of water produced by the combustion of each sample (pure H_2 and admixed boron hydride with hydrogen) were very close to each other.

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[29] F. Jones, R. L. Taylor, “On Boron Hydride”, *Journal of the Chemical Society*, Transactions, 39 (1881), on 215.

[30] F. Jones, R. L. Taylor, “On Boron Hydride”, *Journal of the Chemical Society*, Transactions, 39 (1881), on 217.

To deduce the formula of their hydride, Jones and Taylor performed their most successful experiment, in which 666.8 cc of the mixture yielded 0.5424 g of water. Since the same volume of pure hydrogen should have yielded 0.5377 g of water, the excess 0.0047 g corresponded to 0.0005 g of hydrogen. This corresponded to the hydrogen in combination with boron over and above that required for the formula BH_2. Accordingly, the authors represented the hydride formula as BH_{2+x}. On the other hand, the 0.5424 g of water obtained corresponded to 0.4821 g of oxygen, which should have come from the copper oxide tube. Since the difference measured in the copper oxide weight was only 0.4757 g, the remaining 0.0064 g was ascribed to the deposition of boron in the combustion tube. Thus, the value of x could easily be calculated through the proportion 0.0064: 11 = 0.0005: x, which renders $x = 0.86$. The hydride formula, then, was $BH_{2.86}$ "which may be considered, under the circumstances of the experiment, a sufficiently near approximation to BH_3."

Notice that the atomic weight of boron was then taken to be 11 g/mol. Curiously enough, the present-day value of 10.81 g/mol resulted from Alfred Stock's investigations on the boron hydrides.

In these calculations, Jones and Taylor assumed that only one type of hydride of boron was present in their mixture. Apparently, this seemed to be a rather natural assumption, since they did no discussion whatsoever on the subject. They also assumed that the molecule of their hydride contained a single atom of boron, presenting without any justification the only empirical formula of the hydride obtained by their method as its molecular formula. These two unjustified assumptions may have been a consequence of Buff and Wöhler's discovery of silane, which back then remained the only known hydride of silicon and had a similar formula, SiH_4.

Despite Jones and Taylor's efforts to definitely establish the existence of a hydride of boron, a decade later Paul Sabatier still referred their work as uncertain: "On est mal fixé sur l'existence réelle de l'hydrure de bore. Jones serait parvenu à l'obtenir, mélangé d'hydrogène, en attaquant par l'acide chlorhydrique le borure de magnésium."[31]

In order to test Jones and Taylor's claims, Sabatier repeated their preparative method and observed the liberation of a gas with the characteristic foetid odour and green flame.

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[31] Sabatier, P., "Sur l'hydrogène boré", Compt. rend., 112 (1891). On 865.

By decomposing it through heat, electric current and potash, he was able to establish that it was composed of hydrogen and boron, thus confirming Jones and Taylor's claims:

> Ces divers résultats montrent que le gaz de Jones est constitué par de l'hydrogène renferment une petite quantité d'hydrure de bore. Ce dernier est visiblement un gaz extrêmement fétide, brûlant avec une magnifique flamme vert, détruit en ses éléments par la chaleur rouge et par les étincelles électriques, attaquant le mercure, et immédiatement décomposé par la potasse avec accroissement de volume (qui devient sans doute triple).[32]

Also in 1891, Moissan corroborated Jones and Taylor's results but he made no further work.

Unaware of Sabatier's work, William Ramsay and H. S. Hatfield also began by referring Jones and Taylor's work in their "Preliminary note on the hydrides of boron".[33] They aimed at isolating the hydride of boron by liquefying it with liquid air. This approach was a natural consequence of Ramsay's mastery in isolating gases, and specifically of his wizardry with the inert ones.

They too used Jones and Taylor's method to prepare the gas and observed its foetid odour and its green flame. The boron content of the gas was established using an electrical current upon it. The quantitative analysis of this decomposition led Ramsay and Hatfield to an assumption speculation as to the structure of the boron hydride. The gas probably consisted mainly of the stable compound B_3H_3. Having been unable to reproduce its preparation, they concluded for the existence of a second unstable form of B_3H_3 whose contaminating presence certainly hindered the preparation of the stable form. They further speculated as to the existence of other boron hydride compounds whose formulas they represented as follows:[34]

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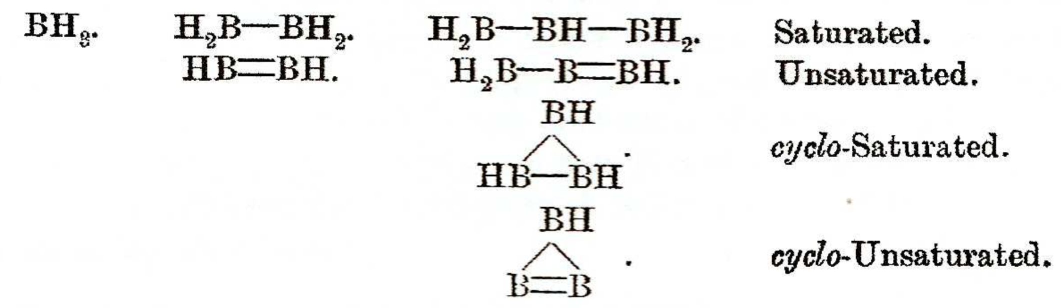
[32] Sabatier, P., "Sur l'hydrogène boré", Compt. rend., 112 (1891). On 865.

[33] Ramsay, W., Hatfield, H. S., "Preliminary note on the hydrides of boron.", Proceedings of the Chemical Society, 17 (239) (1901), 152 – 154.

[34] Ramsay, W., Hatfield, H. S., "Preliminary note on the hydrides of boron.", Proceedings of the Chemical Society, 17 (239) (1901). On 154.



It must be noticed that all these formulas are consistent with a trivalent boron atom.

The stable formula of B_3H_3 was assigned to the corresponding cyclo-compound, which Ramsay and Hatfield named as *cyclotriborene*. To the unstable form of B_3H_3, triborene, they assigned the unsaturated formula H_2B-B=BH.

Ramsay and Hatfield were also convinced that the solid residue that resulted from the action of hydrochloric acid upon magnesium boride contained solid hydrides of boron but did not succeed at isolating them from admixed boron.

Attempts to isolate solid boron hydrides from the residues that resulted from the reactions of boron compounds had already been made by several authors: in 1880, Benjamin Reinitzen became convinced that a mixture of inseparable hydrides of boron resulted from boron trioxide with potassium under sodium chloride; in 1889, Ludwig Gatterman assumed that the interaction between magnesium boride and hydrochloric acid rendered a hydride of boron; Clemens Winkler, who discovered germanium, thought to have isolated B_8H from the action of boiling hydrochloric acid upon magnesium boride; in 1888, Richard Lorenz, wrote an article entitled “The Valence of Boron” claiming the preparation of solid hydrides of boron which he was unable to isolate. All these unreliable claims may have contributed to the discredit of the existence of a compound made of hydrogen and boron.

Thus, the first century in the history of the hydrides of boron was characterized by generalized discredit towards their effective existence, the search for technical improvement to deal with unsurpassable technical difficulties, unawareness of the relevant literature and pervasive silicon contamination. But during this period it was also established the preparative method consisting in the action of hydrochloric acid upon magnesium boride and the analogy between carbon and boron.

The solution to such difficult technical problems clearly required the invention of specific technology, exclusive dedication and unusual perseverance and mastery of chemical science. That was the work of Alfred Stock.

2 - Next to Carbon

At the end of the nineteenth century, the once prominent community of German inorganic chemistry was becoming increasingly overshadowed by the recent successes of its organic congener. To use Egon Wiberg's brilliant metaphor, after its great successes of the eighteenth and beginning of the nineteenth century, inorganic chemistry in Germany was now "living a Cinderella's existence beside its two more attractive sisters, organic chemistry, already in full bloom, and physical chemistry, which was just beginning to flower"[35].

However inaccurate Wiberg's account may be on what concerns German physical chemistry[36], the fact remains that, upon his move to Berlin, the famous organic chemist Emil Fischer had been promised a new building to the Chemical Institute of the University, one that would fit the increasing demands of education in chemistry. Now, in 1899, only one year before its scheduled inauguration, Fischer was resolved to take advantage of the occasion to boost the renaissance of German inorganic chemistry. He accordingly took the decision to send two of his teaching assistants to other laboratories on the very clear mission of learning modern inorganic experimental methods. Alfred Stock went to Paris, to study under Henri Moissan, and Otto Ruff made the journey to Leipzig, to benefit from Wilhelm Ostwald's supervision.

As written by Wiberg, "it is a tribute to Emil Fischer's scientific far-sightedness and perspicacity that his choice fell on Alfred Stock and Otto Ruff whose achievements were later to pioneer the new golden age of inorganic chemistry in Germany."[37]

The extent of Fischer's wisdom in his choice would later be revealed by Ruff's famous witty comment: "I know only two important German inorganic chemists – the other is Alfred Stock!"[38]

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[35] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 691.

[36] Mary Jo Nye, *From Chemical Philosophy to Theoretical Chemistry* (Berkeley: Berkeley University Press, 1993), on p.169, argues differently, namely that German Physical Chemistry was then facing decline too.

[37] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 692.

[38] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 692.

Alfred Eduard Stock was born in 1876, on the 16th of July, in the seaport city of Danzig, in West Prussia (since 1945, the Polish city of Gdansk), but moved to Berlin with his parents when he was only two years old. His father, Hugo Johann Ludwig Stock, an insurance bank official and his grandfather, a court secretary and sub-director of an insurance company, descended from a line of guild workers and farmers. His mother, Hildegard, née Bube, was the daughter of a record office worker and director of the ducal art museum. Her ancestors had been officers in trade and official service.

Stock's interest in the natural sciences began very early in his life. When a young boy, Stock used to press plants, catch salamanders and do butterfly farming. He went further with physical and chemical experiments at home. This early scientific vocation was nurtured by his father with all the necessary books and apparatuses. According to Wiberg, these included the "great Brehm", the botanical "Thomé", an air pump, an electric machine, and "many others."[39]

From 1882 to 1894, Stock completed his studies in Berlin, at the Friedrich Werderschen Gymnasium. For his outstanding performance at school, Stock was awarded the three-year Franz Lange Stipendium and the one-year Wackenroder Stipendium. This support would become important after his father's untimely death in 1895.

In 1894, at the age of 18, Stock went to the University of Berlin to study chemistry. At the time, there were two chemistry institutes: one was under the physical chemist Hans Landolt; the other was under Fischer, whose reputation attracted an increasing number of students:

> By the time he had passed from Erlangen to Würzburg, Fischer's reputation had become magnetic, and from that period on an increasing number of *doctorandi* sought admission to his laboratory. The aggregate of these must be several hundreds, including many nationalities.[40]

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[39] The "great Brehm" is a reference to the famous contemporary work on zoology *"Brehms Tierleben"*, by Alfred Edmund Brehm (1829-1884); The botanical "Thomé" is a reference to the work *"Flora von Deutschland, Österreich und der Schweiz in Wort und Bild für Schule und Haus"* (Flora of Germany, Austria and Switzerland in Word and Picture for School and Home), first of 4 volumes with a total of 572 botanical illustrations, published in 1885 in Gera, Germany, by the German botanist and botanical artist Otto Wilhelm Thomé (1840-1925). Thomé's work can be seen at http://caliban.mpiz-koeln.mpg.de/thome/Alphabetical_list.html

[40] Forster, Martin Onslow, "Emil Fischer memorial lecture", J. Chem. Soc., Trans., 117 (1920). On 1159.

Accordingly, Stock chose to study with Fischer, whose poorly ventilated laboratory was so crowded that Stock had to wait until the third semester to have a work bench. In the meantime, Stock was an avid listener of lectures on art history, physiology (by Du Bois-Reymond) and history (by von Treitschke), besides those on chemistry, physics and mathematics. During the summer breaks, Stock performed further experimental work in van't Hoff's private laboratory, in the context of van't Hoff's extensive investigations on the origins of oceanic salt deposits.

Stock soon became teaching assistant of the organic chemist Oscar Piloty, who supervised his doctoral dissertation. Through Fischer and Piloty, Stock's scientific training can be traced back to Adolph von Baeyer. Indeed, both Piloty and Fischer were Bayer's former students, and, according to William Henry Perkin, himself a former student of Baeyer, Fischer's teaching methods were essentially those by Baeyer:

> Their methods as investigators and teachers were remarkably similar in almost every particular, as indeed might be expected when it is remembered that Emil Fischer was not only a pupil, and perhaps the most distinguished pupil, of Baeyer, but was also, for a long period, Baeyer's principal assistant, and he thus had every opportunity of learning the methods of teaching and the art of experimenting characteristic of his great teacher. In charge of large laboratories overcrowded with students, especially in later years, the first care of both these men was to see that the foundations of the Science, whether the section was Inorganic or Organic, were systematically and very thoroughly taught. With this object in view, the professor himself undertook the first elementary course of lectures and placed his most distinguished Privatdozent in charge of the teaching of practical Inorganic Chemistry, and thus the foundations were truly laid and, when the study of Organic Chemistry was subsequently undertaken, it was not until a sound knowledge of Inorganic Chemistry had been secured. Great stress was laid, both by Baeyer and by Emil Fischer, on a very thorough training in manipulation and the technique of experimenting, with the result that when the time came to engage in original work, the student was in a position to undertake his task with every prospect of success and needed only the minimum of supervision.[41]

Perkins' words indicate that Stock received a solid training on both organic and inorganic chemistry.

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[41] W. H. Perkin, "Baeyer memorial lecture", J. Chem. Soc., Trans., 123 (1923). On 1520.

As Stock showed great experimental skills during his undergraduate studies and doctoral work, Fischer chose him as his teaching assistant for the winter semester in 1898/99 and the summer semester in 1899. That year, on the 10th of May, Stock defended successfully his doctoral dissertation and was awarded the doctor's degree *magna cum laude*. His thesis was entitled "*A Quantitative Separation of Arsenic from Antimony. Monobromacrolien and Tribrompropionaldehyde. Bromnitroso Hydrocarbons and Their Transformation into Pseudonitrole*".

In September of 1899, Stock went to Paris to study with Moissan. From Stock's own words in his biographical work on Moissan[42], it is evident that his stay at Moissan's laboratory was a time of great enthusiasm and joy. According to Stock, despite the many material shortcomings faced by the international group of students that had gathered around Moissan to learn his techniques, in particular to use his *four électrique*, all was dealt with in a humorous and cheerful way. Along with the Parisian atmosphere, Moissan's great teaching and human attributes made an enduring impression on Stock. Wiberg testifies that Stock managed to appropriate Moissan's most remarkable personal and professional features, namely his ability to develop new laboratory apparatuses, his concern for orderliness and his oratory gifts:

> In particular, Moissan's principal lectures on inorganic chemistry gave him [Stock] great aesthetic enjoyment by virtue of their clarity and the elegant often humorous and rhetorically sparkling presentation. An equal ability was thus inspired in Stock, whose lectures and speeches similarly distinguished themselves by a masterful, subtle and elegant command of speech, by lucid exposition of the material and by a sense of humour appropriate to all situations, quick-witted and, if the need arose, also sarcastic.[43]

It was on Moissan's request that Stock first met boron chemistry. His decision to devote himself to the subject goes back to this period and was based on a simple analogy with carbon chemistry:

> C'est là que j'ai pris contact avec la chimie du bore. Le résultat de mon travail à Paris fut la préparation des combinaisons jusqu'alors inconnues du bore et du

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[42] A. Stock, "Henri Moissan", *B. 40 (A)* (1908). On 5099.

[43] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", Pure & Appl. Chem., 49 (1977). On 692.

> silicium SiB^3 et SiB^6. A cette occasion, j'ai pu remarquer qu'on connaissait insuffisamment la chimie du bore, bien que le fait d'être voisin du carbone aurait dû donner à cet étément un intérêt particulier et laissait espérer pour lui des combinaisons plus variées que l'acide borique et les borates qui, à cette époque, étaient presque exclusivement connus.[44]

Stock's ambition was to create a chemistry of boron similar to that of carbon:

> For a long time he had been concerned with the question of whether the immediate neighbour in the periodic table of the chemically so versatile carbon, the element boron, with which he first made contact under Moissan, was really as mundane and "boring" in its behaviour as was then supposed , e. g. whether its chemical affinity was restricted to strongly electronegative elements such as oxygen and chlorine or whether it was indeed possible to uncover hidden affinities for other entities and create a boron chemistry similar to organic chemistry. [45]

In 1900, after attending the Jubilee World Exhibition in Paris, Stock returned to Berlin to resume his duties as Fischer's teaching assistant, now already at Fischer's new building. According to Wiberg, this was no easy transition to Stock:

> The move from the romantic, lively, cosmopolitan Parisian atmosphere and the pastoral, idyllically situated laboratory of Moissan to the new, basic and simple home of the Berlin University chemistry faculty, which was situated amongst large blocks of houses in a lonely corner of the city and, according to Emil Fischer's wishes, devoid of any architectural inspiration, posed initial difficulties for the 24-year old assistant. In Paris everything was poetry: the environment, the city, the people; in Berlin everything was plain. [46]

Stock eventually managed to readapt himself to Berlin but a further setback expected him. His plans to work on boron hydrides were about to be frustrated:

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[44] A. Stock, "La Chimie du Bore", *Bull. Soc. Chim. France*, 51 (4) (1932). On 697.

[45] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977), On 693.

[46] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 692.

> Rentré à Berlin, à l’Institut d’Emil Fischer, je pris bientôt la décision de me consacrer à la chimie du bore et d’examiner en premier lien les hydrures de cet élément, au sujet desquels on ne possédait encore aucun renseignement certain.[...]
> Emil Fischer, à qui j’avais fait part de mon intention de m’occuper des hydrures de bore, me dit quelques jours plus tard, que son ami Ramsay l’avait prévenu que mon travail ne serait pas récompensé, la question des hydrures de bore venant justement d’être résolue dans son laboratoire.[47]

And in fact, shortly after, in 1901, Ramsay and Hatfield published their “Preliminary note on boron hydrides”: “Je renonçai alors à mon plan et me tournai vers d’autres questions”.[48]

In his search for a new research field, Stock spent the next nine years investigating the elements phosphorus, arsenic and antimony and their allotropes and compounds with hydrogen, sulphur and nitrogen. He also investigated boron bromide and boron sulphide. Also, it was during this period that he began developing the numerous improvements to apparatuses which would eventually culminate in his pioneering High Vacuum Technique, which would readily become of generalized use in the work with volatile compounds. Over 60 publications resulted from Stock’s intense work during this period. It was also during this period that Stock wrote his *Praktikum der quantitativen anorganischen Analyse*, whose acceptance is testified by its many editions in numerous languages and which kept being published after his death in extended form by Herman Lux, one of Stock’s co-workers.

In 1906, Stock succeeded Ruff as Professor and head of his research group. The following year, the Prussian minister of cultural affairs appointed Stock to equip the new institute of inorganic chemistry of the Technische Hochschule in Breslau, whose inauguration was scheduled to 1909. Thus, by this time, Stock was already receiving full recognition as an accomplished experimenter of remarkable technical and planning capabilities.

It was in 1909, after his official appointment as full Professor at the Technische Hochschule, that Stock, now with his own laboratory, decided to resume his initial plans to investigate boron hydrides. After all those years, Stock’s expectations for a detailed report on boron hydrides by Ramsay, following his preliminary note with Hatfield, had

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[47] A. Stock, “La Chimie du Bore”, Bull. Soc. Chim. France, 51 (4) (1932). On 697.

[48] A. Stock, “La Chimie du Bore”, Bull. Soc. Chim. France, 51 (4) (1932). On 698.

been frustrated. Why this was so, Stock would learn later, in Ramsay's 1913 book *Vergangenes und Künftiges aus der Chemie*:

> [...] he had made at least twenty-five unsuccessful attempts to reproduce the hydride B_3H_3, even though he had employed boron trioxide from widely different sources and had prepared magnesium boride under all conceivable modifications of temperature, time of heating, and ratios of reactants. Under the most favorable conditions, only a few cubic centimeters of the problematical gas were obtained.[49]

After learning from Fischer that Ramsay had abandoned his work on the boranes, Stock initiated his own investigations on the subject.

2.1 - Stock's preparative method

Already in his initial investigations, published in 1912, Stock was able to dismiss Ramsay and Hatfield's conclusions. He became aware that Ramsay and Hatfield's samples must have been contaminated with "considerable amounts" of silicon hydrides and that these authors had also failed to notice that boron hydrides were completely decomposed when treated with an alkali. This was an essential observation, already communicated by Sabatier, since one crucial step in Ramsay and Hatfield's work was the treatment of the gas containing the boron hydrides with soda lime:

> According to the present writer's observations, a layer of soda lime only a few centimeters long suffices to remove completely the odor of boron hydride from the gas passed over it. The supposed boron, obtained by passing an electric spark through the gas, was not tested further, but undoubtedly consisted almost wholly of silicon in such experiments as those made with "stable B_3H_3" or with "BH_3". Thus all Ramsay's analytical conclusions and the inferences based thereon are invalidated.[50]

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[49] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 14.

[50] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 14.

Even so, Stock followed Ramsay in his method to obtain the hydrides (decomposition of magnesium boride with hydrochloric acid) because "it was found to be the most advantageous method in spite of the poor yield of boron hydride."[51]

The preparation of magnesium boride (Mg_3B_2) by heating metallic magnesium (Mg) with boron trioxide (B_2O_3) and its subsequent decomposition with hydrochloric acid was a rather complex set of chemical and physical proceedings whose mastery Stock could only have achieved by a long "trial and error" process. In fact, it was much of an art, in addition to its scientific nature. A small excerpt of Stock's own description leaves no doubts about it:

> On decomposing the boride with acids, the yield of boron hydride depends not only on the ratio of Mg to B_2O_3, but also to a large extent on the temperature used when preparing the boride. The latter must be prepared at a uniform glowing temperature, without too strong heating. The glowing will take place only if the starting materials are very finely powered and sufficiently free from water. [...] It must pass through silk bolting cloth of 2500 meshes per square centimeter, because if one attempts to powder it by the usual means in the laboratory, the highly hygroscopic oxide takes up too much water, which can not later be removed.[52]

Even a simple reaction equation could be misleading:

> The equation $B_2O_3 + 6\ Mg = 3MgO + Mg_3B_2$ calls for 2 parts by weight of magnesium and 1 part of boron trioxide. At this ratio, however, the reaction between the two is so violent that a great deal of the magnesium vaporizes and the resulting boride gives a very poor yield of hydride. The great rise in temperature is avoided by using an excess of magnesium, that is, 8 parts of magnesium to 3 parts of boron trioxide. If the amount of magnesium drops to 1 part or increases to 5 parts per part of boron trioxide, the yield again decreases.[53]

The crude gas resulting from the action of hydrochloric acid upon magnesium boride was composed of hydrogen (its chief component), boron and silicon hydrides, carbon dioxide and traces of hydrogen sulphide. The presence of boron hydrides could be

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[51] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 14.

[52] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 38.

[53] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 139.

detected by two “very sensitive” qualitative tests: the extremely disagreeable, “chocolate-like” odour - “noticeable even at extreme dilution” – and the green flame resulting from their combustion, due to the broad band in the green region of boron’s spectrum.

Since all crude gas components, with exception of hydrogen, condense on cooling with liquid air, the condensate thus obtained was afterwards transferred to the high-vacuum apparatus, where its components were isolated and purified. According to Stock, the isolation of the individual boron hydrides was a very difficult task that could only be achieved by fractional distillation.

2.2 - The first hydrides of boron

Between 1912 and 1914, Stock and his co-workers published five papers on the hydrides of boron, reporting the discovery of the hydrides B_4H_{10}, B_2H_6, $B_{10}H_{14}$[54] and the hypoborates and halogenated boron hydrides formed by the action of alkali and halogens on them. These results were obtained without the use of Stock’s High-Vacuum Technique, which at this time was still being developed. The formulas of B_2H_6 and B_4H_{10} were the analogues of the corresponding hydrocarbons and Stock was led to believe that his initial ambition had been accomplished: he had proved that boron chemistry was indeed similar to that of carbon.

B_4H_{10}: Due to its relative stability towards water, B_4H_{10} was the first and easiest to be isolated. Its discovery was reported by Stock and Carl Massenez in 1912. At room temperature, B_4H_{10} is a colourless liquid or gas, with boiling point +18 ºC at 760 mm Hg. Its instability rendered the precise determination of its physical constants very difficult. The purification of B_4H_{10}, unlike its isolation, was very difficult and the removal of the hydrides of silicon implied considerable loss of it. When pure, B_4H_{10} does not ignite in air. Its thermal decomposition is quick and forms B_2H_6, B_5H_9, and

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[54] In the following characterization of the boron hydrides discovered by Stock and his co-workers when at Breslau, not all the mentioned properties were studied during this period. Strict chronological order in the writing would result in a somewhat confusing reading with no expectable additional advantages, since Stock continuously sought for improvements or further characterization of the hydrides.

$B_{10}H_{14}$. This led to the discovery, first of B_2H_6, and then to the other hydrides: "It [B_4H_{10}] opened for us the unknown field of the chemistry of the hydrides of boron."[55]

B_2H_6: The existence of B_2H_6 was reported by Stock and Kurt Friederici in 1913. It is the simplest of the hydrides of boron. At room temperature, is a colourless gas with the characteristic disagreeable odour of boron hydrides, somewhat suggestive of hydrogen sulphide. It is the chief product of the thermal decomposition of B_4H_{10}. This reaction was the basis of Stock's method to prepare diborane:

> Six to seven hundred cubic centimeters of B_4H_{10} are placed in a sufficiently large tube and are heated for 5 hour at 90º-95º. The tube then contains B_2H_6 together with hydrogen, a little unaltered B_4H_{10}, and other volatile and non-volatile hydrides of boron. The B_2H_6 is purified by fractional distillation. From 2 ½ liters of B_4H_{10} prepared from 4 Kgm. of magnesium boride, we obtained 1750 cc. of B_2H_6.[56]

No B_2H_6 was formed in the crude gas because its high reactivity towards water precluded its survival after the decomposition of magnesium boride with an aqueous solution of hydrochloric acid. Diborane could also be formed by the thermal dissociation of other hydrides of boron, such as B_6H_{10}. Of all the boron hydrides discovered by Stock and his co-workers, diborane was the most easily purified and one of the most stable. It does not react with dry air (but dissociates readily in the presence of moisture) and dissociates very slowly at room temperature (in the absence of moisture and lubricants). At higher temperatures, decomposition is faster. Decomposition by contact with stopcock lubricants is slower than with any other boron hydride.

$B_{10}H_{14}$: Dekaborane was the only solid, volatile hydride of boron described by Stock. At room temperature, is a colourless well-crystallized solid, belonging to the rhombic system. It was of easy identification, isolation and purification. The production of "considerable" amounts of $B_{10}H_{14}$ through the thermal decomposition of either B_2H_6 or B_4H_{10} was reported by Stock, Friederici and Otto Priess in 1913. It was also produced

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[55] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 60.

[56] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 51.
This description corresponds to the improved method published by Stock and Ernst Kuss in 1923. In 1913, Stock and Friederici studied the thermal decomposition of B_4H_{10} at room temperature and 100ºC.

when B_2H_6 or B_4H_{10} were left to stand at ordinary temperatures for a long time. The rate of this reaction could be accelerated by the use of ultraviolet light. Later, Stock would discover that it was the chief product of the spontaneous dissociation of B_5H_{11} at ordinary temperatures and that it resulted from the spontaneous decomposition of B_6H_{10} too. It was also present in the crude gas resulting from the action of hydrochloric acid upon magnesium boride. The decomposition of 100g of magnesium boride would yield 20 mg of $B_{10}H_{14}$.

According to Stock, dekaborane was best prepared by heating B_2H_6 between -115 ºC and – 120 ºC for 48 hours, or by heating B_4H_{10} between 90 ºC and 95 ºC for 5 hours. When B_4H_{10} was used, dekaborane was a by-product from the formation of B_2H_6. The yield of dekaborane was about 50 mg per 100 cc. of B_2H_6 or B_4H_{10}.

By this time, Stock also believed to have detected the existence of another hydride, with formula B_6H_{12}, in the crude gas resulting from the action of hydrochloric acid upon magnesium boride. However, subsequent investigation, in 1921, with better equipment and methods, immediately led him to realize that it was a mixture of B_4H_{10}, B_5H_9, B_6H_{10} and silicon hydrides.

2.3 - Stock's High Vacuum Apparatus

Ramsay's failure is a good measure of how difficult was to work with the hydrides of boron. In fact, as Stock noticed, "the instability of the hydrides of boron and silicon and their sensitiveness to air, moisture, and lubricants, gave rise to unconquerable difficulties as long as the usual types of apparatus were employed."[57]

According to Stock, this situation stimulated him to build on all the previous work he had made on apparatus improvement in Berlin and to engage in a long and complex struggle to develop a specific type of apparatus and appropriate techniques specially suited to work with highly volatile and unstable substances such as the hydrides, which would become known as Stock's High Vacuum Technique. "Our first attempts were followed by many years of laborious experimentation"[58].

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[57] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 173.

[58] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 15.

Stock's investigations involved no uncommon set of chemical operations and measurements: vapour pressure and melting-point determinations for purification and identification purposes; fractional distillation or fractional condensation to separate mixtures into their individual components, etc. The problem was the high reactivity and instability of the hydrides. A high vacuum glass apparatus, all of whose parts were fused together and evacuated by an automatic mercury pump, allowed overcoming the hydride's sensitivity to air and moisture. Special forms of mercury valves, the float valves, were designed by Stock to replaced the usual lubricated stopcocks and insure that the volatile substances would contact with no materials other than glass and mercury. Due to the hydrides' high sensitivity to grease, the float valves were considered by Stock as his most important improvement. Numerous other equipments were used to perform all the necessary operations involved in many distinct investigations under such demanding conditions: different kinds of porous valves, a tube for weighing substances that react with a lubricant, an apparatus for determination of melting points, the magnetic floating balance, the vapour pressure thermometer, the mercury collecting pump, the vacuum-tube opener, the apparatus for tensimetric molecular weight measurements in liquid ammonia, the zinc electric arc - "a powerful reducing agent in preparative chemistry", the apparatus for analysing boron and silicon hydrides, the apparatus for the treatment of hydrides with sodium amalgam, etc[59].

All these items could be assembled to build a flexible apparatus that could be readily adapted to the specific requirements of a particular investigation:

> The apparatus is assembled to meet the requirements of each individual case. Thus it can comprise portions for separating mixtures by distillation, for carrying out analyses and reactions, for determining physical constants, or for storing samples. It also includes the necessary valves, manometers, comparison barometers, and the like. Volatile substances can be distilled or sublimed, within the apparatus, to any desired part thereof by cooling that point with liquid air, whereupon they condense rapidly and quantitatively. The more volatile the substance the easier it is to work

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[59] An extensive and comprehensive description with photos and diagrams may be found in A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933), on 173. A much shorter account with diagrams was included in A. Stock, "La Chimie du Bore", Bull. Soc. Chim. France, 51 (4) (1932). On 699.

> with. Substances that boil at as high as 150º or even 200º can still be treated in the vacuum-apparatus.[60]

The high accuracy of his vacuum method allowed Stock to carry out an extensive physical and chemical investigation with only a few cubic centimeters of a gas or a few milligrams of a solid. It was specially suited to follow quantitatively the course of the reactions of small quantities of highly unstable and volatile substances between room temperature and that of liquid air.

Stock's High-Vacuum method was applied for the first time in his research on the silicon hydrides formed by hydrochloric acid and magnesium silicide, and its results were published in 1914. Stock kept publishing on apparatus improvement until 1941.

Wiberg wrote that, when he entered Stock's laboratory for the first time in 1927, it looked like a glass primeval forest and that he soon became "overjoyed by the exactness and elegance of the neat methods used by Stock"[61]. He was very clear on how important these technical advances became for chemical research worldwide:

> Stock's High Vacuum Technique enabled the precise and quantitative purification and investigation of the smallest amounts of volatile, sensitive materials under high vacuum by the exclusion of air, moisture and grease in a completely closed, adaptable and easy to operate mercury-sealed glass construction, an apparatus later to become an indispensable and much used aid in modern science and engineering laboratories, and which was to make many researchers, both inside and outside Germany, disciples of Alfred Stock. [62]

Thus, from its very beginnings, research on boron and silicon hydrides made important technical contributions to experimental chemistry by extending its action to highly unstable and volatile substances, until then a forbidden area, as Ramsay's investigations clearly demonstrated.

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[60] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 173.

[61] V. Bartow, "Pioneer Personalities in Borane Chemistry", in Robert F. Gould, (ed.), *Borax to Boranes*, Advances in Chemistry Series, 32, (Washington, D. C.: American Chemical Society Applied Publications, 1961). On 10.

[62] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 695.

2.4 - The Silicon Hydrides

Following the outbreak of World War I in the autumn of 1914, the war effort began to impose severe restrictions on Stock's research activities at the Institute in Breslau, as a considerable number of its students had been recruited to war. Stock himself was spared to any war activities due to health problems. That same year, attracted by the possibility of undisturbed prosecution of his research program and by highly advantageous financial and career conditions, namely a chair at Berlin University, Stock accepted a position at the Kaiser-Wilhelm Institute for Chemistry, in Berlin-Dahlem, thus taking over the laboratory of Richard Willstätter, who had moved to Munich to replace Bayer.

Thus, in 1916, after the unexpected halt at Breslau, Stock, now 40 years old and able to resume his research activities at the Kaiser-Wilhelm Institute in Berlin, turned his attention to silicon hydrides. There were both practical and speculative reasons to render Stock's decision as fully justifiable.

On the practical side, Stock was confronted with the inescapable technical hindrance that was posed by the pervasive character of silicon hydrides as contaminants of the hydrides of boron. This made the preparation of purified boron hydrides from borides an extremely difficult achievement and confronted Stock with an unsurpassable need to learn more about silicon hydrides in order to achieve effective purification of the boron hydrides:

> […] the presence of silicon hydrides in the crude gas was a great obstacle, as the hydrides of silicon and boron are physically and chemically so similar that it is very difficult to separate them. It was impossible to remove the silicon hydrides by chemical methods without simultaneously destroying the less stable boron hydrides. We could not, however, avoid contaminating the boron hydrides with silicon hydrides, because commercial magnesium always contains some silicon which forms magnesium silicide and silicon hydride in the subsequent reactions. Furthermore, with the exception of SiH_4, there was at that time no reliable information on the hydrides of silicon.[63]

On a more speculative plane, it was Stock's belief that, since silicon was an immediate neighbour of carbon in the Periodic Table, moreover in the same group, there should be

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[63] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 15.

possible to unveil a whole new silicon chemistry, as rich and versatile as the chemistry of carbon, in a sense mirroring what he had already done with the chemistry of boron, a few years earlier.

And in fact, Stock's work in this area most certainly met his own expectations, as he was able to synthesize, isolate and study numerous until then unknown silicon compounds, whose existence in nature was precluded by silicon's tendency to polymerize and oxidise outside strictly controlled laboratory conditions.

Stock's investigations on silicon hydrides spread over a seven year period, between 1916 and 1923, and resulted in 16 publications.

Stock was able to increase the yield of silicon hydrides resulting from the reaction of magnesium silicide (Mg_2Si) with hydrochloric acid. This allowed him to establish the existence of a new class of saturated silicon compounds, the silanes, which are the analogues of alkane hydrocarbons and whose general formula is, accordingly, Si_nH_{2n+2}. Stock discovered and/or characterized numerous of its elements: the liquid Si_3H_8 and Si_4H_{10}, the already known gaseous monosilane SiH_4 and the hitherto little known gaseous disilane Si_2H_6. He also ascertained the existence of liquid pentasilane Si_5H_{12} and hexasilane Si_6H_{14}.

Stock also studied the halogenation of these compounds, obtaining and characterizing many of its halogen derivatives in a pure state. He further used these as the starting materials to synthesize many other unknown compounds, such as silicomethylether $(SiH_3)_2O$, silicoformaldehyde SiH_2O, silicoethylether $(Si_2H_5)_2O$ and silicotrimethylamine $(SiH_3)_3N$.

The significance of Stock's achievement in silicon chemistry is more fully conveyed by the passionate words of Wiberg: "Thus a silicon chemistry, comparable in its wealth of formulae to organic chemistry, was created which, owing to silicon's dominating affinity for oxygen, was essentially laboratory born and could only be brought to life by the wand of a experimental magician such as Alfred Stock." [64]

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[64] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977).On 694.

2.5 Back to boron chemistry:

Because of this previously unintended dedication to the development of silicon chemistry, it was only in 1921, while already in Berlin, that Stock finally resumed his work on the boron hydrides. By making use of his High Vacuum Apparatus methods, he was able to achieve immediate advances in the preparation and characterization of B_2H_6 and B_4H_{10} and the higher boranes B_5H_9, B_5H_{11} and B_6H_{10}.

All this work was immediately followed by an impressive systematic characterization of the chemical behaviour of these boranes, which included the study of their reactions with a truly extensive list of compounds, like water, hydrogen halides, ammonia, alkali metals, alkali metal hydroxides and organic substances. Stock also investigated their thermal decomposition at ambient temperature and on warming. This was an essential study, since some of these compounds resulted from the thermal decomposition of others. Thus, the study of thermal decomposition was important, not only to improve the lifetime of highly purified amounts of these compounds, but also because it became the method of production for some of them.

B_5H_9: The isolation of this pentaborane was reported by Stock and Ernst Kuss in 1923. B_5H_9 is a colourless mobile liquid, with a low index of refraction, and not spontaneously inflammable. Stock reported "an extremely disagreeable smell which is the chief source of the nauseating odor of mixtures of boron hydrides".

Along with B_4H_{10}, B_6H_{10} and several hydrides of silicon, B_5H_9 was one of the hydrides present in the mixture that Stock mistakenly thought to be the hydride B_6H_{12} in 1912. Because of its similarity with B_6H_{10}, their separation was difficult: "After great difficulty we then for the first time isolated and described the compound B_5H_9. Its separation from the similar B_6H_{10} was one of the most difficult portions of our investigations."[65]

It could also be formed by heating B_4H_{10} at 100 ºC. Under these conditions, 50 cc. of B_5H_9 could be obtained from 1000 cc. of B_4H_{10}. This yield could be increased to 170 cc. if gaseous B_4H_{10} was slowly passed through a tube warmed to 200 ºC.

Stock also reported that some B_5H_9 seemed to be formed when a current of B_2H_6 was heated to 300 ºC.

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[65] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 68.

B_5H_9 was readily separated from B_4H_{10} by fractional distillation. However, it could not be separated by the usual methods from another hydride physically too similar, to which Stock gave the provisional formula B_6H_{12}?, in which Stock chose explicitly to include the question mark. The presence of this “mysterious” hydride was detectable by a marked drop in the melting point of B_5H_9. However, the isolation of the pentaborane was achievable because the dissociation rates of both hydrides were completely different. If left to stand at room temperature for a few weeks, B_6H_{12}? would change wholly into hydrogen and a solid, yellow, non-volatile hydride, while only a very small amount of B_5H_9 would be lost. This fact was in the origin of the isolation of B_5H_9, because, luckily for Stock, the sample that originally contained a mixture of B_5H_9 and B_6H_{12}? had been standing for several months and, therefore, the B_6H_{12}? was already totally dissociated when the sample was submitted to analysis.

B_5H_9, along with B_2H_6 and $B_{10}H_{14}$, was one of the most stable of the hydrides discovered by Stock and is present in small amounts in the crude gas that results from the decomposition of magnesium boride. It decomposes very slowly into hydrogen and a solid, colourless, non-volatile hydride. According to Stock, the presence of B_5H_9 was detected in tubes used for heating B_4H_{10} four years after such use.

B_6H_{10}: The history of the isolation and description of this hydride was, as already seen, intimately related to that of B_5H_9. Thus, its existence was also reported in 1923 by Stock and Kuss.

B_6H_{10} is a colourless liquid with a high refraction index that does not ignite spontaneously. It decomposes slowly into hydrogen and a solid yellow product even at room temperature.

1g or 300 cc. of gaseous B_6H_{10} could be obtained from 2000 g of magnesium boride.

B_5H_{11}: The isolation of this hydride was reported by Stock and Wolfhart Siecke in 1924. B_5H_{11} is a very mobile colourless liquid that changes very rapidly into $B_{10}H_{14}$ and hydrogen. Along with “beautifully crystallized” $B_{10}H_{14}$, small amounts of hydrogen, and traces of B_4H_{10}, it was prepared through the thermal decomposition of diborane. Alternatively, “considerable amounts” of diborane could be allowed to stand at room temperature for six months. The separation of the admixed B_4H_{10} and B_5H_{11} from the more volatile undissociated B_2H_6 and from the less volatile $B_{10}H_{14}$ was relatively simple, but the isolation of B_5H_{11} from B_4H_{10} was a more difficult task.

Its instability made it very difficult to prepare and, accordingly, only very small amounts could be available: from 1400 cc. of diborane, Stock was able to isolate 0.08 cc of B_5H_{11}; on another occasion, he obtained a few cubic centimeters from 500 cc. of diborane that had stood exposed to daylight for 10 months. This severely restricted the investigation on this pentaborane: “The determination of its odor, its reaction with air and with water, were not undertaken because of the losses attendant upon such tests of this precious compound. So far our investigation of B_5H_{11} has been restricted to a few important reactions.”[66]

Stock also observed that, apparently, B_2H_6 further decomposed into $B_{10}H_{14}$ through the medium of B_5H_{11}: $2B_5H_{11} = B_{10}H_{14} + 4H_2$.

B_6H_{12}: Stock believed that a highly unstable hydride of boron was admixed with the B_5H_9 resulting from the thermal decomposition of B_4H_{10} into diborane. Because it readily decomposed, its study was the most difficult amongst all the hydrides. Analyses showed that it contained more hydrogen than B_5H_9 but the number of boron atoms was still uncertain. In a first moment Stock believed that it had 5 boron atoms and designated it as $B_5H_{>9}$, but subsequent work led him to believe that it had at least 6 boron atoms. Since analysis also came to prove that the molecule contained two hydrogen atoms for every atom of boron, Stock accordingly assigned to it the formula B_6H_{12}?, where the question mark indicated explicitly the associated uncertainty.

According to Stock, the hypothesis of B_6H_{12}? being a mixture of several hydrides was contradicted by a number of observations. Stock was also convinced that the sample used to make those observations still contained about 25 per cent of B_5H_9.

The above description of the basic properties and reactions of each of the hydrides of boron described by Stock and his co-workers, shows very clearly how low the yields of his methods were. This made his investigations very lengthy and difficult. In some cases, as in B_5H_{11}, a full characterization was simply not possible. It also highlights the complexity of inter-relations between the hydrides’ production reactions and gives a very slight hint of the quantity of apparently disperse and unrelated wealth of information Stock both collected and had to deal with, in search for structurally relevant information.

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[66] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 72.

In 1926, severely attacked by his chronic mercury-poisoning condition, Stock decided to leave his contaminated laboratories in Berlin and moved to the Karlsruhe "Hoschule", where he had the opportunity to set up a mercury-free laboratory, which became the object of interest of many fellow chemists from Germany and abroad.

There, between 1926 and 1936, he would lead the final stage of his investigations on boron hydrides, with studies on the more structurally important reactions: the boranes' ammonia compounds and their electrolysis in ammonia solutions, the effect of alkali and alkaline earth metals amalgams on boranes, study of the "inorganic benzene" $B_3N_3H_6$, the effect of halogens and halogen hydrides on boranes.

During this period, Stock conducted an intensive investigation on the poisoning effects of mercury vapour. Among the medical community, Stock is well known for his pioneering investigation on this area. He also started the controversy on the dangers of dental amalgams containing mercury in its filling material that is still going on at the present time. After his retirement, in 1936, Stock dedicated himself exclusively to this area, having set up two special laboratories in Berlin for the effect.

During his stay at Karlsruhe, Stock received numerous honours and invitations to go abroad: France, Holland, United States of America, Switzerland, Austria and Russia. His visit to the United States of America in 1932 deserves special mention. Between February and May of that year, he was the George Fischer Baker Non-Resident Lecturer in Chemistry at Cornell University. As such, he was requested to publish the essential contents of his lectures and he saw in this the opportunity to prepare a systematic and detailed report on his investigations on the hydrides of boron and silicon. This gave birth to his historical book *Hydrides of Boron and Silicon*, published in 1933, and which would become the reference book in the research on boron hydrides for decades to come. It was reissued in 1957, despite the tremendous evolution this field had suffered since its first edition.

Despite the idiosyncrasies of his methods, Stock managed to make an incredibly extensive study of almost all of his hydrides of boron. A sense of the complexity and range of Stock's investigations could hardly be given here. Only the reading of Stock's original papers or their compilation made by Stock in his book can give a more real notion of how incredibly hardworking and persistent Stock had to be to systematically collect and manage a huge and complex wealth of empirical physical and chemical information on the hydrides under very difficult conditions. These included not only the intrinsic experimental difficulties of his investigation, but also those of a more contextual and personal nature, such as repeated changes of workplace and, in particular, Stock’s severely debilitated health due to a chronic mercury-poisoning condition. These and many other aspects of Stock’s life, as his many institutional activities and responsibilities and his educational concerns will not be addressed here, both because it would add nothing to the purposes of this work and because it would inevitably result in no more than a copy of Wiberg’s words. To obtain that kind of information, the reader is referred to the pertinent bibliography. This work is especially concerned with the structural implications of Stock’s work and its subsequent consequences for the history of the quest for the structure of the hydrides of boron. Thus, the following pages will be concerned with a detailed description of some of his investigations that proved to be especially interesting from the structural point of view, to which a small summary about the stability of the hydrides was added:

2.5.1 - Stability

The hydrides of boron did not spontaneously ignite on contact with air (once again, B_5H_{11} and the hypothetical B_6H_{12} had not been tested). Stock refers that this was in contrast with the behaviour of silicon hydrides, B_2H_5Cl, $B(CH_3)_3$ and $B(C_2H_5)_3$.

Room temperature stability of B_2H_6, B_5H_9 and $B_{10}H_{14}$ was reported as very high ($B_{10}H_{14}$ can stand at room temperature in a vacuum for “many months”, without showing any sign of decomposition. It is stable even on warming.) and increasingly less in the cases of B_6H_{10} and B_4H_{10}. The hydrides B_5H_{11} (and B_6H_{12}?) as well as B_2H_5Cl, B_2H_5Br and B_2H_5I had “very much lower” room temperature stability.

Stock was also able to observe that the rate of spontaneous decomposition was influenced by the presence of such impurities as silicon hydride and by traces of moisture or of alkalies. This rate seemed to increase after decomposition had set in. Also, ultraviolet light had an accelerating effect similar to that of warming, but daylight had no perceptible influence.

According to Stock, the spontaneous dissociation of the hydrides led chiefly to the formation of hydrogen and of hydrides that are poorer in hydrogen and higher in molecular weight. The exception was B_4H_{10}, given that its dissociation produces mainly B_2H_6. Stock points out that B_4H_{10} dissociation is “particularly complicated” due to the large number of differing hydrides that result from it and to their many possible cross-reactions: “It is evident that in this case many kinds of reactions take place, and perhaps many equilibria exist side by side and influence one another.”[67]

2.5.2 - Boron Alkyls

Stock and Friedrich Zeidler’s studies on the alkyls of boron, published in 1921, were designed to investigate the eventual dimerization of trivalent boron compounds to learn about the eventual dimerization of the hypothetical BH_3 into B_2H_6. Boron methyl $B(CH_3)_3$ and boron ethyl $B(C_2H_5)_3$ had been reported by Edward Frankland in 1862 but had not been investigated ever since, on account of their volatility and spontaneous inflammability. By making use of his high-vacuum apparatus, however, Stock was able to easily overcome such technical difficulties and decided to investigate these compounds because of the peculiar temperature dependence of boron ethyl’s molecular weight that had been reported by Frankland: 98.4 g/mol at 149ºC, 104.1 g/mol at 132ºC and 108.8 g/mol at 101.6 ºC. The computed value for the molecular weight of $B(C_2H_5)_3$ was only 98.1 g/mol.

This led Stock and Zeidler to the following conjecture: “According to these results it seemed as though boron ethyl polymerized at lower temperatures, and that there existed a $B_2(C_2H_5)_6$ corresponding to B_2H_6.”[68]

The application of this reasoning to boron methyl could not derive from Frankland’s work, since he had made but one determination of the molecular weight of boron methyl (55.3 g/mol at 12.2 ºC; computed value: 56.1 g/mol). However, Stock and Zeidler were able to make an extension of their conjecture to boron methyl by arguing that it could be possible that its vapour density (boiling point: -20 ºC) increased at lower temperatures.

Thus, the idea was to investigate the dimerization of trivalent boron methyl and boron ethyl to learn about the dimerization of the hypothetical trivalent BH_3 into diborane. This implied looking at boron methyl [boron ethyl] and their hypothetical dimer compound $B_2(CH_3)_6$ [$B_2(C_2H_5)_6$] as substitution products of the hypothetical BH_3 and diborane, respectively.

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[67] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 111.

[68] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 99.

Stock and Zeidler were able to produce the boron alkyls from boron chloride and zinc alkyl (Frankland had used alkyl esters of boric acid) and to make, for the first time, a full characterization of these compounds by determining their physical constants (melting and boiling points, vapour pressures at several temperatures, gas densities at several vapour pressures and temperatures). These studies established that the molecular weights of these boron alkyls were independent of temperature and consistent with the computed values for their single molecules. Frankland's allegations that boron ethyl's gas density decreased with increasing temperature were attributed to thermal dissociation into hydrogen and ethane, a fact that had escaped to Frankland's observation.

On these grounds, Stock and Zeidler's conclusion was peremptory: "There can be no doubt that the simplest boron alkyls and boron hydrides are different types of compounds."[69]

2.5.3 - Boron hydrides and sodium amalgam

By making B_2H_6 and B_4H_{10} to react with dilute liquid sodium amalgam, Stock and his co-workers were able to determine that these boron hydrides combined with sodium in stoichiometric proportions to give non-volatile solid compounds, "in a quite different manner than did the silicon hydrides"[70].

Thus, in 1926, Stock and Erich Pohland made two experiments in which an amalgam of known sodium content was made to react with excess B_2H_6: "In both cases, 2 atoms of sodium took up exactly 1 molecule of B_2H_6. Aside from traces of hydrogen, no other product was formed. The B_2H_6 that was not absorbed was found to be still pure."[71]

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[69] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 101.

[70] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 138.

[71] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On138.
In an earlier experiment, in 1923, Stock and Kuss, had already concluded that only 3/2 atoms of Na reacted with each B_2H_6 molecule. Stock explained this contradiction by stating that in the first experiment the amount of sodium was probably not known with certainty.

According to Stock, the reactions of diborane's sodium compound B_2H_6•2Na with water and with gaseous hydrogen chloride led to the conclusion that diborane endured no structural transformation during the reaction with sodium amalgam:

> [...] in water, however, it gave off hydrogen and formed an alkaline solution that reacted like B_2H_6 in caustic potash ($KOBH_3$ reactions), *e. g.* precipitating black Ni_2B from an acetic acid solution of a nickel salt. B_2H_6, therefore, has undergone no deep-seated transformation when changed into its sodium compound; this is also shown by the observation that when the sodium compound was treated with gaseous hydrogen chloride, a large part of the B_2H_6 was again set free.[72]

In 1930, Stock, Wiberg and Hans Martini made a careful study of the reaction of B_4H_{10} with sodium amalgam. They found out that solid, non-volatile B_4H_{10}•2Na was formed after shaking the amalgam with an excess of B_4H_{10} for 24 hours at room temperature.
To investigate the existence of compounds similar to B_4H_{10}•2Na but richer in sodium, the authors treated B_4H_{10} with an excess of sodium amalgam and then tried to determine the unreacted sodium in the residue by two different processes:

- From previous experiments, the authors knew that B_4H_{10}•2Na would not react with diborane. This allowed the use of excess diborane to form B_2H_6•2Na with the remaining sodium, the one that had not been taken up by B_4H_{10}•2Na. From the amount of diborane consumed it would be possible to determine, by comparison with the amount of B_4H_{10}•2Na, the amount of sodium that had been taken up by other sodium compounds of B_4H_{10}. However, "an unexpectedly large amount of B_2H_6 was taken up, much more than if all the sodium originally present in the amalgam had gone over to form B_2H_6•2Na"[73]. This meant that the original goal of determining the amount of free sodium would not be attainable, but one conclusion was still possible, leading to an important structural inference by analogy:

> It must be concluded, therefore, that other sodium compounds besides B_4H_{10}•2Na are produced from the action of B_4H_{10} on an excess of sodium amalgam, and that

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[72] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 138.

[73] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 139.

> they react in some manner with B_2H_6. This recalls the reactions between sodium alkyls and unsaturated hydrocarbons, studied by Ziegler and his co-workers. Probably there is a structural relationship between B_2H_6 and ethylene."[74]

- In the second method, the authors used an excess of hydrogen chloride, a gas that reacted with sodium amalgam according to the equation

$$2Na + 2\ HCl = 2NaCl + H_2$$

However, they found out that the sodium compound of B_4H_{10} was also attacked by the hydrogen chloride:

> Consequently, more hydrogen was produced than corresponded to the total amount of sodium originally present in the amalgam; four-fifths of the B_4H_{10} used in the previous reaction was released as such, and the remainder was converted in boron trichloride. This chlorination went much further than when the hydrogen chloride acted directly upon B_4H_{10}.[75]

Once again, the original goal had been frustrated, but one important structural inference was drawn by analogy:

> The alkali metal compounds of boron aryls studied by Krause and his co-workers since 1924 may be mentioned here. For example, from sodium and an ether solution of boron triphenyl there was formed the crystalline $B(C_6H_5)_3$•Na; it is soluble in ether, and gives up its sodium again when merely shaken with mercury, with reformation of $B(C_6H_5)_3$. There also come to mind the corresponding carbon compounds $C(C_6H_5)_3$•Na and the like, studied by Schlenk and his pupils.
>
> The linkage of sodium to these hydrides indicates a certain degree of unsaturation in B_2H_6 and B_4H_{10}. The liberation of the hydrides when their sodium compounds are treated with hydrogen chloride shows that the sodium addition-products are, relatively, loosely-bound compounds.[76]

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[74] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 139.

[75] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 140.

[76] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 140.

2.5.4 - Halogenation of boron hydrides

In 1914, Stock, Kuss and Otto Priess investigated the halogenation of B_2H_6 and $B_{10}H_{14}$ by chlorine and bromine.[77] These investigations held rather unexpected results, especially if one considers the halogenation of the corresponding hydrocarbons. In fact, Stock and his co-workers found out that the only chlorination product of the reaction between diborane and an excess of chlorine was BCl_3: "With an excess of chlorine the sole chlorination product was BCl_3. No less volatile substance was formed, neither B_2Cl_6 nor any chlorine addition-product of BCl_3. The same held true when that amount of chlorine was used that is theoretically required to form BCl_3."[78]

One must keep in mind that, judging by the paper on the nomenclature of the silicon and boron compounds that Stock would publish two years later, in 1916, at the time Stock viewed boron chemistry as expectably analogous to carbon chemistry with the boron atom matching carbon's tetravalency in its own hydrides. Thus, these preliminary results on the chlorination of diborane were rather odd in this analogical framework, since, unlike what happened in the chlorination of the hydrocarbons (hence the reference to B_2Cl_6), the chlorination of diborane seemed to have the rather strange effect of transforming the tetravalent boron in diborane into the trivalent boron in BCl_3. This led to more careful inquiries: "These observations suggested the questions: How does the change from B_2H_6 to BCl_3 take place? What are the intermediary products? Do substitution products like B_2H_5Cl and $B_2H_4Cl_2$ form, or are the substitution products like $BHCl_2$?"[79]

In order to assure the presence of intermediate products resulting from partial chlorination, Stock, Kuss and Priess used an excess of diborane. Since chlorine's explosive reaction with diborane could be moderated by lowering the temperature, they also tried to slow down the reaction by submitting the reactants and the resulting fractions in the high-vacuum apparatus to the lowest possible temperature. However, the results were far from those expected: "The results were curious, and at first difficult to understand. Even with only one-third as much chlorine as the amount theoretically

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[77] The names Kuss and Priess are here presented in their English versions, following the way they were presented in Stock's book. The original German names, as they were presented in the authors' original article, were Kuß and Prieß.

[78] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 115.

[79] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 115.

required for complete chlorination, BCl_3 was the predominant product of chlorination. Most of the B_2H_6 was recovered as such."[80]

Although Stock and his co-workers, through vapour pressure measurements, were able to establish the transitory presence of the intermediate chlorination products and their subsequent rearrangement into boron hydrides and BCl_3, they were not able to isolate in pure state even the most stable of the partially chlorinated products, the spontaneously combustible gas B_2H_5Cl, which immediately dissociated into B_2H_6 and BCl_3. Even so, they were able to prove that all the intermediate chlorination products were di-boron compounds, like $B_2H_3Cl_3$.

By using bromine instead of chlorine, Stock, Kuss and Priess obtained a much slower reaction with diborane even at room temperature, making possible the isolation and characterization of the compound B_2H_5Br. Other than that, however, all their remaining observations and conclusions were pretty much similar to those resulting from diborane's chlorination:

> The course of the reaction was similar to that of the chlorination, but in this case the resulting monohalide B_2H_5Br could be isolated and investigated. For the rest, there were always formed a large amount of BBr_3, in spite of the presence of excess B_2H_6. The intermediate bromination products also were the B_2-compounds $B_2H_4Br_2$, $B_2H_3Br_3$, and so on, which rapidly dissociated into BBr_3 on the one hand, and into B_2H_5Br and B_2H_6 on the other. None of our observations indicated the presence of $BHBr_2$ or BH_2Br. It was evident that the more highly brominated compounds, like B_2HBr_5, are particularly unstable.[81]

Stock, Kuss and Priess also prepared B_2H_5Br "by warming B_2H_6 at 100º C with about one-third of the theoretical amount of bromine gas required for complete bromination, until the color of the bromine had just disappeared". However, they were not better succeeded in achieving the desired stability for B_2H_5Br, let alone for the other bromination products of diborane:

> Even at room temperature B_2H_5Br dissociates so rapidly that after a few minutes the originally pure gas shows the presence of B_2H_6. After standing for 4 days, 75 per cent of the original quantity had broken down according to the equation:

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[80] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 115.

[81] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 117.

$$6\ B_2H_5Br = 2BBr_3 + 5\ B_2H_6$$

> and the amounts of BBr_3 and B_2H_6 found corresponded precisely with this equation.[82]

The halogenation of the hydride $B_{10}H_{14}$ was also studied by Stock, Kuss and Priess, but this proved to be a very difficult investigation because $B_{10}H_{14}$ was very slowly attacked by either chlorine or bromine. In fact, the reaction with chlorine was slow even at 100ºC and rendered no results at all. After a very complex analytical process in the bromination of $B_{10}H_{14}$, the authors were able to isolate a residue whose empirical formula was $B_{10}H_{11.7}Br_{2.3}$ with an average molecular weight of 348 g/mol. This obviously meant that the residue was a mixture of compounds but the authors concluded that, even so, it probably was essentially $B_{10}H_{12}Br_2$.

Nine years later, in 1923, Stock and Kuss came back with a new approach to boron hydrides' halogenation. This was shortly after Stock's group had resumed the publications on boron hydrides in 1921, following the period dedicated to the investigation on silicon hydrides. During this period, in 1917, Stock and Carl Somieski had obtained the halides SiH_3Cl, SiH_3Br, SiH_2Cl_2, Si_2H_5Cl, "and so on"[83]. Stock and Kuss had begun by using direct halogenation, as they had done with B_2H_6 and $B_{10}H_{14}$ in 1914. However, as the reaction of the silane SiH_4 with chlorine and bromine was explosively violent at room temperature, they decided to introduce the halogen through the use of gaseous hydrogen halide, in the presence of aluminium halide as a catalyst, which was found to be necessary even at elevated temperatures. Thus, for example, they were able to obtain the following reactions:

$$SiH_4 + HCl = SiH_3Cl + H_2$$

$$SiH_3Cl + HCl = SiH_2Cl_2 + H_2$$

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[82] A. Stock, *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933). On 118.

[83] Stock and Somieski were not able to isolate the pure form of Si_2H_5Br and were forced to abandon the isolation of Si_2H_5Cl, $Si_2H_4Cl_2$, etc, due to the formation of isomers.

As Stock himself stressed, this was an unknown reaction in organic chemistry, an absence that he was able to explain with "the weaker positive character of carbon as compared with silicon and boron."[84]

So, by using hydrogen halides instead of free halogens, Stock and Somieski had succeeded in controlling the violent evolution of silicon hydride halogenation. This allowed not only the production of a whole series of partially halogenated silicon hydrides, but also the knowledge of some conversion reactions between some of these, as the formation of SiH_3Cl from SiH_4 and SiH_2Cl_2, for example. In fact, the halogenation products of silicon hydrides became an important resource in silicon hydride chemistry and this was explicitly stated by Stock: "The halides of the silanes opened the way to various further reactions and to new classes of substances."[85]

One may speculate, then, that it was only natural for Stock and his group to be looking forward to extend this success to boron chemistry. Their belief in an overall similarity between the two chemistries may have raised a legitimate hope about a new possibility of isolating further halogenated boron hydride compounds, other than B_2H_5Br. This could not only open the way to a whole new class of reactions and compounds, as it did in the silicon hydrides, but also to make a decisive contribution to finally get a better understanding of the halogenation process in the boron hydrides and especially the process leading to the disturbing production of trivalent BCl_3 and BBr_3, a phenomenon without parallel in carbon and silicon chemistries. One may further speculate that the production of partially halogenated silanes, as SiH_2Cl_2 or SiH_3Cl, may have revived the concern for the existence of trivalent partially halogenated boron hydrides, as BH_2Cl or $BHCl_2$, for example. Should their existence be detected, it could throw some light on the problem of the existence, even if only a transitory one, of the hypothetical BH_3.

The results, though, must have been no less than disappointing. After failing to use hydrogen chloride and hydrogen bromide on diborane at room temperature, Stock and Kuss were able to obtain 75% yields by warming equal volumes of B_2H_6 and HBr at 90ºC for two hours. However, and once again, the products were mainly BBr_3 and B_2H_5Br.

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[84] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 114.

[85] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 26.

In 1926 and 1929, Stock and Erich Pohland studied the iodization of diborane and $B_{10}H_{14}$, respectively. The results for diborane showed to be no different from those previously obtained with chlorine and bromine:

> The principal products of the action of iodine upon B_2H_6 were BI_3 and some oily substances that were difficult to work with. On the other hand, B_2H_5I was readily prepared from B_2H_6 and hydrogen iodide, because the reaction took place at 50º without a catalyst.[86]

The extensive description made above of Stock's investigations on the halogenation of the hydrides B_2H_6, $B_{10}H_{14}$ and B_4H_{10} shows very clearly that this was perceived by Stock and his co-workers as a very important research line. This can be ascertained both from the time extension over which the investigations spread (1914-1929) and from the number of hard-working attempts that were made. One must keep in mind that, in those days, boron hydrides could only be used in minute and expensive amounts and that their preparation (which involved extremely low yielded reactions) and subsequent study took an amount of time and work hardly realizable in present days, as almost all the instrumentation had to be hand-made in the laboratory, including all the glass tubes involved in Stock's high-vacuum apparatus. This is to say that no light-headed decisions could be taken on what concerned any investigation on boron hydrides, let alone such a persistent and systematic effort covering such a time span.

What must have begun as a natural move to study the halogenation of the boron hydrides, as an expectable analogue of the halogenated hydrocarbons, soon became a structural puzzle as the results were markedly different from those occurring in halogenation processes in carbon chemistry and, later, in silicon chemistry. The extreme difficulty in isolating higher halogenated boron hydrides and the pervasive presence of trivalent halogenated boron products made extremely difficult any simplistic analogy between boron chemistry on one side and carbon and silicon chemistries on the other. In particular, the investigations raised serious questions on how the tetravalent boron in diborane could lead to trivalent boron in BCl_3 and BBr_3. To Stock's misfortune, his best efforts proved insufficient to clear these questions. On the purely structural side, all that must have resulted from this long series of investigations was a clear perception of how

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[86] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 119.

unexpectedly odd and complex the subject was, when compared to the relatively straightforward halogenated compounds of carbon and silicon hydrides.

2.5.5 - The ammonia compounds of boron hydrides

By dissolving the hydrides of boron in an excess of liquid ammonia, with subsequent distillation of the remaining ammonia, Stock was able to prepare the ammonia addition-compounds of almost all the hydrides of boron he had synthesized[87]. These were solid, colourless compounds that were readily soluble in ammonia and whose whole behaviour, in particular the electrolysis of their solutions in liquid ammonia, showed, according to Stock, that they were ammonium salts.

Thus, in 1925, Stock and Pohland made a tensimetric molecular-weight determination of diborane's ammonia-compound, establishing the $B_2H_6{\cdot}2NH_3$ formula for it. The next year, they further established that this formula was unique, since it did not depend on the excess of ammonia used.

The study of the electrolysis of $B_2H_6{\cdot}2NH_3$ solutions in liquid ammonia, made by Stock in 1931 (with Wiberg, Hans Martini and August Nicklas), showed that this compound was a "rather good conductor", in comparison with the very low conductivity of ammonia. However, its absolute conductivity, when compared with those of aqueous solutions salts, was low. This led Stock to conclude that the ammonia-compound of diborane, in agreement with its chemical behaviour, was definitely a salt with a low degree of dissociation according to the equation

$$B_2H_6{\cdot}2NH_3 \leftrightarrow B_2H_4^{2-} + 2NH_4^{+}$$

This low degree of association had already been put forward by Stock and Pohland's in 1925, as a result of their tensimetric molecular-weight determination for $B_2H_6{\cdot}2NH_3$. Accordingly, Stock stated that $B_2H_6{\cdot}2NH_3$ was "better written $B_2H_4{\cdot}2NH_4$", establishing a dibasic acidity for diborane.

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[87] Stock did not study the hexaboranes B_6H_{10} and B_6H_{12}? from this point of view.

Stock's interpretation of the electrolysis process of $B_2H_6{\cdot}2NH_3$ solutions in liquid ammonia clearly included some structural assumptions for the explanation of its reaction mechanism and would play an important role in the structural debate over diborane. For this reason, a detailed account of it will be given here.

The description made by Stock of the empirical data resulting from the electrolysis of $B_2H_6{\cdot}2NH_3$ solutions in liquid ammonia sounds somewhat limited:

> A large quantity of gas developed at the cathode at the beginning of the electrolysis, but later decreased in volume, while the volume of gas produced at the anode increased slightly over its original small amount. At the very beginning the gas was largely hydrogen and contained little nitrogen; in the last part of the experiment, however, the gas was a mixture containing between 20 and 25 per cent of nitrogen.[88]

Even so, Stock felt confident enough to state: "The experimental data gives a clear picture of the mechanism of the electrolysis of $B_2H_6{\cdot}2NH_3$."[89] He sustained his claim in a postulated multi-reaction mechanism that allegedly would provide for straightforward explanation of such data.

According to that postulated reaction-mechanism, the anion $B_2H_4^{2-}$ (resultant from the dissociation process $B_2H_6{\cdot}2NH_3 \leftrightarrow B_2H_4^{2-} + 2NH_4^{+}$) could go through two different processes:

1) In the first one, designated by Stock as a "substitution reaction"[90], the anion would take ammonia to form amino-substituted B_2H_6:

$$B_2H_4^{2-} + NH_3 = B_2H_5(NH_2)$$

This would be a compound with an acid character, forming the salt $B_2H_3(NH_2){\cdot}2NH_4$, which by subsequent electrolysis would proceed to further amination:

$$B_2H_3(NH_2) + NH_3 = B_2H_4(NH_2)_2$$

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[88] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 129.

[89] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 129.

[90] Quotation marks in the original by Stock.

At the cathode, other “substitution reactions” would proceed according to the equations

$$B_2H_4{\cdot}2NH_4 + NH_3 = B_2H_3(NH_2){\cdot}2NH_4 + H_2$$

and

$$B_2H_3(NH_2){\cdot}2NH_4 + NH_3 = B_2H_2(NH_2)_2{\cdot}2NH_4 + H_2$$

implying the release of one mole of H_2 for every mole of NH_2 taken on.

2) The second process, designated by Stock as a “re-forming reaction”, represented the recovery of diborane molecules by reaction of the anion with ammonia, with the release of nitrogen:

$$3B_2H_4^{2-} + 2NH_3 = 3B_2H_6 + N_2$$

Summing up with the equation that described ammonium ion’s break up at the cathode,

$$2NH_4^{+} = 2NH_3 + H_2$$

Stock was able to get the overall equation for the re-forming process:

$$3B_2H_4{\cdot}2NH_4 + 2NH_3 = 3B_2H_4{\cdot}2NH_4 + N_2 + 3H_2$$

According to this equation, the released hydrogen and nitrogen during this particular process were in the ration of 3 to 1. This same ratio would still stand in the re-forming process that could also take place in the aminated anions:

$$3B_2H_3(NH_2) + 2NH_3 = 3B_2H_5(NH_2) + N_2$$

which, after summation, would render the overall equation

$$3B_2H_3(NH_2){\cdot}2NH_4 + 2NH_3 = 3B_2H_3(NH_2){\cdot}2NH_4 + N_2 + 3H_2$$

Because B_2H_6 or its amine derivatives were constantly being re-formed, the whole process amounted to the electrolysis of ammonia, with the liberation of nitrogen and hydrogen. According to Stock, there was nothing surprising in this process, since it was analogous to the electrolysis of an aqueous solution of sulphuric acid, which likewise amounted to the electrolysis of water and was used as such in lecture experiments.

The deduced proportions for the releasing of H_2 and N_2 in the re-formation reaction could explain in a straightforward way the observed proportions in the amounts of these gases. Stock justified the discrepancy between the observed and the predicted proportion of N_2 (20 to 25% instead of 33%) with a lag in the substitution reaction, which occurred in the beginning of the electrolysis and released only H_2, giving rise to a slight excess of H_2 during the re-formation reaction.

Stock also argued for additional legitimacy to his postulated process invoking the recent work (1931) of Goldschmidt and Nagel on the electrolysis of solutions of phenols in anhydrous ammonia. These authors had reported similar re-formation reactions and the same 3 to 1 ratio in released H_2 and N_2.

The electrolysis of the ammonia compounds of B_4H_{10} and $B_{10}H_{14}$ had already been studied by Stock, Wiberg and Martini in 1930 and by Stock and Pohland in 1929, respectively. In his book, written in 1932, Stock makes a reference to these studies, but also to some (until then) unpublished results, to state that the results for these compounds were consistent with those obtained for diborane. Thus, according to Stock, the ammonia compounds of B_4H_{10}, $B_4H_{10}{\cdot}4NH_3$, should be regarded as the ammonium salt $B_4H_6{\cdot}4NH_4$. Likewise, the ammonia compound of $B_{10}H_{14}$, $B_{10}H_{14}{\cdot}6NH_3$, was better written as the salt $B_{10}H_8{\cdot}6NH_4$. Consequently, $B_{10}H_{14}$ and B_4H_{10} also behaved like acids.

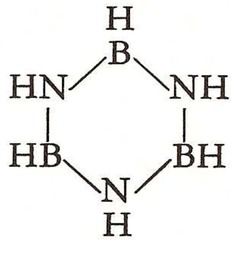
The investigations on the ammonia compounds of the pentaboranes led Stock to conclude for a structural similarity between them, because they formed the same ammonia compound. The reaction of B_5H_9 with ammonia was studied by Stock and Wolfhart Siecke in 1924 and by Stock and Pohland in 1929. According to Stock, these investigations established $B_5H_9{\cdot}4NH_3$ as the ammonia addition-compound of B_5H_9 and its salt-like nature. The reaction of B_5H_{11} with ammonia was studied by Stock and Pohland in 1926. This reaction was more complex and was not stoichiometric. Stock attributed it to the existence of side reactions and became convinced that $B_5H_9{\cdot}4NH_3$ was the principal product. Stock further argued that the reaction of the ammonia compound of B_5H_9 with hydrogen chloride was in agreement with this interpretation.

Stock also investigated the ammonia addition-product of boron methyl, $B(CH_3)_3{\cdot}NH_3$, which had been described by Frankland, to be able to compare it with the ammonia derivatives of the boron hydrides, such as $B_2H_6{\cdot}2NH_3$. This investigation may be related to the investigation on the alkyls of boron. Stock concluded that these two compounds were of a different nature, because $B(CH_3)_3{\cdot}NH_3$ could not be regarded as a salt, due to the much lower conductivity of its solution in liquid ammonia, when compared to the corresponding solutions of the ammonia compounds of the boron hydrides.

$B_3N_3H_6$

$B_3N_3H_6$ was first isolated and studied by Stock and Pohland in 1926. It could be formed by heating the ammonia compounds of B_2H_6, B_4H_{10}, B_5H_9 and B_5H_{11} at 200 ºC for several hours. Stock describes it as a "colourless, mobile liquid that crystallizes readily at low temperatures, forming beautiful, optically uniaxial, rectangular tablets."[91]

$B_3N_3H_6$ is much more stable than all the other hydrides of boron. After enduring 400 ºC for half an hour, as much as 91% remains unchanged. This high stability led Stock to make a careful study of its constitution. Already in 1926, Stock and Pohland became convinced that it had a benzene-like ring structure of alternate BH and NH groups, "in contrast to the probable chain linkage of the hydrides of boron"[92].



Stock's structure for the compound $B_3N_3H_6$

According to Stock, this formula was in agreement with all their experimental observations: its symmetry and being free from B-B linkages, "which all previous

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[91] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 94.

[92] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 97.

experience has shown to be unstable"[93], explained its great stability. Also, its B-N linkages were corroborated by the fact that borimide ($B_2(NH)_3$)[94], which had such linkages, was formed when $B_3N_3H_6$ was heated with excess ammonia. Its behaviour towards water and hydrogen chloride and its thermal dissociation was clearly related to its threefold symmetry. Its molecular weight was also in agreement with Stock's benzene-like structure for the compound.

A very important feature in the study of $B_3N_3H_6$ was the use of contemporary physical methods to get corroboration for all these claims. Thus, H. Mark used X-ray diffraction but his results were inconclusive. However, in 1931, Raimund Wierl applied his electron-diffraction method to the compound, and concluded for a pronounced similarity between benzene and $B_3N_3H_6$, confirming Stock and Pohland's ideas: "A ring formula for $B_3N_3H_6$ may therefore be assumed with a degree of probability approaching certainty-the first case for a single inorganic molecule."[95]

2.6 - Alfred Stock and the structural and theoretical problems in the hydrides of boron

When analysing Stock's thinking on the structural and theoretical questions raised by the hydrides of boron one has to consider three different categories: structure, theory and chemical behaviour. Because Stock, despite his best efforts, had not been successful at establishing structures for the boranes, and because these compounds had managed to keep defying all the theoretical accounts on the nature of their bonds, these levels showed very little integration and were the object of surprising interconnections. Instead of the linear and unidirectional chain of relations that Stock had pursued, that is, to get enough information on the chemical behaviour of the boranes to be able to infer their structures and then to try to explain the nature of their bonds, Stock's failure at getting unequivocal chemical information left him with nothing more than a reluctant

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[93] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 129.

[94] Borimide had been discovered by Stock and Blix in 1901.

[95] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 98.

acknowledgement of the empirical adequacy of what he seems to have thought to be a suspicious explanation put forward by his student Wiberg. He then chose to postpone any conclusion on the structure of the boranes and, consequently, on the nature of their chemical bonds. Since Stock's dilemma was restricted to a choice between his old hint for an alkane-like structure and the alkene-like structures that were increasingly backed up by his investigations on the reactions of the boranes with alkali metal amalgams and on their ammonia compounds, which were advocated by Wiberg's theory, Stock was able to restrict his doubts to open-chain or ring structures entirely analogous to those of carbon chemistry. In this restriction of his dilemma one can find the powerful operative action of his belief in an essential analogy between boron and carbon chemistries, which he was able to force upon his interpretation of the meaning of his own empirical work, despite his acknowledgement of essential differences between boron chemistry and those of carbon and silicon.

2.6.1 - Structure

The structure of the hydrides of boron was an essential problem throughout Stock's work. Besides being directly perceptible from his investigations, this was explicitly expressed by Stock in his book on numerous occasions. In fact, it was the driving force behind virtually all of Stock's investigations:

> It was the further objective to secure, with the aid of these hydrides and by simple, quantitatively controllable reactions, material with which to study structural considerations. Such reactions were: heating, treating with water, with halogens, hydrogen halides, ammonia, sodium amalgam, sodium hydroxide, and the like; they yielded a number of interesting, and often very curious observations. It was often difficult to keep our eyes on the true objective, and to resist being led too far along tempting side-paths.[96]

One may even say that the structural problem was instrumental in Stock's work, in the sense that it was used as a criterion to choose among research lines. For example, when referring to the liquid boron hydrides of low volatility, Stock declared: "So far these

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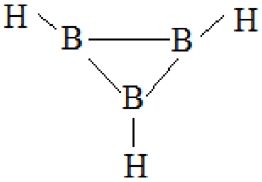
[96] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 17.

substances have not been investigated, because the amount of material was too small and because there was no way to isolate them in homogeneous form; furthermore, the simpler hydrides are of greater theoretical interest."[97]

This was far from being an isolated case. A similar declaration, for example, was made by Stock on the "hypoborates" and the "boron sub-oxides": "A systematic study of this portion of the chemistry of boron has not so far been undertaken, because it seemed to offer a less direct solution to problems involving the constitution of the boron compounds, than does the investigation of the volatile compounds of known molecular weight."[98]

The evolution of Stock's thinking on the structural problem may be followed in his successive suggestions for the nomenclature of the hydrides of boron. Here, one can witness Stock's own struggle to interpret his new hydrides of boron against the contemporary scenario of rapidly changing structure and bonding concepts, heavily derived from carbon chemistry.

Before Stock's investigations, boron, because of its position in the periodic table and the composition of its most widely known compounds, had been regarded as a trivalent element. Plain evidence for this can be found in the mistaken accounts of the boron hydrides' formulas given by "pre-Stock" authors: the BH_3 formula by Sabatier, by Jones and Taylor and by Ramsay and Hatfield; and the B_3H_3 formula by Ramsay and Hatfield, who went as far as assuming the existence of both forms of B_3H_3 consistent with trivalent boron – the open structure $H_2B\text{-}B\text{=}BH$ and the ring structure



Additional structures consistent with trivalent boron could be given by the open chain compounds B_2H_4, B_3H_5, etc, in materialization of the general formula B_nH_{n+2}, consistent with the valence concepts that were current before the introduction of electron theory,

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[97] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 86.

[98] A. Stock, *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933). On141.

and which represented the trivalent analogues of the alkane structures of tetravalent carbon.

There were three distinct moments in Stock's nomenclature suggestions, which testify how Stock became successively more cautious and gradually departed from carbon chemistry nomenclature to his final adoption of an independent phenomenological nomenclature for boron chemistry.

In a first moment, in 1916, close to the very beginning of his investigations, Stock leaned on carbon chemistry in a straightforward way, suggesting the terms monoborane for BH_4, diborane for B_2H_6 and so on. The inclusion of BH_4 means that, at this time, Stock was convinced of the inexistence of BH_3. This must have resulted both from Stock's early dismissal of Ramsay's results and from the fact that, until then, all the hydrides that had been positively identified were consistent with such a direct analogy with the hydrides of carbon. The inclusion of the undetected BH_4 compound as the keystone for this nomenclature scheme may also be justified by Stock's investigations on the silicon hydrides In fact, in 1916, the only hydrides of silicon known to Stock were silane (SiH_4), which had been discovered by Wöhler and Buff, Si_2H_6, which had been first obtained in an impure form by Moissan in 1902, and the higher hydrides Si_3H_8 and Si_4H_{10}, discovered by Stock himself[99]. Consequently, the correspondence with the analogue saturated carbon hydrides was only natural: "All the [silicon] hydrides obviously correspond to the saturated hydrocarbons. No "unsaturated" silicon hydrides were formed; in fact, none are as yet known in low- molecular form."[100]

In the silicon hydride's case, Stock's nomenclature would prove to be an effective and lasting one, able to treat many future silicon compounds, such as $SiH_2(OH)_2$ or $Si(C_2H_5)_4$, as simple substitution compounds, just as in carbon chemistry. These ideas would be reiterated by Stock in his book, in 1933:

> As to nomenclature, it is appropriate to follow the usage of organic chemistry and to call the "saturated" hydrides SiH_4 monosilane, Si_2H_6 disilane, and so forth, to consider the other compounds as substitution products of the silanes, and to name them accordingly.[101]

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[99] Later on, Stock would also discover the hydrides Si_5H_{12} and Si_6H_{14}.

[100] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 21.

[101] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 20.

Stock's nomenclature proposal for the silicon and boron hydrides in 1916 is to be understood as an attempt of supplying silicon and boron chemistries with a nomenclature as flexible and expandable as that of carbon chemistry. Such a heavy reliance on carbon chemistry was justified by Stock's belief that boron, as silicon and carbon, was tetravalent towards hydrogen.

Stock's nomenclatures for the silicon and boron hydrides were also an evident attempt of unification of the carbon, silicon and boron chemistries. Of course, this could only be at the expense of believing in an unsaturated nature for the $B_{10}H_{14}$ compound and in a future discovery of the "monoborane" BH_4. Naturally, Stock actively searched for monoborane and also for triborane, which was also missing to fill the gap between B_2H_6 and B_4H_{10} and would be no more than the expectable analogue of C_3H_8 and Si_3H_8.

Despite his best efforts, Stock failed at detecting their existence:

> The simplest borane that we found is diborane, B_2H_6, and the next simpler is B_4H_{10}. In all our work we have constantly given the greatest attention to the question as to whether monoborane and triborane also exist.[...]
>
> We have sought for such a compound numberless times: in the crude gas when preparing the many boron hydrides; in the manifold reactions observed when passing electric discharges between boride electrodes in an atmosphere of hydrogen; during the action of silent discharges upon mixtures of hydrogen and boron chloride; and especially in those reactions where B_2H_6 is formed from higher boron hydrides by the reduction action of nascent hydrogen. Never have we found the least trace of monoborane. This forces us to the conclusion that monoborane cannot be prepared in identifiable amounts.[102]

Elsewhere, Stock would stress his conclusions in even more definitive terms:

> The simplest hydride of boron is B_2H_6. We have never found a hydride whose molecule has but a single atom of boron, nor have we found one having three boron atoms; even *traces* of a monoborane could not have escaped notice under the sensitivity of our methods. It may be taken as quite certain that such a hydride does not exist in tangible form.[103]

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[102] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 91.

[103] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 17.

Based on his investigations, Stock also dismissed the existence of an isomeric form of B_4H_{10}. Stock's concern about two isomeric forms of B_4H_{10} is easily explained by his belief in an analogy between the boron and carbon chemistries, since two isomeric forms of C_4H_{10} were already known. In fact, this concern was also extended to Si_4H_{10}: "The compound Si_4H_{10} was homogeneous; theoretically two isomers are to be expected, as in the case of C_4H_{10}."[104]

An important feature in Stock's dismissal of the possibility of isolation of monoborane, is that it was grounded in an estimate of the boiling point of this (until then) hypothetical compound made from a comparison of the volatility of CH_4 (boiling point -161º) with those of C_2H_6 (boiling point -89º) and B_2H_6 (boiling point -92.5º). According to Stock, this "leaves no doubt that monoborane must have a volatility similar to that of methane and that – like the latter – must have an appreciable vapor pressure at the temperature of liquid air."[105] Stock proceeded according to this reasoning to plan and interpret the empirical procedure from which he derived his negative conclusions on the isolation of monoborane:

> Condensation of B_2H_6 is practically complete at the temperature of liquid air. In the vacuum-apparatus even a fraction of a cubic millimeter of monoborane could not fail to be observed; it would have to remain uncondensed when cooled with liquid air; and it would be recognized as a borane when its boron was removed by an electric spark, or by the green coloration imparted by its boron to a flame.[106]

Thus, Stock argumentation was entirely derived from his assumption that, because ethane and diborane had similar boiling points, the hypothetical BH_4 would likewise have a boiling point similar to that of methane. Since methane would not condense at liquid air temperature, neither would monoborane. The failure to detect the gas phase of this hypothetical compound in the condensation of diborane automatically implied its inexistence in isolated form.

Notice must be made that this is a clear example in which the assumption of an analogy between diborane and ethane became instrumental to the very planning and interpretation of Stock's investigations.

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[104] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 21.

[105] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 91.

[106] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 91.

In 1926, Stock made his second nomenclature suggestion. This time he was facing a much more complex scenario. After the advent of Lewis' electron pair bond, in 1916, the boron hydrides had become "electron deficient": diborane, for example, had a total of only 12 valence electrons to secure a minimum of 7 bonds, as those in an ethane-like structure. This meant that bonding within the hydrides could not possibly be explained by straightforward resource to Lewis' theory, based on the sharing of a pair of outer-shell electrons. This, of course, had serious implications both to Stock's previous view of boron as a tetravalent element towards hydrogen and to Lewis' theory itself.

In 1922, Stock had already dismissed the generality of Lewis theory, so what really dictated the death of Stock's simple analogy between tetravalent boron and carbon chemistry was his recent discovery of the penta- and hexaboranes B_5H_9, B_5H_{11} and B_6H_{10}. [107]

In 1925, Mark and Pohland (one of Stock's co-workers) had published their work on the X-ray diffraction analysis of crystalline ethane, diborane and disilane. The authors had concluded for an effective similarity between ethane and diborane and a marked difference with disilane. This similarity between diborane and ethane had also been corroborated by infra-red absorption studies conducted by Gerda Laski in 1919[108]. Based on these results, Stock kept the tetravalency of diborane's boron atoms. However, the new penta and hexaboranes forced Stock to accept also the trivalency of boron towards hydrogen. Stock refers that boron already presented a trivalent behaviour in some of its compounds, such as BF_3 or $B(CH_3)_3$, and that carbon itself also presented this ambivalent behaviour: in CH_4 or C_2H_6 it was tetravalent; in $C(C_6H_5)_3$ it was trivalent. The difference was that in carbon chemistry, trivalency had the minor role and in boron chemistry it was the other way around.

Thus, Stock was forced to admit the following structural formulas, which were only suggestions rather than definitive statements (the asterisk indicates tetravalent boron atoms):

B_2H_6: $H_3B^*.B^*H_3$

B_4H_{10}: $H_3B^*.B^*H_2.B^*H_2.B^*H_3$

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[107] Stock's position on the chemical bond theory will be referred ahead.

[108] These studies will be more fully discussed in a subsequent chapter.

B_5H_9: $H_3B^*.BH.BH.BH.B^*H_3$

B_5H_{11}: $H_3B^*.B^*H_2.BH.B^*H_2B^*H_3$

B_6H_{10}: $H_3B^*.BH.BH.BH.BH.B^*H_3$

$B_{10}H_{14}$: $H_3B^*[BH]_8.B^*H_3$

This departure from hydrocarbon structures was naturally reflected in Stock's second suggestion for the hydrides' nomenclature. Having been unable to detect monoborane and confronted with the odd formulas of the penta- and hexaboranes, Stock decided to base his new scheme on a trivalent family of as yet undetected existence, which would follow the rule B_nH_{n+2}: B_2H_4, B_3H_5, $B_{10}H_{12}$, etc. These would be called "diborane", "triborane", "dekaborane", and so on. Apparently, at this time, Stock had not dismissed the existence of triborane yet.

The already detected hydrides would be called hydroboranes, because they were richer in hydrogen. These were further divided in two subclasses:

- Dihydroboranes (two extra hydrogen atoms): B_2H_6 (dihydro diborane), B_5H_9 (dihydro pentaborane), etc

- Tetrahydroboranes (four extra hydrogen atoms): B_5H_6 (tetrahydro pentaborane), etc

The investigation on boron alkyls, in 1921, may, perhaps, be inserted in this context. Forced to accept the trivalency of boron towards hydrogen, Stock probably used his previous negative conclusion on what concerned an eventual dimerization of boron alkyls to draw a similar conclusion on the eventual dimerization of BH_3 into B_2H_6, this way dismissing even an eventual transitory existence of BH_3. Whatever Stock's reasoning was, the fact is that BH_3 is not present in the above trivalent family he used to base his nomenclature suggestion in 1926.

By 1932, however, Stock made his third suggestion for the nomenclature of the hydrides. This time, Stock stopped building his nomenclature schemes on non-existent hydrides such as B_2H_4, B_3H_5, etc. “It seems more appropriate to follow this scheme than to base the nomenclature on hydrides that do not actually exist.”[109]

Besides not having been successful at detecting them, this was, most probably, also a consequence of his investigations on the hydrides’ ammonia, halogen and sodium compounds. These studies indicated a clear departure from a simple analogy with carbon chemistry, and this may have led Stock to adopt a more cautious attitude and put forward a purely phenomenological nomenclature, with no structural assumptions.

Stock divided the empirical formulas of his hydrides into two main groups with distinct general empirical formulas and whose physical and chemical characterization did match such a separation. Thus, this was no arbitrary scheme but rather a purely phenomenological one:

$\mathbf{B_nH_{n+4}}$: B_2H_6, B_5H_9, B_6H_{10}, $B_{10}H_{14}$

$\mathbf{B_nH_{n+6}}$: B_4H_{10}, B_5H_{11}[110]

These groups corresponded to the dihydro and the tetrahydro borane groups that Stock had suggested in 1926. At that time, Stock had already called attention for the differences in the properties of these two groups.

On these groundings, Stock put forward a recommendation for the adoption of a nomenclature based upon the B_nH_{n+4} series, “the normal hydrides” with more stable behaviour, which were to be called “boranes”. Accordingly, the elements of this group were to be designated by diborane, pentaborane, hexaborane and dekaborane, respectively. The other group elements, less stable hydrides because of their higher hydrogen content, should be called “hydroboranes”. In particular, B_4H_{10} and B_5H_{11} should be called dihydrotetraborane and dihydropentaborane, respectively.

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[109] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 18.

[110] Stock did not include B_6H_{12} in this group because its formula had not been definitely established at the time he wrote his book.

2.6.2 - Theory

Until 1916, the hydrides already known (B_4H_{10}, B_2H_6 and $B_{10}H_{14}$) were remarkable for their unexpected non trivalent structures, in particular for the non-detection of BH_3, and for the apparent tetravalency of boron toward hydrogen. However, after the advent of Lewis' ideas on the chemical bond, the hydrides, in addition to being structurally remarkable, also revealed "electron deficiency". To Stock, it was obvious that a straightforward application of Lewis' ideas to the hydrides would not be possible:

> The electronic formulation of the structure of the boron hydrides encounters a number of difficulties. The ordinary concepts of valence will not suffice to explain their structure; this is shown by the fact that in the simplest hydride, diborane B_2H_6, which has 2×3 + 6 = 12 electrons, as many bonds must be explained as are required for C_2H_6 which has two more (2×4 + 6 = 14) electrons available. Thus it is that any structural theory for these compounds requires new hypotheses.[111]

As will bee seen in the next chapter, many efforts were made to articulate contemporary ideas on the nature of the chemical bond in order to accommodate the hydrides odd case. Stock's position on the explanation of the chemical bond in the hydrides was of a very different nature. A preliminary discussion imposes itself at this moment, though. This is about Wiberg's account on Stock's attitude towards theoretical discussions:

> And so in 1937 Stock was able to look back contentedly over a quarter of a century of successful research in the area of boron hydride chemistry, and close this chapter of his experimental activities with the feeling that all the necessary foundations had been laid for a theoretical rationalization of this group of compounds, the boron hydrides, which were so puzzling from a valence point of view. As a dedicated preparative chemist he engaged himself very little in the theoretical evaluation of the accumulated factual material. His preference was here, as in other cases, for the discovery of new compounds and the exploration of unknown reactions. The theoretical evaluation was for him a "cura posterior", which he willingly left to other people. For he did not in general think highly of speculative considerations and theoretical explanations.[112]

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[111] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 154.

[112] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 697.

The danger here is taking the last sentence out of its true context, the boron hydrides research, in which case Wiberg's description may lead to a totally wrong perception of Stock as essentially an empiricist with little or none theoretical concerns. There is good evidence against it. At his inaugural lecture at Cornell University, as the George Fischer Baker Non-Resident Lecture in Chemistry for the year 1932, entitled "The Present State of the Natural Sciences"[113], Stock proves to have a very well informed personal view on the main contemporary sciences. His lecture covers the contemporary state of a wide range of exact sciences, such as mathematics, physics (Stock briefly discusses quantum theory and relativity), chemistry, astronomy, mineralogy and biology (heredity and biochemistry) but also technology, philosophy and sociology. He further discusses their inter-relations and their application to the benefit of man kind, putting forward his own personal view on an ultimate historical process of positivist amalgamation of all these sciences. In particular, he considers the creation of quantum theory "probably the greatest accomplishment in natural science since the days of Copernicus and Newton". Stock's own words do convey an image of someone deeply concerned with the most significant scientific ideas of his time. The conciliation with Wiberg's description comes at once if we limit its validity to the strict domain of the investigation on the hydrides of boron. Hence, what Wiberg most certainly wanted to say was that Stock did not think much of the existent theoretical speculations on the hydrides' structures and that he preferred to continue to gather empirical information to hasten to solve the problem by providing a secure empirical foundation on which a theoretical structural solution could rest. There is plenty of evidence that this was so.

Stock's opinion on the consequences of the hydrides of boron to the theory of the chemical bond was expressed in 1922.[114] Rather than trying to accommodate the hydrides of boron by more or less forced articulation of contemporary ideas, Stock simply denied these ideas' applicability to his hydrides. He argued that the hydrides of boron demonstrated the insufficiency of chemical bond conceptions that had been derived from Organic Chemistry. According to Stock, because of carbon's properties, chemists had been led to believe in a simplicity that did not really exist for other

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[113] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 1. Also as A. Stock, "The present state of the natural sciences", *Science*, 75 (1932). On 345.

[114] A. Stock, "Der Kohlenstoff und seine Nachbarn im periodischen System", *Z. angew. Chem*, 35 (1922). On 341.

elements. The hydrides of boron were to play an important role in the development of chemist's conceptions of chemical bond, affinity and valence.

This can explain Stock's initial attitude towards Wiberg's own model:

> I still have vivid memories of the occasion when, as a young assistant, I showed Stock the reprint of one of my publications on the structure of boron hydrides, in which I proposed that a pair of electrons could bind more than two atoms and that the boron-chlorine bond in boron chloride was stronger than a single bond. He looked at me with a generous forgiving smile; because ideas such as "multicentre bonding" and "back –donation" had at that time, roughly half a century ago, not yet been conceived.[115]

Wiberg's theory[116] pictured diborane as an ethylene-like anion $B_2H_4^{2-}$ to which the remaining two hydrogen ions H^+ would be loosely linked. One can speculate that such a theory must have sounded to Stock a pretty much forced arrangement of a double covalent link between the two boron atoms and some kind of strange electrostatic bond between the positively charged hydrogen ions and the negatively charged ethylene-like core.

Stock's second nomenclature suggestion, in 1926, can be seen as an expression of his opinions on the chemical bond problem in the hydrides of boron. Obviously, his structure suggestions were not according to Lewis theory, but the fact is that, whatever the structure, that would never happen. Thus, Stock most naturally privileged the structure problem over the chemical bond nature problem. Solving the first was a necessary condition to solve the second. Accordingly, he focused on getting empirical evidence that would help to solve the puzzle. Hence Wiberg's words.

However, the investigations on sodium and ammonium compounds of the hydrides of boron gave important empirical support to Wiberg's theory[117] and Stock was forced to acknowledge it. He did so explicitly in his book on more than one occasion and this may have been wrongly mistaken for an explicit support to Wiberg's theory. Indeed, in his review of Stock's book, Lowry said:

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[115] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", _Pure & Appl. Chem._, 49 (1977). On 697.

[116] Wiberg's theory will be more fully addressed in the next chapter.

[117] This will be discussed in the next chapter.

> The author himself [Stock] adopts a different procedure, since he assumes with Christiansen (1927) that diborane, B_2H_6, corresponds in structure and properties with ethylene, C_2H_4, rather than with ethane, C_2H_6, and accepts the formula which Wiburg[118] in 1927 proposed on these lines.[119]

This was an entirely abusive interpretation of Stock's words. All that Stock did in his book was to acknowledge all the experimental evidence that was in accordance with Wiberg's ideas. At this point, it should be mentioned that, by 1932, Mark and Pohland's claim for a structural similarity between the crystalline forms of diborane and ethane was being counter-balanced by some unpublished ultra-violet absorption studies that, according to Stock, had been obtained by Hausser, of the Kaiser Wilhelm Institute in Heidelberg:

> These experiments had not been completed at the time of this writing, but they show very plainly that in this regard B_2H_6 resembles ethylene much more closely than it does ethane.[120]

Therefore, by this time, Stock was facing ambivalence on what concerned the results obtained by contemporary physical methods and consequently the decisive role had to be left for his own investigations.

Even in the chapter of his book dealing with structural problems, Stock is strictly objective and impartial, despite the fact that it had been written with Wiberg's assistance. Although having acknowledged all the evidence in favour of Wiberg's theory, Stock still preferred to continue to investigate. Thus, in 1932, after the advent of Wiberg's theory and after his investigations on the sodium and ammonium compounds of diborane, Stock still wrote in his book: "At Karlsruhe the present objective of our further investigations is the development of the experimental basis for the discussion of the structure of these compounds."[121]

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[118] The correct name would be Wiberg.

[119] T. M. Lowry, "Valence Types and Problems", Nature, 134 (3382) (25 August, 1934). On 269.

[120] Stock, A., *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933), p. 153.

[121] Stock, A., *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933), p. vi.

Also in 1932, Stock explicitly acknowledged the empirical adequacy of Wiberg's theory in his address to the French Society of Chemistry. Once more, he refused to endorse it, preferring to wait for further empirical evidence:

> On a publié dejá un grand nombre de théories sur la structure des hydrures de bore, surtout dans la littérature anglo-saxonne. [...] Je ne voudrais pas encore me prononcer définitivement à ce sujet: j'attendrai le résultat d'experiences en cours qui ont précisement pour but d'eclaircir les questions de la structure.[...]
> En tout cas il est certain que, dans ses combinations avec l'hydrogène, le bore n'est ni tri- ni pentavalent. En se basant sur la théorie électronique, mon collaborateur Wiberg a établi une théorie qui semble expliquer d'une manière satisfaisante les données expérimentales et d'aprés laquelle le bore serait au fond pentavalent mais aurait une coordinance maximum égale à quatre, d'où il résulterait qu'un atome de bore ne peut fixer plus de quatre autres atomes ou groupes d'atomes.
> Toutefois, comme nous l'avons mentionné précédemment, le dernier mot n'a pas encore été dit à ce sujet.[122]

This was so because in 1932, although in a somewhat less assertive way, Stock was still holding to the convictions he had conveyed in his paper in 1922:

> The problem of the structure of the boranes needs still further clarification and experimental confirmation. Our present-day general knowledge regarding the nature of chemical bonds is still deficient, hence all hypotheses can not be more than tentative. In the expected future broadening of this knowledge the chemistry of boron will probably play a very important part, for it is evident that valence phenomena in this field are less simple than those of carbon chemistry.[123]

Stock hoped that, by condensing all his work on boron hydrides up to 1932 in the form of an easily accessible book, he could further contribute to make chemists realize the importance of the hydrides of boron to chemical bond theory and allow them to contribute in an empirically sustained way to the subject:

> It [Stock's book] may also facilitate the developments of theories concerning the constitution of these interesting compounds, for it is steadily becoming more and

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[122] A. Stock, "La Chimie du Bore", Bull. Soc. Chim. France, 51 (4) (1932). On 711.

[123] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 161.

> more evident that the hydrides of boron may have special significance in the development of our general ideas on valency and chemical linkage.[124]

Stock's last words in his chapter on the structural problem are meaningful. He chose to cite J. D. Main-Smith, and it can be read as both an appeal and a warning to his readers: "These compounds must be regarded as a decisive test of any theory of valency."[125]

2.6.3 - Chemical behaviour

Stock looked at his work on silicon chemistry has having shown its fundamental structural and chemical similarity with carbon chemistry, and was able to justify it with the structural similarities of both elements on the atomic level:

> On comparing the chemistry of silicon and of carbon some similarities are found, particularly in the parallelism between the formulas of the compounds. This fact should cause no surprise, because carbon and silicon, in harmony with their atomic structures and their positions in the periodic system, have the same positive (oxygen) and negative (hydrogen) maximum valence. Both have a valence of 4, and their highest hydrides and oxides are CH_4 and SiH_4, CO_2 and SiO_2. A further point of similarity is that, like carbon, the atoms of silicon can unite in chains.[126]

Boron chemistry, however, was a different case altogether. Unlike silicon chemistry, boron chemistry had not fulfilled Stock's initial expectations of an essential analogy with carbon chemistry, as expressed in his nomenclature suggestions in 1916. Its molecular formulas and chemical behaviour were of a diverse and unexpected nature: "The chemistry of boron has proved unexpectedly rich in results and many-sided in character [...]"[127]

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[124] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On vi.

[125] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 161.

[126] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 36.

[127] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 168.

Since silicon chemistry seemed to be no more than a replication of carbon chemistry, the true object of Stock's attention became boron chemistry. Browsing through Stock's bibliography, one can see that his work on silicon hydrides only covered a ten year period, between 1916 and 1926. Even the period between 1916 and 1921, in which Stock published exclusively on silicon chemistry, was justified with its instrumental use for boron chemistry research. Naturally, this asymmetry, motivated by boron's unexpected chemical behaviour and its theoretical implications, became evident in Stock's book:

> This discussion of the hydrides of silicon is somewhat more condensed than will be the following treatment of our work on boron, because the study of the silicon compounds was not so rich in unforeseen results and seems therefore to be of less importance for general theoretical considerations.[128]

Despite having discovered and acknowledged a remarkable difference between boron and carbon chemistries, Stock was not led to view them as fundamentally distinct entities. Instead, forced to change his initial belief in a direct analogy between these two chemistries, he was able to maintain a fundamental relation between them through the creation of a much more complex chemical entity that involved not only boron and carbon, but also silicon and nitrogen.

He saw his own work as the unveiling of the reality of such entity. Although acknowledging that, in their elemental form, carbon, boron, and silicon were "so striking similar than even older chemistry had been able to include them in a limited group"[129], Stock argued that, until his own work, the chemistries of boron and silicon had been restricted by the dominating affinity of these elements for oxygen, which rendered impossible the manifestation of their rich chemical possibilities outside strictly controlled laboratory environment. As for nitrogen, "the similarities in the chemistry of nitrogen and of carbon have long been known"[130].

Having proved the existence of that hidden richness in the chemistries of silicon and boron, Stock was able to build on the electric affinities of the different elements and

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[128] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 20.

[129] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 169.

[130] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 168.

compose his own integrated vision of a gradual chemical continuum unifying all these chemistries, with carbon at its epicentre:

> The chemistry of carbon follows a middle course between that of boron, silicon and nitrogen, as is indicated in the periodic system. Carbon unites in itself the chemical abilities of its neighbors: the manifold reactivity and chain-building powers of boron; the volatile, low-molecular compoundings of nitrogen; the tendency of the compounds of silicon and boron to associate; the power possessed by nitrogen and silicon to form stable molecules containing the positive and negative elements hydrogen and oxygen side by side. These phenomena, only rudimentary in its neighbors, are so extraordinarily developed in carbon that they are the prime reason for the eminent importance of the chemistry of carbon. Corresponding to its central position in the periodic system at an equal distance from the highly positive and highly negative elements, carbon's positive and negative affinities are so perfectly balanced that it has the maximum of symmetry and stability.[131]

The importance of carbon in Stock's chemical thinking was also expressed elsewhere:

> The chemistry of each of these elements [boron and silicon] is in its own way a distorted and simplified image of the chemistry of carbon, that king of the elements in which the chemical abilities of its neighbours are simultaneously magnified and focussed into harmonious unity [...][132]

The "ideal" way to the construction of an understanding of boron chemistry would be to obtain enough "objective" empirical data to discover the structural identity of boron compounds and then to build on it an "understanding" of the nature of the chemical bond in these compounds. This was most probably Stock's own understanding of his activity. As the history of Stock's investigations demonstrates, this would be a totally impossible process, at least in the present case. To begin with, as the hydrides of boron do not exist in nature, the very decision to look for them involved the instrumental use of the analogy with carbon chemistry. So, from the very beginning, carbon chemistry was involved in a fundamental way in Stock's investigations. This was evident in his nomenclature suggestions in 1916. Then, in 1921, he was forced to abandon this simple

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[131] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 169.

[132] Citation in Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", Pure & Appl. Chem., 49 (1977). On 695.

analogy by the discovery of the penta- and hexaboranes. But he kept open-chain "carbon-like" structures for the hydrides of boron in his nomenclature suggestions in 1926. After his investigations on the ammonia compounds, Stock was forced to contemplate another change in the way he saw the hydrides, as it seemed to support Wiberg's ideas. Although recognizing the strong empirical adequacy of Wiberg's theory, Stock always preferred to wait for new evidence. However, when discussing Wiberg's model in his book, he argued: "At the present little may be said regarding the structure of the higher hydrides of boron. The properties of these compounds argue more for chain structures than for ring structures."[133]

And he goes on to present unsaturated open-chain "carbon-like" structures that would be in accordance with Wiberg's theory.

The point here is that carbon-like structures, whether open-chain or ring structures (as in $B_3N_3H_6$), whether saturated or unsaturated, were the real constant in Stock's thinking. It was his justification to associate boron to carbon in his gradual continuum of chemistries involving carbon, boron, silicon and nitrogen – the "chain-building powers of boron". This is the crucial point of Stock's reasoning in which one can see the ruling power of carbon chemistry. In the consulted bibliography, there seems to be no evidence that Stock ever had second thoughts on this crucial aspect of his reasoning.

Of course, one can argue that Stock was much influenced by the results derived from physical methods, namely the x-ray diffraction investigation by Mark and Pohland, the infra-red absorption spectra studies by Gerda Laski and the ultra-violet absorption spectra unpublished results by Hausser. Indeed, Mark and Pohland's work received much attention from Stock in the nomenclature suggestion he gave in 1926. Stock included there a detailed description of their method. And it is also true that Stock, in his discussion of Wiberg's ideas invoked Hausser's conclusions. However, one can also argue that the very interpretation of these studies by Stock was determined by his belief in an analogy with carbon chemistry. In fact, this was the reason why Stock favoured the similarity between diborane and ethane but ignored the contradictory difference observed for disilane, as reported by Mark and Pohland. It must be noticed that the similarity between disilane and ethane had always been considered by Stock as obvious. Thus, the difference between the x-ray diagrams of disilane and those of diborane and ethane, at the very least, had to be interpreted as invalidating any direct inference from

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[133] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 160.

crystallized structures to molecules in the gaseous state. Also, a carefully reading of Stock's words about Hausser's results seems to favour this interpretation: "These experiments had not been completed at the time of this writing, but they show very plainly that in this regard B_2H_6 resembles ethylene much more closely than it does ethane."[134]

The expression "resembles ethylene much more closely than it does ethane" clearly demonstrates an a priori restriction to these two options.

To try to understand why carbon chemistry seemed to be so important in Stock's thinking, the obvious way is taking into account the relative importance of the triumphal contemporary successes of Organic Chemistry and its subsequent domination on a disciplinary level in Germany, to such an extent that Fischer felt the need to fight against it by sending Stock abroad to learn modern inorganic methods. The extent of the impression of the successes of carbon chemistry on Stock is well documented in his work "Der Triumph des Kohlenstoffes", published in 1925[135]. Also, one must keep in mind that Stock began his research career as an organic chemist. His PhD thesis under Piloty, himself an organic chemist, was on organic chemistry themes and he kept publishing on the subject long after he initiated his investigations on boron hydrides. Between 1898 and 1931, Stock published 18 works on carbon compounds. This is only two works less than those he published on the hydrides of silicon. Finally, one must not forget that Stock, as a young boy, became initially interested in science by observing and studying animals and plants. It is not that strange if Stock had a special admiration for carbon's ability to form such an immense wealth of compounds upon which life itself rests.

So, it really comes as no surprise if Stock, just as much as boron in the periodic table, happened to be himself "next to carbon".

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[134] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 169.

[135] A. Stock,"Der Triumph des Kohlenstoffes", *Naturwissenschaften*, 13 (1925). On 1000.

3 - A Perpetual Puzzle

The hydrides of boron defied current ideas on the chemical bond since their discovery was first reported by Stock and Massenez in 1912. At the time, they came to put into question the trivalency that boron exhibited in all its other compounds. In 1916, with the advent of Lewis' electron pair theory to explain covalent bonds and unify the rationale behind the explanation of bond formation in polar and non-polar molecules, the situation got significantly worst, as their electron deficiency could not be dealt with by resourcing to boron's outer shell of electrons. An incredible array of imaginative attempts to solve the situation began then. Peculiar uses of polar bonds, the calling into action of inner shell electrons despite the high energies required for the effect, unexplained or postulated odd interactions between the boron atoms, new bridge structures with no electronic concerns whatsoever or with one-electron bonds, ethane-like configurations with one-electron bonds, pseudo atom structures, were among the many proposals put forward and the list goes on. Most of these suggested formulas were specifically designed for diborane, sacrificing the desired generality for bonding concepts and theories.

Diborane, however, proved to be utterly irreducible. Every time a new structure was put forward, it was at the expense of giving up some important concept or principle: the electron pair; the octet rule; the accepted valence or coordination number for boron or their constancy in boron's link with hydrogen; the idea that only valence electrons could be involved in chemical bonding; the atom-to-atom bond paradigm; the accepted nature for the chemical bond.

These inconsistencies happened at a period of rapid evolution in chemical bond theory, during which chemists struggled to reconcile their own ideas and data on the atomic structure of matter with the fast-emerging atomic theory being developed by physicists. This partly explains the variety of structures that kept being suggested for diborane and, sometimes, for the higher hydrides of boron as well. Another important factor contributing for this situation was the lack of experimental data on the hydrides of boron, notwithstanding Stock's best efforts. That 1914-1921 stop due to WWI and to the investigation on silicon hydrides played here an important role. During the 1920's Stock was still collecting important evidence. In the meantime, the situation allowed creative freedom to researchers. Needless to say, during an important part of this time, the hydrides of boron were far from being the only compounds with which chemists struggled. As time went by, however, bonding theories became increasingly powerful, Stock’s persistence became utterly fruitful, and the hydrides of boron became surprisingly odd. And so they remained until the sixties.

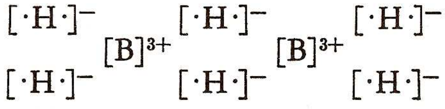
Reviewing all those imaginative suggestions proves how important these compounds became to bond theory. In particular, it clearly shows that the history of the chemical bond cannot be written without taking into account the role played by the hydrides of boron. This is abundantly demonstrated by the obvious concern with these compounds on the part of many of the key contributors to bond theory. In fact, they used systematically the words “puzzling” and “puzzle” to refer to the hydrides of boron:

> [...] the structure of the dimeric B_2H_6 presents a perpetual puzzle, in view of the fact that there are two electrons less than the number which just suffices to provide the single bonds between the atoms in C_2H_6. Much ingenuity has been exercised in deciding which two electrons can be kidnapped with least risk of the loss being detected; but no final conclusion appears to have been reached.[136]

3.1 - “Heteropolar” Structures

Two ionic structures were proposed for diborane, whose obvious common purpose was to account for its structure through the use of widely accepted concepts in bond theory: the polar bond sustained by the electrostatic attraction between opposite charged ions and the tendency of atoms to form closed shell electronic configurations in a chemical interaction.

The first of these suggestions was put forward by Von Arkel and De Boer in 1924, who supposed that in the formation of the diborane molecule each atom assumed the electronic configuration of helium through the capture of the six outer electrons of the two boron atoms by the six hydrogen atoms:[137]



$$\begin{array}{ccccc} [\cdot H\cdot]^- & & [\cdot H\cdot]^- & & [\cdot H\cdot]^- \\ & [B]^{3+} & & [B]^{3+} & \\ [\cdot H\cdot]^- & & [\cdot H\cdot]^- & & [\cdot H\cdot]^- \end{array}$$

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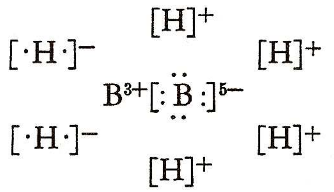
[136] T. M. Lowry, “Valency Types and Problems”, Nature (August 25, 1934). On 269.

[137] Unless otherwise explicitly stated, the illustrations included in this chapter were taken from A. Stock, *Hydrides of Boron and Silicon*, pages 155 to 163.

Ulmann, in 1927, suggested that there were also negative ions in diborane's configuration, according to the following arrangement:

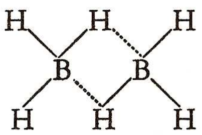


One boron atom assumed the electronic configuration of neon by capturing 5 additional electrons, while the other boron atom surrendered its three valence electrons in order to adopt a helium-like closed shell, which was also assumed by two hydrogen atoms through the capture of one electron each. The four remaining ions in this arrangement were protons.

This type of structures, which implied an ionic nature to diborane and a negative charge for hydrogen were independently refuted by Stock and Müller in 1927, on empirical grounds.

3.2 - *The bridge model*

On 11 November 1921, in an address to the Chemical Society of Erlangen, Walter Dilthey argued that the bimolecular nature of diborane was better accounted for by the following tetrahedral structure, in which boron was considered to be tetravalent:[138]



Dilthey's suggestion was concerned with structure alone. He made no consideration whatsoever on the electronic distribution in his configuration.

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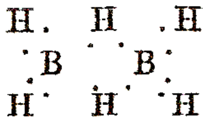
[138] W. Dilthey, "Chemische Gesellschaft Erlangen", Z. angew. Chem., 34 (1921). On 596.

In July 1927, Angus F. Core, of the chemistry department of the University of Manchester, wrote a letter to the editor of the *Journal of the Society of Chemistry and Industry*, suggesting the following structure for diborane:[139]



Core's structure for diborane.

When explaining his idea, Core presented it as being adaptable both to the old and the new quantum mechanics: "The dots in this formula represent, in a necessarily imperfect manner, the electrons revolving in orbits, or certain extended distributions of negative charge which, according to some interpretations of the quantum theory, constitute the electronic configuration."[140]

In this structure, the two inner hydrogen atoms shared one electron with each boron atom, but each of these electrons were under the attraction of both boron atoms. The hydrogen atoms could tentatively be seen as negative ions whose negative charge was greatly deformed in the direction of the boron nuclei.

Core did not make explicit whether the links between the bridging hydrogen atoms and the boron atoms were to be understood as one-electron bonds or three-nucleus bonds.

Core's contribution was triggered by Ulman's 1927 proposal, and seems to have been motivated by a concern with the symmetry of molecular structures. Core argued that there was not sufficient evidence that the intrinsic stability of Ulman's octets would be enough to support such an asymmetrical configuration as $(BH_4)^- (BH_2)^+$. According to Core, Ulman's octets were not necessarily able to attain the stability of the neon and helium elements, because these had greater nuclear charges. Core suggested that Ulman's polarity for diborane could be tested by measurements of the dielectric constant at different temperatures.

Core argued for the plausibility of his configuration on energetic grounds, stating that its energy would be lower than the two uncombined BH_3 molecules, even if its hydrogen existed as undeformed negative ions. Thus, his structure could explain the

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[139] A. F. Core, "Chemical Combination and the Constitution of Boron Hydride", J. Soc. Chem. Ind., 46 (1927), 642 – 643.

[140] A. F. Core, "Chemical Combination and the Constitution of Boron Hydride", J. Soc. Chem. Ind., 46 (1927). On 642.

association into diborane of the BH_3 molecule, whose existence Core seems to take for granted, even if undetected at the time. Moreover, the deformation of the negative hydrogen ions greatly improve the stability of the "double molecule", because more negative charge would be drawn in between the boron nuclei.

Despite having the same basic configuration, Core and Dilthey's structures were entirely distinct from each other. Indeed, Core was concerned with the electron distribution within diborane, but not with its three-dimensional arrangement. As already seen, Dilthey's concern was the other way around. A further major difference was that Core's suggested structure, unlike Dilthey, was not tetravalent. In fact, he argued that his structure allowed dispensing the postulation of tetravalent boron in diborane.

3.3 - Under the Carbon Spell

3.3.1 - The k electrons

In 1922, E. D. Eastman, from the Chemical Laboratory of the University of California, proposed his own account of the double and triple bonding in unsaturated molecules.

Eastman's theory was heavily based on the concepts and ideas published by Lewis in 1916, namely the cubic atom, the octet rule and the shared electron pair. However, Eastman departed from Lewis' ideas in his use of the two inner shell electrons to extend the sharing of a single electron pair to multiple valence bond formation, as opposed to Lewis' sharing of two or three pairs of electrons for higher order bonding:

> Adopting this hypothesis, the picture of the double bond which is now proposed is that of one atom in which the central electrons have been drawn into the outer octet, joined by two electrons to another atom in which the normal arrangement is preserved. In cases of triple bonding the inner two electrons are assumed to have been drawn into the outer shell in each of two adjacent atoms, there being again two electrons held in common.[141]

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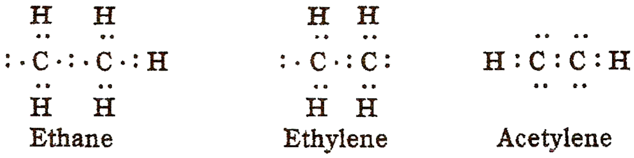
[141] E. D. Eastman, "Double and Triple Bonds, and Electron Structures in Unsaturated Molecules", J. Am. Chem. Soc., *44* (3) (1922). On 438.

The figure below illustrates Eastman's proposed structures for ethylene and acetylene. The ethane structure is included for comparison purposes, namely to facilitate the identification of the inner shell electrons, here represented as the horizontal electron pairs with the carbon nucleus symbol in between.



Eastman's structures for ethylene and acetylene.

As mentioned by Eastman, the double bond in Ethylene is formed with the inner electrons of only one carbon atom. Only in acetylene's triple bond, electrons from the inner shells of both carbon atoms are brought into play.

Eastman discusses how his theory depended on the particular example of a periodically changing law of force proposed by Dushman in 1917, having the inverse square law of force as a limiting case for great internuclear distances. His proposal was a materialization of the periodically changing force argued for by Lewis in 1917, in accordance with his postulated refutation of the inverse square law for small internuclear distances in 1916. Also, Eastman argues that his theory provided a natural explanation for Lewis' hitherto unpublished results on the restriction of multiple bond formation to first period elements, since any element belonging to a higher period had a completed octet between its valence shell and the two inner electrons of its first shell.

After discussing the general suitability of his theory to some of the empirical properties of unsaturated compounds, such as their reactivity and stability, for example, Eastman proceeds to apply his theory to some classes of compounds, such as chain hydrocarbons, benzene, oxides of carbon, etc, ending with a discussion of boron compounds.

Along with diborane, Eastman discusses two pre-Stock fictitious hydrides whose existence had been claimed by Ramsay and Hatfield: "The simplest well recognized gaseous hydrides of boron are the formulas B_3H_3, BH_3 and B_2H_6 [...]. The last two obviously offer difficulty in representation by the ordinary theory."[142]

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[142] E. D. Eastman, "Double and Triple Bonds, and Electron Structures in Unsaturated Molecules", J. Am. Chem. Soc., 44 (3) (1922). On 450.

Evidently, Eastman was not sufficiently aware of the relevant literature, because Stock and Massenez, in their inaugural paper on the hydrides of boron in 1912, were very clear about the inadequacy of Ramsay and Hatfield's conclusions.[143]

This fact was explained by Stock in his book, when discussing Ramsay and Hatfield's conclusions:

> According to the present writer's observations, a layer of soda lime only a few centimeters long suffices to remove completely the odor of boron hydride from the gas passed over it. The supposed boron, obtained by passing an electric spark through the gas, was not tested further, but undoubtedly consisted almost wholly of silicon in such experiments as those made with "stable B_3H_3" or with "BH_3". Thus all Ramsay's analytical conclusions and the inferences based thereon are invalidated.[144]

The application of Eastman's ideas to "his" boron hydrides can be visualized in the next set of figures, where the squares represent the planar projection of Lewis' cubic atoms and the inner electrons of diborane's first boron atom are represented by the small circles inside its square (the inexistence of these circles inside the squares of the other boron atoms means that their inner electrons were brought into play):[145]

Eastman's structures for B_3H_3, BH_3 and B_2H_6

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[143] "Alle diese Berechnungen Ramsays und Hatfield sind hinfällig. Die untersuchten Gase müssen außer Borwasserstoffen auch Siliciumwasserstoffe enthalten haben." In A. Stock, C. Massenez, "Borwasserstoffe", Ber., 45 (1912). On 3542.

[144] Treatment with soda lime was one of the steps in Ramsay and Hatfield's experimental method to obtain the hydrides of boron. A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 14.

[145] Eastman, "Double and Triple Bonds, and Electron Structures in Unsaturated Molecules", J. Am. Chem. Soc., *44* (3) (1922). On 450.

One may notice that Eastman did not include among his structures the open chain structure of B_3H_3 (H_2B-B=BH) proposed by Ramsay and Hatfield. This was probably a consequence of Eastman's belief in the universality of the octet rule, since the use of the inner electrons of this structure's last boron atom to comply with it implied that its hydrogen would share two pairs of electrons. However, in the ring structure of B_3H_3 each of its three hydrogen atoms share an electron pair with each of its two neighbouring boron atoms. This possibility was a general feature of Eastman's theory.

Nevertheless, Eastman was able to use a valid argument in favour of the saturated character of his structures: "It is also interesting to note that B_2H_6 substitutes rather than adds halogen. It is therefore saturated in the sense that benzene is, i.e., because the boron atoms are almost completely protected by the outer atoms."[146]

The following year, 1923, the idea of using boron's K electrons to solve the electron deficiency of the hydrides of boron made an independent appearance at a famous discussion on the theory of the chemical bond held by the Faraday Society at the Department of Physical Chemistry, University of Cambridge on 13 and 14 July. Robert Robinson, commenting on Lowry's "depleted octet" (or "sextet"), stated that the chemical behaviour of boron atom afforded "striking confirmation" of Lowry's view that such an arrangement was possible in certain cases, but such was not the case in the hydrides of boron:

> On the other hand, BH_3 does not exist, and Stock and his collaborators have shown that in the hydrides boron simulates carbon, or rather B_2 simulates C_2 and is a sexavalent group. The hydrides are B_2H_6 ($BH_3.BH_3$), B_4H_{10} ($BH_3.BH_2.BH_2.BH_3$), B_6H_{12} (analogue of cyclohexane?) and $B_{10}H_{14}$ (analogue of an isomeride of hexahydronaphthalene).[...] In terms of the octet theory the obvious explanation is that the inner duplet from one of the boron atoms is brought into play in order to provide the connecting valency and complete the octets. In B_2H_6 we have, therefore, $H_3B{:}BH_3e_2$, where e_2 represents the inner duplet not called out.[147]

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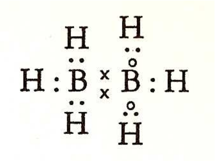
[146] E. D. Eastman, "Double and Triple Bonds, and Electron Structures in Unsaturated Molecules", J. Am. Chem. Soc., *44* (3) (1922) On 450.

[147] R. Robinson, G. Shearer, A. W. Porter, A. O. Rankine, "Discussion", *Trans. Faraday Soc*., 18 (1923). On 299.

Thus, just like Eastman, Robinson believed that only one of the boron atoms contributed with its inner electrons to the boron-boron link. Stock used the following structure to express Eastman and Robinson's proposals:



However, this is somewhat misleading because, while Eastman's configuration involved a single boron-boron bond, Robinson's proposal involved a double boron-boron bond. In fact, by calling upon the K electrons of only one of the boron atoms, Robinson considered that the B^+ - B^- structure was created within the molecule, which he referred to Lowry's theory of mixed double bonds. These were constituted by two different types of bonds: one covalent link due to sharing of one electron pair (in diborane's case, the inner pair of one of the boron atoms) and one electrostatic or polar bond (which was provided by the asymmetrical distribution of electrons that resulted from Robinson's decision to engage the inner electrons of only one of the boron atoms).

In his reply to Robinson, Lowry was naturally delighted to agree with his proposal: "Professor Robinson's application of the "depleted octet" to the hydrides of boron is a fascinating example of the way in which the use of mixed double bonds throw light on some of the most puzzling phenomena of chemistry."[148]

However, Lowry carried the subject even further, arguing that boroethane (diborane) $B^+H_3 – B^-H_3$ was the analogue of ethylene C^+H_2-C^-H_2 and should behave as an unsaturated compound.

He also argued that "borobutane" (B_4H_{10}) B^+H_3-B^-H_2-B^+H_2-B^-H_3 was the analogue of butadiene and that the "hydrocarbon" B_6H_{12} was the analogue of benzene and should resemble it in its properties:[149]

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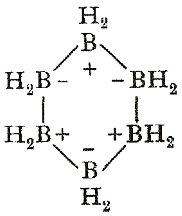
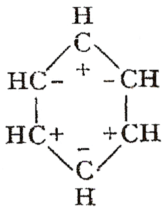
[148] R. Robinson, G. Shearer, A. W. Porter, A. O. Rankine, "Discussion", _Trans. Faraday Soc._, 18 (1923). On 301.

[149] R. Robinson, G. Shearer, A. W. Porter, A. O. Rankine, "Discussion", _Trans. Faraday Soc._, 18 (1923). On 301.

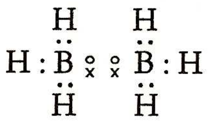




However, in the “hydrocarbon” $B_{10}H_{14}$ two missing atoms of hydrogen broke the analogy to naphthalene.

Robinson though of boron to be trivalent or quinquevalent as nitrogen, their difference stemming from the use of free electrons in the outer shell in being in nitrogen while boron had to use its inner electrons (the helium duplet, as Robinson called them). According to Robinson, this was in agreement with the fact that the trialkylborons formed additive compounds with ammonia. In fact, boron methyl was prepared by Frankland, who attributed it the formula $B(CH)_3{\cdot}NH_3$ and had been reinvestigated by Stock and Zeidler in 1921, who corroborated Frankland’s formula.

Müller, in 1925, thought that both boron atoms contributed to the link between them with one inner electron each:



$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & \cdot\cdot & & \cdot\cdot & \\ \mathrm{H}: & \mathrm{B} & \overset{\circ}{\times}\;\overset{\circ}{\times} & \mathrm{B} & :\mathrm{H} \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

An important argument against this theory was the high energy value required to involve the inner electrons in the chemical bond of boron. This was pointed out by Lowry in 1923. Even so, Lewis was able to support Eastman’s proposal:

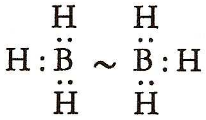
> This is an interesting theory, and not only offers a new picture of the multiple bond, but affords the only explanation which has so far been offered to account for the existence of the two hydroborons, B_2H_6 and B_4H_{10}, which appear to be so similar to ethane and butane. Nevertheless, there are some serious objections to the acceptance of Eastman’s view, the chief of which is that our X-ray data seem to indicate that the removal of electrons from the inner shell would require a far greater expenditure of energy than is available in ordinary chemical processes. It seems not impossible, however, that a modification of his theory may be useful in which it is assumed that

> the electrons of the inner shell of one atom, help fill the outer octet of another atom.[150]

However, Fritz Ephraim (1928) and Wiberg (1929) dismissed the inner electrons hypothesis based on the empirical properties of the hydrides of boron too.

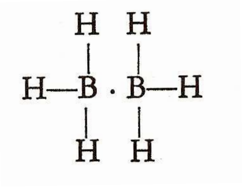
3.3.2 - *Different boron-boron bonds*

Later on, in 1929, W. Hellriegel suggested that the K electrons co-operated in an "electrostatic-electromagnetic" bond (~) between the boron atoms. For Stock, Hellriegel did not explain this concept more explicitly, and so he took the liberty of representing his structure as follows:



$$\begin{array}{ccccc} & H & & H & \\ H: & \underset{\cdot\cdot}{\overset{\cdot\cdot}{B}} & \sim & \underset{\cdot\cdot}{\overset{\cdot\cdot}{B}} & :H \\ & H & & H & \end{array}$$

Stock related this structure to one put forward by Alfred Benrath in 1921, where the point (•) indicated a different valence:



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H— & B & \cdot & B & —H \\ & | & & | & \\ & H & & H & \end{array}$$

3.3.3 - *Electron sextets and trivalent structures*

In 1923, H. Henstock proposed a structure in which one boron atom had six outer electrons and was linked to two hydrogen atoms, while the other was able to fill the octet and was linked to the other four hydrogen atoms:

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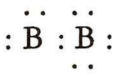
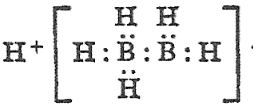
[150] G. N. Lewis, *Valence and The Structure of Atoms and Molecules*, American Chemical Society Monograph Series (New York: The Chemical Catalog Company, Inc., 1923).



$$:\overset{..}{B}:\underset{..}{\overset{..}{B}}:$$

This meant that, with the other boron atom included, the latter boron atom was bonded to five different atoms, a situation that was unique in chemistry. This singularity was by-passed by J. Böesenken (1922) and W. A. Wahl (1925), who placed one hydrogen ion in an outer sphere:



$$H^+\left[H:\underset{\ddot{H}}{\overset{H}{\ddot{B}}}:\overset{H}{\ddot{B}}:H\right]$$

Stock dismissed this formula because his investigations on the ammonia compound of diborane had convinced him that diborane was a di-basic acid, while according to Böeseken and Wahl's configuration it was monobasic.

In 1922, Maurice L. Huggins published his theory of trivalent structures for the hydrides of boron. At the time, only B_2H_6, B_4H_{10}, B_6H_{12} and $B_{10}H_{14}$ were known. Stock had published his classification scheme based on tetravalent boron in 1916 and there was still a great deficit in the experimental knowledge about the hydrides of boron.

Huggins argued that Stock's tetravalent boron was opposed to what was already known about atomic structure. Moreover, the formula of $B_{10}H_{14}$ would not be simply accounted for by boron's tetravalency. Huggins also questioned why boron showed its tetravalency only in its hydrogen compounds.

Based on these considerations, Huggins was led to look for structures in which boron had three valence electrons. He proposed the following configurations:[151]

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[151] Huggins, "Boron Hydrides", J. Phys. Chem., 26 (1922). On 834.

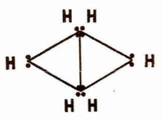

FIG. 1 - B_2H_6

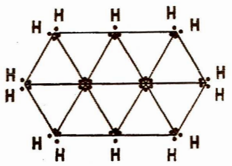

FIG. 4 - $B_{10}H_{14}$

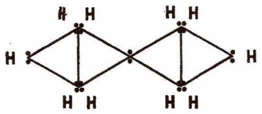

FIG. 2 - B_4H_{10}

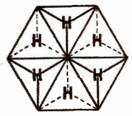

FIG. 5 - C_6H_6

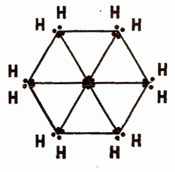

FIG. 3 - B_6H_{12}

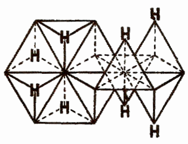

FIG. 6 - $C_{10}H_8$

The key feature of these configurations was their 4 electron bonds, which were shared by four atoms. According to Huggins, these structures showed very striking analogy with those of the carbon compounds ethylene (diborane), butadiene (B_4H_{10}), benzene (B_6H_{12}) and naphthalene ($B_{10}H_{14}$).

Huggins believed that the double and triple bonds possessed a residual affinity that resulted in the attraction of other unsaturated structures and the formation of a bond of three or four (sometimes more) electrons. Usually, these were only temporary structures but he admitted that boron atoms had a greater tendency to form and hold such complexes than had carbon atoms. He also admitted that the residual affinity of the boron-boron double bond was strong enough to hold onto hydrogen atoms, but it was not strong enough to hold heavier atoms. This accounted for his structures. However, Huggins acknowledged that further experimental evidence was needed before his or any other structures could be considered to be proved.

3.3.4 - Pseudo-atoms

In 1928, George Glocker suggested a structure for diborane based on the hydride displacement law that had been put forth by Grimm in 1925: “Atoms anywhere up to four places in the periodic system before an inert gas change their properties by uniting with one to four hydrogen atoms, in such a manner that the resulting combinations behave like pseudoatoms, which are similar to elements in the groups one to four places respectively, to their right."[152]

Thus, as the following table represents, a CH group would behave like a pseudo-atom of nitrogen, a CH_2 group would behave as an oxygen atom, and so on.[153]

C	**N**	**O**	**F**	**Ne**	**Na**
	CH	NH	OH	FH	
		CH_2	NH_2	OH_2	FH_2^+
			CH_3	NH_3	OH_3^+
				CH_4	NH_4^+

Grimm had not included boron in his law, but Glocker extended it to the hydrides of boron by considering the BH group as a pseudo-atom of carbon. Diborane would then become a "pseudo-ethylene" molecule $H_2(BH)=(BH)H_2$. By doing so, Glocker claimed, a whole boron chemistry could be conceived of in complete analogy to carbon chemistry. The following table is a transcription of two tables by Glocker. Here they were put together, side by side, to render the analogy more clear:[154]

Hydrocarbons			**Hydroborons**		
Ethane	$CH_3 - CH_3$	$\mathbf{C_nH_{2n+2}}$	-	$BH_4 – BH_4$	$\mathbf{B_nH_{3n+2}}$
Ethylene	$CH_2 = CH_2$	$\mathbf{C_nH_{2n}}$	Borethane	$BH_3 = BH_3$	$\mathbf{B_nH_{3n}}$
Acetylene	$CH = CH$	$\mathbf{C_nH_{2n-2}}$	-	$BH_2 = BH_2$	$\mathbf{B_nH_{3n-2}}$

These formal classes were not intended to include all the hydrides of boron. In fact with the exception of B_2H_6 and B_4H_{10}, no hydride of boron discovered by Stock was included in Glocker's three formal classes. Thus, Glocker became convinced that he had discovered the explanation for diborane's structure and led by his belief in an analogy

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[152] Patani, LaVoie, "Bioisosterism: A Rational Approach in Drug Design" Chem. Rev., 96 (1996). On 3148.

[153] Patani, LaVoie, "Bioisosterism: A Rational Approach in Drug Design" Chem. Rev., 96 (1996). On 3148.

[154] G. Glocker, "The Structure of Boron Hydrides", Science, 68 (1928). On 305.

between the carbon and boron chemistries predicted the existence of other boron compounds.

Glocker argued that although Stock had assumed boron to be tetravalent in diborane, which he compared to ethane, it seemed equally reasonable to compare diborane with ethylene, since physical properties, such as the melting and boiling points, were as close to ethylene as they were to ethane. He nevertheless admitted that the chemical properties could differ, due to the different positions held by the positive nuclear charges in diborane and ethylene. Even so, in both cases the positive charges were thought to be located inside an octet of electrons.

On these grounds, Glocker was able to dismiss a number of other suggestions, namely those by Eastman, Stock, Huggins and the k-electrons theory: "If the idea of the pseudo-atom is extended to the hydrides of boron it is possible to write formulae for these substances that conform more nearly to our usual notion of molecular structure than do formulae advanced up to date."[155]

3.3.5 - One-electron bond

According to Stock, the one-electron bond concept was first suggested independently by J. D. Main-Smith and Samuel Sugden in 1927. However, the reading of Sugden's paper reveals that the origin of this concept can be placed much earlier, should one be willing to view it as a fundamentally plastic concept that went through several different bond conceptions, ranging from the early electronic valence theories to Pauling's resonance. Sugden himself adopts this view and traces the concept back to the early electronic theories of Stark (1916) and to a suggestion for the hypothetical NCl_5 by Thomson (1921). In 1923, Prideaux suggested the following formula for phosphorus pentachloride (this formulation, in which each bond indicates a single shared electron and the superscript figures give the number of unshared electrons, was due to J. D. Main-Smith):[156]

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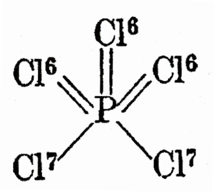
[155] G. Glocker, "The Structure of Boron Hydrides", Science, 68 (1928). On 305.

[156] S. Sugden, "The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorous and Antimony", J. Chem. Soc. (1927). On 1174.



Thus, Prideaux maintained the octet rule but discarded the electron pair in two of the chlorine atoms, which are supposed to be bound by sharing one-electron with the phosphorus atom.

According to Sugden, Prideaux's formula was subsequently applied by Ingold and Ingold in 1926 to explain certain cases of substitution in aromatic compounds. These authors viewed the one-electron bond (also called a singlet link) in Prideaux's formula as a "semipolar single bond", that is, as consisting of half a covalency and half an electrovalency. This concept was directly derived from the mixed type of valency that had been defended by Lowry in 1923, at the Faraday Society Meeting:

> If a shared electron is counted as half value for each of the atoms which share it, there is found to be a positive charge on the phosphorus atom and an effective half negative charge on each of the chlorine atoms held by a singlet. This half charge does not, of course, signify a splitting of the electron, but may be interpreted dynamically on the lines suggested by Højendahl (1924) as a statistical average obtained by integrating the field of the electron in the neighbourhood of a particular atom over a time interval which is large compared with the period of revolution in its orbit. From this point of view it is obvious that the effective polarity of a shared electron will only be exactly 0.5 if its orbit lies symmetrically about or between the two atoms which share it;[157]

Obviously, the singlet link constituted a departure from Lewis duplets, but Sugden offered the following justification:

> The conception of duplets is based upon the occurrence of electrons in pairs at each quantum level throughout the structure of atoms, and the presence of an even number of valency electrons in by far the greater number of stable molecules. This, however, can scarcely be regarded as proving the invariable covalency linkage of two electrons. Sufficient "odd" molecules exist to show that the pairing of electrons, although very common, is not necessary for the formation of stable molecules; also

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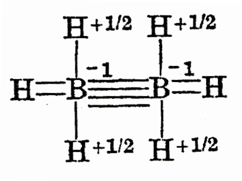
[157] S. Sugden, "The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorous and Antimony", *J. Chem. Soc.* (1927). On 1175.

> pairs of singlet linkages, as in [Prideaux's] formula III, may well be present in molecules containing an even number of valency electrons.[158]

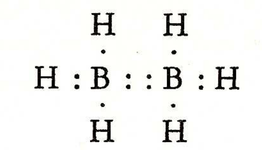
Sugden then analyses the eventual effect of one-electron bonds on the parachor and concludes that parachor can be used to detect the presence and number of such bonds in a molecule: "The extension of the electronic theory of valency to include singlet linkages, or more generally odd-electron linkages, can therefore be subjected to a direct experimental test and has no longer a purely speculative basis; it opens up a wide field for future investigation [...]"[159]

In his paper, Sugden applies the one-electron bond concept to explain numerous compounds, which could contain odd-electron bonds (1, 3 or 5 electrons) formed by an odd-number of singlet links.

Sugden's structure for borethane (diborane) included 4 singlet links:[160]



which Stock translated into its modern version



$$\begin{array}{ccccc} & H & & H & \\ & \cdot & & \cdot & \\ H: & B & :: & B & :H \\ & \cdot & & \cdot & \\ & H & & H & \end{array}$$

Curiously enough, in his letter on the constitution of the boron hydrides, Core included a *post scriptum* note in which he called attention to the publication of Sugden's paper and acknowledged that such a configuration would be more stable than his own.

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[158] S. Sugden, "The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorous and Antimony", J. Chem. Soc. (1927). On 1175.

[159] S. Sugden, "The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorous and Antimony", J. Chem. Soc. (1927). On 1175.

[160] S. Sugden, "The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorous and Antimony", J. Chem. Soc. (1927). On 1179.

In that same year, 1927, a modified version of the one-electron bond ethane-like structure was put forward by Nevil Vincent Sidgwick in his book *The Electronic Theory of Valency*.[161]

Sidgwick did not agree with the pervasive presence of Sugden's singlet link and began his account of this kind of bond with a clear statement about its peculiar nature: "While in all ordinary cases the evidence is strongly in favour of every covalent link being constituted of two shared electrons, there are a small number of compounds in which it is almost certain that a single shared electron can form a link."[162] This constituted a remarkable departure from the opinion he had defended just a few years ago, in the discussion held by the Faraday Society in 1923:

> The idea that the shared electrons occupy binuclear orbits makes it clear why two electrons are required for the purpose. When one of the two is near to, or on the far side of, one of the nuclei, its attraction on the other is negligible and it does nothing to prevent the two nuclei from separating; whereas if there are two, they may be so arranged in phase that one of them is always available to hold the nuclei together.[163]

It is significant that, in addition to the hydrides of boron, the hydrogen ions H_2^+ and H_3^+, which inevitably had a one-electron bond, were the only compounds referred by Sidgwick. One must conclude that Sidgwick's departure from his omnipresent electron pair in 1923 was caused by the hydrides of boron, since the hydrogen ions were already known then. These ions had a transitory existence restricted to experiences in a positive ray tube. Their instability and very limited existence, which Sidgwick considered being common features to diborane (in dry air diborane was not that unstable), and the fact that they all were hydrogen compounds, led him to the following conclusions: "We may therefore conclude that the occurrence of links formed of a single shared electron is very rare: that such links are always unstable: and that they are only possible at all when one of the atoms so linked is hydrogen."[164]

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[161] N. V. Sidgwick, *The Electronic Theory of Valency* (London: Oxford University Press, 1927).

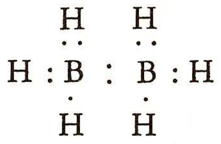
[162] N. V. Sidgwick, *The Electronic Theory of Valency* (London: Oxford University Press, 1927). On 102.

[163] N. V. Sidgwick, "The nature of the non-polar link", Trans. Faraday Soc., 19 (1923). On 469.

[164] N. V. Sidgwick, *The Electronic Theory of Valency* (London: Oxford University Press, 1927). On 103.

Sidgwick restriction of the one-electron bond to the hydrides of boron constituted the major argument put forward by its opponents against it. Such singularity in the chemical world appeared rather suspicious.

Sidgwick believed that only an ethane-like structure with a single bond between boron atoms and two hydrogen atoms attached by one-electron bonds could possibly describe diborane:



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ \mathrm{H} & : & \mathrm{B} & : & \mathrm{B} & : & \mathrm{H} \\ & & \cdot & & \cdot & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

The only other option considered by Sidgwick was the use of the inner electrons of the boron atoms, but he immediately dismissed it on energetic grounds.

Sidgwick's belief in an ethane-like structure seems to have been empirically founded on the similarity of ethane and diborane's boiling points. He justified the assumption that the one-electron bond was restricted to B-H links with Stock's results on the stability of diborane's halogen and alkyl derivatives: "The halides and the alkyl derivatives are all of the type BX_3 and careful investigation by Stock has shown that they give no sign of association to B_2X_6 down to the lowest temperatures, while the hydride has no tendency to dissociate into BH_3 up to the temperature at which it begins to decompose with loss of hydrogen."[165]

One important aspect of Sidgwick's discussion on the structure of diborane is his omission to discuss the structure of the higher hydrides. Sidgwick seems completely satisfied with a single reference to their existence and with applying his ideas only to the simplest of all cases, leaving the reader with the impression of a straightforward extension of his reasoning to the higher hydrides.

The important problem of the exact location of the one-electron bonds among the six B-H bonds is not addressed either. In particular, Sidgwick does not even clarify if these special bonds are to be understood as having a fixed location.

In 1931, Pauling published his second paper on the nature of the chemical bond, which dealt with the one-electron and the three-electron bond concepts[166]. As with Sidgwick,

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[165] N. V. Sidgwick, *The Electronic Theory of Valency* (London: Oxford University Press, 1927). On 103.

Pauling's one-electron bond was restricted to diborane, apart from the hydrogen ions. Pauling's concern with diborane can be traced back to 1928, at least, when he took some notes in which he discusses the application of London's ideas to the ion H_3^+ and diborane.[167]

Apparently, having been unable to use the work by Heitler and London to understand these molecules, Pauling was led to argue for a chemical bond theory which also included the one-electron bond:

> The work of Heitler and London and its recent extensions have shown that the Lewis electron-pair bond between two atoms involves essentially a pair of electrons and two eigenfunctions, one for each atom. It will be shown in the following paragraphs that under certain conditions bonds can be formed between two atoms involving one electron or three electrons, in each case one eigenfunction for each atom being concerned.[168]

Although acknowledging that quantum resonance was essentially due to the identity of two shared electrons, Pauling argued that the application of the first-order perturbation theory of quantum mechanics to a system consisting of one electron and two nuclei, although not leading to accurate numerical results, revealed that such a bond was indeed possible. In most cases were the two nuclei had different nuclear charges such an analysis showed that only repulsive states were attained, but when the unperturbed system was degenerate or nearly degenerate, a resonance energy leading to molecule formation was possible. Thus, the criterion for the stabilization of the one-electron bond was:

> *A stable one-electron bond can be formed only when there are two conceivable electronic states of the system with essentially the same energy, the states differing in that for one there is an unpaired electron attached to one atom, and for the other the same unpaired atom is attached to the second atom.*

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[166] L. Pauling, "The Nature of the Chemical Bond. II. The One-Electron Bond and the Three –Electron Bond", J. Am. Chem. Soc., *53* (9) (1931), 3225–3237.

[167] Ava Helen and Linus Pauling Papers, Special Collections & Archives Research Center, Oregon State University Libraries. Box 209. On 21.

[168] L. Pauling, "The Nature of the Chemical Bond. II. The One-Electron Bond and the Three –Electron Bond", J. Am. Chem. Soc., *53* (9) (1931). On 3225.

> By “essentially the same energy” it is meant that the energies of the states of the unperturbed system differ by an amount less than the possible resonance energy.[169]

After exemplifying the application of his theory to the hydrogen ions, Pauling discussed the boron hydrides case, recognizing their importance to bond theory “on account of their unusual and previously puzzling properties.”[170]

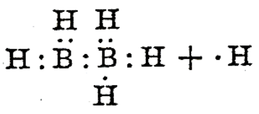
In his discussion of the empirical data on the boron hydrides, Pauling repeated Sidgwick’s arguments, including his dismissal of the inner electrons contribution on energetic grounds. One should keep in mind that Stock published his paper (with Wiberg, Martini and Nicklas) on the electrolysis of the ammonia compound of diborane in that same year, 1931 and that, most probably, Pauling was not aware of it at the time.

Although Sidgwick had restricted his discussion to diborane, without including any figure of his structure, Pauling attributed to Sidgwick the following structures for diborane and tetraborane, arguing that these were to be accepted in view of the quantum mechanical discussion of the one-electron bond:[171]

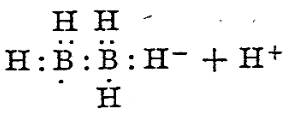
$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H}\\ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\end{array}\qquad\qquad \begin{array}{c}\mathrm{H}\ \ \mathrm{H}\ \ \mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H}\\ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\end{array}$$

Sidgwick's structures for diborane and tetraborane, according to Pauling.

To apply his stability criterion to diborane, Pauling considered the structures below:



$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H} + \cdot\mathrm{H}\\ \dot{\mathrm{H}}\end{array}$$



$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H}^- + \mathrm{H}^+\\ \dot{\mathrm{H}}\end{array}$$

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[169] L. Pauling, “The Nature of the Chemical Bond. II. The One-Electron Bond and the Three –Electron Bond”, J. Am. Chem. Soc., *53* (9) (1931). On 3225.

[170] L. Pauling, “The Nature of the Chemical Bond. II. The One-Electron Bond and the Three –Electron Bond”, J. Am. Chem. Soc., *53* (9) (1931). On 3225.

[171] L. Pauling, “The Nature of the Chemical Bond. II. The One-Electron Bond and the Three –Electron Bond”, J. Am. Chem. Soc., *53* (9) (1931). On 3227.

Through successive *estimates* of the energies of formation and electron affinities of these compounds Pauling struggled to prove that their resonance energies could be sufficiently close to obey his stability criterion. It must be noticed that, even giving full credit to his criterion (its deduction was not presented in the paper), one can not help to realize that Pauling did not deduce the necessity for the one-electron bond; he rather strove to prove its plausibility. Moreover, his reasoning is clearly circular, as both structures above are postulated to have another one-electron bond. Even so, Pauling put forward the following conclusion:

> We accordingly conclude, in default of another structure, that the one-electron bond is to be accepted for the boron hydrides, whose existence provides the strongest evidence that the condition for the formation of this bond is satisfied.[172]

This conclusion is doubly fallacious: first, Pauling uses the false inexistence of another structure to force the acceptance of his theory, thus postulating (wrongly) the inadequacy of Wiberg's (or any other) theory; second, he uses the very existence of diborane to argue for his theory. This was a direct consequence of his first fallacy.

Besides his alleged theoretical substantiation of the one-electron bond, Pauling put forward an important amplification of Sidgwick's account of this concept. Although Sidgwick was not explicit about a possible static character for the two one-electron bonds in diborane, Pauling argued against it. According to him, the various configurations obtainable by the mobility of the one-electron bond among all the B-H links further stabilized the molecule through additional degeneracy, since it was obvious that all these configurations had the same energy. Further distance from Sidgwick's account was provided by Pauling's rejection of Sidgwick's conclusion for the mandatory presence of a hydrogen atom in this kind of link. In fact, Pauling argued that his stability criterion would be necessarily obeyed by such structures as Li_2^+, Na_2^+, etc, and that it was possible that other compounds involving one-electron bonds between two unlike atoms would be discovered.

Finally, it must be perfectly clear that Pauling's departure from the electron pair bond must be seen in a wider context that also includes his three-electron bond concept.

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[172] L. Pauling, "The Nature of the Chemical Bond. II. The One-Electron Bond and the Three –Electron Bond", J. Am. Chem. Soc., *53* (9) (1931). On 3237.

Robert S. Mulliken built on the one-electron bond ethane-like structure to account for diborane's structure according to his molecular orbital theory. In 1932 and 1933, Mulliken predicted a paramagnetic behaviour for diborane but was forced to change his account because diborane was found to be diamagnetic by indirect measurements by Farkas and Sachsse in 1935. This result was confirmed by Mulliken through direct measurements in that same year. He then built on this result and his own previous theory for C_2H_6 structure to account for diborane, whose structure he considered to be that of ethane deprived of two electrons. Mark and Pohland's results played an important role in Mulliken's justification for taking *a priori* an ethane-like structure for diborane.

Stock dismissed the one-electron bond because it had no application other than the boron hydrides and also because it infringed the octet rule: "The assumption of singlet bonds seems arbitrary and unsatisfactory because, however appropriate it may be in some other cases [the hydrogen ions], it does not in this instance attain the end aimed at –viz., the building of noble-gas electron shells for all the atoms involved."[173] Its "arbitrariness" would be systematically pointed out as its major shortcoming.

On the empirical level, the one-electron bond was able to explain some of Stock's results, such as the addition of two sodium atoms, pointing to a special position for two of the hydrogen atoms in diborane. This fact accounts for the survival of his configuration for diborane as the only ethane-like structure to outlast the confrontation with empirical evidence. However, it did not explain the reaction mechanism Stock had put forward to account for the action of diborane upon ammonia. Its supporters preferred to hold to the X-ray diffraction results obtained by Herman Francis Mark and Pohland in 1925. They had studied the X-ray photographs of solid B_2H_6 and compared it with ethane and disilane Si_2H_6. They concluded for a marked similarity between diborane and ethane. Disilane was found to belong to a different symmetry system. The B-B distance was found to be 1.8 to 1.9 Å; the distance between neighbouring molecules was 3.7 Å. The corresponding values for ethane were 1.5 - 1.6 Å and 3.5 Å, respectively. This indicated that in diborane the boron atoms were farther apart that were the carbon atoms in ethane.

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[173] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 157.

It is somewhat surprising the way these results were systematically invoked by those actively involved in defending the ethane-like structure for diborane. It is also surprising how long they did it. As will be seen ahead, direct extrapolations of results taken from crystalline structures to their gaseous phase did not constitute sound science. This much was acknowledged by Pauling later on (this issue will be addressed in chapter 5).

In corroboration of the ethane-like structure for diborane, Stock also referred the infra-red absorption spectra studies made by Gerda Laski in 1919 but these results were never mentioned by anyone else. This may have been due to the fact that he never included the reference of her work in his own work, despite having mentioned it on several occasions. Apparently, Laski was the first woman ever that worked with the hydrides of boron.

3.3.6 - Lewis' structures

In 1933, Lewis proposed an alternative to the one-electron bond. He conceded the existence of the one-electron bond in the hydrogen ions, but thought that it was very doubtful that there was good evidence for its existence in any known stable molecule. Lewis argued that any atom or molecule containing one or more unpaired electrons would exhibit paramagnetic behaviour and that this was the most effective criterion to detect the existence of unpaired electrons.

Addressing the structures proposed by Sidgwick and Pauling, Lewis expressed his conviction that they did not pass his criterion: "As far as I am aware, the magnetic properties of these substances have not been studied, but when they are, I shall be surprised if any paramagnetic behavior is observed."[174]

To comply with his prediction of a magnetic behaviour for diborane, Lewis proposed an ethane-like structure in which all electrons remained paired but would occupy each link only six sevenths of the time on average.

> We shall then have a picture of a molecule in which all the electrons remain paired, but in which the orbits are not fully occupied. If we imagine the electrons in rapid motion throughout the several orbits, and in such phase relations as to preserve the

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[174] G. N. Lewis, "The Chemical Bond", *J. Chem. Phys.*, 1 (1933). On 20.

> pairs at all times, we should presumably diminish the strength of the bonds without altogether destroying their stability.[175]

Lewis did not include any representation of his structures, but later on, in 1937, Simon H. Bauer used Pauling's resonance to put together Pauling and Lewis structures in a resonating set for diborane (Bauer's work will be addressed in chapter 5). These were the configurations he attributed to the structures proposed by Lewis:[176]

Lewis' structures according to Bauer

3.3.7 - Wiberg's structure

Another ethylene-like structure was suggested by Wiberg in 1928. His theory was based on the hypothesis that boron was pentavalent toward the more positive hydrogen (to achieve a neon-like electronic configuration) but that its maximum co-ordination number was only 4, thus combining only with four atoms or groups of atoms. The result of this essential tension between the valency and coordination number of boron led to the association of two boron atoms according to the following structure:

The capture of two hydrogen electrons allows each boron atom to achieve a neon-like electronic configuration, benefiting from five additional electrons, while making only four chemical bonds. Thus, four hydrogen atoms were linked to this structure by

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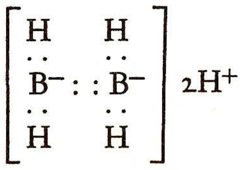
[175] G. N. Lewis, "The Chemical Bond", J. Chem. Phys., 1 (1933). On 27.

[176] S. H Bauer, "The Structure of Diborane", J. Am. Chem. Soc., *59* (6) (1937). On 1100.

“regular” covalent bonds, in which one electron pair is shared. The remaining two hydrogen nuclei, which were deprived from their electrons, were, according to Wiberg, loosely bound, supposedly by an electrostatic attraction with the negative structure above arranged within the electron shell of the boron atoms. Analogous structures were subsequently put forward in 1928 by Stackelberg and Ephraim.

In his book, Stock presented the following two figures to express Wiberg’s configuration:



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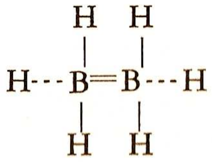


II

As Stock himself stressed, both these figures are incomplete: figure I does not make evident that the two hydrogen positive ions are inside the electron shell of the boron atoms; figure II only hints that the two protons are bound differently from the other. Stock’s difficulty in displaying Wiberg’s structure is symptomatic of one of its major shortcomings: since Wiberg had been rather vague on what concerned the exact position of the two hydrogen ions, his structure could not be visualized. Later on, this shortcoming brought about serious methodological implications.

One of the theoretical arguments for Wiberg’s structure resulted from amplifying the original scope of Grimm’s hydride-displacement law. Thus, it was argued that B_2H_6 and C_2H_4 were, to a certain extent, isomers that differed in the position of two protons within their molecules. Such vision was corroborated by the marked similarity between the chemical and physical properties of both molecules. This had already been pointed out in 1927 by Christiansen, who did not say anything about the electronic configuration of diborane. Stock considered this an important argument for Wiberg’s formula.

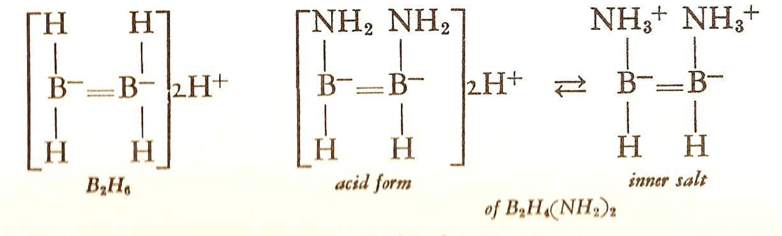
According to Stock, the unsaturated nature of diborane was evident from the addition reaction of two sodium atoms, which could be expressed using Wiberg’s ideas as

$$[BH_2{=}BH_2]\,H_2 + 2Na \rightarrow [BH_3{-}BH_3]Na_2$$

The special position of the two hydrogen atoms was also shown by the formation of the ammonium salt of diborane, which Wiberg's structure rendered easy to express as

$$[B_2H_4]\ H_2 + 2NH_3 \rightarrow [B_2H_4]\ (NH_4)_2$$

If one recalls Stock's mechanism for this reaction, it is evident that Wiberg's structure for diborane was specially suited to it. Moreover, Stock used Wiberg's structure to explain the empirical formula $B_2H_8N_2$ of the solid residue that resulted from the electrolysis of the ammonia compound of diborane. According to him, this formula should be expressed as $B_2H_4(NH_2)_2$, indicating that during the electrolysis two of the hydrogen atoms of B_2H_6 had been replaced by NH_2: "The much lower conductivity and acidity of $B_2H_4(NH_2)_2$ as compared with B_2H_6 are explained by the fact that, as in many similar cases, the insertion of NH_2- groups causes an intramolecular neutralization or salt formation."[177] According to Stock, this reaction could be easily written using Wiberg's structure, as expressed by the following figure:



Wiberg's structure for B_4H_{10} could be deduced by noticing that this hydride could be synthesized from B_2H_6 by means of the iodine compound B_2H_5I:

$$2B_2H_5I + 2Na = B_2H_5{\cdot}B_2H_5 + 2NaI$$

Thus, the structure of B_4H_{10} could be obtained by combining two B_2H_6 molecules and dropping two hydrogen atoms. This would result in two double bonds and four specially bound hydrogen atoms, in a structure that resembled that of butadiene:

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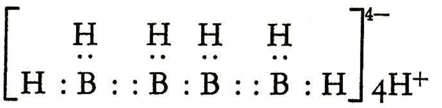
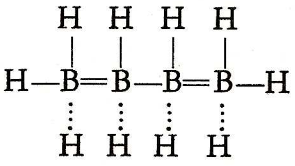
[177] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 131.



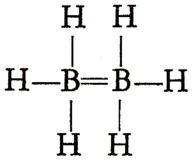
$$\left[\mathrm{H}:\overset{\mathrm{H}}{\underset{}{\overset{\cdot\cdot}{\mathrm{B}}}}::\overset{\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{B}}}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{B}}}::\overset{\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{B}}}:\mathrm{H}\right]^{4-}4\mathrm{H}^{+}$$

or

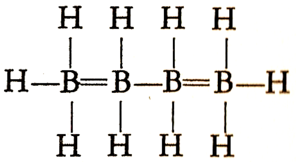


$$\mathrm{H{-}\overset{H}{\underset{H}{B}}{=}\overset{H}{\underset{H}{B}}{-}\overset{H}{\underset{H}{B}}{=}\overset{H}{\underset{H}{B}}{-}H}$$

The similarity between the ultra-violet absorption spectra of tetraborane and butadiene was pointed out by Stock. Moreover, like certain derivatives of butadiene, B_4H_{10} took up two sodium atoms and it also took on four NH_3 molecules, in accordance with its Wiberg structure: "Again, the results of the electrolysis of B_4H_{10} and of B_2H_6 in liquid ammonia may be explained by the above formula without doing them violence."[178]
Stock also pointed out that Wiberg's formulas for diborane and tetraborane reproduced, with the modifications implied by contemporary electronic theory of valence, the very first formulas suggested for these compounds, written by R. C. Ray back in 1916:

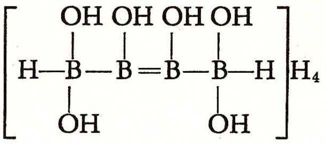


$$\mathrm{H{-}\overset{H}{\underset{H}{B}}{=}\overset{H}{\underset{H}{B}}{-}H}$$

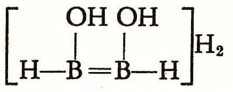


$$\mathrm{H{-}\overset{H}{\underset{H}{B}}{=}\overset{H}{\underset{H}{B}}{-}\overset{H}{\underset{H}{B}}{=}\overset{H}{\underset{H}{B}}{-}H}$$

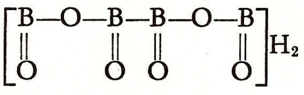
Ray, Gupta and Travers had done important work on the boron hydrates and, in 1930, Wiberg argued for an intimate connection between their researches and those of Stock and his co-workers on the boron hydrides. Using knowledge gained investigating the boron hydrides, he was able to apply his theory to draw structures for the compounds discovered by Ray, Gupta and Travers that were according to the electronic theory of valence:



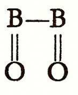
(*a*) $H_{12}B_4O_6$



(*b*) $H_6B_2O_2$



(*c*) $H_2B_4O_6$



(*d*) B_2O_2

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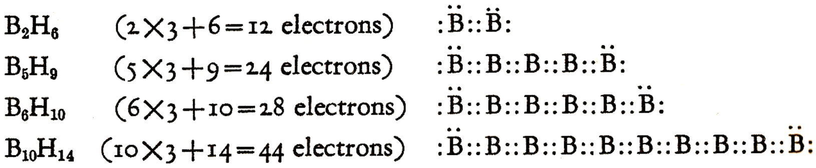
[178] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 160.

But Wiberg did not stop at the structures of these compounds; he drafted a very complex scheme of their sources and reactions in order to explain the formation of the boron hydrides when acids reacted with magnesium boride[179]. Apparently, this had never been done before. The action of hydrochloric acid upon magnesium boride had been Stock's only method to produce the hydrides of boron since the beginning of his investigations, but no full explanation was provided for.

Stock acknowledged that Wiberg's scheme was fruitful and showed empirical adequacy: "The scheme shows very plainly the close connection between the hydrides of boron and the boron compounds found by Travers, Gupta and Ray. [...]

Taken on a whole, the facts considered above lend a remarkable degree of probability to Wiberg's assumptions"[180]

Despite being aware that little might be said about the structure of the higher hydrides of boron, Stock put forward the configurations of some according to Wiberg's theory, based on the conviction that their properties were more consonant with chain structures than with ring structures:[181]



B_2H_6	$(2 \times 3 + 6 = 12$ electrons$)$	$:\ddot{B}::\ddot{B}:$
B_5H_9	$(5 \times 3 + 9 = 24$ electrons$)$	$:\ddot{B}::B::B::B::\ddot{B}:$
B_6H_{10}	$(6 \times 3 + 10 = 28$ electrons$)$	$:\ddot{B}::B::B::B::B::\ddot{B}:$
$B_{10}H_{14}$	$(10 \times 3 + 14 = 44$ electrons$)$	$:\ddot{B}::B::B::B::B::B::B::B::B::\ddot{B}:$

By 1931, only two structures seemed to have survived the evolution of bond theory and tests of empirical evidence: the one-electron bond ethane-like structure and Wiberg's configuration. Stock himself acknowledged this situation: "For the rest, the Sidgwick and Pauling formula approximates one of Wiberg's [...] and corresponds with it in that it assigns to two hydrogen atoms bonds that differ from those of the other four hydrogen atoms, thereby adapting itself to the experimental facts."[182]

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[179] Wiberg's impressive scheme may be found in Stock's book, on page 164.

[180] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 167.

[181] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 160.

[182] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 157.

No direct evidence favoured any of these structures, although the ability to explain the reaction of diborane with ammonia seemed to give Wiberg's ideas a clear advantage on the empirical level:

> In any event, it seems to be clearly established that two of the hydrogens differ from the other four in being acidic, and electrolysis of solutions in liquid ammonia confirms the deductions made above, since the main effect is a replacement of two non-acidic hydrogens by NH_2 radicals, followed perhaps by the formation of an "inner salt" [...][183]

Despite the apparently overwhelming indirect evidence in favour of Wiberg's structure, a small community engaged in the defence of the ethane-like structure took its initial steps starting in 1929-1930 in the United States of America. Their commitment took the form of a very cautious initial attitude towards the debate, while persisting in a systematic research program, their "stubborn" opposition to Wiberg's theory can not be unequivocally justified. However, a comment made by Bauer a few years latter leads one to suspect that the "strange" nature of the electrostatic bond between the two hydrogen ions and the $[BH_2{=}BH_2]^-$ core was one of the reasons behind their attitude. Another reason may have been the difficulty in visualizing Wiberg's structure. Also, although this was an issue that has never been raised by those actively working in the field, it was a fact that Wiberg's structure involved a simultaneous link between three atoms. That this may have been a key aspect that earned Wiberg strong opposition is disclosed by Lowry's words:

> The difficult problem of the structure of the boron hydrides continues to attract investigators. F. Ephraim considers that they can be satisfactorily explained on the octet theory of distribution of the outer electrons, but in his suggested structures some electrons are shared between three atoms, which will doubtless be considered unsatisfactory.[184]

Lowry was referring to Ephraim's structure but since it was analogue to that by Wiberg, his words also applied to the latter.

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[183] T. M. Lowry, "Valency Types and Problems", Nature (August 25, 1934). On 269.

[184] H. Bassett, "Inorganic chemistry", Annu. Rep. Prog. Chem., 26 (1929), 34-73.

Pauling and Mulliken’s theoretical accounts were important in legitimizing the ethane-like structure, but its real importance in the commitment of those engaged in analytical chemistry must not be overestimated, as will be seen ahead.

Despite their different commitments and evaluation of available evidence, there was one issue on which all were willing to agree: the solution to the puzzle could only be achieved by developing better production methods, whose higher yields would render the hydrides more prone to investigation, a necessary pre-condition to collect decisive evidence in order to settle such complex problem.

4 - A Spark is the Method

4.1 - Baby Steps

By 1930, the hydrides of boron were produced out of Stock's laboratory for the first time. Not surprisingly, the driving force for such evolution was the structural puzzle that the hydrides of boron were imposing to chemistry and the clear perception that better yields in the preparative methods had to be achieved in order to make possible a more intensive and extensive program of research that would lead to the solution of the problem.

Thus, three different research groups, in three very distinct geographical locations, were now actively involved in the search for improved methods of production: besides Stock's group in Germany, Bertram Dillon Steele and James Edward Mills in Australia and Hermann Irving Schlesinger and Anton Burg in America were trying to develop their own new production methods.

One of Stock's attempts was to substitute magnesium boride by beryllium boride, which was prepared from boron trioxide and beryllium just as magnesium boride was. Beryllium was produced commercially by a process developed by Stock, Wiberg and Hans Martini prior to 1930[185]. The results came out very similar to those of magnesium boride both in quantity and in quality. As with magnesium boride, B_4H_{10} was the chief product of the acid decomposition of beryllium boride. This was a more expensive process, but in the preparation of small quantities of boron hydrides, its higher cost could be offset by using pure silicon-free beryllium. This would render hydrides of boron free from silane contamination and the difficult and destructive separation could be avoided.

Another interesting attempt was published in 1930 by Bertram Dillon Steele and James Edward Mills, of the University of Queensland at Brisbane[186]. Despite the work of these authors was about to be made quite ephemeral by the work of Schlesinger and Burg in

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[185] Stock refers a paper published by these authors in 1930, thus placing the development of this method before that date.

[186] B. D. Steele, J. E. Mills, "XII – The Hydrides of Boron", J. Chem. Soc., (1930), 74 – 79.

1931, there are several reasons which justify a more careful look at both the work and life of Bertram Steele (unfortunately Mills proved to be a really inconspicuous character): Steele and Mills were the first investigators, other than Stock and his co-workers, to produce their own hydrides of boron after Stock's first publication in 1912; also, it is somewhat intriguing that Australia was to be the first place in which the hydrides appeared during "Stock's era", other than Germany. This led to a natural curiosity about Steele and Mills and the developments that led them to work on the hydrides. Unfortunately, this part of their work has been entirely neglected in the biographical accounts that were found available on Steele (no secure biographical information on Mills was obtained). Thus, one could not really find out what led them to work on this subject, other than their own explicit concern with the structural problem. In fact, the following quotation makes it very clear that their intention was to render the investigations more amenable to the search for the BH_3 molecule: "The conclusions of Jones and Taylor, Sabatier and Ramsay and Hatfield as to the existence of BH_3 are without sufficient experimental foundation, yet a doubt remains that the existence of the simpler hydrides might be established if the field of investigation were widened."[187]

Meanwhile, Steele turned out to be a very interesting character, both on the scientific and on the personal planes, and since it seems that he became largely forgotten by the history of science, the decision was made to include a biographical note on him. After all, he and Mills did make a contribution, although a minor one, to the improvement of the production methods of the hydrides that was readily incorporated by Stock in his practice. This biographical note will also establish Bertram's high intellectual and scientific status, adding to the pattern of first-rate scientists that was to be maintained throughout the whole investigation on the hydrides of boron.

Bertram Dillon Steele was born in 1870, on May 30, at the English city of Plymouth. As a young man, Steele emigrated to Australia. He first studied Pharmacy, took the Society's Gold Medal at the qualifying examination, and started a pharmaceutical business. He then became dissatisfied with the routine and entered the University of Melbourne at the age of 25 to become a medical student. In his first year, Steele realized that his true vocation lay in Chemistry, having caused a sensation by obtaining one

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[187] B. D. Steele, J. E. Mills, "XII – The Hydrides of Boron", <u>*J. Chem. Soc.*</u>, (1930). On 74.

hundred per cent in his Chemistry examination. In 1899, he graduated as a Bachelor of Science, taking first-class honours in the School of Chemistry.

One year after graduation, Steele was awarded a research scholarship and travelled to London to work one year with Professor Collie at the University College. A joint paper on Dimethyldiacetylacetone, which became a standard work on the subject, was then published. On the advice of William Ramsay, Steele went to Breslau in 1901, to work under Professor Abegg on a problem of his own – the development of the Moving Boundary method of measuring Transport Numbers. After completing the preliminary work, which showed the great possibilities of the method, Steele became nonetheless interested in another problem, which involved the measurement of Transport Numbers of Calcium and Barium halides in dilute solution by the Hittorf Method. This work gained him the degree of Doctor of Science, awarded *in absentia*, by the University of Melbourne.

After his stay at Abegg's laboratory, Steele was invited by Ramsay to return to London and become associated with him in research in his private laboratory.

When this extended scholarship ended, Steele was appointed senior demonstrator of Chemistry at the McGill University, in Montreal. A year later, he accepted a similar position at the Heriot-Watt College, in Edinburgh, Scotland, where he engaged in research on Solution theory. Steel became a worldwide authority on this subject.

In 1906, Steel returned to Australia to accept the position of Senior Lecturer and Demonstrator of Chemistry in the University of Melbourne. In December of 1910, he was elected by the senate of the new University of Queensland to fill the post of Professor of Chemistry. Steele worked very hard to build from scratch the chemical laboratory of the new university, whose sound development owed much to his commitment, at the expense of his research work:

> Students of the University to-day will find difficulty in visualising the University of those early days. Professor Steele delivered his early lectures in Brisbane in an almost bare room, the sole furniture being a chair, a table and a black-board. There were seventy students at the opening of the University, they had no laboratory and had to improvise one out of kitchen tables, chairs and sundry culinary implements. Professor Steele set himself to change all this, and it was due to his untiring efforts that the Queensland University eventually had the best-equipped chemical laboratory in Australia. Moreover, the fact that the University of Queensland has a

> standard as high as that of any University in the world is due in no small measure to Professor Steele's efforts.[188]

Besides his contributions to knowledge in Chemistry, Steele was also the inventor of valuable laboratory apparatus, the most famous of them being the so-called "Steele-Grant Micro Balance". Steele devoted to this project every spare moment in his laboratory or in his home during many months. Later, he invited Kerr Grant, a brilliant younger colleague, to join him. Together, they succeeded at making the most precise balance in the world, so delicate that it had to be kept and used in a vacuum case. It could sense one thirty millionth part of a grain[189]. This instrument was later copied by Ramsay, with Steele's permission, who never patented his invention so that it would be available to other scientists, in the hope that they, in turn, could make further contributions to the advancement of science.

It was as an inventor that Steele went back to England in 1915, during WWI. Steele invented a new gas mask and some sort of submarine detector device for which he was sworn to secrecy before the Board of Admiralty, to whom he presented it. However, Steele also made important contributions to England's war effort as a chemist. Having been appointed as an inspector of factories supplying ammunition and chemicals to the British Government, Steele immediately denounced the fabulous profits that were being made by private factories. He then developed a new route to the synthesis of phenol, allowing a major reduction in the cost of this product to the British Government, who instructed Steele to design, build and manage a Government factory to produce it. Steele did it with astonishing efficiency and success, attracting the attention of one of the American suppliers of ammunitions for the British Government. Steele was offered a fabulous contract to go to America but to great surprise of the American, Steele refused it, as had refused all the payments and the highest honours offered by the British Government: "Professor Steele would accept neither money nor honour for what he considered a duty to his country."[190]

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[188] A. Hardman-Knight, R. B. Denison, *A Tribute to a Great Scientist: Bertram Dillon Steele*, (1935). On 9.

[189] 1 gr (grain) = 64.79891 mg (source: Bureau International des Poids et Mesures)

[190] A. Hardman-Knight, R. B. Denison, *A Tribute to a Great Scientist: Bertram Dillon Steele*, (1935). On 14.

Steele's devotion to Britain led him to produce a new mustard gas, which was not used in the battlefields because the war ended in the mean time. However, the "awful deadliness" of the new gas was tragically demonstrated by the instant death of two men who were passing the factory in a small rowing boat: "If Hitler ever breaks his undertaking no to use poison gas and Britain is forced to retaliate, then the whole German nation will be shaken to its foundations by the deadly effect of that gas which Professor Steele was producing at the close of the great war of 1914-8."[191]

Before his departure to help Britain to win the war, Steele was able to give birth to a long nurtured idea whose implementation proved a demanding task involving numerous journeys to Sidney looking for funding. This was the creation of the first school of applied science in Australia, which opened in 1915 and whose mission was to train industrial students as technical industrial experts.

Steele made also a decisive contribution to the eradication of the prickly pear, an infestant species of cactus in Australia. There is no secure information on exactly how the prickly pear was introduced in Australia from America. It seems that is was first used as a garden plant. Having been able to become rapidly acclimatised, it could rely on the inexistence of natural enemies and on the usual political negligence to spread at an alarming rate. By 1925, it was completely out of control, claiming 25 million hectares (60 million acres) and spreading at the rate of half a million hectares a year.

Extensive chemical and mechanical treatments programs were implemented but nothing seemed to be able to hold its progress. Many people were forced to abandon their lands.

The solution was biological control, using cactoblastis caterpillars (*Cactoblastis cactorum*). The first liberations of cactoblastis were made in 1926, after extensive laboratory testing to ensure they would not move into other plant species. Within six years, the problem was solved, becoming the world's most spectacular example of successful weed biological control.

Steele was actively involved in the whole process. He was the first chairman of the Prickly Pear Board, which was established in 1912, and in 1923 was invited to act as chairman of the Royal Commission on prickly pear. He also supervised the experimental station at Dulacca, where the first cochineal insects brought to Queensland were nursed. Steele travelled over 8,000 miles of pear-infested country with his

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[191] Hardman-Knight, A., Denison, R. B., *A Tribute to a Great Scientist: Bertram Dillon Steele*, (1935). On 14.

committee to write a report for the Government. Every suggestion in his report was made an act of Parliament within two and a half months. Steele never accepted to be paid a sum larger than his own modest salary as a Professor.

In 1927, Steele suffered a cerebral haemorrhage and nearly two years of severe illness followed, from which Steele never fully recovered. One cannot fail to make notice that it was on his return to the professorial activity, which was only made possible "with the help of his loyal staff", that his work on the hydrides of boron was realized and that this must have some meaning about the importance Steele attributed to this work.

Steele's fragile health condition finally dictated his forced resignation shortly after, in 1931. He died on April 12th, 1934.

In 1930, Steele and Mills reported their own new method for producing B_4H_{10} (and probably B_5H_9 and B_6H_{10}) from aluminium or cerium boride. Apparently, they did not use Stock's High-Vacuum Technique. Cerium boride was silane free and, consequently, was exempt of purification. Both yields were low, especially the aluminium boride one. In addition, Steele and Mills referred that, in 1911, Hoffmann had already reported the synthesis of unidentified boron hydrides from commercial iron and manganese borides. According to Stock, however, technical commercial borides of heavy metals such as iron, nickel and manganese were not suitable for making boron hydrides: "They either are not decomposed by acids or else give much smaller yields than does magnesium boride. The same is true of the products of the reaction between boron trioxide and aluminum or cerium."[192]

Thus, the efforts made by either Stock himself or by Steele and Mills or even those apparently incipient by Hoffmann were doomed to failure, in the sense that they all had not succeeded in overcoming Stock's extremely low yields. Of course, this was no coincidence, as all these efforts relied on the action of acidic aqueous solutions upon the borides, whatever their kind was. Steele and Mills used phosphoric acid instead of hydrochloric acid because it appeared to improve their very low yields, a progress that Stock would confirm and incorporate in his magnesium boride method. However, this represented a relatively minor advance, as the yields kept being discouraging low - an intrinsic and inescapable consequence of using an acidic aqueous solution to obtain the readily hydrolysable boron hydrides.

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[192] A. Stock, *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933). On 48.

Thus, a major breakthrough in the production methods of the hydrides of boron could only be achieved through a truly independent method, one that would not use aqueous solutions. That would be the work of Schlesinger and Burg, at the University of Chicago. Curiously enough, as so many times in the history of science, that would also be the work of chance.

4.2 –The Pungent Smell of Failure

In 1931, Hermann Irving Schlesinger and Anton Behme Burg, from the George Herbert Jones Laboratory of the University of Chicago, announced an entirely new and much more effective method for producing diborane. This was the fortuitous result of Anton Burg's work for his Ph. D. thesis under Schlesinger's supervision. In an attempt to produce pure boron from boron trichloride and hydrogen in an electric arc, diborane was detected. Two decades later, Schlesinger's mention to this episode in his 1951 Edgar Fahs Smith Memorial Lecture would be reported as follows: "The hypothesis which led to the selection of this method was soon shown to be incorrect, but demonstrated the importance of having a hypothesis even if it later proved to be wrong as several of theirs did."[193]

Hermann Irving Schlesinger was born in 1882 on October 11, in Milwaukee, Wisconsin, having moved to Chicago with his family at the age of six. The first studies were completed at a private grammar school that had been established by the German-American community. It was in high school that Schlesinger made an early and firm decision upon his future career in chemistry. This was the result of young Schlesinger's tutelage by Charles Elijah Linebarger, a remarkable science teacher that managed to keep researching and publishing despite his heavy duties as chemistry and physics teacher[194].

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[193] N/A , *Chemical and Engineering News*, 29 (13) (March 26, 1951).

[194] Charles Elijah Linebarger became Chairman of the Chicago Section of the American Chemical Society in 1899, a position that would be held by Schlesinger in 1930. This must have been a remarkable achievement for a high school teacher, as all the other chairmen held an academic position or a professional association to chemical industry.

In 1900, Schlesinger initiated his study of chemistry at the University of Chicago, where he attended classes held by John Ulric Nef, Alexander Smith, Julius Stieglitz, Albert Michelson and Robert Millikan. After a brilliant progression as undergraduate student, Schlesinger completed his Ph. D. thesis under the orientation of Julius Stieglitz in 1905.

That very same year he travelled to Germany, to spend a year with Nernst, in Berlin, where he attended the lecture courses delivered by Emil Fischer, Van't Hoff and Planck. At that time, Stock was in Berlin too, but no evidence was found that the two men ever met each other then.

In August of 1906, Schlesinger left Berlin to work on the diazotization of dichlorostilbene with Thiele, at Strasburg. He returned to the United States in February of 1907 to join Abel, one of the world's leading physiological chemists, at Johns Hopkins University. There, Schlesinger worked on the isolation of the toxic principle of *Amanitas phalloides*, a deadly poisonous mushroom, commonly known as the *death cap* and involved in most human deaths from mushroom poisoning.

At this point, an invitation by Nef to return to the chemistry department of the University of Chicago led Schlesinger to an unexpected career change. Since he had no prior experience in inorganic chemistry and was due to teach general chemistry, Schlesinger proceeded to fill that gap in his training by researching in inorganic chemistry.

For more than 20 years, Schlesinger published on a variety of subjects: pioneer work on the application of absorption spectra to inorganic chemistry; the conductivities of electrolytes in formic acid as a solvent (which led to an appointment as cooperating expert to the International Critical Tables); determination of the structure and properties of the complex compounds of chromium, iron, cobalt and platinum; studies on the manganates, permanganates and inorganic sulphur compounds.

At the time Schlesinger turned his attention to the hydrides of boron, in 1929, he was already a highly reputed expert in inorganic chemistry whose career had covered with notorious success a variety of distinct fields. An anonymous faculty member at the University of Chicago once said that Schlesinger could pick out an error in an experiment he had never seen, much less done, from half a mile away.

According to Schlesinger's statements in his Edgar Fahs Smith Memorial Lecture (1951), the main reason for his entrance in the boron hydrides field was the fact that "their formulas did not fit any of the theories about the nature of chemical bonds".[195] It has also been reported that Schlesinger was intrigued by the apparent link between organic and inorganic chemistries suggested by Stock's work on the hydrides of boron[196].

Schlesinger was joined by Anton Burg in 1930. Burg had graduated from the chemistry department of the University of Chicago and was coming back to the University after taking an industrial position. Burg's personal quest for the understanding of bonding in boron compounds probably had its origins in 1927, when he attended a lecture by Lewis at the University of Chicago: "He said that nobody understood the boron hydrides well", Burg would later recall.

Born on October 18, 1904, in Dallas City, Illinois, Burg was the grandson of a German immigrant who had made a fortune building carriages. William Lipscomb described him as the first American-born, American educated boron chemist.[197] While studying at the University of Chicago (B.S., 1927, Ph.D., 1931), Burg was also a world-class high jumper, five times winner of the U.S. national championship and barely missing the qualification for the 1928 Olympics[198]. Burg would become known both for his athletic eccentricities[199] and for being a very precise and meticulous chemist with a special ability to make "astute observations in ordinary experiments revealing unexpected new chemistry"[200]. Burg was also an excellent glass blower, a skill highly recommended in

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[195] The other reason was Schlesinger's perception that the study of compounds in which hydrogen behaved as if it were a negative constituent of compounds had been neglected. N/A, _Chemical and Engineering News_, 29 (13) (March 26, 1951), 1202 - 1203.

[196] "An American Contemporary...Herman I. Schlesinger", _Chem. Eng. News_, *27* (8) (1949). On 496.

[197] W. Lipscomb, In Memory of Anton Burg.
Available at http://chem.usc.edu/dept/IN_MEMORY.PDF.

[198] In 1926, and being "only" 5'11'' tall (1,80m), Burg cleared 6'6 1/4" (1,99m), one quarter-inch higher than the winning mark in the 1924 Olympics.

[199] Burg never walked upstairs. He ran, taking two, four or even five steps at a time. Coming down, he would take six or eight at a time. Burg's agility would become legendary when, on one occasion, the fire department wanted to close down Burg's chemistry labs at the University of Southern California for security reasons. Those labs were located on the second floor of some World War II prefabricated structures and lacked fire escapes. To prove the Fire Department inspectors that people could still safely get out of there, Burg "agilely leapt out the second story window, landing on the pavement like a cat".
Burg's bicycle became his brand. He never bought a car, a true eccentricity by American standards, and his ability to go anywhere on his bike did make an impact on people. At the age of 90, Burg still used his bicycle to go to his lab to run personally his experiments.

[200] W. Lipscomb, "In Memory of Anton Burg". Available at
http://chem.usc.edu/dept/IN_MEMORY.PDF.

that time for those who wanted to use Stock's High-Vacuum Technique, which he mastered with great imagination.[201]

Schlesinger and Burg's debut in the chemistry of the hydrides of boron can be read as having multiple historical significances. While constituting another unexpected break in the German monopoly of the experimental mastering of the hydrides, it also marks the first appearance of the hydrides in America. A spectacular one, it may be said, as its practical relevance resided in the incredibly higher yields that the new method was able to render (55%), when compared with the ones Stock had to deal with (3%).

Schlesinger and Burg's intention of seizing their new method to break such restrictive scenario was clearly stated in the first paragraphs of their paper. While acknowledging the "unusually ingenious and careful way" by which Stock and his co-workers had investigated the hydrides of boron, they were also aware that these "evidently deserve much further experimental study". However, Stock's poor yields in the production of the hydrides severely hampered systematic investigation:

> The main obstacle to the advance of knowledge of these substances has been the great difficulty and expense of preparing them in quantities sufficiently large for thorough study. Stock´s preparation method, which consists in the reaction between an acid in aqueous solution and an alloy of boron, seems to be inherently inefficient because the presence of water excludes the possibility of obtaining the instantly hydrolyzable diborane. The yields at best are only 3% and the process must be operated so slowly that a month of tedious work is required for the production of a few grams of a mixture of several hydrides.[202]

Schlesinger and Burg's explicit intention was then to overcome this situation and establish a new production rate that could sustain a more intensive and comprehensive investigation program of such demanding compounds:

> In order to render this field of chemistry more accessible to experiment, we have developed a comparatively efficient new method of preparing diborane. [...] we

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[201] Simon H. Bauer. Private Communication.

[202] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. I. An Efficient New Method of Preparing Diborane; New Reactions for Preparing Bromo-Diborane and the Stabler Pentaborane B_5H_9", J. Am. Chem. Soc., *53* (12) (1931). On 4321.

> believe that the new method solves the problem of obtaining diborane in quantities suitable for long series of experimental work. [203]

The new method consisted in the reduction of gaseous boron trichloride (BCl_3) by hydrogen in an electric discharge at low pressure. The volatile products of this reaction were large yields of monochlorodiborane (B_2H_5Cl), hydrogen chloride (HCl) and small quantities of diborane. B_2H_5Cl could not be separated by any contemporary physical means from the large parcel of BCl_3 that went unchanged through the electric discharge (three-quarters, under the most favourable conditions).

The hydrogen chloride and the small quantity of diborane (3% to 5%) directly produced by the discharge were separated from BCl_3 and B_2H_5Cl by distillation. These remaining compounds were then warmed up to 0 ºC, inducing the latter's decomposition according to the equation (already observed by Stock in 1914)

$$6B_2H_5Cl = 5B_2H_6 + 2BCl_3.$$

The diborane thus produced was then distilled off and easily purified by fractional condensation.

A perception of the yields the new method was able to render can be learned through Schlesinger and Burg's detailed description of one of their experiments: 17.8 litres of BCl_3 (gaseous state, at 0º C and 760 mm. pressure) was added to the hydrogen steam at -43 ºC and passed through a 15,000 V discharge maintained by a 250 VA transformer, at 9 mm. total pressure. This led to the formation of 14.06 litres of HCl, corresponding to the destruction of 4.69 litres of BCl_3. 150 cc. of diborane was directly produced and isolated in 90% purity by repeated fractional condensation through a U-tube at -140 ºC. The resulting mixture of BCl_3 and B_2H_5Cl was then freed from HCl and warmed up to 0 ºC during 4 hours, resulting in 700 cc. of nearly pure diborane that was isolated through distillation. The residue was allowed to stand at 0 ºC and a further 450 cc. of diborane was produced until the vapour pressure of the residue had fallen to 500 mm (at 0 ºC), which rendered thermal decomposition impracticable.

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[203] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. I. An Efficient New Method of Preparing Diborane; New Reactions for Preparing Bromo-Diborane and the Stabler Pentaborane B_5H_9", *J. Am. Chem. Soc.*, *53* (12) (1931). On 4321.

Hence, after 16.5 hours of operation, the experiment yielded a total of 1300 cc. of pure diborane, corresponding to the destruction of 2.60 litres of BCl_3, 55% of its initial amount (4.69 litres destructed by the electric discharge).

To carry the reduction of gaseous boron trichloride (BCl_3) by hydrogen under the electric discharge, Schlesinger and Burg used an experimental apparatus similar to the one that had been used by Weintraub in 1909 to synthesize pure boron. The volatile products thus obtained were further studied in a vacuum apparatus whose principles of operation where similar to that developed by Stock, although with a very different design.

Schlesinger and Burg's entrance in the boron hydrides chemistry was hailed by Stock: "It is gratifying to note that workers in other laboratories are beginning to enter this field, as is evidenced by a recent paper of Schlesinger and Burg." [204]

Stock acknowledged the importance of Schlesinger and Burg's method, while revealing that a similar method was then simultaneously under investigation in his lab:

> This method now makes B_2H_6 more readily available. By accident, a very similar reaction was being studied at the same time in the writer's laboratory, viz., the effect of a silent electric discharge upon a current of mixed hydrogen and boron chloride at decreased pressure. Our small-scale experiments with an ordinary Berthelot ozonizer led to a qualitatively similar, but less satisfactory quantitative result. [205]

While recognizing the superiority of the new method, Stock nevertheless pointed out its major technical shortcoming: "It seems to be more convenient to prepare B_2H_6 by this short method than by the use of magnesium boride and B_4H_{10}; but it probably will be difficult to separate the B_2H_6 completely from the equally volatile hydrogen chloride that is formed at the same time."[206]

Indeed, Schlesinger and Burg's method had such a technical difficulty, but this had to do only with the small amount of diborane that was directly produced (3 to 5%):

> The small quantities of diborane directly produced by the reaction in the discharge always are mixed with large quantities of hydrogen chloride, whose complete

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[204] Stock, A., *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933), p. vi.

[205] Stock, A., *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933), p.48.

[206] A. Stock, *Hydrides of Boron and Silicon*, (New York: Cornell University Press, 1933). On 52.

> removal is rather difficult. We have found that samples of diborane, from which most of the hydrogen chloride has been removed, may be completely purified by allowing them to stand for several months at room temperature. The hydrogen chloride is used up, evidently by the reaction $B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2$. The reaction proceeds without any catalyst other than glass or mercury.[207]

The implications, thus, were restricted to time performance in the purification of the small initial amount of diborane.

Since they could now easily access relatively high amounts of diborane, Schlesinger and Burg's explicit ambition was to extend their success to the higher hydrides of boron by devising new production methods that would use diborane as the departing reactant: "The development of a rapid and efficient method of preparing diborane (B_2H_6) has made desirable the finding of efficient methods of preparing from it the less volatile hydrides of boron."[208]

In fact, already in their first paper, Schlesinger and Burg reported that the now readily available diborane could be used to produce useful quantities of the more stable pentaboron hydride B_5H_9. This discovery was a consequence of their attempts to separate hydrogen chloride from the small amount of diborane that was directly produced by the electric discharge. They observed that, when heated at 120-130 ºC, in the absence of mercury, diborane containing a small quantity of hydrogen chloride produced a substance whose melting point and vapour pressure allowed identification with B_5H_9 by comparison with the values that had been determined by Stock and Kuss in 1923 (an accident had prevented Schlesinger and Burg from a direct elementary analysis). As Schlesinger and Burg were keen to stress, this was an entirely new reaction; the direct production of B_5H_9 from diborane had never been reported. Moreover, it came out with yields of about 20%, which they considered sufficiently promising: "We hope to find the conditions most favorable to this reaction, as it promises to be the means of making B_5H_9 readily available for experiment."[209] In fact,

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[207] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. I. An Efficient New Method of Preparing Diborane; New Reactions for Preparing Bromo-Diborane and the Stabler Pentaborane B_5H_9", *J. Am. Chem. Soc.*, *53* (12) (1931). On 4323.

[208] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", *J. Am. Chem. Soc.*, *55* (10) (1933). On 4009.

[209] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. I. An Efficient New Method of Preparing Diborane; New Reactions for Preparing Bromo-Diborane and the Stabler Pentaborane B_5H_9", *J. Am. Chem. Soc.*, *53* (12) (1931). On 4332.

in their next paper, they were able to report the improvement of the yields of this reaction to a maximum of 33%, as a consequence of their investigation on the production of B_5H_{11} from diborane.[210]

Contrary to the diborane and B_5H_9 cases, Burg and Schlesinger's production methods for B_5H_{11} were no novelty. Stock had already reported the production of "a few cubic centimetres" of B_5H_{11} from diborane, either through slow decomposition of diborane at room temperature (Stock's reported decomposition periods of six and ten months) or through thermal decomposition of diborane at higher temperatures. However, unlike Stock, who did not try to enhance B_5H_{11} production from diborane, which is quite understandable in face of his poor production rates for diborane and also in face of the pioneering character of his investigations, Burg and Schlesinger were aiming at the preparation of large quantities of B_5H_{11}. Dissatisfied with Stock's yields, they devised a flow method, which allowed them the thermal decomposition of diborane at temperatures between 100 and 120 ºC. This process had to be limited to short periods of time in order not to risk B_5H_{11} own thermal decomposition but could be "repeated again and again, to convert any desired fraction of the diborane into B_5H_{11} and B_4H_{10}."[211]

Thus, what was new here was not the complex thermal decomposition phenomena of diborane, which had already been reported and investigated by Stock and his co-workers, but the development of a new experimental procedure designed to build on it and on the now readily available diborane to achieve a larger scale production of B_5H_{11}.

This meant an empirical breakthrough on what concerned B_5H_{11} investigation, as this was, as Burg and Schlesinger put it, a "hitherto little known substance". In fact, Stock had explicitly admitted that B_5H_{11} production was too low to enable an extensive investigation of its properties.

Hence, Burg and Schlesinger, unlike Stock, were now able of a much more thorough study of B_5H_{11} physical properties and chemical behaviour. And so they did. For example, by this time, contamination of B_5H_{11} samples with B_5H_9 was still posing problems to both Stock and Schlesinger's work: "Present analytical methods do not

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[210] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", J. Am. Chem. Soc., *55* (10) (1933), 4009–4020.

[211] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", J. Am. Chem. Soc., *55* (10) (1933). On 4012.

permit a determination of the amount of B_5H_9 in a sample of nearly pure B_5H_{11}."[212] This had led Stock and Siecke, in 1924, to a mistaken belief in the existence of a third pentaborane, distinct from B_5H_9 and B_5H_{11}. Stock would still argue for the existence of this "$B_5H_{>9}$" hydride in his book, in 1933, but this was refuted by Burg and Schlesinger in that same year. Not having been able to find any evidence in support of that assumption, and arguing that, on the contrary, their observations had always been consistent with those of Stock and Siecke for either B_5H_{11} alone or B_5H_{11} admixed with a large proportion of B_5H_9, Burg and Schlesinger put forward the following conclusion: "It is reasonable to believe that "$B_5H_{>9}$" and B_5H_{11} are identical."[213]

Since contemporaneous chemical methods would not allow the detection of the pervasive B_5H_9 in B_5H_{11} samples, Burg and Schlesinger turned their attention to B_5H_{11} physical constants. They determined the vapour tensions at several temperatures, having established the value 53.0 mm at 0 ºC. They also made two determinations of the melting point: -123.3 ºC and -123.4 ºC. Burg and Schlesinger's values for the vapour tensions were in close agreement with those that had been reported by Stock and Pohland at low temperatures, but a significant deviation occurred at higher temperatures (Stock and Pohland had reported 57mm at 0ºC). In addition, Stock values for the melting point were markedly distinct from those reported by Burg and Schlesinger: -129.1 ºC, -128.3 ºC and -128.5 ºC. Burg and Schlesinger explained these discrepancies with the contamination of Stock's samples with B_5H_9:

> It evident that their sample was free from tetraborane, but must have been considerably contaminated with B_5H_9. This is to be expected in a sample accumulated in a period of ten months. One of our samples, obtained from diborane which had stood for thirteen and one-half months at room temperature, was analysed by complete thermal decomposition and found to contain about 12% B_5H_9. Its vapor tension at 0º, after the most rigorous fractionation, was 57 mm.[214]

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[212] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", J. Am. Chem. Soc. *55* (10) (1933). On 4016.

[213] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", J. Am. Chem. Soc., *55* (10) (1933). On 4010.

[214] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", J. Am. Chem. Soc., *55* (10) (1933). On 4013.

Burg and Schlesinger were able to demonstrate the vapour pressure at 0ºC as a very sensitive test of the degree of contamination: “The presence of B_5H_9 in carefully purified pentaborane samples is indicated very well by the deviation of the vapor pressure at 0º from the value 53.0 mm.”[215]

Burg and Schlesinger studied the thermal decomposition of B_5H_{11} and found out that it decomposed to give hydrogen, diborane, tetraborane and almost undetectable traces of B_5H_9 and $B_{10}H_{14}$. They also identified a mysterious slightly volatile substance whose quantity was always too small to allow definite conclusions on its composition. By the repeated application of a flow method, they were, nonetheless, able to get enough of that substance to determine its vapour pressure at 24 ºC: 1.2 mm. Then, since they were unable of an analytical study of that substance, they appealed to a linear regression curve between the number of boron atoms in each hydride molecule and its vapour pressure at 24 ºC to justify their identification of that substance as a new hydride, an octaborane:

> The most direct evidence for the belief that this substance is an octaborane is derived from the value of its vapor tension at 24º. The temperature at which each of the of the known hydrides of boron has a vapor tension of 1.2 mm. may be calculated from the vapor tension-temperature curves, and found to be as follows: B_2H_6, -162º; B_4H_{10}, -90º; B_5H_{11}, -58º; B_6H_{10}, -28º; $B_{10}H_{14}$, 63º. If we plot the temperature against the number of boron atoms in the molecule, we obtain a very regular curve whose intercept at 24º corresponds to 8.05 ± 0.10 boron atoms. It seems reasonable safe to conclude that the slightly volatile substance was an octaborane.[216]

Burg and Schlesinger’s investigations on B_5H_{11}, in turn, gave rise to a new method for preparing “useful quantities” of B_4H_{10}, “without recourse to the less efficient procedures involving the use of boron alloys”. This new method was based on the reaction between B_5H_{11} and hydrogen: $2B_5H_{11} + 2H_2 \leftrightarrow 2B_4H_{10} + B_2H_6$.

> [...] the reaction of B_5H_{11} with hydrogen gives us an efficient means of preparing tetraborane. The development of a convenient technique for carrying on this reaction

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[215] A. B. Burg, H. I. Schlesinger, “Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen”, *J. Am. Chem. Soc.*, *55* (10) (1933). On 4014.

[216] A. B. Burg, H. I. Schlesinger, “Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen”, *J. Am. Chem. Soc.*, *55* (10) (1933). On 4015.

> on a large scale should make this substance considerably more easily available than it has been before. A flow method should be suitable for the purpose.[217]

Schlesinger and Burg were also able to improve diborane's halogenation. By sheer analogy with the reaction $6B_2H_5Cl = 5B_2H_6 + 2BCl_3$, which they had proven to be a reversible equilibrium, Schlesinger and Burg decided to study the reaction $5B_2H_6 + 2BBr_3 = 6B_2H_5Br$. Having discovered that in this case the equilibrium was even more favourable to the formation of the halogen derivative, they concluded that this reaction was "a convenient and efficient means of preparing bromodiborane" and that this type of reactions suggested the possibility of using boron halides to substitute hydrogen for halogens in the higher hydrides of boron. According to Schlesinger and Burg, this method for preparing bromodiborane presented considerable advantage over that used by Stock, Kusz and Priesz in 1914, since it did not require special apparatus for handling bromine under vacuum conditions.

Schlesinger and Burg's new production method was improved by Stock and Sütterlin in 1934. They used boron bromide instead of boron chloride because the decomposition of bromodiborane to diborane could be more easily brought to completion:

$$6\ B_2H_5Br \leftrightarrow 5\ B_2H_6 + 2\ BBr_2$$

This was due to two reasons: the volatility of the boron bromide BBr_2 made it relatively easy to remove from the reaction mixture. According to the Le Chatêlier principle, if BBr_2 is continuously removed from the above chemical equilibrium, the reaction will continuously evolve to produce it and diborane, eventually leading to the complete transformation of B_2H_5Br into diborane; diborane's purification was also more easily achieved with bromine-containing impurities than with the corresponding chlorine compounds. This allowed improving the reaction yields up to 80%.

However, it must be said that, by 1942, Stock's original method was still used with advantage in the production of hexaborane.

The importance of the new method by Schlesinger and Burg was not restricted to the achievement of much higher production rates. It was also a major achievement in the simplification of the production methods as well. As already stated, Stock's method to

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[217] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", <u>*J. Am. Chem. Soc.*</u>, *55* (10) (1933). On 4010.

prepare magnesium boride embodied a very complex set of knowledge that could be more properly described as an art, rather then just a scientific process. Schlesinger himself described it as a “cumbersome task”.

This description of Schlesinger and Burg’s investigations shows very clearly that a major characteristic of their work was their ability to departure from a fortuitous finding to develop a fully autonomous production program which, in a consistent and consequent effort, rendered for the first time production rates that could sustain the growth and expansion of boron hydride chemistry for academic purposes.

Although Schlesinger and Burg had an autonomous research program with differentiated methodologies that were able to outshine Stock’s production rates and even to correct some of his results, conclusions and quantitative determinations, the undeniable truth is that all of their work was entirely built on Stock’s achievements. They relied heavily on Stock’s investigations, making constant references to it. In fact, their references were exclusively to Stock’s work. That can hardly be a surprise, since at that time, apart from Steele and Mill’s brief incursion in the field, the production and analytical investigation was circumscribed to Stock and Schlesinger’s groups.

This genetic filiation between the two groups was especially strong on what concerned the experimental apparatus and techniques used by Schlesinger and Burg. They did frequent design adaptations of Stock’s basic apparatus to their momentary needs and Burg is even to be credited for some important modifications and additions to Stock’s High-Vacuum Technique, namely by new designs for the float valves, the application of fractionating columns and a simplified technique of fractional condensation, which allowed the isolation of extremely unstable compounds.[218] With these improvements, Burg was able to isolate and determine the melting point and vapour tension of chlorodiborane (B_2H_5Cl), one of the compounds involved in their production method for diborane and which until then could not be isolated. Even so, Schlesinger and Burg never really departed from Stock’s inventions, at least in the same way they departed from Stock’s production methods.

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[218] A. B. Burg, “The Isolation of Chlorodiborane; Some Additions to the High-vacuum Technique for Chemical Work with Volatile Substances”, J. Am. Chem. Soc., *56* (3) (1934), 499–501.

5 – The American Way

The most striking feature of Schlesinger and Burg's research on the boron hydrides in the first ten years is its profound commitment to the structural problem. It is certainly true that this issue had been Stock's major driving force in his investigations. However, the fact the Stock had already made such an extensive exploratory research, allowed Schlesinger and Burg to build on his results to make an even greater commitment to the structural question, which had been in the origin of their decision to enter this field.

Thus, after having introduced new and much more effective production methods in their first two papers, Schlesinger and his group completely focused on the structural question. To be rigorous, Burg and Schlesinger's concern with this issue is quite evident already in their second paper, where B_5H_{11} thermal decomposition and its reaction with hydrogen, $2B_5H_{11} + 2H_2 \leftrightarrow 2B_4H_{10} + B_2H_6$, prompted them to put forward an assumption about its structure:

> The thermal decomposition of B_5H_{11} and its reaction with hydrogen are most easily understood by supposing that the structure of this substance is an open chain, whose most probable mode of decomposition is a break at one end. This picture accounts very well for the reaction with hydrogen, which produces one molecule of tetraborane from each molecule of pentaborane used up. This reaction may be an addition of hydrogen to the tetraboryl and monoboryl radicals produced by the breakdown of the five-atomic chain. The same assumption would account for the formation of an octaborane in the absence of hydrogen, under which conditions some of the tetraboryl radicals might unite to form eight-atomic chains.[219]

There is a substantial difference in kind between these statements and the subsequent research, in the sense that the latter was entirely guided by the search for information on the structure of the hydrides. This is not to say that there was a real change in attitude between their third paper and the previous one, since they were literally published one after the other (the last page of their second paper is also the first one of their third work on the hydrides of boron).

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[219] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen", J. Am. Chem. Soc., *55* (10) (1933). On 4010.

Before beginning the description of Schlesinger's research on diborane's structure, it is important to mention that Schlesinger's methods, like those by Stock, were a direct product of his scientific training, and, for that reason, his only instruments to probe diborane's structure were those of analytical chemistry. Therefore, he could only aim at indirect evidence from the chemical behaviour of the hydrides and their compounds and one cannot really understand how clever and imaginative he and Burg had to be in their approach without "plunging" into their work.

5.1 – Not a Wild-Goose Chase

At the time Schlesinger and Burg began their researches, the empirical adequacy of Wiberg's theory was already forcing it as a serious candidate to the solution of the structural puzzle that the hydrides of boron were imposing to chemistry. However, Schlesinger and Burg were not willing to embrace it, since they believed that BH_3 was the fundamental structural unit of the hydrides of boron. The isolation of the BH_3 molecule had been ruled out by Stock, but they believed that it was not due to any fundamental impossibility in its existence but rather to an experimental incapacity to prevent its great tendency to dimerization. They accordingly devised an ambitious research program that was intended to bring some light on the conditions under which diborane, supposed to be a dimer of BH_3, would break its boron-boron link or, inversely, what would make molecules of the type BX_3 to aggregate. More succinctly, Schlesinger and Burg were aimed at studying the stability of the boron-boron bond and wanted to establish the transitory existence of BH_3. Of course, this would be a powerful argument against Wiberg's ideas.

The first paragraph of Burg and Schlesinger's third paper (1933) is very informative:

> Linkages between boron atoms seldom occur in compounds of boron with elements other than hydrogen. A striking contrast to this situation is presented by the boron hydrides, in all of which the boron atoms are linked together. The tendency for such linking is so strong that monoborine (BH_3) seems incapable of existence and the

> simplest hydride is diborane (B_2H_6), a circumstance not easily explained by any generally acceptable theory of valence.[220]

These statements show very clearly that Burg and Schlesinger assumed that the boron atoms were linked together in all boron hydrides. Since this assumption was not justified (they did not refer the reader to any such discussion either), one can conclude that this was by then a generalized assumption. These statements also show that they regarded monoborine (BH_3) as the expectable fundamental structural unit for the hydrides, an implicit dismissal of Wiberg's theory.

In fact, two years later, Schlesinger would make this explicit: "Although diborane has an atomic arrangement similar to that of ethane, as show by x-ray data taken at low temperatures..."[221]

Here Schlesinger makes an explicit reference to the X-ray diffraction study of crystallized diborane made by Mark and Pohland in 1925, declaring it as his empirical substantiation for an ethane-like structure of diborane. This was an explicit dismissal of Wiberg's theory.

In their first paper, in 1931, Schlesinger and Burg had already stated that "[...] their [the hydrides] formulas [...] seem not to be explained by any widely applicable theory of valence and molecular structure."[222] In 1933, they repeated their evaluation of the situation: "...a circumstance not easily explained by any generally acceptable theory of valence"[223]. Schlesinger and Burg were not willing to give up a general solution to the chemical bond. In particular, this constitutes explicit evidence that, at that time, they did not endorse the one-electron bond theory. It may also constitute evidence that Schlesinger and Burg criticized Pauling's one-electron bond for its suspicious lack of applicability beyond boron hydrides.

Besides the inexistence of BH_3 in a stable form, Schlesinger and Burg were also puzzled by the strange behaviour of diborane towards halogenation, reported by Stock, Kusz and

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[220] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. III. Dimethoxyborine", J. Am. Chem. Soc., *55* (10) (1933). On 4020.

[221] H. I. Schlesinger, A. O. Walker, "Hydrides of Boron. IV. The Methyl Derivatives of Diborane", J. Am. Chem. Soc., *57* (4) (1935). On 621.

[222] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. I. An Efficient New Method of Preparing Diborane; New Reactions for Preparing Bromo-Diborane and the Stabler Pentaborane B_5H_9", J. Am. Chem. Soc., *53* (12) (1931). On 4321.

[223] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. III. Dimethoxyborine", J. Am. Chem. Soc., *55* (10) (1933). On 4020.

Priesz in 1914 and Stock and Pohland in 1926: "Substitution of halogens for hydrogen in diborane leads to compounds of the type B_2H_5X and possibly $B_2H_4X_2$, but further substitution leads only to the boron trihalide."[224]

The only explanation for this behaviour would be a different kind of stability in the B-B bond, as compared to the C-C bond in carbon hydrides. Burg and Schlesinger were willing to elucidate why this was so and tried to use their analytical approach to reach some conclusions:

> It is thus of considerable interest to prepare compounds of the types HBR_2, H_2BR, HBX_2, and H_2BX, in the hope that a compound showing a tendency toward association by boron linkages may be obtained. Such a work might lead to a better understanding of the factors which stabilize the boron to boron bond.[225]

In an attempt to implement this line of research, they were able to prepare dimethoxyborine, $(CH_3O)_2BH$, from the reaction of diborane with methyl alcohol. Aside from the study of its physical properties and its decomposition equilibrium, Burg and Schlesinger's results were somewhat disappointing: "Dimethoxyborine shows no tendency toward association, beyond that common to most volatile oxygen compounds."[226]

In 1935, Schlesinger and Walker came up with a different kind of approach to the same strategy. For the first time, Schlesinger made an explicit reference to the discussion on the structure of the hydrides, in the form of a foot-note reference to the contributions of Eastman (1922), Robinson (1922), Main Smith (1927), Sugden (1927), Wiberg (1928), Sidgwick (1927), Pauling and Mulliken. This was the first time that Schlesinger made a direct reference to Wiberg. Lewis' contribution was not mentioned at all.

While disclosing their preference for the one-electron bond solution, Schlesinger and Walker were not able to justify it. On the contrary, they argued that no theory had a solid empirical basis:

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[224] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. III. Dimethoxyborine", J. Am. Chem. Soc., *55* (10) (1933). On 4020.

[225] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. III. Dimethoxyborine", J. Am. Chem. Soc., *55* (10) (1933). On 4020.

[226] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. III. Dimethoxyborine", J. Am. Chem. Soc., *55* (10) (1933). On 4025.

> Many suggestions have been made concerning the structure of diborane, although all of these lack the support of an adequate experimental basis, those assuming some type of single electron bond between boron and hydrogen seem at present most satisfactory as working hypotheses.[227]

In this statement, Schlesinger and Walker made very clear that they were not endorsing any particular account of the one-electron bond concept, but that they rather opted by an instrumental approach to the concept itself. Of course, the fact that they chose the one-electron bond gives away a subjective preference for that concept. Thus, this statement also shows how cautious Schlesinger and his group were determined to be. The hydrides of boron constituted a truly dangerous mined field.

Still, they were forced to distance themselves from Mulliken's version of the one-electron bond, because of his failed anticipation of a paramagnetic behaviour for the hydrides. While revealing that their own preliminary investigations contradicted Mulliken's conclusions, Schlesinger and Walker were able to sustain the one-electron concept by distrusting the certainty of Mulliken's theoretical argumentation for his conclusions.

Schlesinger and Walker's strategy to use the one-electron bond concept as a working hypothesis to refine Schlesinger and Burg's previous use of substitution derivatives of diborane was as simple as brilliant. While the two H-B one-electron bonds in diborane would not necessarily have to be in a particular H-B bond but rather could resonate among all the six existing B-H bonds, this would not be possible if four of the hydrogen atoms had been substituted by other atoms or groups, since "boron compounds containing no boron to hydrogen links had, in general, formulas consistent with the ordinary present-day concepts of valence"[228]. Thus, such a substitution of four of diborane's hydrogen atoms would force the one-electron bonds to fixed positions. Clearly, Schlesinger and Walker were trying to "ambush" the one-electron bonds:

> Should there be marked differences in properties and stability of the tetra and pentamethyl derivatives, or should the latter prove incapable of existence, this result would itself have some bearing on the problem in question; further detailed study of

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[227] H. I. Schlesinger, A. O. Walker, "Hydrides of Boron. IV. The Methyl Derivatives of Diborane", *J. Am. Chem. Soc.*, *57* (4) (1935). On 621.

[228] H. I. Schlesinger, A. O. Walker, "Hydrides of Boron. IV. The Methyl Derivatives of Diborane", *J. Am. Chem. Soc.*, *57* (4) (1935). On 621.

> these compounds might ultimately lead to a far better understanding of the nature of the anomalous valence relations in the boron hydrides.[229]

By analogy with the halogenation of diborane by boron halide, used by Schlesinger and Burg in 1931, Schlesinger and Walker were able to methylate diborane through its reaction with boron trimethyl. The following equations express their results:

$$5B_2H_6 + 2B(CH_3)_3 \rightarrow 6B_2H_5CH_3$$
$$2B_2H_6 + 2B(CH_3)_3 \rightarrow 3B_2H_4(CH_3)_2$$
$$B_2H_6 + 2B(CH_3)_3 \rightarrow 2B_2H_3(CH_3)_3$$
$$B_2H_6 + 4B(CH_3)_3 \rightarrow 3B_2H_2(CH_3)_4$$

In spite of their best efforts, Schlesinger and Walker never succeeded at synthesizing pentamethyldiborane or at detecting any tendency to boron-boron bond disruption.

For the first time, Schlesinger's strategy gave its fruits, for he and Walker, by studying the hydrolysis of these compounds, were able to draw some important conclusions on their structure:

> Dimethyldiborane, prepared according to the reaction mentioned, appears to have an unsymmetrical structure in which both of the methyl groups are attached to the same boron atom, for, when hydrolyzed, it yields one mol of boric acid, one mol of dimethylboric acid and four mols of hydrogen. In the trimethyl derivative, two of the methyl groups are shown to be attached to one of the boron atoms and the third to the other, for hydrolysis yields no boric acid and but one mol of dimethylboric acid. Tetramethyldiborane yields two mols of dimethylboric acid and hence has a symmetrical structure. [230]

In conjunction with the inexistence of pentamethyldiborane, this was interpreted as a corroboration of Stock's conclusion that each boron atom in diborane always had to be attached to, at least, one hydrogen atom. Otherwise, there would be no apparent reason for the inexistence of either pentamethyldiborane or an unsymmetrical tetramethyldiborane or even a totally unsymmetrical trimethyldiborane.

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[229] H. I. Schlesinger, A. O. Walker, "Hydrides of Boron. IV. The Methyl Derivatives of Diborane", J. Am. Chem. Soc., *57* (4) (1935). On 622.

[230] H. I. Schlesinger, A. O. Walker, "Hydrides of Boron. IV. The Methyl Derivatives of Diborane", J. Am. Chem. Soc., *57* (4) (1935). On 622.

Of course, these were not conclusions on the structure of diborane itself but they had rather important bearings on it as well:

> It appears that the boron-boron linkage in compounds of this type can exist only when each boron atom is also attached to at least one hydrogen atom. More broadly stated, this observation lends support to the view mentioned in the introductory paragraph that (at any moment) two of the hydrogen atoms in diborane are held by a type of bond different from that which holds the other four hydrogen atoms.[231]

According to H. J. Emeléus, Stock expressed the same conclusion[232].

The reference to their introductory paragraph shows that Schlesinger and Walker interpreted these results as corroborative of the one-electron bond concept, but one has to keep in mind that Wiberg's theory also contained a different kind of bonding in two of diborane's hydrogen atoms. Therefore, the legitimacy of Schlesinger and Walker's conclusions cannot come from this investigation alone. These conclusions can only make sense in a pre-existent framework of rejection of Wiberg's theory.

Moreover, Schlesinger and Walker were forced to an inevitable additional assumption to explain the inexistence of pentamethyldiborane: "It must be admitted, however, that substitution of four methyl groups for four hydrogen atoms in diborane may so alter the character of the molecule as to prevent further substitution."[233]

So, to conciliate their results with the application of the one-electron bond concept to an ethane-like structure for diborane, Schlesinger and Walker were forced to acknowledge that diborane was different from ethane in that the substitution of four of its hydrogen atoms would necessarily change the molecule's capacity of further substitution, very much unlike ethane.

Schlesinger's next publication, co-authored by Leo Horvitz and Burg, reported the extension of this investigation to the ethyl and n-propyl derivatives of diborane. This was done "to determine whether increase in the molecular weight of the radical replacing hydrogen in diborane is accompanied by marked changes in the stability of

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[231] H. I. Schlesinger, A. O. Walker, "Hydrides of Boron. IV. The Methyl Derivatives of Diborane", J. Am. Chem. Soc., *57* (4) (1935). On 622.

[232] H. J. Emeléus, A. J. E. Welch, "Inorganic chemistry", *Annu. Rep. Prog. Chem.*, 37 (1940). On 141.

[233] H. I. Schlesinger, A. O. Walker, "Hydrides of Boron. IV. The Methyl Derivatives of Diborane", J. Am. Chem. Soc., *57* (4) (1935). On 622.

the compounds."[234] They hoped that a detected decrease in stability might led to a better understanding of boron-boron bond in diborane, but the new compounds' behaviour was entirely similar to that of the methyl derivatives of diborane.

In that same year, Schlesinger, Horvitz and Burg used the methyl derivatives of diborane to test Stock and Pohland's benzene structure for $B_3N_3H_6$, the relatively stable, volatile compound that Stock and Pohland had synthesized in 1926 through the rapid heating to 200ºC of the diammoniate of diborane, the salt-like substance first prepared by Stock and Kuss in 1923. A further study of the adequacy of the ring structure was to be achieved through the study of the synthesis and hydrolysis of the methyl derivatives of $B_3N_3H_6$.

According to Schlesinger, Horvitz and Burg, this ring structure had been proposed by Stock and Pohland in 1926 "on the basis of fairly convincing but not perfectly conclusive experience"[235]. Thus, they were able to obtain one, di and tri-methyl derivatives of the inorganic benzene by rapidly heating the diammoniate of the corresponding methyl derivatives of diborane at low temperatures (or a mixture of ammonia and the methyldiborane). They found the yields to be greatly improved by using higher pressures than those reported by Stock and Pohland.

Schlesinger, Horvitz and Burg postulated a reaction mechanism for the synthesis of each methyl derivative of $B_3N_3H_6$ and then confronted the experimental outcomes with those expectable according to the corresponding postulated mechanism.

Only the reaction between ammonia and tetramethyldiborane (which held no methyl derivative of $B_3N_3H_6$) held quantitative results in agreement with its supposed reaction mechanism. However, Schlesinger, Horvitz and Burg ascribed the observed discrepancies to side reactions, in particular to the production of a non-volatile solid of unknown composition, already reported by Stock and Pohland.

Schlesinger, Horvitz and Burg then studied the hydrolysis of the methyl derivatives of $B_3N_3H_6$ and considered that the good agreement between the calculated and observed quantities of released hydrogen was corroborative of all their assumptions: the ring structure for $B_3N_3H_6$, their postulated reaction mechanisms and that the hydrogen freed in the hydrolysis of the methyl derivatives of $B_3N_3H_6$ resulted only from B-H bonds. On

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[234] H. I. Schlesinger, L. Horvitz, A. B. Burg, "Hydrides of Boron. V. The Ethyl and n-Propyl Diboranes", J. Am. Chem. Soc., *58* (3) (1936). On 407.

[235] H. I. Schlesinger, L. Horvitz, A. B. Burg, "Hydrides of Boron.VI. The Action of Ammonia on the Methyl Diboranes", J. Am. Chem. Soc., *58* (3) (1936). On 409.

that basis, they concluded that the methyl radicals were only linked to boron atoms in $B_3N_3H_6$. The empirical outcome of their investigation was the synthesis of the new compound dimethylaminoborine $(CH_3)_2BNH_2$, a product formed in small amounts in the reaction between ammonia and the methyl derivatives of diborane, and the synthesis and isolation of the new methyl derivatives of $B_3N_3H_6$: $CH_3B_3N_3H_5$, $(CH_3)_2B_3N_3H_4$ and $(CH_3)_3B_3N_3H_3$. As usual, its vapour densities, vapour tensions, freezing points and other physical constants were determined.

Aside its empirical achievements and being one further example of how structural concerns guided Schlesinger's research, the investigation on the structure of $B_3N_3H_6$ had no direct bearings on the structure of boron hydrides, since, due to nitrogen's lone pair of electrons, this was not an electron deficient molecule. However, one should notice that Schlesinger and Burg, while endorsing Stock and Pohland's structure for $B_3N_3H_6$, did not say a word about Wiberg's structure for this molecule, which was genetically related to his structures for the hydrides of boron.

Burg and Schlesinger were never able to isolate borine (BH_3), but they were successful at discovering new compounds that resulted from reactions of diborane with molecules containing unshared electron pairs, and which seemed to be better explained by reaction mechanisms that implied the transitory existence of BH_3.

This was the case of the gaseous compound BH_3CO, produced by the reaction of diborane with carbon monoxide:

$$B_2H_6 + 2CO \leftrightarrow 2BH_3CO$$

In their study of the reverse reaction, Burg and Schlesinger verified that the initial rate of decomposition of BH_3CO at room temperature was relatively high but decreased very rapidly under the inhibiting effect of carbon monoxide, diborane's effect being negligible. They concluded for the existence of two steps in the reverse reaction ($2BH_3CO \leftrightarrow B_2H_6 + 2CO$): the first was described by the equation $BH_3CO \leftrightarrow BH_3 + CO$ and implied the transitory existence of borine. Presumably, this was a rapid and easily reversible reaction that was carried forward by the removal of borine through the almost irreversible secondary reaction $2BH_3 \rightarrow B_2H_6$, whose rate determined the initial rate of the entire process.[236] The inhibiting effect of carbon monoxide in the overall

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[236] This was an assumption based on the failed attempts by Stock and Kuss, in 1923, to obtain borine through the thermal decomposition of diborane up to 155ºC. In fact, Burg and Schlesinger's only

reaction would be explained by its effect in reversing the first reaction, diminishing the borine available to form diborane.

Due to the speculative nature of their reasoning, Burg and Schlesinger proceeded to complement it with more compelling evidence for the transitory existence of borine based on the displacement effect of trimethylamine on BH_3CO, which produced the new compound borine trimethylammine $(CH_3)_3NBH_3$:

$$BH_3CO + (CH_3)_3N \rightarrow (CH_3)_3NBH_3 + CO$$

In Burg and Schlesinger's opinions, these reactions supported the assumption of a borine carbonyl structure for BH_3CO. Whether it was the carbon atom or the oxygen atom that was actually linked to boron it did not really matter to them.

These investigations gave birth to a whole research program on the behaviour of the alkyl diboranes and some of the higher boranes with carbon monoxide and with trimethylamine. In addition, they also searched for compounds, other than carbon monoxide and trimethylamine, which might unite with borine, because "these lines of work should lead to a better understanding of the nature of the boron hydrides and of the numerous "addition compounds" which they seem to be capable of forming."[237]

Trimethylamine-borine $(CH_3)_3NBH_3$ could also be obtained from the reaction of the higher boranes with trimethylamine. B_5H_9 reacted with it to give the compound $B_5H_9{\cdot}2N(CH_3)$, which when heated gave trimethylamine-borine and "other products not yet characterized"[238]. Tetraborane and B_5H_{11} reacted with trimethylamine to yield impure samples of trimethylamine-borine and a non-volatile solid residue. These were inconclusive preliminary results, but Schlesinger and Burg believed that these reactions could lead to important structural results: "These reactions deserve further, more highly detailed study, since they may be helpful in elucidating the structure of the higher hydrides."[239]

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evidence that the reaction was reversible at all derived from their proposed reaction mechanism for the formation of BH_3CO from diborane and carbon monoxide.

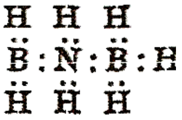
[237] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. VII. Evidence of the Transitory Existence of Borine (BH_3): Borine Carbonyl and Borine Trimethylammine", J. Am. Chem. Soc., *59* (5) (1937). On 781.

[238] H. I. Schlesinger, A. B. Burg, "Recent Developments in the Chemistry of the Boron Hydrides", Chem. Rev., *31* (1) (1942). On 16.

[239] H. I. Schlesinger, A. B. Burg, "Recent Developments in the Chemistry of the Boron Hydrides", Chem. Rev., *31* (1) (1942). On 16.

The existence of borine, however transitory, would soon be used to legitimize the assignment of a particular structure to the volatile compound B_2H_7N, which had been obtained in small quantities in the preparation of triborine triamine ($B_3N_3H_6$) from the direct action of diborane upon the diammoniate $B_2H_6 \cdot 2NH_3$[240]. In the discussion on the “conceivable structures” for B_2H_7N, Schlesinger, David Ritter and Burg considered that only two hypotheses were consistent with some of its physical and chemical properties: an amine of diborane, $B_2H_5NH_2$, or a structure involving a B-N-B skeleton. The first structure was rejected because B_2H_7N only took one molecule of ammonia, while all derivatives of diborane took up two molecules of ammonia per molecule of diborane derivative to form stable compounds. Thus, only two structures with a B-N-B skeleton were possible: BH_3NHBH_3 and $BH_2NH_2BH_3$. One must notice that, since both remaining structures implicitly assumed that diborane split into two borine molecules, the previous results on the transitory existence of borine were a strong co-adjuvant for the rejection of the $B_2H_5NH_2$ solution.

The structure BH_3NHBH_3 was rejected, mainly because B_2H_7N could only take one molecule of NH_3 but also because this structure required additional assumptions about its electronic distribution that were unjustified by any of the B_2H_7N chemical properties. Thus, only one structure remained for B_2H_7N, which was $BH_2NH_2BH_3$. Schlesinger, Ritter and Burg proposed the following electronic structure for it:



$$\begin{array}{ccccccc} H & & H & & H & & \\ \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ B & : & N & : & B & : & H \\ \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ H & & H & & H & & \end{array}$$

This structure, they argued, explained in a straightforward way the addition of one and only one molecule of ammonia to B_2H_7N as an addition to the “unsatisfied” boron with only two B-H bonds. Schlesinger, Ritter and Burg justified the presence of this boron atom with only six bonding electrons in the molecule with the common existence of compounds, such as BF_3, BCl_3 or BR_3, in which the boron atom only had six bonding electrons too and which, like B_2H_7N, were able to take up only one molecule of ammonia. These compounds were also capable of adding trimethylamine in the same

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[240] H. I. Schlesinger, D. M. Ritter, A. B. Burg, “Hydrides of Boron. X. The Preparation and Preliminary Study of the New Compound B_2H_7N”, *J. Am. Chem. Soc.*, *60* (10) (1938), 2297–2300.

ratio as B_2H_7N did. On the other hand, the authors argued, B_2H_7N should have a BH_3 group as well, since when the addition compound $B_2H_7N{\cdot}N(CH_3)_3$ was heated with an excess of the amine, borine trimethylammine $BH_3{\cdot}N(CH_3)_3$ was produced, a characteristic reaction of compounds containing a BH_3 group. Further chemical evidence was put forward to strengthen their views on the structure of the B_2H_7N compound:

> Its stability is characteristic of compounds containing a B-N-B pattern of linking, rather than of those containing B-B bonds; the B-N-B skeleton explains why the compound, when heated, gives good yields of $B_2N_3H_6$, a substance containing the
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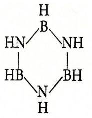
> 
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> ring; its rapid hydrolysis in acid solution to give five volumes of hydrogen suggests the existence of five B-H bonds.[241]

Further legitimacy for the hypothesis of BH_3 as the fundamental structural unit of diborane was claimed in 1939 by Schlesinger, Flodin and Burg, as a result of the successful synthesis of a symmetrical isomer of dimethyldiborane: “The success of this search was a direct consequence of the hypothesis that the molecular group BH_3 (borine) plays an important role in many of the reactions of diborane; the usefulness of this hypothesis is thus further demonstrated.”[242]

One may notice that the authors were cautious enough to claim the demonstration of the usefulness of the hypothesis rather than the hypothesis itself.

This investigation was a continuation of the previous work on the methyl derivatives of diborane by Schlesinger and Walker in 1935 and on the ethyl and n-propyl diboranes by Schlesinger, Horvitz and Burg in 1936. These investigations had failed at substituting more than four of diborane’s hydrogen atoms by methyl, ethyl or propyl radicals. They had also failed at the synthesis of the symmetrical isomers of di- methyl, ethyl or propyl diborane, leading the authors to the present investigation on the synthesis of the

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[241] H. I. Schlesinger, D. M. Ritter, A. B. Burg, “Hydrides of Boron. X. The Preparation and Preliminary Study of the New Compound B_2H_7N”, J. Am. Chem. Soc., *60* (10) (1938). On 2299.

[242] H. I. Schlesinger, N. W. Flodin, A. B. Burg, “Hydrides of Boron. XII. Symmetrical Dimethyldiborane and the Methyl Derivatives of Borine Trimethylammine”, J. Am. Chem. Soc., *61* (5) (1939). On 1078.

symmetrical isomer of dimethyldiborane $CH_3BH_2BH_2CH_3$. This formula could equally be accounted for either by the one-electron ethane-like structure or by Wiberg's theory. Thus, it was not the synthesis of the compound itself that gave birth to the authors' claim, but rather the way they did it, since the reactions they had designed to that purpose explicitly assumed that BH_3 functioned as the basic structural unit of diborane.

The intention was to find a reagent X that would remove a borine group from mono methyl diborane, leaving the resultant methylborine free to form the symmetrical isomer of dimethyldiborane by subsequent direct association:

$$2CH_3BH_2BH_3 + 2X \rightarrow 2BH_3X + 2BH_2CH_3$$

$$2BH_2CH_3 \rightarrow CH_3BH_2BH_2CH_3$$

Dimethyl ether proved to be a good choice to play the reagent X role and Schlesinger, Flodin and Burg were able to achieve their initial goal by conducting the reaction

$$2CH_3BH_2BH_3 + 2(CH_3)_2O \leftrightarrow 2BH_3(CH_3)_2O + CH_3BH_2BH_2CH_3$$

They also tried to account for the failure in detecting the presence of this symmetrical form of dimethyldiborane a few years earlier. They observed that this compound would only take some minutes to begin decomposing into its unsymmetrical form. After three days, decomposition into monomethyl- and trimethyldiborane was detectable and after long-standing, equilibrium would be reached with nearly equal volumes of these derivatives. This was in full agreement with the observations held by Schlesinger and Walker in 1935, thus proving that the instability of the symmetrical isomer of dimethyldiborane was the reason why Schlesinger and Walker had failed at detecting it back then.

At this point of their investigations, Schlesinger and Burg could hardly claim victory over Wiberg's theory. Their methyl derivatives could easily be appropriated by both sides of this informal debate, and in fact, Wiberg did use them as further chemical evidence for his structures. Schlesinger and Burg relied instead on their work on the existence of borine. While acknowledging that it gave only indirect evidence, they were at the same time convinced that it proved that the BH_3 was indeed the fundamental structural unit in the hydrides: "The formation of compounds of this type [coordination compounds of BH_3] is of such importance in the chemical behavior of diborane, and probably of the other boranes as well, that most of the chemical reactions of these substances cannot be adequately discussed without reference to this property."[243]

However, this conviction was seriously put to test by Wiberg in 1936. Schlesinger's response proved his resilience but in the process his investigation became inseparable from the electron diffraction studies made by Simon H. Bauer at Pauling's laboratory, at the California Institute of Technology. Together, they formed a formidable opposition to Wiberg's theory and were able to annihilate an increasing tendency to accept Wiberg's structures as the solution to the puzzle. Together, Schlesinger, Burg and Bauer can be properly termed the American stronghold of boroethane's (as the ethane-like structure was commonly denominated).

5.2 - Going Physical

Since Stock's argumentation for a salt-like nature of the ammonia compound of diborane, Wiberg's theory had been regarded by everybody as a serious candidate to the solution of the structural problem, even by those who opposed it: "The structure of B_2H_6 is a perpetual puzzle, and in spite of the great ingenuity displayed by numerous writers, it appears that no completely satisfactory solution has yet been reached. The most important reagent for diagnosing the structure of the boron hydrides is ammonia."[244]

However, it was the publication of Wiberg's extensive review of the field, in 1936, that imparted a clear advantage to his theory, over the ethane-like structure for diborane:

> In the December issue of the *Berichte der Deutschen chemischen Gesellschaft,* Dr. E. Wiberg reviews at considerable length the experimental evidence from which the structure of the puzzling hydrides of boron may be deduced. That considerable difficulty has been encountered during the last decade in formulating the electronic structure of these compounds will be apparent from the fact that such unsatisfactory

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[243] H. I. Schlesinger, A. B. Burg, "Recent Developments in the Chemistry of the Boron Hydrides", Chem. Rev., 31 (1) (1942). On 16.

[244] E. S. Hedges, W. Wardlaw, R. Whytlaw-Gray, "Inorganic chemistry", Annu. Rep. Prog. Chem., 31 (1934). On 109.

> devices as singlet linkages, polyvalent hydrogen, a co-ordination number of five for boron, electronic septets, even the sharing of K-electrons, a new but unexplained kind of "electrostatic-electromagnetic" valency and inequality of the two boron atoms, have all been requisitioned at various times in order to find plausible explanations of the existence of the simple compound known, perhaps wrongly, as boroethane, B_2H_6.
>
> Recent work has thrown new light upon this problem, which has been greatly simplified. The author brings forward both chemical and physical evidence to show that, instead of ethane, one should rather regard ethylene as the carbon analogue of diborane (boroethane), since it possesses an unsaturated character.[245]

One should note that the author explicitly dismisses the one-electron bond theory ("singlet linkages") as one of the "unsatisfactory" solutions that had been proposed.

An even more assertive judgement was put forward that same year: "[...] it is interesting to recall the fact that this very problem was brilliantly solved quite recently by Dr. E. Wiberg [...]"[246]

In his review, Wiberg was able to use recent research to argue further for his theory. Thus, in 1935, Stock, Sütterlin and Kurzen used potassium amalgam on the hydrides B_2H_6, B_4H_{10} and B_5H_9 to prepare their potassium salts. In each case, they found two atoms of potassium per molecule of hydride in the composition of the salt: $K_2B_2H_6$, $K_2B_4H_{10}$ and $K_2B_5H_9$. In 1936, Stock and Laudenklos proceeded with more detailed analysis of these salts as well as the corresponding sodium and calcium salts of diborane ($Na_2B_2H_6$ and CaB_2H_6) and tetraborane ($Na_2B_4H_{10}$). Wiberg interpreted these formulas as corroborating the unsaturated nature of the hydrides, since addition of potassium, rather than substitution, occurred.

$$BH_3{=}BH_3 + 2K \rightarrow K^+ [B^- H_3 - B^- H_3]K^+$$

$$BH_3{=}BH_2\text{-}BH_2{=}BH_3 + 2K \rightarrow K^+[B^- H_3 - BH_2 = BH_2 - B^- H_3]K^+$$

The structural formula for the addition of sodium, according to Wiberg, would be

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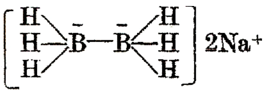
[245] N/A, "Hydrides of Boron", Nature (February 27, 1937). On 381.

[246] N/A, "A Theory of Atomic Structure", Nature (June 12, 1937). On 996.



Despite quite logical, this argument was easily dismissed by Schlesinger and Burg, who contended that the addition of two alkali atoms by diborane was equally well explained by assuming an ethane-like structure with two one-electron bonds:

> [...] he [Wiberg] explains the reaction of sodium (amalgam) with diborane as an addition to the assumed double bond. This reaction may equally well be interpreted as the result of the tendency of the electronically unsaturated molecule
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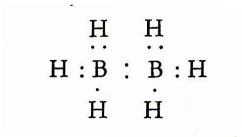
> 
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> to gain electrons; in either case the result would be the saturated compound $Na_2B_2H_6$.[247]

This appropriation of the same empirical facts by the two opposing theories also occurred with the work on the methyl derivatives of diborane by Schlesinger and Walker. This work was naturally interpreted as corroborating Stock's interpretation of a different nature for the boron-hydrogen link in two of diborane's hydrogen atoms. This interpretation, of course, could be easily appropriated by both theories, as Stock himself stressed in his book.

Of course, Wiberg was aware of this ambiguity in the chemical evidence. He even went further, by acknowledging that chemical evidence alone did not allow solving the problem in a definitive manner. He was fully convinced that recent investigation on the physical properties of diborane argued for his theory and he accordingly stressed the importance of these results.

Thus, further support for the ethylenic structure of diborane was claimed from parachor measurements by Stock, Wiberg and Mathing in 1936. Their measured value (121.9) was in good agreement with Wiberg's structure $[H_2 - B = B - H_2]^{-2}\ H^{+2}$, i.e., with two single parachors for 2 boron atoms (2×16.4), 4 hydrogen atoms (4×17.1), a double link (23.2), and 2 electrovalencies (-2×1.6) = 121.2.

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[247] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938). On 290.

Wiberg also invoked ultra-violet absorption spectra studies: the unpublished results of K. W. Hausser and A. Smakula in 1931/1932, already referred by Stock in his book, and recent work by E. Blum and G. Herzberg, who, in 1936, using samples provided by Stock, studied the ultra-violet absorption spectrum of diborane from 2200 Å to about 1550 Å. They obtained a continuous absorption curve whose interpretation in the context of Mulliken's molecular orbital theory was inconclusive on what concerned the choice between the ethane-like and the ethylene-like structures: "With the material at present available it is not possible to decide definitely between the two possibilities discussed above."[248] Despite these inconclusive results, Wiberg invoked the similarity between the ultra-violet spectra of ethylene and diborane as additional data in favour of his position.

In 1935, K. L. Ramaswamy, from the Departments of General Chemistry and Physics of the Indian Institute of Science at Bangalore, reported the measurement of the dielectric constant of diborane and $B_3N_3H_6$. Structural concerns gave rise to this study: "The chemistry of fluorine and boron compounds are of considerable interest from the valency and structural points of view. It was therefore desired to study the electrical and optical properties of some of these compounds available in the pure gaseous state."[249]

Ramaswamy worked with samples provided by Stock, on a request by Chandrasekhara Venkata Raman, who had received the Noble Prize in 1930 for the discovery and explanation of the "Raman Effect" and was a Professor at the Indian Institute of Science at Bangalore since 1933.

From the original 100 c.c. of diborane provided by Stock, Ramaswamy had to remove 25 c.c. of incondensable gas at liquid air temperature, due to extensive decomposition. A further condensable impurity, which measured 1.5 c.c. when warmed to room temperature, was removed separately.

Even so, Ramaswamy was able to calculate a null electric dipole moment for diborane. This result could only be taken as implying a symmetrical structure for diborane. Further conclusions were not possible: "The absence of an electric moment for the diborane can only indicate that the molecule has a symmetrical structure with possibly a

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[248] E. Blum, G. Herzberg, "On the Ultra-Violet Absorption Spectrum of Diborane", J. Phys. Chem., 41 (1937). On 95.

[249] K. L. Ramaswamy, "Dielectric Coefficients of Volatile Compounds of Fluorine and Boron", *Proc. Indian Acad. Sci.* 2A (630) (1935). On 364.

co-valent linkage between the two boron atoms. The question of exact configuration cannot be settled without other experimental data."[250]

In the $B_3N_3H_6$ case, the dipole moment obtained by Ramaswamy was 0.67×10^{-18}.[251] This was in contradiction with the expected null value for such a symmetrical structure as the benzene-like one advocated by Stock, based on several chemical and physical data, namely the electron diffraction study made by Wierl.

However, Ramaswamy acknowledged that, despite careful measurements, the results obtained for $B_3N_3H_6$ required further confirmation. Indeed, he had to work with a "rather small" sample, because "an unfortunate delay" in taking up the investigation on this compound caused the crystallization of a considerable part of the original sample provided by Stock. Moreover, $B_3N_3H_6$ is a liquid at ordinary temperatures (boiling point is 53 ºC) and the sample was vaporized before some of the measurements were taken. Further decomposition, presumably into hydrogen, was then detected at steam temperature (95.2 ºC), rendering the calculated moment a very uncertain result: "On account of the uncertainty in the values at the steam temperature, the significance of the observed moment cannot be emphasised. If the moment is assumed to be correct, it cannot be explained by such a plane symmetrical structure."[252]

According to Wiberg, the null electric dipole moment for diborane was in good agreement with his symmetric ethylenic structure and in contrast with an expected non-null dipole moment for an ethane-like diborane (assuming tetrahedral boron atoms), since the coexistence of double and single electron bonds introduced an asymmetry in the structure.

In 1934, Farkas and Sachsee published a study in which they tested the theoretical treatment of diborane put forward by Mulliken in 1933[253]. They did so by testing Mulliken's prediction of a paramagnetic behaviour for diborane, using the para-ortho-hydrogen intraconversion caused by the inhomogeneous magnetic field of paramagnetic

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[250] K. L. Ramaswamy, "Dielectric Coefficients of Volatile Compounds of Fluorine and Boron", *Proc. Indian Acad. Sci.*, 2A (630) (1935). On 377.

[251] Ramaswamy did not include the unit he used to express this value, but it was most probably expressed in statC·cm.

[252] K. L. Ramaswamy, "Dielectric Coefficients of Volatile Compounds of Fluorine and Boron", *Proc. Indian Acad. Sci.*, 2A (630) (1935). On 376.

[253] L. Farkas, H. Sachsee, *Trans. Faraday Soc.*, 30 (1934), 331 – 333.

molecules.[254] They concluded that, in opposition to Mulliken's prediction, the ground level of diborane was diamagnetic: "The reaction velocity constants and the corresponding collision efficiencies show that the observed conversion of para-hydrogen cannot be caused by paramagnetism of B_2H_6: from the fact that at 195º K there is no reaction at all we can definitely conclude that the ground level of B_2H_6 must be diamagnetic."[255]

Farkas and Sachsse also concluded that, should any paramagnetic excited state exist above the diamagnetic ground level, its energy would be larger than 3000 calories.

From Farkas and Sachsee's article, it is not possible to know whether they produced their own diborane or they relied on sample supply by an outside laboratory. They did not refer to their hypothetical method of production and they did not include any note thanking a hypothetical supply of diborane, as would be expected.

Farkas and Sachsse's results were confirmed that same year by Mulliken, who seems to be referring to measurements by Schlesinger and Burg.

The diamagnetism of diborane was used by Wiberg to argue for the superiority of his theory over the one-electron bond ethane-like structure. According to Wiberg, the latter contained two magnetically uncompensated electrons and this would make diborane a paramagnetic molecule. On the contrary, his structure contained only atoms with noble gas-like electronic shells, which justified diborane's diamagnetism.

Wiberg's reliance on the physical methods was not an isolated opinion. In 1936, Simon H. Bauer and Pauling published an electron diffraction study on the stable pentaborane B_5H_9 in which they claimed that the debate could only be solved by calling upon the physical methods:

> Despite the large amount of experimental and theoretical work which has been done in this field in recent years, little progress has been made in assigning structural formulas to these substances, and it seems probable that in order for this to be done with confidence it will be necessary to obtain information about the structure of the molecules by the application of physical methods.[256]

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[254] Ortho and para-hydrogen are spin isomers of molecular hydrogen. In ortho-hydrogen, both nuclei have the same spin. In para-hydrogen, the two nuclei have opposing spins.

[255] L. Farkas, H. Sachsee, "On the Magnetism of B_2H_6", *Trans. Faraday Soc.*, 30 (1934). On 332.

[256] S. H. Bauer, L. Pauling, "The Structure of the Pentaborane B_5H_9", *J. Am. Chem. Soc.*, 58 (12) (1936). On 2403.

Although this statement might imply some sort of disciplinary clash with those practicing classical analytical chemistry, like Stock and Schlesinger, the historical facts tell a very different story. In fact, on a conceptual plane, Stock himself was no less than a great enthusiast of the new physical methods:

> The possibilities of these optical methods (in the widest sense of the world) are truly miraculous. They bring us information of what is going on in the most remote sections of the universe, as well as in the interior of the minute chemical atoms; they disclose to us the existence of chemical compounds so short-lived that we can not hope ever to be able to grasp and keep them; they enable us to determine magnitudes that at first seem to have nothing at all to do with optics, as, for example, the measurement of chemical forces.[257]

Stock's enthusiasm built on the full awareness of the great impact that the new physical methods had had upon chemistry in recent years:

> Chemical research has profited particularly from the progress of modern physics. Spectrum analysis, the quantum and the electron theories, together with "wave mechanics", have enabled the chemist to draw up such a picture of the chemical atom as was never dreamed of a few decades ago when it was considered to be a rigid, unchangeable object. [...]
>
> Reaction velocities, heretofore one of the least understood fields of chemistry, have been opened up for study by these new ideas. As Haber has expressed it, "We have now gained a first impression of the actual nature of the play staged by chemical processes while heretofore, as Schönbein put it, we have known only what happens before the curtain rises and remains when it has fallen." [...]
>
> Band spectra have enabled us to detect the transitory existence of unusual compounds such as hydroxyl and have thus supplied us with an explanation of many hitherto obscure reactions. Great progress has also been made in our knowledge of the special forces acting on a particle at the surface of a substance, where, contrary to the conditions in its interior, there is no longer that uniform effect due to neighboring surrounding particles. This knowledge has illuminated the once dark and obscure fields of colloid chemistry, adsorption phenomena, contact effects and catalysts.[258]

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[257] Stock, A., *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 3.

[258] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 6.

This enthusiasm over the new methods available to probe the structure of matter even led Stock to write a book on such recent achievements by physics. This work resulted from a series of lectures he had been asked to deliver to the chemists working at the Farbwerken vorm. Fr. Bayer & Co, in September of 1919:

> When I was asked to give to the chemists at these works an account of the most recent advances in chemistry I was not for a moment in doubt as to the choice of a subject, namely, the astonishing advances in our knowledge of the fine structure of matter which have been made during the last few years. Chiefly by the work of the physicist a new region has here been revealed to us; a fertile country which even now has yielded many blossoms and fruits and many more most promising buds, a veritable Wonder-garden, as yet little known to chemists but one which on closer acquaintance can offer a wealth of inspiration and enjoyment. It is, however, by no means easy for the chemist to wander in this garden and pursue knowledge along its winding paths, for the way is set about with the thorns of theoretical physics and mathematics.[259]

From Stock's words, one can learn that, although there seemed to be no conceptual or disciplinary clash between classical structural chemistry and the new microphysics, the latter's theoretical and mathematical complexity could represent an effective barrier to the ordinary chemist. To go over such difficulties, Stock wrote an essentially qualitative account and referred any further interest to the bibliography.

The nature and goals of this book were well described by Stock when justifying its name - "*Ultrastrukturchemie*": "Just as Ultramicroscopy takes us beyond the smallest particles seen in the ordinary microscope so in "Ultrastrukturchemie" we go beyond the boundaries of ordinary structural chemistry into the realm of the smallest building stones of matter, and discuss the laws governing the structure of atoms as well as molecules."[260] Thus, Stock believed that the justification for structural chemistry had to be found in microphysics. Samuel Sugden, the translator of the English version, argued

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[259] A. Stock, *The Structure of Atoms* (London: Methuen & Co. Ltd., 1923). Translation by S. Sugden. On v.

[260] A. Stock, *The Structure of Atoms* (London: Methuen & Co. Ltd., 1923). Translation by S. Sugden. On v.

that this title could scarcely be translated literally and rendered it instead the more innocuous title “The Structure of the Atoms”.

The translation of all this enthusiasm had a very concrete translation into Stock’s practice. It included numerous attempts to get structurally useful information on the hydrides of boron, using several different available methods. Thus, one can recall the X-ray diffraction analysis of diborane, made by Mark and Pohland (one of Stock’s chief co-worker) in 1925. Stock’s enthusiasm with this work is evident in the paper on the nomenclature of the hydrides he published next year, in 1926. This paper included a detailed discussion of Mark and Pohland’s work, which Stock used to substantiate his decision to maintain his old vindication of a tetravalent boron atom in the hydrides, although he had already been forced to acknowledge the trivalency of boron in the hydrides as well. This work was followed by Stock’s collaboration with Wierl in 1931, to study the structure of $B_3N_3H_6$ through Wierl’s new electron diffraction method. Stock next measured the parachor of diborane, with Wiberg and Mathing, in 1936. In that same year, Stock, with Laudenklos, also published his work on the alkali salts of the hydrides of boron, in which he included an X-ray diffraction analysis of these compounds.

Therefore, in 1936, the debate was largely focused in the physical analysis of diborane and the situation was becoming very uneasy to those supporting the ethane-like structure of diborane. However, this did not last long, as in that same year Simon H. Bauer published the first of a series of electron diffraction analysis of the hydrides of boron. Bauer’s work inflicted severe damage to Wiberg’s allegations, as he was able to reverse all the physical arguments previously collected by Wiberg. Moreover, for the first time ever, Bauer claimed direct and definitive evidence for the structure of some of the hydrides, including diborane. As will be discussed ahead, his work took place in the context of Pauling’s extensive program of structural analysis by the electron diffraction method, at the California Institute of Technology. In his dismissal of Wiberg’s structures, Bauer was able to put forward very powerful empirical evidence, completed by his own theoretical discussion based on Pauling and Mulliken’s quantum chemical theories.

5.2.1 – Just Shoot Them and Take a Picture

In 1926, Herman Mark was invited by K. H. Meyer, one of the directors of the I. G. Farbenindustrie's, the largest chemical corporation in Germany, to direct the company's research laboratory of high molecular compounds, in Ludwigshafen. With Meyer's support, Mark was able to go ahead with a number of personal projects that were expected to result in no financial benefit for the corporation. One of those projects was a new method to investigate molecular structure: the diffraction of electrons.

In 1931, Raimund Wierl, Mark's student, reported the first experiments on the diffraction of electrons by gas molecules. In his introduction, Wierl acknowledged the X-ray diffraction of crystals as the method that, at the time, became nearest to render direct information on the structure of individual molecules. However, Wierl also pointed out its major shortcomings: the effect of the individual molecules was screened by the effect of the lattice and complications such as the temperature effect, the mosaic structure and the zero point energy, arose.

Wierl's point on what concerned the screening effect of the lattice, that is, the essential error in inferring the structure of a single molecule from its crystal structure, was clearly explained by Pauling:

> Whereas the investigation of any structure was a gamble, in that a simple molecule might interact with its neighbors in the crystal in such a way as to make the structure complex, no such complicating effect was possible in a gas. For example, Dickinson in 1923 had found that the unit of structure of tin tetraiodide is a cube containing eight molecules, with atomic positions determined by five parameters, which he succeeded in evaluating. But the SnI_4 molecule is tetrahedral, with its structure determined by a single parameter, so that one could predict with confidence that the investigation of the vapor by the electron diffraction methods would surely permit the verification of the tetrahedral structure and the determination of the value of the one parameter, the tin-iodine bond length without trouble.[261]

This meant, for example, that Mark and Pohland's results for crystallized diborane and ethane could not be directly transposed to their gas phases.

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[261] L. Pauling, "Herman F. Mark and the Structure of Crystals", in M. Joan Comstock (ed.), *Polymer Science Overview – A Tribute to Herman F. Mark,* ACS Symposium Series 175 (Washington, D.C.: American Chemical Society, 1981). On 98.

According to Wierl, the answer to these idiosyncrasies was to investigate gas molecules. Obviously, electron-diffraction was better suited to such purpose, as X-ray diffraction of gas samples would involve much longer incidence periods.

A fundamental advantage of electron-diffraction over X-ray diffraction was that there was little scattering from the electronic structure of atoms. The scattering was effected primarily by the molecule's nuclei and the method was especially well adapted to the study of internuclear distances.

In his papers, Wierl discussed the structures of many molecules. He made accurate measurements of the single, double and triple bond carbon distances and found that carbon atoms in propane, butane, pentane and hexane make bonds at approximately the tetrahedral angle. Wierl was able to determine the interatomic distances in carbon tetrachloride. He also showed that the assumption of free rotation about the carbon-carbon bond was in contradiction with his results for 1,2-dibromoethane and 1,2-dichloroethane.

In 1930, Pauling visited Mark and Wierl at Mark's laboratory in Ludwigshafen:

> In 1930, when I visited Herman Mark in Ludwigshafen, I learned that he and his young associate R. Wierl had constructed an apparatus for scattering a beam of electrons from gas molecules and had determined the interatomic distances in carbon tetrachloride and a number of other molecules by analysis of the diffraction pattern. [...]
>
> I was overwhelmed by my immediate realization of the significance of this discovery.[262]

Structure determination by X-ray diffraction of crystal structures had proved to depend on too many parameters to determine the positions of atoms in the unit cell and, by 1930, the technique allowed no more than the determination of half a dozen parameters from the X-ray photographs. According to Pauling, this rendered the determination of relatively simple structures, such as $K_2Ni_2(SO_4)_3$, an often impossible task. Another such example was the X-ray study made by Möller of some crystals of $B_{10}H_{14}$. According to Stock, although this study was able to show that two molecules of $B_{10}H_{14}$ were associated in the crystals to form a double molecule, the large number of

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[262] L. Pauling, "Herman F. Mark and the Structure of Crystals", in M. Joan Comstock (ed.), *Polymer Science Overview – A Tribute to Herman F. Mark*, ACS Symposium Series 175 (Washington, D.C.:, American Chemical Society, 1981). On 98.

parameters to be determined prevented the calculation of the atomic arrangement within the unit cell from the observed diffraction rings. This problem had also frustrated the many attempts to use X-ray diffraction in the study of such structures as amino acids and simple peptides, intimately related to the protein problem in which Pauling was interested.

> As the impact of the significance of this discovery burst upon me I could not contain my enthusiasm, which I expressed to Mark – my feeling that it should be possible in a rather short time, perhaps ten years, to obtain a great amount of information about bond lengths and bond angles in many different molecules. I asked Mark if he and Wierl were planning to continue with such a program, and he said that they were not. He added that if I were interested in building an electron-diffraction apparatus he would be glad to help, and in fact he gave me the plans of their apparatus.[263]

Although Mark is widely known as a pioneer in polymer science and the founding father of this branch of chemistry in the United States, Pauling thought of Mark also as a pioneer in modern structural chemistry and considered his electron-diffraction of gases technique as his most important contribution to it.

Back to America, Pauling initiated an ambitious program of systematic and extensive analysis of molecules by the new electron-diffraction method.

> On my return to Pasadena in September I talked with a new graduate student in the California Institute of Technology, Lawrence Brockway, about this project, and he agreed to undertake the construction of the apparatus (with the help and advice of my colleague Professor Richard M. Badger).[264]

According to Pauling, during the next twenty-five years the structures of 225 different molecules were determined by this method at the California Institute of Technology, involving 56 graduate students and post-doctoral fellows.

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[263] Pauling, L., “Herman F. Mark and the Structure of Crystals”, in M. Joan Comstock (ed.), *Polymer Science Overview – A Tribute to Herman F. Mark,* ACS Symposium Series 175 (Washington, D.C.: American Chemical Society, 1981). On 99.

[264] Pauling, L., “Herman F. Mark and the Structure of Crystals”, in M. Joan Comstock (ed.), *Polymer Science Overview – A Tribute to Herman F. Mark,* ACS Symposium Series 175 (Washington, D.C.: American Chemical Society, 1981). On 99.

At that time, Pauling had already developed the stochastic approach to the X-ray diffraction analysis of matter:

> I developed what I later called the stochastic method. The name is drawn from the Greek meaning “the art of divining the truth by conjecture." Really only a small fraction of the crystals that we attacked could be solved in terms of their structure by logical methods. My attitude was, why shouldn't I use the understanding that I have developed of the nature of crystals in inorganic substances and proceed to predict their structures? I would predict the structure and then I would calculate the X-ray pattern and if it agreed with the observed pattern, then I felt I had the right to say that it was the right structure. Of course, if I were to predict a hundred structures and then one of them agreed roughly with the observed pattern, it certainly could be an accident. The period when it became possible to determine complicated structures in a straightforward way was far in the future and people really didn't know how to refine the approximate structures at that time. I had unique success in predicting structures as well as the shape and size of structural units as well as the coordinates of atoms all of which suggested that I was on the right track with my total structure.[265]

Pauling, most naturally, employed this stochastic approach to Mark and Wierl’s electron diffraction method: the experimental electron diffraction pattern was converted in an intensity curve that was compared with the computed intensity curves for those theoretical models assumed to be in agreement with all the known data for the compound under study. Tedious calculations were involved in this process, but its major shortcoming was its dangerous model-dependency:

> The stochastic nature of the electron diffraction treatment (excepting the radial distribution method) is not always recognized. Excellent agreement between the photographs and the intensity curve for a particular model of a molecule does not constitute a unique determination of the structure. Other values of the configuration parameters are possible unless they are specifically eliminated by treatment of the corresponding intensity curves. It is always desirable to limit the uncertainties in the configuration parameters by testing a series of molecular models until definite disagreement with the photographs is found and unless this is done the configuration of the molecule has not been determined. It is permissible and often necessary to

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[265] D. Ridgway, “Interview with Linus Pauling”, *Journal of Chemical Education*, 53 (8) **(**August 1976). On 471.

> assume some of the parameter values which have been determined by other methods; but assumed parameters values are not determined by the electron diffraction results. The assumed values are merely shown to be compatible with the results of the experiment. In this respect an investigator should not be satisfied with only rough agreement between theory and experiment; changes in the parameters may lead to definite improvement in the agreement and hence to an actual determination of parameter values. The report of the results is incomplete without a list of the various molecular models tested showing which interatomic distances or bond angles were assumed and which were determined.[266]

In 1935, Pauling and Brockway published a new approach to the electron diffraction technique, the radial distribution method, which they had developed building on the method of interpretation of X-ray data developed by Zernike and Prins in 1927 for the study of the structure of liquids and applied by Warren and Gingerich to crystals in 1934.

The radial distribution method was a non-stochastic method that led directly to the values of the internuclear distances, within 1 or 2 % error. Therefore, it was a powerful tool that allowed risk minimization when using the stochastic method. The correct procedure would be to use the radial distribution method to obtain directly the relevant internuclear distances and use these to rule out all structures of the molecule except those compatible with them. This granted much greater security in choosing the structure models to be tested.

Articulation between X-ray and electron diffraction results proved difficult in the beginning, but electron diffraction eventually was able to prove its superiority over x-ray diffraction:

> For three or four years after 1930 there existed general skepticism as to the reliability of electron-diffraction results. This was due mainly to the existence of a discrepancy of about four per cent between the values of interatomic distances in gas molecules reported from electron diffraction and x-ray studies. The skepticism regarding electron diffraction was fostered in articles and lectures by the investigators who had used the X-ray results which were wrong.[267]

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[266] L. O. Brockway, "Electron Diffraction by Gas Molecules", *Reviews of Modern Physics*, 8 (3) (1936). On 258.

[267] R. Spurr, L. Pauling, "The Electron-diffraction Method of Determining the Structure of Gas Molecules", *Journal of Chemical Education* (October 1941). On 459.

Already in his comprehensive review of the field, in 1936, Brockway was able to write on some of the recent successes in structural chemistry achieved by electron-diffraction:

> The need for solving many problems in structural chemistry really led to the development of this field since it afforded direct answers to some questions of long standing. Examples of these are the configurations of geometric isomers, the tetrahedral arrangement of bonds in aliphatic carbon derivatives, the planar character of the benzene ring, the angles between chemical bonds on atoms of the various elements and the more recent considerations of the relation between the internuclear distance of chemically bonded atoms and other properties of the bond, such as electronic structure, force constant, dissociation energy, electric moment, etc. As a result the experimental method has been used primarily as a means of determining the structures of molecules.[268]

In 1942, Bauer had the following to say on the reliability of the electron-diffraction method:

> As a tool for determinations of molecular structure the electron-diffraction method needs no justification in this review. It appears to be ideally suited for sufficiently volatile compounds which are available only in small quantities and which are not stable for a matter of days or even hours. The final structures are deduced by means of a stochastic process; to date, all conclusions have been found to be in agreement with chemical intuition, and have been repeatedly confirmed by x-ray and band-spectral investigations.[269]

The most used method to interpret diffraction patterns was the so-called "visual method", which had been first used by Wierl. It consisted in a visual evaluation of the intensity of the well-defined circular bands which constituted the diffraction pattern printed on the photographic plates and had an apparent correspondence to intensity maxima and minima. However, a detailed study of the perception of these intensity patterns made by Pauling and Brockway showed that, in general, such maxima and

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[268] L. O. Brockway, "Electron Diffraction by Gas Molecules", *Reviews of Modern Physics*, 8 (3) (1936). On 233.

[269] S. H. Bauer, "Structures and Physical Properties of the Hydrides of Boron and of their Derivatives", Chem. Rev., *31* (1) (1942). On 44.

minima did not really exist. This mistaken perception was the result of the limited sensitivity of the human eye/brain system, which did not react to absolute intensity, but rather to the ratio between the molecular scattering and the background intensity (coherent and incoherent atomic scattering) for a large range of background intensities. This meant that human visual perception magnified the contribution of the molecular structure to the diffraction pattern, rendering the visual method especially apt to molecular structure determinations.

Since what was taken from the diffraction patterns was a relative quantity, it had to be compared with a computed relative quantity also. Thus, the theoretical curve calculated for the specific chosen model had to result from the ratio between the computed molecular scattering and the sum of the coherent and incoherent scattering:

$$\frac{I_{mol}}{I_{coh} + I_{incoh}}$$

The list and location of the computed maxima and minima was then compared with correspondent ones obtained by visual inspection of the diffraction patterns. Quantitative comparison was achieved by calculating the ratio between the calculated and observed angles for each of the maxima and minima. This proportion was then multiplied by one specific internuclear distance belonging to those that had been postulated to build the theoretical molecular model being tested. The same procedure was applied to all maxima and minima in relation to that specific internuclear distance. The list of values thus obtained was then inspected to evaluate their constancy. This procedure aimed at the visual match of the maxima and minima of the observed and the calculated curves by shifting the calculated curve along the angle axis. If the values were very nearly constant, there was a match and the best estimate of the real value for that specific internuclear distance was obtained by averaging all those nearly constant values. An identical procedure was then applied to all other internuclear distances in the postulated model. In the absence of such constancy in the values, the postulated model was either to suffer alterations and be tested again or be abandoned in favour of another type of model.

Since only the matching of specific points (maxima and minima) had been tested, an agreement was arrived at between the observed molecule and the internuclear distances of the postulated model, but not its geometry. An agreement in the geometry could as well be tested by a qualitative visual comparison between all the features of both curves: the intensity correlation between neighbouring peaks, slopes, existence of shelves, etc. Only in this case the procedure corresponded to a visual match of the whole curves by shifting the calculated curve along the angle axis. If there was no such agreement, one had to try another molecular geometry with the same internuclear distances. According to Brockway, "this criterion for the choice of a model is very useful and represents one of the advantages of the visual method since this treatment is based chiefly on the molecular scattering".[270] This brought confidence to the choice of models. The implicit assumption here was that it would be very unlikely that two different models could have sufficiently close resemblance to the empirical curve. Even so, there was evidence that this had already happened in very special cases and careful judgement should be used:

> Extensive experience has shown that when the computed intensity curve for a specific model checks with the observed pattern, it is very unlikely that a totally different model will also agree. However, each compound should be treated individually, and safe predictions may then be made to decide whether two configurations are sufficiently unlike. For example, with the visual method of interpreting electron-diffraction photographs, normal pentane may be distinguished from neopentane, but not readily from isopentane.[271]

However, the methodological limitation of the visual method was largely overtaken by its simplicity, essential in the study of large numbers of molecules, and by its use of a greater number of maxima and minima compared with any other method, which increased the number of independent determinations of the molecular size. This was an important outcome because outer rings were more sensitive to model changes in model than inner rings.

The chief disadvantage of the visual method was its vulnerability to subjective measurement errors. This issue had to be handled very carefully and experienced readers of the intensity of the diffraction rings should be employed:

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[270] L. O. Brockway, "Electron Diffraction by Gas Molecules", Reviews of Modern Physics, 8 (3) (1936). On 252.

[271] S. H. Bauer, "Structures and Physical Properties of the Hydrides of Boron and of their Derivatives", Chem. Rev., *31* (1) (1942). On 44.

> The accuracy of the visual method has been specifically tested by comparison of its results on the diatomic molecules, chlorine, bromine, and iodine monochloride with the results of the rotational analysis of the absorption spectra of the same compounds. The deviations in the electron diffraction interatomic distances are +1.1, +0.4 and -0.6 percent, respectively.[272]

5.3 – Checkmate or Perpetual Check?

Simon H. Bauer was one of Pauling students at the California Institute of Technology. Born in Lithuania in 1911, Bauer emigrated with his family to the United States, more specifically to Chicago, in 1921. He attended the University of Chicago, where he earned his B.S. and Ph.D. degrees, having studied with T. R. Hogness, W. D. Harkins and H. I. Schlesinger.

Bauer's electron diffraction work on the hydrides of boron was first published in 1936 with a paper on the structure of the stable pentaborane B_5H_9, written together with Pauling. This work was followed by publications on the structure of diborane in 1937 and on the structures of tetraborane (B_4H_{10}) and pentaborane (B_5H_{11}) in 1938. Bauer also made important electron diffraction studies on some of the compounds synthesized by Schlesinger and his co-workers, such as borine carbonyl and borine trimethylamine (1937) and B_2H_7 and $B_3N_3H_6$ (1938). This cooperation was prompted by the personal friendship between Burg and Bauer, which went back to Bauer's period as a student at the University of Chicago. Bauer first proposed it to Burg in early 1936:

> Relative to the electron diffraction studies, I first proposed that this tool, which at that time was available in the USA only at CalTech, be used to determine the gas phase structures of the newly prepared boron hydrides. I wrote to Anton, and I am certain he checked with Prof. Schlesinger, who agreed to establish this collaboration. Anton then developed the procedure for freezing tiny amounts of the gases, packing the tubes in dry-ice and sending them by air mail to Pasadena. He estimated that each tube contained about 10 mmoles of the compound. As best as I recall, I was

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[272] L. O. Brockway, "Electron Diffraction by Gas Molecules", Reviews of Modern Physics, 8 (3) (1936). On 253.

> able to record no more that four successive exposures- plates that I carefully developed and visually inspected.[273]

The difficult work conditions due to the instability of the hydrides are evident. This was, most probably, the reason why the stable pentaborane B_5H_9 was the first to be studied by Bauer and Pauling, in 1936.

Further work proceeded in the forties and beyond.[274] Bauer investigated many other compounds using this technique, to which he made important contributions, both at the technical and in the theoretical level. He was also the author of a very important review of the structural problem in the hydrides of boron, in 1942.[275]

Bauer's work on the hydrides of boron may be divided into three distinct but intimately related dimensions: the radial distribution method, the stochastic approach and the theoretical discussion of results.

As already referred, the radial distribution method was always applied first, because it allowed the determination of the relevant internuclear distances in the molecule and this, in turn, automatically imposed a significant restriction on the number of eligible models whose computed intensity curves could be compared with the observed one in the stochastic phase of the method. Because it was not model-dependent, the radial distribution method was used as a powerful instrument to get some insight on the nature(s) of the chemical bond in the molecule under study. However, to make such a transition from simple knowledge of the internuclear distances in the molecule, one had to accept a definitive correlation between bond length and bond nature. According to this criterion, a comparison between the observed length and single-bond length provided an answer to the nature of the bond: double if the observed value was clearly less than the single bond length, a looser bond (like the one-electron bond) if the observed length was significantly greater than the single bond one. Bauer justified this criterion on the grounds of recent publications by Pauling and his co-workers on the correlation between interatomic distances and the electronic structures of molecules. In

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[273] Simon H. Bauer. Private Communication.

[274] With the exception of work on the aluminium borohydride (1940), Bauer's work on the hydrides of boron in the forties will not be addressed here.

[275] S. H. Bauer, "Structures and Physical Properties of the Hydrides of Boron and of their Derivatives", Chem. Rev., *31* (1) (1942), 43–75.

fact, in 1932, Pauling published a paper in which he pointed out that the observed values of interatomic distances provided useful information on the electronic structures of molecules, especially in what relates to resonance between two or more valence bond structures.[276] He concluded that resonance between two or more structures led to interatomic distances that were closer to the smallest value for those individual structures. For example, in benzene each carbon-carbon bond resonated equally between a single bond and a double bond, as given by Kekulé structures; the observed carbon-carbon distance, 1.39 Å, was much closer to the carbon-carbon double bond distance, 1.38 Å, than to the single bond distance, 1.54 Å. It is very interesting to notice that, in this paper, Pauling used the boron-boron distance in $B_3N_3H_6$, measured by Stock and Wierl in 1931, to argue for the resonance between a single bond and a double bond in this compound, just as in benzene.

Of course, the benzene case was a especially simple one, since both Kekulé structures contributed equally. In general, however, the two or more structures contributed differently to the wave function of the molecule and, in such cases, a bond between two atoms could have any intermediate character between single bond and double bond.

To determine this intermediate character, Pauling, Brockway and Beach went as far as establishing a continuous correlation curve between bond length and the resonance character of the bond nature.[277] This smooth curve was constructed with four points: the carbon-carbon single bond distance in diamond and aliphatic compounds (1.54 Å); the carbon-carbon double bond length (1.38 Å), taken from Pauling's table of covalent radii and corroborated by Badger's value for ethylene (1.37 Å); the 1.39 Å value for benzene, which had fifty per cent double bond character, was used as the middle point of the curve; finally graphite provided the last point in this curve. To each of its bonds was attributed one-third of double bond character. Pauling, Brockway and Beach then used the resulting curve/function to obtain information about the electronic structures of a number of resonating molecules whose experimental interatomic distances were available.

On these grounds, Bauer was able to use the interatomic distances obtained through the radial distribution to immediately dismiss all Wiberg's structures for diborane,

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[276] L. Pauling, "Interatomic Distances in Covalent Molecules and Resonance between two or more Lewis Electronic Structures", Proc. Nat. Acad. Sci., 18 (1932), 293 – 297.

[277] L. Pauling, L. O. Brockway, J. Y. Beach, "The Dependence of Interatomic Distance on Single Bond-Double Bond Resonance", J. Am. Chem. Soc., 57 (1935), 2705 – 2709.

tetraborane and both pentaboranes. Bauer simply argued that none of the boron-boron distances he had determined for all these compounds were consistent with a double bond nature. They were all too big. In fact, they were even bigger than in a single boron-boron bond. The same happened with all the boron-hydrogen bonds: "Actually, the values for the B-B and B-H distances in B_2H_6 are both considerably larger than the single-bond separations, showing that all the bonds in the molecule have to some extent the character of bonds weaker than single bonds."[278]

Besides the absolute value of the bond lengths, their relations between them also constituted a powerful argument against the structures proposed by Wiberg: "[...] direct evidence is available that all the hydrogen atoms are equivalent in diborane and, indirectly, a case of non-equivalence in tetraborane would have led to differing B-B distances within the molecule, contrary to observation."[279]

Thus, based on these results alone, Bauer was immediately able to claim: "The structural theory of Wiberg was unquestionably eliminated."[280]

By using the stochastic method, Bauer was able to put forward very concrete structures for some of the boron hydrides. He did it by computing the theoretical intensity curves for a number of different structures that were consistent with the bond distances he had obtained from the radial distribution method. One must call attention to the fact that, despite having claimed the elimination of Wiberg's theory through the radial distribution method, Bauer did try to test it through the stochastic method also. Naturally, he limited his models to ethane-like or ethylene-like structures, since the debate at the time was restricted to such structures. He immediately discarded the ethylene-like structures. However, these results were a lot less secure than those obtained from the radial distribution method were. Because, independently of its experimental idiosyncrasies, the stochastic method was model-dependent. In fact, Bauer assumed his struggle to assign a testable model to Wiberg's ethylenic structure: "I found it difficult to construct a spatial model which would correspond unambiguously to the structure proposed by Wiberg".[281]

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[278] S. H. Bauer, "The Structure of Diborane", J. Am. Chem. Soc., *59* (6) (1937). On 1099.

[279] S. H. Bauer, "The Structure of the Hydrides of Boron. V. Tetraborane B_4H_{10} and the Pentaborane B_5H_{11}", J. Am. Chem. Soc., 60 (4) (1938). On 812.

[280] S. H. Bauer, "The Structure of the Hydrides of Boron. V. Tetraborane B_4H_{10} and the Pentaborane B_5H_{11}", J. Am. Chem. Soc., 60 (4) (1938). On 812.

A similar observation was included in his paper on the structure of the tetraborane and the pentaborane B_5H_{11}. The fact that Wiberg's structure could not be easily displayed by a visual diagram, due to the awkward position of its two hydrogen ions, had already been referred by Stock in his book, and was most probably a major cause for the resistance faced by Wiberg's theory. This intrinsic feature of Wiberg's structure for the hydrides of boron was a severe inconvenience, not to say danger, in such a spatial model-dependent method as the electron diffraction analysis.

Even so, Bauer's confidence in his results was doubly justified: the difficulty in assigning a spatial model to Wiberg's structure (Bauer only tried one of these for each hydride of boron) was nothing to be concerned with, since the radial distribution method had already ruled out its plausibility; on the other hand, Bauer visually compared the observed curve for diborane with the analogous ones for ethane and ethylene. He was keen in calling the attention to the obvious similarity between diborane and ethane: "The similarity of the pattern produced by diborane to the one produced by ethane should be noted.[...] The contrast with the features presented by the ethylene photographs is apparent."[282]

From the several ethane-like structures tested for diborane (obtained by assigning different bond-lengths and bond angles), Bauer was able to find one whose data was in full agreement with the observed curve, allowing him to reach the following conclusions:

- Diborane's atoms were arranged in the form of two pyramids with coincident axes, at whose apices the boron atoms were located, pointing toward each other.

- The boron-boron distance was 1.86 ± 0.04 Å; the B-H distance was 1.27 ± 0.03 Å.

- The valence angles of the boron atoms were tetrahedral to within three degrees.

Similar conclusions were deduced for the tetraborane, which was found to have a chain-like structure corresponding to butane, with the following interatomic distances: B-B =

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[281] S. H. Bauer, "The Structure of Diborane", <u>J. Am. Chem. Soc.,</u> *59* (6) (1937). On 1099.

[282] S. H. Bauer, "The Structure of Diborane", <u>J. Am. Chem. Soc.,</u> *59* (6) (1937). On 1096.

1.84 ± 0.04 Å; B-H = 1.28 ± 0.03 Å. The valence angles were close to tetrahedral and rotation about the various B-B bonds should be assumed.

Likewise, the pentaborane B_5H_{11} was found to have a configuration that corresponded either to that of pentane or isopentane, with the following interatomic distances: mean B-B = 1.81 ± 0.03 Å; B-H = 1.26 ± 0.03 Å. The observed angles were close to tetrahedral and, once again, internal rotation should be assumed.

This similarity between the structures of diborane, tetraborane and the unstable pentaborane B_5H_{11} should lead any chemist to expect similar chemical properties for all of them. However, this was in full contradiction with the distinction among them made by Stock in his classification scheme. In fact, Stock divided the hydrides into two distinct families: B_nH_{n+4} and B_nH_{n+6}. Stock had stressed that this was not just a formal scheme; it also expressed a marked division among the hydrides on what concerned their observed chemical behaviour. Since diborane belonged to the first family and tetraborane and the pentaborane B_5H_{11} belonged to the second one, their different chemical properties also implied marked differences on a structural level, in contradiction with the results Bauer obtained. Of course, Bauer was fully aware of this problem, which was behind his arguing against Stock's scheme, which he dubbed was a purely formal one with no chemical basis. Thus, according to Bauer, diborane behaved as though it belonged to the B_nH_{n+6} family and to put together his own interpretation of the chemical facts, in full opposition to Stock's view, he argued:

> Unlike B_5H_9 and $B_{10}H_{14}$, but like B_4H_{10}, B_5H_{11} and B_6H_{10}, diborane melts at a temperature at which its vapor tension is not observable on an ordinary mercury manometer. Diborane, tetraborane and the unstable pentaborane also react far more readily with water and ammonia than does the stable pentaborane or decaborane. In further contrast to the latter two compounds, B_2H_6 reacts with hydrochloric acid to give a chloro derivative and hydrogen, a behavior shown also by B_4H_{10} and B_5H_{11} (except that the derivatives of these cannot be isolated). It is significant that di-, tetra- and the unstable pentaboranes are converted easily one into the other by the proper choice of experimental conditions, while B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ are formed slowly and irreversibly from that equilibrium mixture.[283]

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[283] S. H. Bauer, "The Structure of the Hydrides of Boron. V. Tetraborane B_4H_{10} and the Pentaborane B_5H_{11}", J. Am. Chem. Soc., 60 (4) (1938), 805 -812.

Evidently, Bauer's work was unique and Wiberg had rested his case on physical evidence derived from several other physical methods. That meant that Wiberg had no electron diffraction evidence to oppose to Bauer, other than a possible dismissal of the method itself. It also meant that Bauer still had to argue against Wiberg's arguments in order to build a truly consistent case. Otherwise, the situation would just become too confusing, with different physical methods allowing to draw opposing conclusions. To overcome this situation, Bauer used the theoretical accounts of Pauling and Mulliken as a powerful intellectual instrument against Wiberg's compelling arguments. Therefore, he did not contest the experimental results put forward by Wiberg, but rather their interpretation. By using the electronic configurations of Pauling, Lewis and Mulliken, Bauer built immediate theoretical justifications for the striking results he obtained with the radial distribution method. Bauer thereby added empirical legitimacy to the theoretical accounts of the hydrides he had used and having done so, he in turn used this legitimating strategy to overthrow all the interpretations on which Wiberg had rested his claim of an empirical inadequacy of the ethane-like structure for diborane.

The importance of the theoretical accounts by Pauling and Mulliken in Bauer's thinking about the hydrides of boron is explicit in the following statement:

> Only within the past few years has it been realized that the existence of diborane may be accounted for without the introduction of *ad hoc* hypotheses; theoretical justifications based on the currently accepted theories of valence have been formulated favoring the structure initially proposed by Sidgwick.[284]

Therefore, Bauer considered the structures of Wiberg as grounded on *ad hoc* hypotheses. On the other hand, the one-electron bond, despite its alleged existence being strictly restricted to the hydrides of boron, could not be considered an *ad hoc* hypothesis because it was accounted for by both main theoretical constructions in quantum chemistry.

The main argument that Bauer used to legitimize the one-electron bond structures was, naturally, the higher bond lengths he had find in his application of the radial distribution method. Bauer began by stressing that weaker and longer B-H bonds were expected on the basis of Sidgwick's structure

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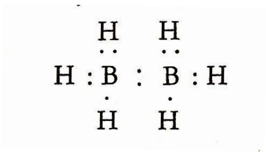
[284] S. H. Bauer, "The Structure of Diborane", J. Am. Chem. Soc., *59* (6) (1937). On 1096.



$$\begin{array}{ccccc} & H & & H & \\ & \cdot\cdot & & \cdot\cdot & \\ H: & B & : & B & :H \\ & \cdot & & \cdot & \\ & H & & H & \end{array}$$

which gave each B-H bond two-thirds single-bond and one third one-electron bond character. Of course, Sidgwick's structure could not account for a looser B-B bond and Bauer put forward a "slight extension of this configuration" by considering resonance to structures such as

$$\begin{array}{ccccc} & H & & H & \\ & \cdot\cdot & & \cdot\cdot & \\ H\cdot & B & \cdot & B & :H \\ & \cdot\cdot & & \cdot\cdot & \\ & H & & H & \end{array}$$

Bauer also considered that both B-H and B-B looser bonds were equally compatible with the seven Lewis structures

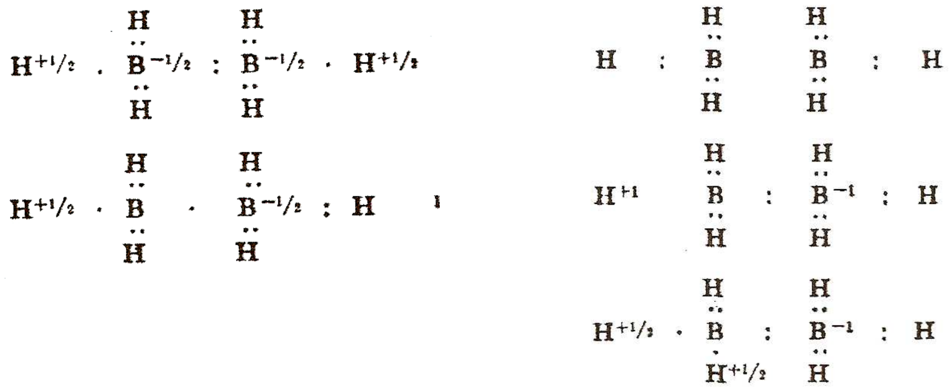
$$\begin{array}{ccccc} & H & & H & \\ & \cdot\cdot & & \cdot\cdot & \\ H: & B & & B & :H, \\ & \cdot\cdot & & \cdot\cdot & \\ & H & & H & \end{array} \qquad \begin{array}{ccccc} & H & & H & \\ & \cdot\cdot & & \cdot\cdot & \\ H & B & : & B & :H, \\ & \cdot\cdot & & \cdot\cdot & \\ & H & & H & \end{array}$$

which gave each bond 6/7 single bond character.

Apparently, Bauer was the first author to take into consideration Lewis structures for diborane. This may have been because a no-bond character could be even stranger than a one-electron bond. However, Bauer's interest may have been triggered by the fact that these structures did account for his observations and, at the same time, it gave the highest mean value for the single bond character in each bond, thus minimizing the odd nature of diborane. Another important feature of these structures was that they accounted in a natural way for diborane's diamagnetism. Moreover, this was no coincidence, since they had been devised by Lewis precisely to account for his prediction of a diamagnetic behaviour for diborane.

Bauer sustained then that "strong theoretical arguments may be given to support the view that the molecule resonates among all the structures of the Sidgwick and Lewis types, the B-B and the B-H bonds having single-bond, one-electron-bond and no-bond character".[285]

In his discussion of the structure of diborane, Bauer "translated" all these structures into Mulliken's molecular orbital language:



$$\mathrm{H}^{+1/2}\cdot\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}{}^{-1/2}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}{}^{-1/2}\cdot\mathrm{H}^{+1/2}\qquad \mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}\quad\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}:\mathrm{H}$$

$$\mathrm{H}^{+1/2}\cdot\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}\cdot\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}{}^{-1/2}:\mathrm{H}\qquad \mathrm{H}^{+1}\ \overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}{}^{-1}:\mathrm{H}$$

$$\mathrm{H}^{+1/2}\cdot\overset{\mathrm{H}}{\underset{\mathrm{H}^{+1/2}}{\mathrm{B}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{B}}}{}^{-1}:\mathrm{H}$$

These were the valence bond configurations contributing to the ground state. The wave function of diborane might be represented approximately by a linear combination of the wave functions of the above structures. Only four hybrid sp^3 orbitals with tetrahedral orientations were allowed, each of them filled with a shared electron pair, a single electron or no electron at all. By suitable manipulation of this theoretical frame, Bauer was able to "conclude" that diborane had a diamagnetic ground state. However, it should be noticed that he predicted the existence of a low-lying paramagnetic state too, whose existence had not been verified yet.

The electronic symmetry and the equivalence of all the hydrogen atoms in his structures allowed Bauer to dismiss in a straightforward way the part of Wiberg's argumentation based on the symmetry of his structures, which comprised both the diamagnetism and the null dipole moment of diborane.

He also dismissed Wiberg's use of the similarity between the ultraviolet spectra of diborane and ethylene as "fallacious". Moreover, Bauer argued, Blum and Herzberg had put forward an explanation for their observed absorption spectra that was derived from Mulliken's theory, the same he had used in his discussion of diborane. However, Bauer recognized that Mulliken's recent report (1937), according to which diborane showed no absorption in the near ultraviolet, visible and infrared (2500-12000 Å) regions, was

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[285] S. H. Bauer, "The Structure of Diborane", J. Am. Chem. Soc., *59* (6) (1937). On 1099.

"somewhat puzzling since various low-lying electronic levels to which transitions from the ground state are not forbidden have been predicted."[286]

Bauer also dismissed Stock's determination of diborane's parachor, arguing that this was the first time that such determination was made for molecules involving one-electron bonds. Since the contribution to the parachor of any type of bond could only be determined experimentally, one could not draw any conclusions on the structure of diborane from parachor determinations. Wiberg used deductions from phosphorus and arsenic pentachlorides but Bauer found them without fundament because most chemists believed that these molecules did not contain one-electron bonds.

Despite having built a formidable empirical and theoretical firewall against the spreading of Wiberg's structures, Bauer's claims for their definitive elimination still faced a major obstacle. In fact, although he had been very successful in discrediting Wiberg's claims on the physical side of the debate, this success implied perfectly homogeneous structures, which accounted for the null dipole moment and the diamagnetic behaviour of diborane. This homogeneity was clearly implied by the homogeneity of all B-B and B-H bonds in diborane, tetraborane and the pentaborane B_5H_{11} and Bauer endeavoured to provide them with suitable electronic structures through a resourceful use of a number of resonating structures. In this process, however, he sacrificed all chemical evidence pointing to the existence of two different B-H bonds. In particular, he could do nothing against Wiberg's strongest card on the chemical side: the ammonia compound of diborane. It is somewhat ironic that this compound should be involatile and, consequently, not suitable for an electron diffraction analysis. In a way, diborane seemed to have some fractal kind of irreducibility. Thus, after so much work and debate on the physical properties of diborane, one great battle remained before anyone could declare *checkmate* on Wiberg. Bauer's claims for a definite elimination of Wiberg's structures may well be understood as a declaration of the superiority of his physical results upon the available chemical evidence. However, for those who valued chemical evidence, Bauer had forced Wiberg to retreat to its original stronghold, the chemical action of diborane upon ammonia, but was now risking a *perpetual chess* situation that would prevent the debate to get to its closure. Then Schlesinger and Burg decided to play a card they had been holding for years.

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[286] S. H. Bauer, "The Structure of Diborane", J. Am. Chem. Soc., *59* (6) (1937). On 1102.

In fact, in 1938, Schlesinger and Burg published a surprising claim for the annihilation of Wiberg's advantage in the explanation of the ammonia salt of diborane[287].

Building on the results of their own research program on the transitory existence of BH_3, they were now in a position to give a full coherent interpretation of some unpublished experiments they had done years earlier on the action of sodium upon a solution of the diammoniate of diborane (diborane's ammonia compound) in liquid ammonia.

Schlesinger and Burg began by disputing Stock's interpretation of his own observations and, consequently, the reaction mechanism he had postulated to explain them:

> It is true that the production of hydrogen before any nitrogen is liberated during the electrolysis of liquid ammonia solutions of this compound, suggests the presence of ammonium ions in such solutions. Nevertheless, the possibility that at least a part of the production of hydrogen is due to the cathodic reduction of ammonia (during which anodic oxidation of the boron hydride occurs instead of liberation of nitrogen) renders it impossible to estimate the quantity of ammonium ion furnished by the original salt.[288]

Even more striking was the dismissal of Stock's interpretation of the ammonia compound of diborane as a diammonium salt. They argued that "a solution of a true diammonium salt in liquid ammonia would be expected to produce a greater lowering of the vapor tension and a greater electrical conductivity than were actually observed."[289]

Instead, Schlesinger and Burg further argued that the ammonia compound of diborane had one single ammonium ion, rather than the two defended by Stock. It should be noted that they did not dispute Stock's conclusion that two ammonia molecules reacted with each diborane molecule. They rather disputed that both ammonia molecules were transformed into ammonium ions. Schlesinger and Burg's reasoning was based on experiments that showed that only one atom of sodium reacted with the ammonia

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[287] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938). On 290.

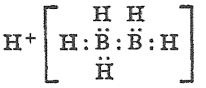
[288] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938), 290–299.

[289] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938). On 290.

compound of diborane and not the two that were expected to replace the two ammonium ions of a true diammonium salt:

> Some years ago, we undertook a further test of Wiberg's interpretation, through a study of the action of sodium upon a solution of the diammoniate of diborane in liquid ammonia. One mole of a true diammonium salt should react with two gram atoms of sodium to liberate two equivalents of hydrogen. Actually we found that the diammoniate, prepared at the lowest feasible temperature (-120º) and allowed to react with excess sodium in liquid ammonia just above its freezing point (-77º), produce only one equivalent of hydrogen per mole of diborane used. [...] In experiments in which the quantity of sodium was just one equivalent per mole of diborane, a stable salt having the empirical formula NaB_2H_8N could be obtained by subliming away the ammonia after the reaction was complete.[290]

According to Schlesinger and Burg, at first glance, this seemed to favour the structure proposed by Böeseken and Wahl:



$$H^+\left[\begin{array}{ccccc} & H & & H & \\ H: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{B}} & : & \overset{\cdot\cdot}{B} & :H \\ & H & & & \end{array}\right]$$

This structure could bind one molecule of ammonia by coordination with the "unsatisfied" boron atom and the other by formation of the ammonium ion detected by the reaction with sodium.

Recall that Stock's dismissal of Böeseken and Wahl's structure was justified with the alleged dibasic acidity he had attributed to diborane because of his interpretation of diborane's ammonia compound. Since Schlesinger and Burg were disputing that very interpretation by Stock, this structure was a possibility again.

However, according to Schlesinger and Burg, this structure failed to explain some evidence. The first one, "a minor logical difficulty, although not an insuperable one", was pretty obvious: in the diborane molecule, only four hydrogen atoms could be replaced by alkyl radicals, however great the excess of boron alkyl used. It was not easy to explain why Böeseken and Wahl's structure would fail to substitute the fifth hydrogen atom.

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[290] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938). On 290.

Even so, a more serious objection to this structure was the result of a further study of the reaction of the ammonia compound of diborane with sodium in liquid ammonia. Schlesinger and Burg observed that further hydrogen was released if the temperature was allowed to rise. However, the total amount of hydrogen never exceeded 1.4 moles of atomic hydrogen H (not molecular hydrogen H_2) per mole of diborane, thus never achieving the two moles that would be expected with Wiberg's structure. Since the exposure of the liquid ammonia solution to temperatures as high as -40ºC, before any sodium had been added, led to an immediate production of 1.25 moles of atomic hydrogen by reaction with sodium at -77ºC, Schlesinger and Burg concluded that the immediate release of those additional 0.25 mol of atomic hydrogen resulted from a very slow secondary reaction between ammonia and the ammonia compound of diborane that had not been previously detected at lower temperatures.

Wiberg or Wahl's structures could hardly explain this secondary reaction, and Schlesinger and Burg proceeded to explain it by postulating a new mechanism for the reaction between ammonia and diborane. According to them, the basis for their new approach was their recent work on borine carbonyl BH_3CO and borine trimethylammine $BH_3N(CH_3)_3$:

> The direct formation of the latter compound [$BH_3N(CH_3)_3$], by the action of trimethylammine upon diborane at temperatures as low as -110º, suggests that the product of the action of ammonia at similar temperatures also may be a complex compound of borine. Another clue to the problem is found in the fact that borine trimethylammine, dissolved in liquid ammonia, does not react with sodium. This observation suggests that the hydrogen produced by the action of sodium upon the diammoniate of diborane[291], comes not from the BH_3 group now assumed to be present in that compound, but rather from ammonia involved in the original reaction with diborane.[292]

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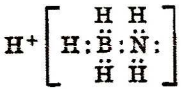
[291] Schlesinger and Burg kept referring to the ammonia compound of diborane as "diammoniate of diborane" or simply as "diammoniate" because it was a convenient and empirically correct name for the compound, whose empirical formula was $B_2H_6{\bullet}2NH_3$. They, nevertheless, opposed to Stock's idea that it was a real diammonium salt.

[292] H. I. Schlesinger, Anton B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938). On 291.

Building on these ideas, Schlesinger and Burg assumed that the action of ammonia upon diborane was the hypothetical borine ammine $BH_3{\cdot}NH_3$, whose ionization would render the formula

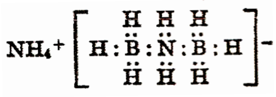


$$H^+\left[\begin{array}{c} H\;\,H \\ H:\ddot{\underset{\cdot\cdot}{B}}:\ddot{\underset{\cdot\cdot}{N}}: \\ H\;\,H \end{array}\right]^-$$

which, in liquid ammonia, should lead to the formation of the salt

$$NH_4^+\left[\begin{array}{c} H\;\,H \\ H:\ddot{\underset{\cdot\cdot}{B}}:\ddot{\underset{\cdot\cdot}{N}}: \\ H\;\,H \end{array}\right]^-$$

However, it was evident that this salt's structure could not be reconciled with the empirical formula $B_2H_6{\cdot}2NH_3$ of the ammonia compound of diborane, determined by Stock and not disputed by Schlesinger and Burg. This difficulty could be solved by admitting further reaction of a borine molecule with the unsaturated nitrogen in the anion of this salt to give the compound



$$NH_4^+\left[\begin{array}{c} H\;\,H\;\,H \\ H:\ddot{\underset{\cdot\cdot}{B}}:\ddot{\underset{\cdot\cdot}{N}}:\ddot{\underset{\cdot\cdot}{B}}:H \\ H\;\,H\;\,H \end{array}\right]^-$$

This formula of a mono-ammonium salt containing a B-N-B skeleton, rather than a direct derivative of diborane, was in agreement with all the observations by Schlesinger and Burg and with the empirical formula $B_2H_6{\cdot}2NH_3$, determined by Stock.

Schlesinger and Burg tried to detect direct evidence for this mechanism through the study of borine ammine or its ammonium salt, but "all the attempts to prepare these compounds have failed, evidently because they either are unstable or undergo secondary reactions."[293] These attempts involved not only the reaction of ammonia with diborane and borine carbonyl, but also the action of ammonia upon two very unstable compounds formed by the low-temperature addition of diborane to phosphine and methyl ether.

Still, Schlesinger and Burg were able to argue for indirect evidence that corroborated their postulated reaction mechanism. By making methyl ether to react with diborane

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[293] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938). On 291.

they obtained the unstable borine derivative $BH_3{\cdot}(CH_3)_2O$[294], which when dissolved simultaneously with sodium in liquid ammonia rendered a residue whose analysis after the removal of excess ammonia proved to be $NaBH_3NH_2$. Since not only the amount of released hydrogen (0.5 H_2 per boron atom), but also the rate of this release was consistent with a process that consisted first in the formation of the compound $NH_4BH_3NH_2$ by reaction of $BH_3{\cdot}(CH_3)_2O$ with ammonia (all methyl ether $(CH_3)_2O$ was recovered), followed by the replacement of the ammonium ion $NH4^+$ by the sodium ion Na^+, Schlesinger and Burg considered that the presence of the ion $BH_3NH_2^-$ had been indirectly demonstrated, thus substantiating their postulated mechanism for the formation of the mono-ammonium salt of diborane.

A reference to this investigation was already included in a footnote on a previous publication, dating it no later than 1935[295]. Thus, approximately two years, at least, had elapsed between this footnote and the actual publication of the investigation. One can speculate that this delay may have been due to Wiberg's 1936 review paper. Schlesinger and Burg may have refrained from publishing their reaction mechanism for the action of diborane upon ammonia by Wiberg's argumentation based on diborane's physical data. The publication of this new reaction mechanism was probably triggered by Bauer's work.

In fact, Schlesinger and Burg submitted their paper in November 1937 and Bauer's paper on the structure was submitted on March 2, 1937. Schlesinger and Burg must had been aware of Bauer's results. Either they were already in the possession of the reaction mechanism, or they rushed to get it, because in September 1937 Bauer submitted a paper on the structure of B_2NH_7 and $B_3N_3H_6$. At that time, Schlesinger, Ritter and Burg had not yet published their paper on B_2NH_7 (it was only submitted in April 11, 1938), but a sample of it was sent to Bauer because they suspected that both compounds (B_2NH_7 and the ammonia compound of diborane) had a B-N-B skeleton. Since the ammonia compound of diborane was not volatile, and consequently, not suitable to electron diffraction analysis, their best chance of obtaining indirect evidence for its B-N-B structure was through the volatile B_2NH_7, because there was evidence that this new

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[294] Schlesinger and Burg assigned the formula $BH_3{\cdot}(CH_3)_2O$ to this compound by analogy with borine trimethylammine $BH_3N(CH_3)_3$, although it might have been formulated also as $B_2H_6{\cdot}2(CH_3)_2O$, since its molecular weight had not been determined yet.

[295] H. I. Schlesinger, L. Horvitz, A. B. Burg, "Hydrides of Boron.VI. The Action of Ammonia on the Methyl Diboranes", J. Am. Chem. Soc., *58* (3) (1936). On 409.

compound was formed by the action of diborane upon the ammonia compound of diborane. Thus, a B-N-B structure for B_2NH_7 would be a good indication that the ammonia compound of diborane had a B-N-B skeleton itself, in full agreement with Schlesinger and Burg's mechanism for its formation.

Indeed, Bauer confirmed the B-N-B structure for B_2NH_7, although he was not able to get decisive evidence favouring the H_3B-NH-BH_3 structure over the alternative configuration H_3B-NH_2-BH_2. Bauer also determined that the boron atoms were closely equidistant from the N atom and that the mean B-N separation was 1.56 ± 0.3 Å. The B-N-B angle was tetrahedral within four degrees, while the B-H distance was close to 1.20 Å. As a part of this process, Bauer decided to reinvestigate the interatomic distances in $B_3N_3H_6$, because the high relative error in the value obtained by Stock and Wierl in 1931 (1.47 ± 0.07 Å) prevented the deduction of a sufficiently secure value for the single covalent separation of boron and nitrogen. Bauer confirmed Stock and Wierl's benzene-like structure for $B_3N_3H_6$, with a B-N separation equal to 1.44 ± 0.02 Å. Assuming a resonance similar to that of benzene, Bauer deduced that the boron-nitrogen single bond separation was 1.59 Å long.

This was not the first time that Bauer analysed a new compound discovered by Schlesinger and Burg. In July of 1937, he had already submitted his analysis of borine carbonyl and borine trimethylammine, establishing their structure and discussing their electronic structures.[296]

When Schlesinger and Burg submitted their paper on the ammonia compound of diborane, they were keen to present Bauer's result as further evidence for their reaction mechanism:

> Finally, attention is called to a recent paper by S. H. Bauer, who, at our suggestion, investigated the electron diffraction of the vapor of this compound, and concluded that the data obtained can be explained only by the existence of a B-N-B skeleton for the molecule. [297]

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[296] S. H. Bauer, "The Structures of the Hydrides of Boron. III. Borine Carbonyl and Borine Trimethylammine.", *J. Am. Chem. Soc.*, 59 (10) (1937), 1804 – 1812.

[297] H. I. Schlesinger, D. M. Ritter, A. B. Burg, "Hydrides of Boron. X. The Preparation and Preliminary Study of the New Compound B_2H_7N", *J. Am. Chem. Soc.*, *60* (10) (1938). On 2300.

On these grounds, Schlesinger and Burg felt they were finally in a privileged position allowing them to participate openly in the debate. They knew that their reaction mechanism, despite all their arguments, still sounded speculative. They also knew that all they needed was to claim they had established a reaction mechanism that was as consistent as that by Stock, thus putting both reaction mechanisms on an equal footing. Then they could call into action Bauer's work, which provided compelling direct structural evidence and dealt with all the physical evidence on diborane. But most important to Schlesinger and Burg, they were also finally able to claim that their own research program on the structural relevance of borine (BH_3) could sustain Bauer's conclusions on a chemical level:

> Whether or not one considers the indirect evidence sufficiently cogent for the acceptance of the structural formula here proposed, the arguments presented here make it evident that the structure of the "diammoniate of diborane" cannot properly be used for the support of hypothetical structures of diborane, since the present work has shown that the diammoniate is not necessarily a direct derivative of diborane. The tendency of diborane to yield the transitory molecules of borine, the chemical evidence of its unsaturation, and the electron diffraction pattern which it produces, all seem best in accord with formulas containing bonds involving less than two electrons.[298]

However, a problem still remained: the chemical evidence for the existence of two B-H bonds in diborane with a different nature was not restricted to its ammonia compound. For example, Schlesinger and Walker's 1935 work on the methyl derivatives of diborane led them too to such a conclusion. This incongruence between the physical and the chemical data may have been the reason behind Schlesinger and Burg's search for further physical evidence, for, in 1938, Burg published a joint paper with T. F. Anderson on the Raman spectrum of liquid diborane, in which they stated:

> The x-ray and electron diffraction patterns of diborane (B_2H_6) show that its atomic arrangement is analogous to that in ethane. However, the formulation of its electronic structure is made difficult by the deficiency of two electrons. In the hope

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[298] H. I. Schlesinger, A. B. Burg, "Hydrides of Boron. VIII. The Structure of the Diammoniate of Diborane and its Relation to the Structure of Diborane", J. Am. Chem. Soc., *60* (2) (1938). On 293.

> of contributing toward the solution of this problem, we have obtained the Raman spectrum of diborane in the liquid condition.[299]

Schlesinger and Burg's concern with this investigation may be corroborated by two facts: Burg did participate in this investigation, rather than just providing the samples; large amounts of diborane were prepared with Schlesinger's material help.

It is somewhat surprising that, at this stage, Mark and Pohland's work was still being used as valuable evidence for the ethane-like structure of diborane. Bauer had used it too. According to this statement, it was the electronic structure that was problematic for the authors. This is well explained by the clash between Bauer's electronic structures for diborane and important chemical evidence. For Schlesinger and Burg, the only way out of this deadlock was to distrust Bauer's electronic structures. On a theoretical level, this should not be very hard to do, as Bauer's argumentation based on Pauling's resonance, with its intrinsic teleological character, may have sounded to them as some sort of a scientific "mumbo-jumbo". After all, Schlesinger and Walker had already explicitly distrusted Mulliken's theoretical consistency before, because of his prediction of a paramagnetic behaviour for diborane. The real problem must have been the homogeneous B-H distances that Bauer had determined through the radial distribution method. To preserve their results on the methyl derivatives, Schlesinger and Burg were forced to distrust them as well. Thus, Bauer on one side and Schlesinger and Burg on the other, were at this point forced to evaluate differently the same empirical evidence according to their own work (and consequently, their disciplinary commitments).

Since Anderson and Burg's work came up with no structural implications whatsoever, the debate seemed doomed to a somewhat confusing situation, forcing its audience to an attitude of cautious objectivity in describing both parties' arguments. Later on, in their 1942 review of the field, Schlesinger and Burg gave up on the necessity of the structural significance they had attributed to the methyl derivatives of diborane, stating that other explanations, as steric hindrance, were conceivable. This statement may be understood as an attempt by Schlesinger and Burg to contribute for the debate's closure. Anyway, at this time, Schlesinger and Burg were already waving a surprising goodbye to the structural debate, acknowledging that chemical evidence was not enough to decide its

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[299] T. F. Anderson, A. B. Burg, "The Raman Spectrum of Liquid Diborane", *Journal of Chemical Physics*, 6 (1938). On 586.

outcome and leaving the discussion to the review published by Bauer, which dealt only with the physical evidence on the hydrides of boron:

> Nevertheless, it must be recognized that no single picture of diborane is in satisfactory agreement with either the total chemical behavior of the substance or deductions from the various physical properties so far studied.
>
> Numerous structures have been proposed for the higher boron hydrides, but knowledge of their chemical properties is still too meagre to give support to any of these suggestions. Since Bauer in the following review discusses in detail the physical data bearing upon the structure of diborane and of the higher hydrides, structural problems will not be further discussed in this review, except as they are directly related to the chemical aspects of the subject.[300]

These statements may be considered as one of the key points in which Schlesinger and Burg explicitly assumed that the chemistry of the hydrides of boron should be independent of the structural problem. As a result of a decade devoted to the structural problem, they had been able to collect a huge amount of new data that allowed establishing the chemistry of the hydrides of boron as an autonomous field *per se*: "Quite aside from these structural problems, the chemistry of the boron hydrides is so unusual as to be a matter of considerable interest in itself."[301]

This sudden evolution was largely based on the surprising results of very recent investigation on the metallo borohydrides, which had been published in 1940. However, at the time he wrote his 1942 review with Burg, Schlesinger was already holding back truly historical secret developments that had been obtained by his team in the context of their participation on the Manhattan Project...

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[300] H. I. Schlesinger, A. B. Burg, "Recent Developments in the Chemistry of the Boron Hydrides", Chem. Rev., *31* (1) (1942). On 3.

[301] Schlesinger, H. I., Burg, Anton B., "Recent Developments in the Chemistry of the Boron Hydrides", Chem. Rev., *31* (1) (1942). On 3.

6 - Graduating from College

By 1942, the community actively engaged in producing boron hydrides was still very restricted. In America, with a few occasional exceptions, only Schlesinger's group produced and studied the chemical behaviour of the hydrides of boron and its derivatives.[302]

An important step forward in spreading this kind of chemistry occurred in 1939. Unable to find tenure in Chicago, Burg accepted the invitation of the University of Southern California to direct their chemistry department. He was credited for having rescued that department from the "alchemy era", building one the finest chemistry departments in the United States. Burg kept actively researching on boron chemistry until his nineties.

Thus, despite Stock's "American road show" in 1932, no interest in boron hydride chemistry was gathered outside Schlesinger's group. This situation resulted certainly from the secondary status of inorganic chemistry had at that time, when compared with organic chemistry. In those days, engaging in inorganic chemistry was definitely not the best way to get a job in chemical industry. Much worse if one decided to do research on a subject with absolutely no practical applications whatsoever, as the hydrides of boron were.

Stock did try to encourage American chemists to go into his field. His book was explicitly written with such intention. This is also evident in the way its organization was meant to render its consultation very easy. Despite a somewhat confusing and repetitive account of his investigation, it served his purposes quite well. The incredible fact is that, despite having been largely ignored by his targeted audience, it did have the desired effect on (at least) one chemistry student who was to make all the difference, as he was about to play a decisive role in the most dramatic revolution in the history of the boron hydrides.

Herbert C. Brown was born in London on May 22, 1912. His family emigrated to Chicago when he was two years old. Brown had an irregular education. The untimely death of his father forced him to abandon high-school to find a job and help to support his family. After three years of fruitless attempts, he decided that further education was the only way to get a job.

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[302] One of these few occasions in which diborane was produced independently, was Lee Gamble and Paul Gilmont's failed attempt in MIT to use the similarity between phosphine and ammonia to clarify the structure of the ammonia compound of diborane.

Brown entered Crane Junior College in February 1933, having registered for a degree in electrical engineering. Someone had told him that electrical engineers made good money...

All engineers had to go through chemistry and Brown felt in love for it. He decided to forget about the money and study chemistry. Due to an exceptionally good memory, Brown did well in the course work and exams. He read a lot about the history of chemistry. He was fascinated by Lowry’s historical approach in his general chemistry textbook *Historical Introduction to Chemistry* (1915). Many years later, he would adopt it in his book *Boranes in Organic Chemistry* (1972).

After his first year at Crane, the college closed due to a lack of funds. It was the Great Depression. By that time, Brown had taken two courses in general chemistry.

It was then that Nicholas D. Cheronis, an instructor at Crane, invited ten of the students at Crane to use the small commercial laboratory he operated in the converted garage of his home to do whatever experiments they wanted to do, using his reagents for free. He wanted to keep the students off the streets. Brown then registered for a correspondence course on qualitative analysis given by the University of Chicago. He did all the experimental work in Cheronis’ laboratory.

Brown first met Julius Stieglitz as his listed instructor for the correspondence course. He also took Harold A. Fales’ *Inorganic Quantitative Analysis* (1925) and worked through it independently. Later on, when Brown entered the University of Chicago, he showed his note books to W. Conway Pierce and received full credit for the two undergraduate Quantitative Analysis courses.

In 1934, Brown entered the Wright Junior College, which had just opened in September. He took courses in organic chemistry and physics. He was permitted to experiment freely with the physical equipment and used to publish a weekly journal on physics and held a monthly museum exposition at which he demonstrated the equipment.

> It was a wonderful time there, and I could experiment there. One time I read about the Foucault pendulum, and I went to the engine house where the ceiling was accessible through three or four floors. I assembled several heavy weights and suspended them from the ceiling to just above the bottom floor. I caused the

> pendulum to swing and followed the plane of its motion for a full day. The experiment worked as described.[303]

Also, Cheronis was writing a book on teaching organic chemistry (*Semimicro and Macro Organic Chemistry*, 1942) and Brown did many tests and experiments on his request.

Brown graduated from Wright Junior College with the first class in 1935. He was persuaded to apply for a competitive scholarship at the University of Chicago, which he won.

At the University of Chicago he was able to complete both his junior and senior years in three quarters, by June 1936. At this point, Brown did not intend to apply for admission to Graduate School or for an assistantship. He planned to get a job as a chemist and marry his girlfriend Sarah Baylen, who had been his classmate since Wright Junior College. It was on the advice of Stieglitz, who had become impressed with Brown in his classes, that Brown, with Sarah's support, postponed his plans and accepted Stieglitz's offer of an assistantship through his Ph.D. degree.

At this point Stock's book became instrumental in Brown's decision to research on inorganic chemistry. Sarah had offered him the book and Brown became interested in the field. Stieglitz also encouraged him to go into organic chemistry and study with Schlesinger, who had been one of Stieglitz students: "At that time, inorganic didn't attract the best students. [...] You know, I didn't do it lightly, because at that time, people looked down upon inorganic as a field of research, and there were very few students getting Ph.D.s in it."[304]

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[303] Herbert C. Brown, interview by James J. Bohning at Purdue University, 11 November 1994 (Philadelphia: Chemical Heritage Foundation, Oral History Transcript # 0117).

[304] Herbert C. Brown, interview by James J. Bohning at Purdue University, 11 November 1994 (Philadelphia: Chemical Heritage Foundation, Oral History Transcript # 0117).

6.1 - Metallo Borohydrides

The discovery of the metallo borohydrides led to a true revolution in the character of the investigation on the boron hydrides, namely by fostering its departure from the structural problem. It also paved the road to large scale production and industrialization, a dramatic unexpected revolution which occurred under the sad accelerating power of war.

The first metallo borohydride was reported by Schlesinger, R. Thomas Sanderson and Burg in 1940. Once again, structural concerns related to the investigation on the existence of borine and the forces leading to its hypothetical dimerization in diborane were in the origin of this investigation. Since trimethyl aluminium $Al_2(CH_3)_6$ was also an electron deficient dimer, it occurred to Sanderson to attempt to prepare the mixed compound $H_3BAl(CH_3)_2$ by combining a borine unit with a trimethyl aluminium unit. According to Brown, "this was obviously an impractical idea, but the general policy of academic research favoured the testing of impractical ideas, sometimes with startling results."[305] Sanderson was not successful at obtaining $H_3BAl(CH_3)_2$ but the new compound aluminium borohydride AlB_3H_{12} was unexpectedly synthesized. Although it had only a remote connection to the structural debate over diborane, its interesting properties, namely its high hydrogen content, raised immediate interest and, shortly after, beryllium borohydride and lithium borohydride were synthesized. Their discovery and study were also reported in 1940. In their review of the field in 1942, Schlesinger and Burg were very clear on the importance of these discoveries: "Among the more striking results of recent investigations in the chemistry of the boron hydrides is the discovery of metal-boron-hydrogen compounds containing unusually large proportions of hydrogen."[306]

All these metallo borohydrides were prepared by the action of diborane upon the alkyl compounds of the corresponding metals. For example, in the aluminium borohydride case the reaction was given by the equation

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[305] Herbert C. Brown, "The Borohydrides – A Case History of Academic Exploratory Research", Chemical and Engineering News, 29 (50) (December 10, 1951). On 5231.

[306] H. I. Schlesinger, Anton B. Burg, "Recent Developments in the Chemistry of the Boron Hydrides", Chem. Rev., *31* (1) (1942). On 35.

$$Al_2(CH_3)_6 + 4\ B_2H_6 \rightarrow 2B(CH_3)_3 + 2AlB_2H_{12}$$

The similarity between aluminium and beryllium suggested to Burg and Schlesinger that beryllium borohydride could be formed by an analogous action of diborane upon dimethyl beryllium. In fact, they were able to obtain a stable volatile compound of molecular formula BeB_2H_8, after a series of intermediate steps in which several other compounds such as $(CH_3)BeBH_4$ and $HBeBH_4$ were also isolated.

In turn, the isolation of the aluminium and beryllium borohydrides led Schlesinger and Brown to attempt the synthesis of an alkali metal borohydride. According to Schlesinger and Brown, the existence of salts with a BH_4^- ion had long been postulated. In 1936, Stock and Laudenklos had tried to prepare $K^+(BH_4^-)$ by the action of active hydrogen upon potassium diborane, $K_2B_2H_6$, but had failed at it.

Since ethyl lithium could be readily prepared and purified, Schlesinger and Brown decided to use it as the starting material. They found out that, at room temperature, gaseous diborane was readily absorbed by ethyl lithium to form the various ethyl derivatives of diborane and a white solid whose salt-like character was established through its remarkable stability and low volatility (no decomposition or volatilization was observed at 240 ºC and 10^{-5} mm Hg. At 275 -280 ºC it melted to a clear liquid which slowly evolved hydrogen). By comparing the composition of the volatile products with that of the starting materials and by treating the white solid with methyl alcohol, Schlesinger and Burg were able to establish its formula as $LiBH_4$: “At present we can say no more than that it seems very probable that the two constituents of the compound, Li and BH_4, are probably ions.”[307]

Since this compound could be obtained through the reaction of aluminium borohydride with ethyl lithium in a benzene solution,

$$3\ LiC_2H_5 + AlB_3H_{12} \rightarrow 3\ LiBH_4 + Al(C_2H_5)_3$$

Schlesinger and Burg interpreted this reaction as indicating that the basic structures of aluminium and lithium borohydrides were closely related and assigned the molecular formula $Al(BH_4)_3$ to aluminium borohydride. Such a formula was in agreement with the

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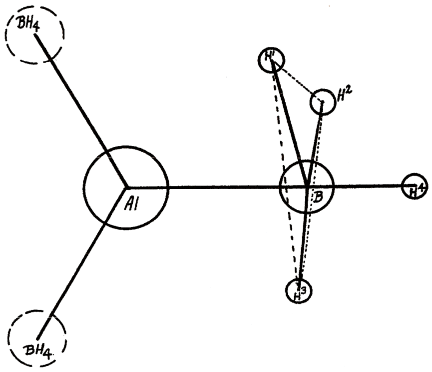
[307] H. I. Schlesinger, H. C. Brown, “Metallo Borohydrides. III. Lithium Borohydride” J. Am. Chem. Soc., *62* (12) (1940). On 3431.

ability of the compound to add one molecule of dimethyl ether or of trimethylamine, thus producing molecules in which the coordination number of aluminium is four. Moreover, this formula was corroborated by the electron diffraction study made by J. Y. Beach and Bauer[308]. Indeed, Beach and Bauer calculated theoretical intensity curves for nine different molecular models. Four of them pictured the aluminium atom as being bonded to three BH_3 groups and three H atoms. The B –AL-B angle was varied from 100 to 110 ° and the B – H distance was varied from 1.20 Å to 1.28 Å. Another model considered the aluminium atom as being surrounded by three BH_4 groups in a plane, the four H atoms being in a plane perpendicular to the B-H bond. In all these cases the calculated intensity curve compared poorly with the observed one.

Beach and Bauer then tried another version of this last model, in which the H atoms were arranged about the B atom at the corners of a trigonal bipyramid. This was also unsatisfactory, but by distorting the trigonal bipyramid so that the three equal Al –B – H angles were 85° instead of 90°, they were able to get agreement. Beach and Bauer presumed that this distortion was a consequence of the repulsion between hydrogen atoms. They found the best ratio of B-H to Al-B distances to be 1.28/2.15. This model is shown in the next figure:[309]



The structure of $Al(BH_4)_3$ according to Beach and Bauer

The structures of lithium and beryllium borohydrides prompted Burg and Schlesinger to assign the formula $Be(BH_4)_2$ to the beryllium borohydride compound. This was also

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[308] J. Y. Beach, S. H. Bauer, "The Structure of the Hydrides of Boron. VI. AlB_3H_{12}", J. Am. Chem. Soc., 62 (1940), 3440 – 3442.

[309] S. H. Bauer, "Structures and Physical Properties of the Hydrides of Boron and of their Derivatives", Chem. Rev., *31* (1) (1942). On 47.

done, without further work, by Beach and Bauer, to whom the extension of their model of the $Al(BH_4)_3$ molecule to the beryllium and lithium borohydrides was obvious; in the case of $Be(BH_4)_3$ the B-Be-B valence angle was presumed to be 180º.

Brown and Schlesinger were then led to propose a qualitative explanation to the gradual transition in the physical and chemical properties from diborane to lithium, with beryllium and aluminium holding intermediate positions in between, just as might be expected from the Periodic Table.

Thus, according to Schlesinger and Burg, at one end of this series, there was diborane ($BH_3.BH_3$), with its high volatility and very low freezing point, characteristics of non-polar compounds. Lithium, at the other end of the series, showed a relatively high melting point and extremely low volatility, which together with the appearance of its crystals and its insolubility in benzene denounced a far more polar character. Aluminium and beryllium borohydrides, as far as these properties were concerned, occupied intermediate positions, with the aluminium compound more near diborane and the beryllium compound similar to lithium borohydride.

Similar relations could be observed in their chemical behaviour: diborane's instability was in opposition to the relative stability of lithium borohydride; diborane is very reactive toward air and oxygen. Lithium borohydride does not react with dry air at ordinary temperatures. Once again, the other borohydrides revealed intermediate behaviour, although Schlesinger and Burg recognized that this judgement was entirely qualitative because no reaction rates or equilibria had been studied.

To Schlesinger and Burg, the most striking feature was the difference in the behaviour of these substances towards trimethylamine, that is, in the easiness with which the borine group was dislodged from the different metallo borohydrides: lithium borohydride did not react at all. Beryllium borohydride required a temperature as high as 90 ºC to unfold a reversible reaction with trimethylamine. On the contrary, aluminium borohydride and diborane reacted irreversibly at 0 ºC and -100 ºC, respectively.

According to Schlesinger and Brown, these observations indicated very clearly that diborane behaved as "a molecule consisting of two BH_3 groups not too firmly bound to each other"[310]. On the contrary, the whole chemical and physical behaviour of $LiBH_4$ indicated the presence of a BH_4^- ion. The presence of a BH_4 group in diborane was not

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[310] H. I. Schlesinger, H. C. Brown, "Metallo Borohydrides. III. Lithium Borohydride", J. Am. Chem. Soc., *62* (12) (1940). On 3430.

to be expected: “Nothing in the behavior of diborane would lead one to suspect that it could possibly yield a BH_4 group or ion, unless one were to use the relatively slow reaction of diborane with ethyl lithium to produce lithium borohydride as the basis for such a conclusion.”[311] Similarly, “nothing in the chemical behaviour of lithium borohydride is in any way suggestive of the presence of a BH_3 group.”[312]

The properties of aluminium and beryllium borohydrides were intermediate in character. For example, aluminium borohydride physical properties were those of a non-polar compound, but its reaction with ethyl lithium in a benzene solution to give lithium borohydride was very similar to an ionic double decomposition. Schlesinger and Brown explained this gradual transition in aluminium and beryllium borohydrides’ behaviour with a less pronounced, but still definitely recognizable, “BH_3 character” when contrasted with diborane.

> All these facts seem to us most satisfactorily interpreted by considering lithium borohydride to be a polar compound consisting of a lithium and a borohydride ion. It is possible that the degree of ionization of the compound may not be so high as that of a typical salt because of slight deformation of the borohydride ion; decision on this question must await accumulation of further data. It is evident, however, that the smaller and more highly charged aluminum and beryllium ions would exert a much greater deforming influence on the BH_4^- ion. As a result, the polar character of the beryllium compound would become less than that of the lithium borohydride and still less in the aluminum compound, as is actually the case. Furthermore, the deformation of the BH_4^- would make it susceptible to disruption, an interpretation which explains why BH_3 groups are relatively readily “extracted” from the aluminum and the beryllium compounds.
>
> But by far the most pronounced deforming influence should be exerted by the very small, highly charged boron ion. Such an aggregate as $B\text{-}BH_4^{++}$ would not be expected to be capable of existence. Disruption into BH_3 groups should be essentially complete, and association of such groups to diborane molecules is then easily understood.[313]

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[311] H. I. Schlesinger, H. C. Brown, “Metallo Borohydrides. III. Lithium Borohydride”, J. Am. Chem. Soc., *62* (12) (1940). On 3431.

[312] H. I. Schlesinger, H. C. Brown, “Metallo Borohydrides. III. Lithium Borohydride”, J. Am. Chem. Soc., *62* (12) (1940). On 3431.

[313] H. I. Schlesinger, H. C. Brown, “Metallo Borohydrides. III. Lithium Borohydride”, J. Am. Chem. Soc., *62* (12) (1940). On 3431.

Thus, the metallo borohydrides provided Schlesinger and Brown a new understanding of diborane which finally allowed a qualitative contextualization of its odd tendency to dimerize. This was to be achieved not by the study of the stability of BH_3 molecules or BH_3 containing compounds as Schlesinger and his co-workers had tried so far, but rather by viewing BH_3 as resulting from the deformation of its hyper structural parent, the BH_4 ion.

This was not an explanation for diborane's structure and in fact, they explicitly denied it, assuring that it had no relation to Bauer's interpretation of diborane in terms of numerous resonating structures.

Schlesinger and Brown were now willing to suspend the debate until further investigations by physical methods could be put forward:

> Chemical evidence alone cannot decide these questions, and since ours is a chemical study of these compounds, we are not entering into a discussion of the problem the further elucidation of which requires many additional data.[314]

The previous statement may be considered to signal the very first moment in which Schlesinger and his group explicitly admitted to be abandoning the structural debate to focus on the chemistry of boron hydrides. This emancipation of boron chemistry as a full autonomous body of chemical knowledge was the result of a long process of data collection that had been entirely formatted by the structural debate, but a sudden shift seems to have been triggered by the discovery of the unexpected properties of the metallo borohydrides in a perpetual puzzle scenario. Remarkable as it may have been, this was just the first step in the dramatic mutation that metallo borohydrides were about to bring to boron chemistry.

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[314] H. I. Schlesinger, H. C. Brown, "Metallo Borohydrides. III. Lithium Borohydride", J. Am. Chem. Soc., *62* (12) (1940). On 3431.

6.2 - I WANT YOU!

Late in 1940, the National Defence Agency asked Schlesinger to investigate the synthesis of new compounds of uranium with a volatility as low as 0.1 mm Hg at a temperature at which the material was stable enough for long periods of time. The purpose of such an investigation was not disclosed to Schlesinger.

Brown had just completed his work on lithium borohydride and was working on gallium borohydride when he was asked by Schlesinger to drop his academic research and engage in the Defence Project. Brown assembled a small group and began studying several possible uranium compounds that might do the work. Uranium hexafluoride UF_6 was already known, but its extreme reactivity raised too many technological problems. Brown and his group focused on uranium (IV) acetonylacetonate and related derivatives, but the volatility of acetonylacetonate was too low. They tried to solve the problem by changing acetonylacetonate's structure and were being well succeeded with two fluorine derivatives when they were informed that it was very important that the molecule had a low molecular weight, preferably not greater than 238 g/mol. This was a blow in the investigation: one of the fluorine derivatives of acetonylacetonate had a molecular weight of 1066 g/mol.

Brown then decided to prepare uranium (IV) borohydride $U(BH_4)$ by treating uranium (IV) fluoride with aluminium borohydride:

$$UF_4 + 2\ Al(BH_4)_3 \rightarrow U(BH_4)_4 + 2\ AlF_2(BH_4)$$

The first experiment was successful and the National Defence Agency requested the creation of a large research team to synthesize and study uranium borohydride $U(BH_4)_4$ and to discover simple synthesis methods for large scale production. Schlesinger took care of the analytical study of $U(BH_4)_4$ and other promising derivatives (volatility, stability, etc) and Brown was in charge of their production (both test quantities and large scale methods).

Brown could get uranium (IV) fluoride from government sources but he had to synthesize aluminium borohydride.

Aluminium borohydride was produced by treating trimethylaluminium with excess diborane. To synthesize trimethylaluminium one had first to use mercuric chloride and methylmagnesiumchloride to obtain dimethylmercury, which in turn was treated with aluminium:

$$2\ CH_3MgCl + HgCl_2 \rightarrow (CH_3)_2Hg + 2\ MgCl_2$$

$$3\ (CH_3)_2Hg + 2\ Al \rightarrow 2\ (CH_3)_3Al + 3\ Hg$$

$$(CH_3)_3Al + 2\ B_2H_6 \rightarrow Al(BH_4) + B(CH_3)_3$$

As the last equation shows, diborane production was an essential step in the whole process. Brown used Schlesinger and Burg's method as modified by Stock and Sütterlin in 1934, that is, he used boron tribromide instead of borontrichloride. Borontrichloride was synthesized from calcium boride and subsequently reduced by an electric discharge method:

$$CaB_6 + 10\ Br_2 \rightarrow CaBr_2 + 6BBr_3\ (900\ ^{o}C)$$

$$BBr_3 + H_2 \rightarrow BHBr_2 + HBr\ (15\ mm\ Hg\ ;\ 12{,}000\ volts)$$

When subjected to high temperatures, $BHBr_2$ renders B_2H_5Br, which in turn decomposes into diborane and boron tribromide:

$$B_2H_5Br \rightarrow B_2H_6 + BBr_3$$

By treating $U(BH_4)_4$ with trimethylboron, it was possible to synthesize a monomethyl derivative of $U(BH_4)_4$ that was even more volatile than its parent compound.

According to Brown, most of their effort had to be devoted to the synthesis of sufficient uranium borohydride and its methyl derivative for detailed study of their volatilities, stabilities and the like. However, it was clear that this production method would not be suited for large-scale industrial production.

A small group had almost immediate success in finding a simpler and better-suited process, though. By making a suspension of finely divided lithium hydride LiH to react with boron trifluoride etherate, diborane was produced. In that same solvent (diethyl ether – ($(C_2H_5)_2O$), diborane reacted with lithium hydride to produce lithium boron hydride $LiBH_4$:

$$6\ LiH + 8\ BF_3 \rightarrow B_2H_6 + 6\ LiBF_4$$

$$2\ LiH + B_2H_6 \rightarrow 2\ LiBH_4$$

Lithium borohydride then reacted with aluminium trichloride (in the absence of solvent) to produce the desired aluminium borohydride:

$$3\ LiBH_4 + AlCl_3 \rightarrow Al(BH_4)_3 + 3\ LiCl$$

When these discoveries were reported to the National Defence Agency, a second blow fell:

> When we reported this to the headquarters, our delight was severely dampened. There was a serious shortage of lithium hydride and none could be spared for this application. (Every plane going over water carried two 1-pound charges of lithium hydride, which could be used to inflate a balloon with hydrogen to carry aloft an antenna for distress signals.)[315]

They were then asked to use sodium hydride NaH.

Because of war, they could not resort to the usual solvents tetrahydrofuran and diglyme and ethyl ether and other solvents were shown not to work. The problem was solved with sodium trimethoxyborohydride, which was readily prepared by heating sodium hydride with excess methyl borate:

$$NaH + B(OCH_3)_3 \rightarrow NaBH(OCH_3)$$

This compound was then used to produce sodium borohydride

$$2\ NaBH(OCH_3)_3 + B_2H_6 \rightarrow 2\ NaBH_4 + 2\ B(OCH_3)_3$$

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[315] H. C. Brown, *Boranes in Organic Chemistry* (New York: Cornell University Press, 1972). On 44.

which, in turn, could be combined with aluminium chloride to give aluminium borohydride.

Sodium trimethoxyborohydride was also a source of diborane:

$$6\ NaBH(OCH_3)_3 + 8\ BF_3 \rightarrow B_2H_6 + 6\ NaBF_4 + 6\ B(OCH_3)_3$$

$$6\ NaBH(OCH_3)_3 + 2\ BCl_3 \rightarrow B_2H_6 + 6\ NaCl + 6\ B(OCH_3)_3$$

Finally, the production procedure for $U(BH_4)$ was completed and it was time to test it:

> Our results indicated that uranium (IV) borohydride possessed sufficient volatility and stability to meet the specifications. A supply of uranium (IV) borohydride was prepared, and I received priority to fly to New York for testing at Columbia University (a four-stop flight aboard a DC3). At Columbia I worked with Dr. Willard E. Libby, subjecting the material to the metal barriers that would be used in the diffusion plants. Alas! Uranium borohydride proved unstable to these metal barriers.[316]

Meanwhile, the U.S. Army Signal Corps had been having problems with field generation of hydrogen, needed to elevate their radio antennas to the required altitudes. They used a mixture of ferrosilicon and sodium hydroxide, whose reaction left a solid residue of silicates that had to be chipped out before the generator could be used again. This took a soldier’s full day. Even worst, the handling of sodium hydroxide pellets often resulted in hospitalization due to caustic burns. Also, the large and bulky cylinder required was difficult to transport to battle areas around the world. Finally, these silicates had a salty taste much loved by cows, but the acid in their stomachs converted it to silica. The farmers had been complaining because, with their stomachs filled with silica, the cows slowly starved to death without ever being hungry. The Army was facing too many damage suits.

In the meantime, someone in the Signal Corps read one of the reports from the Schlesinger group and noticed the high yield of hydrogen in the hydrolysis of lithium borohydride. However, the entire world supply of lithium was not enough to sustain such use for lithium borohydride and Schlesinger and his team suggested the use of sodium borohydride. Its hydrolysis should produce almost as much as lithium

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[316] Herbert C. Brown, *Boranes in Organic Chemistry* (New York: Cornell University Press, 1972). On 45.

borohydride and far better than calcium hydride or ferrosilicon. Moreover, the reaction product was the easily disposable sodium borate. The Signal Corps asked for a demonstration.

> Interested, they asked for a demonstration. This led to one of the greatest shocks of my life.
>
> In research involving the hydrogen compounds of carbon one customarily oxidizes them to carbon dioxide and water and collects and weighs these to get an analysis. One does not normally anticipate that a given hydrocarbon will fail to burn. Similarly, in research involving the hydrides of boron it is customary to treat the compound with water to form boric acid and hydrogen. It is ingrained in one always to protect such compounds from air and water. We had always so protected sodium borohydride.
>
> Since our visitors wanted a demonstration, I weighed out a sample of sodium borohydride in a dry box and placed the sample in a flask fitted with a gas outlet tube connected to a gas meter. A dropping funnel containing water was attached to the flask. The entire assembly was mounted behind a safety screen. (I expected a violent reaction, similar to that which occurs with lithium aluminum hydride.)
>
> With the several colonels and civilians of the visiting party surrounding me, I cautiously allowed the water to flow from the dropping funnel into the flask. To my amazement, the sodium borohydride simply dissolved and no significant gas evolved.
>
> This was embarrassing indeed![317]

Even so, the Signal Corps kept its interest and the search began for a simpler and more economical procedure to obtain sodium borohydride and its hydrolysis. It was achieved by combining methyl borate with sodium hydride at 250 ºC:

$$4\ NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3\ NaOCH_3$$

And this reaction was behind the industrial method for the production of sodium borohydride.

In 1944, a contract was signed between the Signal Corps and the Ethyl Corporation to build a pilot plant, but shortly afterwards Washington gave instructions to stop the

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[317] H. C. Brown, *Boranes in Organic Chemistry* (New York: Cornell University Press, 1972). On 46.

construction of any new war plants as the war was nearing its end. Once again, the hydrides of boron failed at engaging in combat.

According to Brown, their efforts were not fruitless: “Nevertheless, the research opened up major new areas. It completely revolutionized the methods used by the organic chemists for the reduction of functional groups. And sodium borohydride, a product developed under the exigencies of war research, later found its main application in the pharmaceutical industry.”[318]

6.3 - Inorganic meets Organic

In 1938, Brown was persuaded by Schlesinger and Burg to explore the reaction of diborane with aldehydes, ketones and other compounds containing carbonyl groups. In his book, Stock had already referred some incidental observations on reactions between boron hydrides and carbon compounds, namely the reactions between B_4H_{10} and ethane and alcohol and the reactions of acetylene with B_2H_6 and B_4H_{10}: “These are set down here briefly, because if followed up they may lead to the preparation of compounds that contain both boron and carbon.”[319] Brown’s PhD. thesis was published in 1939[320]. It was a joint paper with Schlesinger and Burg and contained some unpublished work on the reactions of diborane with acetaldehyde and methyl formate that Burg had carried out in the summer of 1934. References to studies on these reactions can be found in an earlier publication by Schlesinger and Burg:

> These results have not yet been published. We have found that diborane reacts rapidly with acetaldehyde to give diethoxyborine, with acetone to give a compound which seems to be diisopropoxyborine, and far more slowly with methyl formate to

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[318] H. C. Brown, *Boranes in Organic Chemistry* (New York: Cornell University Press, 1972). On 48.

[319] A. Stock, *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 150.

[320] H. C. Brown, H. I. Schlesinger, A. B Burg, “Hydrides of Boron. XI. The Reaction of Diborane with Organic Compounds Containing a Carbonyl Group”, *J. Am. Chem. Soc.*, *61* (3) (1939), 673–680.

> give dimethoxyborine. The aldehyde and ketone reactions are completed in ten minutes at room temperature.[321]

Brown, Schlesinger and Burg hoped that their work could shed some light on the structure of diborane, but also that results of significance to organic chemistry might be observed. In fact, as pointed out by Brown later on, it gave birth to a revolution in organic chemistry. It reported the first use of inorganic hydrides for the reduction of organic functional groups.

According to Brown, before this development, organic reductions were carried out by using active metal, such as iron, zinc, or sodium with acetic acid or alcohols. Elevated temperatures (100 ºC) and extended reaction times (9 hours) were required. The introduction of aluminium alkoxides in the late 1920's did not change these requirements. On the other hand, the reduction by diborane took only 1 minute and required 0 ºC!

Because only milligram quantities of diborane were available at that time, produced through Stock or Schlesinger and Burg's methods, this incredible development could not be adopted by organic chemists. It was of theoretical interest only. Interestingly, Brown recognized that neither of them realized then the need for the improvement of preparative methods:

> It would be nice to tell you that one of these three researchers [Brown, Schlesinger and Burg] recognized the desirability of developing a practical synthesis of diborane, one that would make this chemical readily available and lead organic chemists throughout the world to use our convenient procedure for reducing organic compounds.
>
> Regrettably, that was not the case. At the time faculty members at universities tended to look down upon research directed toward inorganic synthesis.[322]

This deadlock was overcome due to work on sodium borohydride during the war. In 1943, Brown failed to achieve tenure at the University of Chicago and went to Wayne University, Detroit. While there, he was associated as a consultant with Ethyl Corp. to develop a commercial process for the manufacture of sodium borohydride. However,

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[321] A. B. Burg, H. I. Schlesinger, "Hydrides of Boron. VII. Evidence of the Transitory Existence of Borine (BH_3): Borine Carbonyl and Borine Trimethylammine", *J. Am. Chem. Soc.*, *59* (5) (1937). On 781.

[322] H. C. Brown, "Hydride reductions: A 40-year revolution in organic chemistry", *Chemical & Engineering News* (March 5, 1979). On 24.

the research on the reducing potential of sodium borohydride was still under classification and he could not continue his work on this specific issue.

After the war, lithium hydride, a compound with exceptionally powerful reducing capabilities, was synthesized by Albert Finholt, Arthur C. Bond Jr. and Schlesinger at the University of Chicago. Because the declassification problem held up the publication and commercialization of sodium borohydride, lithium hydride was available sooner to the organic chemist. However, in 1947-48, both aluminium hydride and sodium borohydride were being produced by Metal Hydrides Inc. Lithium hydride was originally their major product soon to be surpassed by sodium borohydride. Large scale production sustained by the world-wide construction of several large plants followed these early developments.

An important step in this process was the selective reduction research program initiated by Brown at Purdue University, where he moved in 1947. The available reducing agents at the time were very different in character: sodium borohydride was a very mild reducing agent capable of reducing aldehydes, ketones and acid chlorides; and lithium aluminium hydride was a very strong reducing agent which reduced practically all organic functional groups. Brown and his co-workers tried to enhance the reducing power of sodium borohydride and to decrease that by lithium aluminium hydride. This was achieved by adding lithium chloride or bromide to a solution of sodium borohydride and by introducing alkoxy substituents in lithium aluminium hydride.

Since sodium borohydride, a simple source for diborane, was now commercially available, Brown decided to explore diborane’s reducing characteristics. They turned out to be completely distinct from those of sodium borohydride and lithium aluminium hydride and this fact allowed playing with their differences to obtain selected results. For example, in a mixture of chloral and trimethylacetaldehyde, sodium borohydride would reduce the chloral and diborane would reduce the acetaldehyde.

According to Brown, the most unexpected characteristic of diborane as a reducing agent was its rapid reduction of carboxylic acids to alcohols and of amides to amines. This was a significant breakthrough because carboxylic acids were especially resistant towards reduction.

The following table illustrates how the organic chemist had now at his disposal a versatile range of reducing agents which he could select for his specific purposes:[323]

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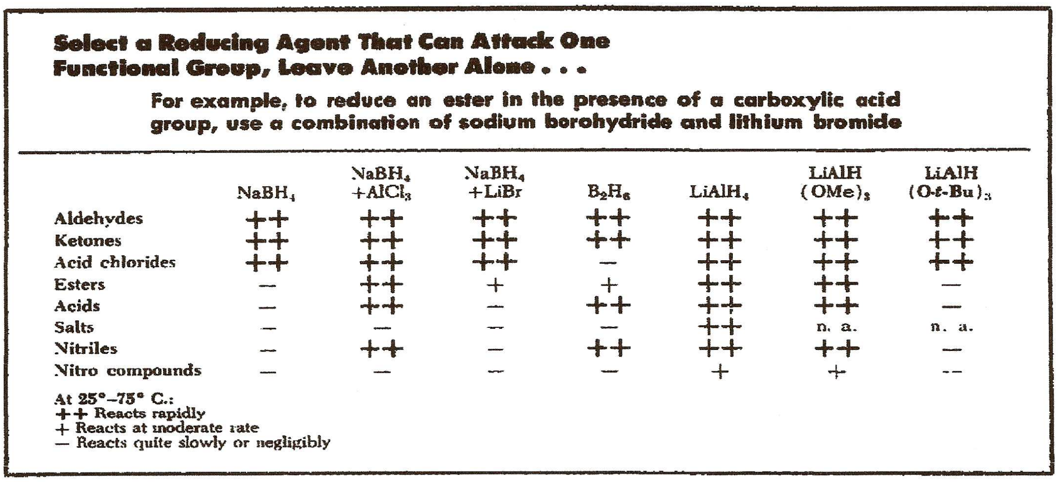
[323] N/A, “Versatile Hydroborons”, Chemical and Engineering News (May 6, 1957). On 28.



Select a Reducing Agent That Can Attack One Functional Group, Leave Another Alone . . .

For example, to reduce an ester in the presence of a carboxylic acid group, use a combination of sodium borohydride and lithium bromide

	$NaBH_4$	$NaBH_4$ $+AlCl_3$	$NaBH_4$ $+LiBr$	B_2H_6	$LiAlH_4$	LiAlH $(OMe)_3$	LiAlH $(O\text{-}t\text{-}Bu)_3$
Aldehydes	++	++	++	++	++	++	++
Ketones	++	++	++	++	++	++	++
Acid chlorides	++	++	++	—	++	++	++
Esters	—	++	+	+	++	++	—
Acids	—	++	—	++	++	++	—
Salts	—	—	—	—	++	n. a.	n. a.
Nitriles	—	++	—	++	++	++	—
Nitro compounds	—	—	—	—	+	+	--

At 25°–75° C.:
++ Reacts rapidly
+ Reacts at moderate rate
— Reacts quite slowly or negligibly

The instrumental use of boron hydride derivatives was readily assimilated by the drugs industry and Brown's research was supported by grants from Upjohn, Parke-Davis, and Merck.

6.4 - *Fuelled by War*

One of the most notorious properties of boron hydrides was their high energy content. They could achieve as much as 30,000 BTU per pound (hydrocarbons yielded 18,500 BTU per pound), making them excellent potential fuel components. Naturally, now that industrial production was in reach, this characteristic immediately got the attention of the US Army and Navy and, after WWII, research programs were implemented to determine if boron hydrides could be used as fuel additives in the recently developed jet-engine. Initial work was done at universities and in 1946 the US Army contracted with General Electric Company (GE) the classified "Project Hermes" research program. The US Navy initiated its own research program in 1948 with Callery Chemical Company, a subsidiary of the Mine Safety Appliance of Pittsburgh, and in 1952 a program with code name "Project Zip" began - boron hydride fuels were nick-named "zip" fuels due to their potential high speed power. Twenty chemical companies were asked to try boron for high-energy aircraft fuel. Callery Company and the Mathieson

Chemical Corporation of Niagara Falls, N.Y., were elected. Universities and smaller chemical companies were subcontracted for research.

In the late 1940's and early 1950's GE built a small pilot plant at its research and development facility at Malta, NY. This was operated for several years, producing diborane, pentaborane and small amounts of decaborane. The production and handling of the hydrides of boron got so problematic (several accidents and one death) that GE decided it was too risky and terminated its contract with the Army. The Malta Pilot Plant was taken over by the Olin Mathieson Corporation. This company also erected, mostly with its own funds, a $5,500,000 plant at Niagara Falls, NY, under the first contract with the Navy for Project Zip. In 1954, a second plant was built under a cost-covering Navy contract. This was a small pilot plant installation which paved the way to a bigger one inaugurated at 1957, at Model City, NY. $4,500,000 were invested here. By this time the Air Force expressed its interest in the fuel and the plant got under its supervision that same year.

In the meantime, the Navy continued its cooperation with the Callery Company. Thus, in 1948, the Callery Chemical Company had started research on high-energy fuels for the U. S. Navy, building pilot scale facilities on its property in Pennsylvania. In June 1956, a $38,000,000 contract for the construction of the HiCal plant at Muskogee was signed. At the time, Rear Admiral Robert E. Dixon, Chief of the Navy's Bureau of Aeronautics, stated that the Muskogee workers would produce the fuel "that will enable American air power to maintain the ascendency necessary to guarantee the democratic way of life to the peoples of the free world"[324]. Another plant at Lawrence, KS, was contracted with Callery Company in 1957.

On June 21, 1955, the Malta pilot plant exploded, causing the death of two employees and the total destruction of its facilities. The explosion is attributed to the use of the cleaning solvent carbon tetrachloride CCl_4 on some reaction vessels. They had been warned against it by Burg, but they decided to go ahead anyway. Subsequent research showed that pentaborane and carbon tetrachloride combine to form a highly shock-sensitive compound.

The Malta pilot plant kept experiencing several accidents, some of them fatal, involving detonation of material in lines, failure of processing equipment and incidental exposure to toxic vapour that affected the victims' nervous system.

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[324] J. Raymond, "200 Million went into "exotic" fuel", *The New York Times* (August 16, 1959).

At Callery Company, one single accident with three deaths and three injured was recorded. The fatal victims had taken on themselves the construction of a rocket using one of the company products...

The research on high-energy fuels derived from boron hydrides found its context in the Cold War and the Race to Space. Zip fuels or “exotic” fuels, as they were known, were intended to extend the range of existing bombers by at least one-third and perhaps one-half or more. This would allow a B-58 bomber to fly to any point in the world and return without refuelling. But its major application was to power the new J-93-5 engines of the new B-70 Valkyrie supersonic long-ranger bomber. It was to achieve speeds up to 2000 mph, allowing it to evade its pursuers or to advance on a target by surprise. Two prototype B-70 were built and tested, but the high costs of their operation prevented the constitution of a fleet. Indeed, each of its four engines would consume 20 tons of fuel per hour at a cost of $5 per pound. The boron fuels were to be used with conventional fuels and used to power the bomber only for short durations. Other than being based on boron, any information on the composition of the new fuels was classified.

The interest in boron hydride fuels was further enhanced when the second soviet satellite was launched, reportedly powered by a new type of super-fuel that some observers believed to contain a combination of boron, carbon and hydrogen.

An authentic “race to boron” was triggered by all these developments, with Wall Street rising to euphoria, powered by sky-rocketing records for missile and boron companies: “It was a missile market yesterday in Wall Street” - one could read in the New York Times in November 7, 1957 - “Eleven of the fifteen most active stocks were in the missile rocket fuel or aircraft fields. [...] Companies involved in solid fuels shared the limelight with the missiles.”[325] The madness continued the next day: under the title “Talk of a new rocket fuel stirs feverish buying – Missiles also active”, one could read “Stocks of companies in the high energy fuel field boomed for the second day. It has been reported that the second soviet satellite was launched by a new power source – a liquid super fuel. [...] Trading in one high-energy fuel companies was suspended. [...] High energy fuel companies, like Borax, and aircraft-missile stock also played a major role in pulling the market up”.[326]

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[325] N/A, “Missile Shares Star in Market”, *The New York Times* (November 7, 1957).

[326] N/A, “Boom continues in Boron Shares”, *The New York Times* (November 8, 1957).

In November 13, 1957, the world biggest borax mining operation was inaugurated in Mojave Desert, with the presence of representatives of the Air Force and the Navy. For the first time, the biggest deposit of pure borax (big enough to ensure the production for 100 years) was going to be exploited by the open-pit mining method.

In 1958, the major borax mining companies joined chemical giants to achieve large-scale production: Stauffer Chemical Company, one of the three major world producers of boron raw materials joined the Aerojet General Corporation, the largest chemical corporation in the West of the United States specialized in rocket fuel research, to develop and produce boron compounds for rocket and missile propulsion fuels; the Dow Chemical Company, the leading producer of chlorine, and the US Borax Research Company combined their previously independent efforts to develop a profitable procedure to synthesize trichloride – a rocket fuel intermediary.

However, boron fuel science was still in its infancy. Besides the dangers involved in large-scale production and handling of the hydrides of boron, several fundamental problems were plaguing the use of the new fuels as jet propellants. Thus, when burned in the jet engine, they left boron oxide deposits that blocked fuel injection parts and eroded the engine's precision parts. This required an after burner and another fuel system. Also, during the flight, vast areas of land were sprayed with a toxic residue that particularly affected citrus crops and tobacco.

Despite these problems, the report on accomplishments in the aeronautics and space fields sent by President Eisenhower to the Congress on February 2, 1959, stated: "During 1958 an after burner of new design was tested. It was found appreciably freer of the boron-oxide deposit problem than were earlier versions. Although much research and development in this program is classified, it can be stated that boron now appears feasible as a high-energy jet fuel".[327]

Only six months after, the blow fell on everybody. The Air Force cancelled a $45,000,000 contract with GE for producing the J-93-5 engine, after having spent $10,000,000 on it. This engine was being produced for the B-70 bomber and the F-108 fighter plane. The Navy cancelled the 1956 contract of $38,000,000 with the Callery Company for the construction of the HiCal plant at Muskogee.

Apparently, GE had up-graded the J-93-3 engine to achieve, with conventional fuels, efficiency and performance standards that were near those that were expected with zip

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[327] N/A, *The New York Times* (12 August, 1959).

fuels. The high cost and the technical difficulties of operating the J-93-5 engine with boron fuels were no longer acceptable. The B-70 bomber and the F-108 fighter plane would be reprogrammed to operate with the conventional J-93-3 engine. After an investment of $240,000,000 and the occurrence of several deaths and injured workers, 8 plants were to be dismantled or reprogrammed for the production of small amounts for research purposes and 2000 people were out of job. “A disastrous blow”, was claimed by the companies involved...

In the early 1960’s, the US Air-Force and NASA became interested again in diborane and pentaborane as storable space propellants for intercontinental ballistic missiles, low-orbit rockets and the U-2 and Blackbird spy planes. The Muskogee plant was brought to life again to produce a large amount of pentaborane to be used at Edwards Air Force Base as a missile propellant. This was a short lived contract and the pentaborane was never used. Small quantities were used for tests at many facilities belonging to the Air-Force and the Navy. The remaining pentaborane has been stored in bunkers and storage igloos all across the United States ever since. Research on the hydrides of boron as solid propellants continues at the present.

It is somewhat ironic that war research was the great responsible for leading boron hydride chemistry to industrialization and commercialization, with a wide range of applications in the pharmaceutical and medical areas, while collecting a long list of failures on what concerned its military applications. As Schlesinger had put it, “for defense purposes the boron hydrides would always be a bridesmaid but never a bride!”[328]

Stock did not live long enough to see these incredible developments in the chemistry he had created. Although he strongly opposed the utilitarian view of science, he believed that science should contribute to the advancement of mankind. In his inaugural lecture at Cornell, in 1932, Stock stated: “The highest problem for the scientific mind to solve will be: How to free mankind from political, economic and social limitations and how to give it a purer and broader minded understanding of humanity and sympathetic mutual co-operation.”[329] He also had high expectations for the future of science: “Although no field of natural science is lacking in vastly important unsolved problems, their outlines

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[328] G. Urry, “Hermann Irving Schlesinger–October 11, 1882–October 3, 1960,” *Biographical Memoirs of the National Academy of Sciences*, 64 (1994), 369–394.

[329] Stock, A., *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 11.

are recognizable; and no one knows what lies hidden in the obscurity of the future. If Archimedes escapes the death by the rough hand of the soldier, the natural sciences may long continue their triumphant march."[330]

Tragically, this last sentence became his own epitaph. Forced to leave his home, shortly after being heavily bombed, and to become a war refugee by the advance of the Russian Army, Stock lost all his possessions. "My entire scientific notes were lost in Warmbrunn. I have only managed to save a summary of my complete publications together with some biographical notes in my portfolio, a fact which I am particularly keen to let you know. My wife and I send our very best wishes to you, my dear friend, and to your wife, Yours, Stock."[331] These were the last words Stock sent to Wiberg.

On the 12th August 1946, under appalling conditions, severely disabled and distressed with the future of German chemistry, Stock died in peaceful loneliness with his wife. His death went unnoticed to the outside world.

As with Archimedes, the rough hand of the soldier came too late. Stock had already escaped death through the triumphant march of his masterful creation.

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[330] Stock, A., *Hydrides of Boron and Silicon* (New York: Cornell University Press, 1933). On 11.

[331] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem*., 49 (1977). Translation from the German by H. Nöth and R. H. Walter. On 700.

Concluding Remarks

Humphry Davy, Friedrich Wöhler, Henri Sainte-Claire Deville, Paul Sabatier, William Ramsay, Alfred Stock, Egon Wiberg, Herman F. Mark, Nevil V. Sidgwick, Samuel Sugden, Maurice L. Huggins, Robert Robinson, Thomas M. Lowry, Linus Pauling, G. N. Lewis, Robert S. Mulliken, Gerhard Herzberg, Simon H. Bauer, Hermann I. Schlesinger, Anton B. Burg, Herbert C. Brown.

This list, presented without any guiding context, is undoubtedly recognized by any chemist or historian of chemistry as an impressive array of many of the top chemists of the last two hundred years. Unfortunately, before the present work, probably no chemist or historian of science would be able to identify what linked all these men together. Most probably, they would be much surprised by the answer. Most probably, they would be even more surprised to know that all these brilliant men failed at it.

The path to the solution of the structure and the nature of the chemical bond in the hydrides of boron required an additional list of equally famous names in chemistry, such as Kenneth S. Pitzer, Y. K. Syrkin, M. E. Diatkina, H. C. Longuet-Higgins, R. P. Bell, William C. Price and William N. Lipscomb.

This simple list proves that the development of the chemistry of the hydrides of boron was no "alternative" or "underground" historical development running parallel to the main stream development of chemistry in the twentieth century. The present work proves that the chemistry of the hydrides of boron was an integral and important part of theoretical chemistry in the twentieth century. There is no doubt this was indeed the perception of many of those who built bond theory. "Puzzling", "perpetual puzzle", "one of the most puzzling phenomena of chemistry", these expressions were systematically repeated when referring to the hydrides of boron. Most articles on these compounds begin by stating their importance to chemical bond theory: "Much attention has been paid recently to the structure of the B_2H_6 (diborane) molecule" (E. Blum and G. Herzberg, 1936); "The chemistry of fluorine and boron compounds are of considerable interest from the valency and structural points of view." (K. L. Ramaswamy, 1935); "The structure of diborane (B_2H_6) is a problem of very general interest because it raises the important question of the occurrence, in simple compounds, of covalent bonds involving less than a pair of electrons." (Schlesinger and Burg, 1938). The obvious corollary here is simple: *no diachronic account of the history of chemistry in the twentieth century can ignore the history of the hydrides of boron.*

The history of these compounds is essential to put into a more inclusive perspective the history of chemical bond.

But even if one chooses to adopt an anachronistic understanding of history, the hydrides of boron will easily force their way into it. This is so due to their pervading presence in modern chemistry, with crucial applications to chemical and pharmaceutical industry, to medicine, nanotechnology, etc. Even on a purely theoretical level, their history is still be unavoidable because these compounds eventually forced chemists to abandon the paradigm of the atom-to-atom chemical bond with William Lipscomb's *three centre-two electrons* concept in 1956.

In a sense, Lipscomb solution gave finally reason to Stock's claims that the understanding of the nature of the chemical bond in the hydrides of boron would force chemists to abandon such simple concepts as those derived from the chemistry of carbon. However, Lipscomb solution would, most probably, be politely rejected by Stock. This may be inferred by his reaction to Wiberg's structures:

> I still have vivid memories of the occasion when, as a young assistant, I showed Stock the reprint of one of my publications on the structure of boron hydrides and other boron compounds, in which I proposed that a pair of electrons could bind more than two atoms and that the boron-chlorine bond in boron chloride was stronger than a single bond. He looked at me with a generous forgiving smile; because ideas such as "multicentre bonding" and "back-donation" had at that time, roughly half a century ago, not yet been conceived.[332]

Published in 1977, just after Lipscomb's Nobel Prize in 1976, Wiberg's new version of his biographical article on Stock in 1950 may be seen as an attempt to remember the history behind the prize and the long intellectual and experimental struggle necessary before things got to that point. In particular, Wiberg's last sentence may be also interpreted as a sarcastic observation to fact that multicentre bonding was already been conceived by him fifty years ago.

This raises the question of how ideas are able to evolve and be appropriated by other participants in new theoretical contexts. How much credit should Wiberg have received

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[332] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 697.

for Lipscomb's work? This question is especially relevant because Wiberg's structures assumed an important role after William C. Price's definite dismissal of the ethane-like structure in 1948. Should Wiberg have shared Lipscomb's Nobel Prize? Stock's opinion would no doubt be positive. As Wiberg tells in his article, he once said: "The value of theories should not be overestimated, even if they seem very attractive and bring intellectual satisfaction. So often it is only a case of old wine in new skins!"[333]

Extra cases can easily be identified in the history of the hydrides of boron. One example is the evolution of the one-electron bond concept, from the first conceptions of the electron as the source of the chemical bond by Thomson to Pauling's one-electron bond. Another one is the relation between Dilthey and Core's bridge model and how both are related to the bridge structure for diborane accepted presently. Since the beginning of the latter's emergence, they were revived and identified as its phylogenetic parents, for example by Schlesinger in his 1942 review article. But this is not straightforward, since Dilthey's suggestion, for example, had no electronic concerns. This argument was used by Longuet-Higgins in his essay "The Hydrides of Boron", in 1943. Besides stressing an interesting historiographic question to be also tackled through the hydrides of boron, the point is that their past can not be ignored because it is directly related to its present concepts and theories. There was no refoundation, no break, no gap between the past and the present, but rather a long and laborious evolution.

Ignoring the history of the hydrides of boron can only lead to a mistaken perception of their own identity. Such is the case with the presently prevailing idea that up until their use outside the academic environment, they had been laboratory curiosities. The present work demonstrates that during their laboratory phase they were rather seen as a pressing theoretical problem and this perception entirely guided all investigations. All chemical data collected on the hydrides of boron and their derivatives, with the exception of Stock's very first research, were driven by the structural problem. This scenario only began to change with the investigations on the metallo borohydrides and the action of diborane upon some organic compounds in the late thirties. Even those were partially motivated by the structural problem.

Another interesting historiographic issue raised by the hydrides of boron is the dramatic role played by war in their mutation into industrial and commercial products. It was not

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[333] E. Wiberg, "Alfred Stock and the renaissance of inorganic chemistry", *Pure & Appl. Chem.*, 49 (1977). On 697.

only a matter of bigger investment, better material conditions or larger research groups. As Brown explicitly admitted, war changed the objectives of their investigation. Up until then, they had purely academic aims and even their results on the possible applications of their work to organic chemistry did not commit them to seek ways to make applications possible. It was the need of the Signal Corps for field generation of hydrogen that led them to the industrial process for the production of sodium borohydride.

This discussion is intertwined with the everlasting debate on the funding of fundamental investigation. The boron hydrides may be presented as the perfect example of one entire field of knowledge that resulted from purely academic research funded for many years with no expectable or at least foreseeable practical application. And in fact, Brown did so on several occasions, expressing his concern with the increasing dependence of research from private or military funding. However, the present work also shows that it was due to external demand that the departure from academic research occurred. Brown was very clear on this issue too. Together with Schlesinger, they would not have taken by themselves the hydrides of boron to the outside world. Thus, the hydrides of boron do not allow one to take ranks with one of the parties in this debate. Without public funding or at least non profitable funding, Stock and Schlesinger's work would have not been possible. On the other hand, it would not have stepped outside the university threshold if it were not for the war. In the fact, the Atomic Energy Commission did not ask Schlesinger to specifically use his research on the boron hydrides. They simply outlined the technical problems they had with UF_8 and asked him for a substitute. It was a coincidence that Schlesinger and Brown were already in the possession of the metallo borohydrides and decided to try their use. So, it seems undisputable that non-profitable funding was absolutely essential to support so many years of purely academic investigation. However, the transmission of society's needs, and specifically war related problems, to the academic world, was also an essential step in this story. Schlesinger's willingness to help his country was the last but not the least of the needed ingredients. Everybody profited from this collaboration.

A key chapter in the history of the hydrides of boron is the relation between the work by those engaged in analytical chemistry and the results obtained by those involved in the new physical methods for structure determination. The present work shows that ultraviolet and infra-red absorption spectra, as well as X-ray and electron diffraction analyses, played an important role both to Stock and Schlesinger and Burg. In fact, the difficulty in preparing and handling the hydrides of boron led to some momentary overlap between the two communities. There were several examples of an active cooperation that resulted in joint papers: Mark and Pohland, Stock and Wierl, Anderson and Burg. In some other cases, Stock or Schlesinger supplied the necessary samples to Herzberg, Ramaswamy, and Bauer. There were no *a priori* disciplinary clashes between the two communities. Stock's enthusiasm with the new physical methods was evident. Mark and Pohland's work played an important role in his understanding of the hydrides in 1926. He subsequently adopted a more cautious attitude due to conflicting ultraviolet absorption spectra and chemical data. But he continued to work to collect physical data on the hydrides and their derivatives. He and Wierl submitted $B_3N_3H_6$ to electron diffraction analysis, made parachor measurements on diborane and X-ray diffraction analysis of the alkali addition compounds of diborane.

Mark and Pohland's work was even more important to those supporting the ethane-like structure, like Schlesinger, Burg and Bauer. Until Bauer's work on diborane in 1937, it offered the only physical data supporting the ethane-like structure. In fact, it is surprising how important it became, since no direct extrapolations to gaseous diborane could be drawn from the crystallized sample of diborane that Mark and Pohland analysed. This was explicitly acknowledged in general terms by Pauling, as discussed in chapter 5. The obvious conclusion is that, until Bauer's appropriation of all the physical data invoked by Wiberg in 1936, Mark and Pohland's work assumed a relevance to Schlesinger, Burg and Bauer that can only be justified by a subjective *a priori* adoption of the ethane-like structure. Thus, Mark and Pohland's work was instrumentalized rather than instrumental. Despite being an inverted relation, there was no conflict at this point because Schlesinger and Burg did not have access to Hausser's unpublished data on the ultraviolet absorption spectra that had been invoked by Stock. The conflict came only later, with Wiberg's 1936 paper, but thanks to Bauer's work it was rapidly put under control. However, this was done at the expense of an irreducible conflict between Bauer's work and Schlesinger and Burg's evidence on the special nature of two of the hydrogen atoms of diborane. A confusing situation ensued which resulted in an intellectual deadlock that forced everybody to hold to their disciplinary commitments. Later on, it also forced Schlesinger and Burg to abandon the structural debate and leave it to those engaged in its physical dimension.

Nevertheless, this forced disciplinary division was enhanced by much more relevant and evident disciplinary gap between the analytical approach of Schlesinger and Burg and the theoretical rationalization attempted by Pauling, Mulliken and Bauer. It was not a disciplinary conflict but rather a insurmountable gap. Schlesinger and Burg seem to have been always uneasy towards Pauling and Mulliken's theoretical accounts of diborane. They never really endorsed them, they rather focused on the ethane-like structure itself, but never entered into the theoretical debate on the electronic configuration. However, after Bauer's use of Pauling's resonance in 1937 to achieve a homogeneous electronic structure for diborane, the theoretical dimension directly collided with their work on the methyl derivatives of diborane and also with Stock's work on the alkali addition compounds of this compound. Most probably, this is the reason behind Burg's involvement in Raman spectra analysis of diborane. Inconclusive results forced them to a disciplinary retreat and to a subsequent dismissal in 1942 of their previous interpretation of their work on the methyl derivatives of diborane. The sad irony is that it was this disciplinary barrier between Schlesinger and theoretical chemistry that really prevented him and his team to solve the puzzle. That is, Schlesinger was led to believe that chemical evidence alone did not suffice. The historical truth is that he held the solution in his hands but his disciplinary commitments forbade him to go for it, preferring instead to abandon the debate.

Indeed, Brown was the one that got the solution and the story, as told by him, happened this way:

> I had a classmate in Chicago named Norman Davidson. He had won a Rhodes Scholarship in 1937 or 1938, and had gone to Oxford. When the war broke out, they sent all these Rhodes scholars back to the United States, and he came back to the University of Chicago. He had started to work on aluminum alkyls at Oxford, and he wanted to continue in this area. By that time I had become Schlesinger's research assistant. Schlesinger was too busy to be involved into a new field, so he turned him over to me. We began working together. When we examined the molecular weight of gaseous trimethylaluminum, it was a dimer. We examined aluminum bromide; it was a dimer. We took dimethylaluminum chloride; it was a dimer. And so on. So I came to the conclusion that both methyl groups and halogen atoms can bridge, forming dimers. Perhaps hydrogen could also bridge, accounting for the dimeric structure of B_2H_6.
>
> I went to Schlesinger with this theory, and he said: "This is not our field. We should be very careful. I will correspond with Mulliken and with Pauling, tell them your ideas and see what they think of it". I've never seen the correspondence, but he told

> me the answer came back and they said the one-electron configuration of Pauling was valid, even for these compounds.
>
> Well, I couldn’t fight that. After all, I was his research assistant.[334]

Schlesinger did write to Pauling and the answer was negative indeed:

Schlesinger to Pauling, January 3, 1941:

> May I now turn to a personal problem--that is, a problem connected with my own research? As result of our work on the metallo borohydrides I definitely feel that a structure for diborane quite different from those generally proposed, would aid in correlating many of the observations we have made. I am at present writing a review of this field, and would like to include a statement to the effect that this other structure merits serious consideration. Curiously enough I have just now received a reprint of a Russian article on hydrides of boron. Unfortunately I have not had this translated as yet, but in spite of the fact that I cannot even read the Russian alphabet, I gather from some of the formulae in the article that the author has come to a conclusion very similar to mine.
>
> The structure I have in mind is a bridge structure, in which the two boron atoms are joined to each other through an unusual type of hydrogen bond, perhaps best represented by the following formula: [bridge model formula]
>
> As I picture it, the two BH_3 molecules are bound together by a resonance involving the two boron and the bonding hydrogen atoms. Such preliminary calculations as I have been able to make indicate that the boron-boron distance that might result from such a picture is not in disagreement with the results of the electron diffraction measurements that have come out of your laboratory. Furthermore, the fact that there is apparently an unusual hindrance to free rotation, as recently found by Stitt, seems to fit in with this suggestion quite satisfactorily. I must confess, however, that I do not feel myself sufficiently firmly grounded in the concepts of resonance to be sure that the suggestion is in accordance with the best ideas on this subject. I would greatly appreciate a comment from you on this point.

Pauling to Schlesinger, January 7, 1941:

> I do not feel very friendly toward the structure which you mention in your letter for the diborane molecule. So long as the suggested structure remains vague and

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[334] Herbert C. Brown, interview by James J. Bohning at Purdue University, 11 November 1994 (Philadelphia: Chemical Heritage Foundation, Oral History Transcript # 0117). On 17.

> indefinite, it is not easy to say that it is eliminated by electron diffraction data or other data. However the force constant for the B-B vibration is I think much stronger than would be expected for a structure of this type, in which there is no direct B-B bond. [335]

This story is directly linked with one of the most important lessons one can derive from the history of the hydrides of boron, which is related to the relation between diborane and theoretical chemistry. In terms of results, theoretical chemistry's attempts to appropriate diborane were undeniable clamorous failures. Pauling and Mulliken's accounts of diborane served as serious obstacles to achieve the right structure because they were used as a powerful legitimation of the ethane-like structure. On what concerns diborane, both Pauling's resonance theory and Mulliken's molecular orbital theory accounts offered teleological constructions based on an *a priori* adoption of the ethane-like structure. However, one must make a distinction between Mulliken's and Pauling's accounts. Mulliken assumed that his work on diborane was built on his previous work on the ethane molecule and made a prediction on the magnetic behaviour of diborane that constituted an objective though not a definitive test of his theory. Worst than this was Pauling's reasoning which was based on the completely fallacious assumption that diborane should pass his stability criterion. This case study may have profound consequences for the debate over the nature of quantum chemistry. Namely, the "diborane affair" may lead one to ask if the failure of theoretical chemistry to deal with such a "simple" molecule as diborane does not show that it just offered a construction meant to give calculations in agreement with experimental observations rather than be willing to make realist claims about its objects of study. Put in another way: does quantum chemistry really relates, even if only partially, to its objects or is it just some kind of incredibly sophisticated calculating device? Can quantum chemistry be some kind of a modern version of Ptolemy's circles, a theory to "save the phenomena"? Those who advocate that this is precisely what a theory of atomic or molecular systems should amount to, should look at diborane's case and be prepared to abdicate from predictive power and a unified theory of matter.

Of course, diborane alone won't solve the question, but its history may contribute to the debate in a very fruitful way.

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[335] Courtesy Ava Helen and Linus Pauling Papers, Special Collections & Archives Research Center, Oregon State University Libraries. Folder 357.7.

Diborane's history also has important bearings on the debate over the reducibility of chemistry to physics. It clearly falsifies it. Quantum physics was not able to account for diborane's structure. Lipscomb's three centres–two electrons theory was an a posteriori construction in the sense that it was developed after the ethane-like structure was definitely eliminated by Price's infra-red analysis in 1948.

The above considerations, as the culmination of the present work, find their historiographic basis in a critical assessment of the past, in which theories, opinions and ideas are evaluated for their empirical foundations, logical consistency and inter-relations, within their proper historical contexts. Thus, it is in complete agreement with the historiographic vision expressed a few years ago by Jed Buchwald and Allan Franklin.[336] One must stress, however, that the historiographic approach adopted here was not the result of an *a priori* affiliation but rather a natural consequence of the historical interpretative process and the available documentary sources. It became rapidly obvious that the intelligibility of the historical process under investigation depended on such a critical assessment. The unavailability of documentation on the social or cultural factors involved imposed an investigation focused on the scientific debate itself. Proving the richness of such a historiographic approach is one further claim of this work. Of course, this claim must be balanced by the fact that the historical process analysed occurred within the last 100 hundred years. The documents accessed were entirely intelligible and no significant differences in scientific culture were found. In fact, the scientific and intellectual rigour of all participants, with the exceptions already addressed, is one of the most impressive features in this story. This gives diborane's history a significant educational value.

The claim for the intellectual and scientific rigour of all key scientists directly involved in the debate may seem somewhat displaced, since, in addition to their conflicting and irreconcilable positions, all of them were wrong in their structural commitment.

The history of diborane constitutes a very interesting case, in which the emergence of the correct structure (in the sense that it is the presently accepted one) allowed to understand the different positions as partially correct accounts of the same reality rendered irreconcilable by different commitments to the analogy between the boron and carbon chemistries.

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[336] J. Buchwald, A. Franklin, "Introduction: Beyond Disunity and Historicism", in Buchwald and Franklin (eds.), *Wrong for the Right Reasons* (New York: Springer, 2005), pp. 1 – 17.

This wrong analogy was the only reason that led Stock to revolutionize the field. His initial failure to support his expectations of such a simple correlation sustained and guided Stock's persistence. The same belief played a decisive role in Schlesinger and Burg's decision to enter the field. And it sustained their resilience and persistence. As their belief never had true solid scientific foundations, it cannot be reduced to the sort of critical analysis adopted in this work. Its proper analysis would require a very different kind of historical documents. Even so, one can go as far as proving how omnipresent and instrumental this analogy was from the very beginning of boron chemistry. It was the sole responsible for its emergence. Its power is well evident in the fact that all knowledge and data used to build the route to the industrialization and commercialization of the hydrides of boron was already available before the presently accepted structure emerged in 1940. Until then, the discussion was restricted to the discussion between an ethane-like and an ethylene-like structure. This debate shaped this field evolution. All other options devised by so many authors never really had any influence among those actively involved in the analytical work on the hydrides of boron. Stock never gave any credit whatsoever to such proposals and by the time Schlesinger and Burg initiated their work the debate was already restricted to existing evidence. Although a proper analysis of such belief or shall I call it metaphysical principle cannot be attempted here, I cannot end without identifying and calling attention to the pervading role of analogical reasoning in analytical and theoretical chemistry.

Thus, the present work proves how important and instrumental metaphysical beliefs or principles can become to scientific communities. The lack self awareness of their implicit role may act as a constraint preventing faster research developments. The awareness of such constraining factor in diborane's puzzling history should be taken into due account by science policy makers. Scientists do not have the appropriate intellectual training or technical background necessary to such exercise in reflexivity. Furthermore, most of them do not even have such a vocation and even fewer would be willing to learn from it. Diborane's puzzling history proves that historic analysis can become instrumental to modern research if viewed within interdisciplinary cooperation. Of course, one can deny such pretension. And state that diborane's case was just an isolated case, as odd as diborane. Based on the scientific status of all of those involved in the search for diborane's structure and in the incredible quality of their work, I venture that the proper answer to such an argument is captured by John Donne’s famous words:

Therefore, send not to know
For whom the bell tolls,
It tolls for thee.

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