

**STELLINGEN**  
**THESES**

*Everard Peter van Emmerik*

1. De beslissing van Van Laar's voogden om Van Laar in 1876 naar het Koninklijk Instituut voor de Marine te sturen, heeft bij hem geleid tot een achterstand, die zijn levensloop sterk heeft beïnvloed.  
(Dit proefschrift)

The decision by Van Laar's guardians to send Van Laar to the Royal Naval Institute in 1876, left him at a disadvantage academically which had a considerable influence on the course of his life.

(This dissertation)

2. Als Van der Waals leiding had gegeven aan Van Laar dan zou dat in het belang zijn geweest van de thermodynamica en de faculteit der wis- en natuurkunde van de Universiteit van Amsterdam.  
(Dit proefschrift)

Had Van der Waals supervised Van Laar, this would have been to the advantage of thermodynamics and the Faculty of Mathematics and Physics at the University of Amsterdam.

(This dissertation)

3. Van Laar is in de periode 1907-1908 ten prooi gevallen aan een negatief oordeel door verschil van mening tussen fysici en chemici over de positie van de 'chemische thermodynamica' en 'mathematische chemie' aan de faculteit der wis- en natuurkunde.  
(Dit proefschrift)

In the period 1907-1908 Van Laar became a victim of negative opinions due to a difference of opinion between physicists and chemists about the position of 'chemical thermodynamics' and 'mathematical chemistry' at the Faculty of Mathematics and Physics.

(This dissertation)

4. De uitspraak van Lorentz dat het werk van Van Laar, hoewel gedeeltelijk, van blijvende waarde is, is juist gebleken.  
(Brief van Schreinemaker aan Waller van 10 mei 1928, ARAG, 2.14.20, O.K.& W. No.345; dit proefschrift)

Lorentz's statement that Van Laar's work is in part of lasting value, proved to be correct. (Schreinemaker's letter to Waller of 10 May 1928, ARAG, 2.14.20, O.K.& W. No.345; this dissertation)

5. De betekenis van Van Laar als werkelijke vernieuwer, is gering; wel is het aan hem te danken dat in het begin van deze eeuw de thermodynamica van Gibbs snel is doorgedrongen bij de Nederlandse scheikundigen.  
(Dit proefschrift)

Van Laar's significance as a true innovator is slight; it is however to his merit that Gibbs' thermodynamics were introduced to Dutch chemists relatively quickly.

(This dissertation)

6. Een zeker superioriteitsgevoel van de school van Van der Waals ten opzichte van het buitenland, in het bijzonder Duitsland, moet onderdeel van de Amsterdamse cultuur zijn geweest rond de eeuwisseling.  
(Dit proefschrift)

Around the turn of the century a certain feeling of superiority in Van der Waals' school with regard to foreign countries, especially Germany, must have been part of the culture in Amsterdam.

(This dissertation)

7. Het volstrekt afwijzen door Kohnstamm en Van Laar van het Warmtetheorema van Nernst, vindt zijn oorsprong in het botsen van twee thermodynamische tradities: die van Gibbs en die van Helmholtz.  
(Dit proefschrift)

Kohnstamm's and Van Laar's total rejection of Nernst's heat theorem at the start of this century finds its origins in the clash of opinions of two thermodynamic traditions, the tradition of Gibbs on the one hand and of Helmholtz on the other.

(This dissertation)

8. Na zijn eerste afwijzing in 1906, maakt Van Laar geen positieve ontwikkeling meer door ten aanzien van het Warmtetheorema van Nernst.  
(Dit proefschrift)

After his first rejection in 1906, Van Laar did not make any positive scientific developments concerning Nernst's heat theorem.

(This dissertation)

9. Ter bevordering van het inzicht in het (ir)reversibel proces in het elementaire thermodynamica onderwijs is het gewenst de entropieproductie bij reële processen in het curriculum op te nemen.

To enhance the understanding of the (ir)reversible process in the education of elementary thermodynamics it is advisable to include the entropy production of the natural process in the curriculum.

10. Het ware gewenst dat archieven die beheerd worden door gesubsidieerde instellingen vallen onder de archiefwet van 1962.

It be desirable that archives which are managed by subsidised establishments be subject to the Dutch law on archives of 1962.

11. Een relatie krijgt de beste kans als beide partners in het eerste contact harmonisch en gelukkig zijn.  
(de SwA., van E., B.-de B.)

A relationship will have a good chance to succeed if both persons feel happy at the moment they meet each other for the first time.

(de SwA., van E., B.-de B.)

12. Het in 1983 verwijderen van de staketsels met het woord 'CINEAC' van J. Duiker's (1890-1935) Cineacgebouw (1934) in de Reguliersbreestraat te Amsterdam is een grove verminking; restauratie en herstel zijn dringend geboden.

The removal, in 1983, of the stockades with the word 'CINEAC' of J. Duiker's (1890-1935) Cineacbuilding (1934) in the Reguliersbreestraat in Amsterdam is a flagrant mutilation; restoration and repair are required urgently.

13. Dat Wolfgang Amadeus Mozart (1756-1791) een groter componist is dan zijn tijdgenoot Karl Ditters von Dittersdorf (1739-1799) is objectief onbewijsbaar, maar wel waar.

That Wolfgang Amadeus Mozart (1756-1791) was a greater composer than his contemporary Karl Ditters von Dittersdorf (1739-1799) cannot be proved objectively, but is nevertheless true.

14. De romantische woorden van de Weense dichter F. Grillparzer (1791-1872): 'Ein menschenleben, ach, es ist so wenig. Ein Menschenschicksal, ach es ist so viel'; weerspiegelen het leven en werk van Van Laar volledig. (J. Romein, 'De biografie', Amsterdam: Ploegsma (1946) 9; dit proefschrift)

The romantic words of the Viennese poet F. Grillparzer (1791- 1872): 'Ein Menchenleben, ach, es ist so wenig. Ein Menschenschicksal, ach es ist so viel' fully reflect Van Laar's life and work.

(J. Romein, 'De biografie', Amsterdam: Ploegsma (1946) 9; this dissertation)

**J.J. VAN LAAR (1860-1938)**

**A**

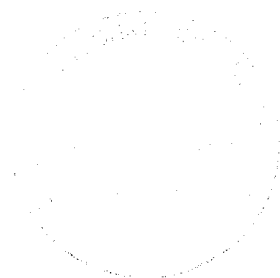
**MATHEMATICAL CHEMIST**

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus, Prof.dr.s.P.A. Schenck, in het openbaar te verdedigen ten overstaan van een commissie aangewezen door het College van Dekanen op donderdag 21 maart 1991 te 14.00 uur,

door

Everard Peter van Emmerik  
scheikundige  
geboren te Amsterdam.



Dit proefschrift is  
goedgekeurd door de promotor  
Prof.Dr.Ir.J. de Swaan Arons

In grateful memory of my friendship with  
Drs Maarten A. Kostelijk (1918-1983), his wife Kiki and their son Herman;  
in remembrance of my courageous brother Johan Adriaan (1943-1989).





# VOORWOORD

Het verschijnen van dit proefschrift biedt mij de welkome gelegenheid mijn dankbaarheid uit te spreken jegens allen die bereid zijn geweest mij terzijde te staan met hun soms zeer uiteenlopende kennis en kundigheden. In de eerste plaats geldt dit U, hooggeleerde De Swaan Arons, hooggeschatte promotor. Ik ben er trots op bij U te mogen promoveren. Reeds vanaf het eerste contact bleek onze verstandhouding optimaal; dit is niet alleen met U zo gebleven, doch ook met alle leden van Uw sectie. Voor Uw vele suggesties en stimulerende begeleiding wil ik U oprecht zeer hartelijk bedanken.

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Zeergeleerde Oonk, steeds als wij gesproken hebben over Van Laar's persoon en werk bleek U enthousiast en was Uw hulp daadwerkelijk. Hiervoor en voor de collegiale sfeer ben ik U zeer dankbaar.

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Voorts wil ik een ieder die mij behulpzaam is geweest in de Sectie Toegepaste Thermodynamica en Fasenleer te Delft, in mijn werk te Amsterdam en in de vele bibliotheken en archieven in binnen- en buitenland mijn zeer grote erkentelijkheid betuigen.





*Van Laar in his forties.<sup>1</sup>*



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## INTRODUCTION

*'For the workers in the vineyard of science, despondency and misfortune often await, and a single encouraging word by you often works miracles.'*

In the fields of chemical thermodynamics and phase equilibria, the name of the mathematical chemist J.J. van Laar (1860-1938) is closely connected with the equation for the excess Gibbs' energy, which was named after him, and to the theory of binary mixtures developed by J.D. van der Waals (1837-1923). Van Laar is regarded as having been Van der Waals' assistant and in modern literature on the subject his name is inextricably linked with Van der Waals. In older publications, Van Laar's work is also mentioned in connection with H.W. Bakhuis Roozeboom (1854-1907) and is sometimes associated as well with J.H. van 't Hoff (1852-1911).

Van Laar's position among these three great Dutch scientists, who have been considered leading figures in this field of study since the end of the last century, was the first incentive for further research into his person, his work and his life. The study shows that Van Laar was a great admirer of Van der Waals and in his own book 'Die thermodynamik in der Chemie' (1893) he expands the lectures given by Van der Waals. In 1900 Van Laar even wrote a biography on Van der Waals and followed closely in the tracks of his great example, although this does not alter the fact that, certainly after 1900, Van der Waals regarded Van Laar as an unwanted person at the Faculty of Mathematics and Physics at the University of Amsterdam, and that conflicts subsequently occurred. After a close study of the available material it has to be admitted that Van Laar was a self-willed man who was strict in his convictions. However, the same can also be said about Van der Waals. Unfortunately, it was often Van der Waals who started the trouble and, in a sense, stood alone. It is certain that Bakhuis Roozeboom admired Van Laar's expert knowledge and that

there was a friendship between these scientists. The same appreciation was also shown, although curtly, by Van 't Hoff.<sup>2</sup>

Van Laar wrote many letters and an important collection of them is undoubtedly the one found in the General State Archives in The Hague, taken from Lorentz's archives. It consists of 72 letters and postcards and also contains five rough drafts of letters to Van Laar in Lorentz's handwriting. This famous physicist from Leiden, H.A. Lorentz (1853-1928), was very important in Van Laar's life and contacts between Van Laar and the remarkable scientist continued from 1893 until 1928. They met in Leiden and later in Haarlem and Lorentz was always a father figure to Van Laar. He asked Lorentz for advice, argued with him and opened his heart to him. Lorentz's guidance made these contacts particularly productive.<sup>3</sup> Lorentz celebrated the 25th anniversary of his receiving his Ph.D. on 11 December 1900 and everyone who congratulated him sent a photograph. When Van Laar received his copy, he expressed great kindness in what was possibly his most beautiful letter.

Utrecht, 3 April, 1901.

Dear Professor,

May I thank you very much for sending me your portrait, with its great likeness, and the handwritten caption. It was a truly pleasant surprise.

Looking at the picture will not only bring one of the most excellent scientists to mind, but also an excellent man, who is always willing to spend time to support and help others in their scientific endeavours, and is always willing to encourage others, both in word written and spoken.

For the workers in the vineyard of science, despondency and misfortune often await, and a single encouraging word by you often works miracles. I myself have often benefitted from them. Again, thanking you deeply, greeting you, I remain, yours faithfully,

Yours obd.

J.J. van Laar.<sup>4</sup>

Neither Van Laar's working life, nor his private life were easy. In a sense, he often stood at the margins of scientific life and of society in general. He occupied a very special place in the scientific world. He worked hard and put everything aside for science but his interpersonal skills were weak and he left a trail of conflicts. All his life he was opposed to W. Nernst (1864-1941) and his theorem of heat. Study of this opposition shows that he was not alone in this respect and his resistance can be interpreted as a part of the scientific culture at the Faculty in Amsterdam, originating in the differences in the application of the first and second laws of thermodynamics. Van der Waals in Amsterdam based his studies on Gibbs' work and Nernst in Berlin used Helmholtz's function as a foundation for his theories.

To get a better impression of Van Laar's life, most of the places he lived in have been revisited in 1987. In the Netherlands these include Middelburg, Utrecht, Hilversum, Baarn, Amsterdam and Haarlem and in Switzerland, La Tour de Peilz and Tavel-sur-Clarens. His house 'Villa Les Arolles' in La Tour de Peilz and the apartment buildings 'Maison les Brayères' and 'Maison les Tilleuls' in Tavel-sur-Clarens still exist (in 'Maison les Tilleuls', Igor Stravinsky (1882-1971) composed the 'Sacre du Printemps' in 1911/12).<sup>5</sup> 'Hôtel de la Gare' in Clarens appears to contain some of the original furniture and the paddle steamers on Lake Geneva are, albeit modernized as far as the engines are concerned, still the same as the ones used during Van Laar's time. The places where Van Laar worked in the periods from 1895-1897 and 1898-1912, the Rijks Hoogere Burgerschool at the Kruisstraat 1 in Utrecht, and the Scheikundig Laboratorium at the Nieuwe Prinsengracht 126 in Amsterdam (which was demolished in 1988) were also visited.<sup>6</sup> The Rijks Hoogere Burgerschool in Middelburg was destroyed during the early days of World War II.

The chapter concerned with Van Laar's work discusses his work chronologically and assesses its significance today. The academic traditions and the scientific policy and cultural background of the Faculty of Natural Sciences of the University of Amsterdam were illustrated when Nernst published his heat theorem in 1906 as the 'Neue Hypothese'. The moment of publication more or less coincided with the filling of the vacancies left by Bakhuis Roozeboom in 1907 and by Van der Waals in 1908, as described in the chapter about Van Laar's life in the Netherlands. It is assumed that the scientific reception of the theorem in the Netherlands reflected the aforementioned tradition and scientific policy, and by mapping out the reception of the heat theorem, it appears that such a culture must have existed. All those opposing the theorem appear to have

worked as physicists or chemists at the Faculty in Amsterdam. Ph.A. Kohnstamm (1875-1951), Van der Waals' successor as professor of thermodynamics, led the way and Van Laar's opposition to the theorem originally appears not to have been only a private matter. The fact that Van Laar was lacking in social skills is of considerable importance in this affair as is explained in the retrospect on his personality. Although this study certainly highlights Van Laar's personality and his place in science, it is like every dissertation about life and work, a weak reflection of the reality of his time.

The order of the chapters has been chosen in such a way that the description begins in the year of Van Laar's birth, 1860, and ends in 1938, the year of his death.

To summarize, answers have been sought to the following questions:

1. Who was Van Laar and what were his scientific achievements?
2. Did his work have a lasting significance?
3. Why did he become a lecturer of mathematics to chemistry and biology students in 1908 and not remain within his subject of mathematical chemistry?
4. What led to his departure for Switzerland in 1911 and his resignation from his position as lecturer in 1912?
5. What policy was pursued by the Faculty with regard to Van Laar?
6. Can this policy be traced back to a scientific standpoint?
7. Did Van Laar learn from his experiences with regard to the heat theorem?

Where necessary, letters or passages from letters are quoted and for clarity's sake, abbreviations are written out fully and the punctuation has been completed.

The subject of this study is written within the scope of the author's principal doctoral subject, chemical technology, and the subsidiary subjects of industrial economy, labour psychology and library science. Experience gained from his present position at the Algemeen Pedagogisch Studiecentrum in Amsterdam has been invaluable.

The following abbreviations have been used in the notes after each chapter:

- AC      Archives College van Curatoren (Board of Governors)  
          University of Amsterdam in GAA
- AF      Archives Faculty of Natural Sciences of the University of  
          Amsterdam in GAA

AHC	Archives Historical Commission 'Koninklijke Nederlandse Chemische Vereniging'
AL	Archives H.A. Lorentz in ARAG
ARAG	General State Archives The Hague
ASAO	Archives of the Secretary of the Departement of Education in GAA
AWL	Akademie der Wissenschaften Leipzig
AWNG	Archive Wolters-Noordhoff Groningen
BML	Boerhaave Museum Leiden
DMM	Deutsches Museum München
GAA	Town Archives Amsterdam
GAG	Town Archives The Hague
GAH	Town Archives Haarlem
GAM	Town Archives Middelburg
GAU	Town Archives Utrecht
KB	Koninklijke Bibliotheek The Hague
LMG	Letterkundig Museum The Hague
MMH	Museum Maritieme Historie The Hague
MOKW	Archives of the Ministry of Education, Culture and Sciences in ARAG
RAG	State Archives Groningen
RAH	State Archives Haarlem
UBA	University Library Amsterdam
UBL	University Library Leiden
ULH	University Library Harvard (USA)
UMA	University Museum Amsterdam
UMU	University Museum Utrecht

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1. Photograph (BML).
2. Foreword by J.H. van 't Hoff in: J.J. van Laar, *Die Thermodynamik in der Chemie*, Leipzig: Barth (1893).
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5. L. Andriessen and E. Schönberger, *Het apollinisch uurwerk*. Amsterdam: De Bezige Bij (1983) 189.
6. E.P. van Emmerik, *Het Van 't Hoff laboratorium*, *Laboratorium Praktijk* (1987) 318-320.



## LIFE IN THE NETHERLANDS

*'I would wish that, they, too had been lacking something, so that I could congratulate them on obtaining it!'*

### 1. Introduction

This chapter gives an outline of Van Laar's life until 1914, the year in which he received his honorary degree. It focuses on his time at the University of Amsterdam from 1898 until 1912, and on his conflict with Van der Waals during this period.

### 2. Youth, naval cadet and teacher

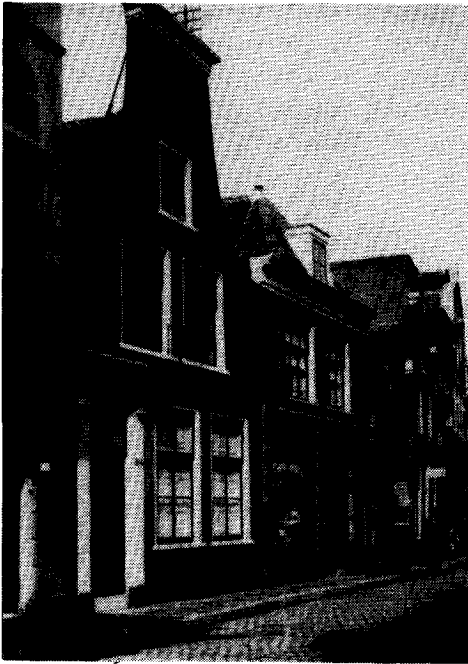
Johannes Jacobus van Laar was born in The Hague on 11 July 1860, the son of Johannes Jacobus van Laar (1818-1873), a veterinary surgeon in the Royal Armed Forces, and Johanna Rost van Tonningen (1829-1862), an educated woman with a wide knowledge of languages and gifted in mathematics.<sup>1,2,3</sup>

Nearly a year after the death of his mother on 20 May 1862, he moved to Haarlem, with his father and younger sister Emilie Carolina.<sup>4</sup> After having had some private tuition from his father and having finished elementary school, he attended the Hoogere Burgerschool (H.B.S., a former grammar school for the 12-18 year age group) at the Prinsenhof.<sup>5,6</sup> At this school he became acquainted with the later well-known writer and psychiatrist Frederik van Eeden (1860-1932).<sup>7</sup> It was his physics teacher W.M. Logeman (1821-1894), his chemistry teacher A.E. van Roijen (1838-1899) and his mathematics teacher E. van der Ven (1833-1909) who evoked in young Van Laar an enthusiasm for the exact sciences.<sup>8,9</sup> He must have

been an active pupil:

'Never since that time has there been such romping and hiking and botinazing in the delightful dunes near Haarlem (still without barbed wire!)'.<sup>10</sup>

By the age of 14, he knew the three volumes of Koppeschaar, a H.B.S. text-book on chemistry, by heart.<sup>11</sup> After the death of his father on 15 May 1873, his uncle N.A. Rost van Tonningen (1819-1878), a senior civil servant and ex-Governor of the Dutch Caribbean Island of St. Eustatius, was legally appointed as his guardian. The co-guardian was C.W. Vinkhuyzen (1813-1893), the personal physician to King Willem III from 1868 to 1890.<sup>12</sup>



*Van Laar's house in Haarlem.*<sup>13</sup>

His guardians decided that he was to become a naval officer and after the fourth form of the Hoogere Burgerschool they sent him to the Koninklijk Instituut voor de Marine (Royal Naval Institute) at Willemsoord in 1876. Rost van Tonningen petitioned the Naval Minister for that purpose and Van Laar was accepted.<sup>14</sup> He was promoted to naval cadet and sub-lieutenant on 1 September 1876, 1877 and 1879 respectively.<sup>15</sup> From 11 November 1879 to 1 August 1880 he was a crew member on H.M.S. 'Zilveren Kruis', a propeller-driven steamship with sailing facilities



commanded by Lieutenant-Commander W.H.F. Cramer (1833-1904).<sup>16</sup> From 10 December 1879 to 24 June 1880 he made a trip to Curacao and from 1 August to 6 November 1880 he served on H.M.S. 'Marnix', another propeller-driven steamship with sailing capabilities.<sup>17,18</sup> He took part in an inspection trip to Edinburgh and Copenhagen under the command of Lieutenant-Commander Jhr. J.A. Roëll (1838-1924).<sup>19</sup> After a short period of service on the guard ship 'Willemsoord', he was assigned to H.M.S. 'Koningin Emma der Nederlanden', also a propeller-driven steamship with sailing facilities, on 1 December 1880. The 'Emma' was iron-built and covered with wood. The double-bladed propeller had a diameter of 4.88 m and had a sailarea totalling 1585 m<sup>2</sup>. The maximum speed when engine propelled was 14.1 miles per hour. Its length was 91.85 m, its width was 12.50 m and it drew 6.10 m.<sup>20</sup> It was commissioned on 1 December 1880 and had a complement of 276 men. On 15 January it sailed on its maiden voyage to Batavia, via Rio de Janeiro.<sup>21</sup> Just before the 'Emma' was due to sail, Van Laar visited Professor J.H. van 't Hoff from Amsterdam and asked him what subjects he should study in order to be able to take the kandidaatsexamen (comparable to a B.Sc. examination).

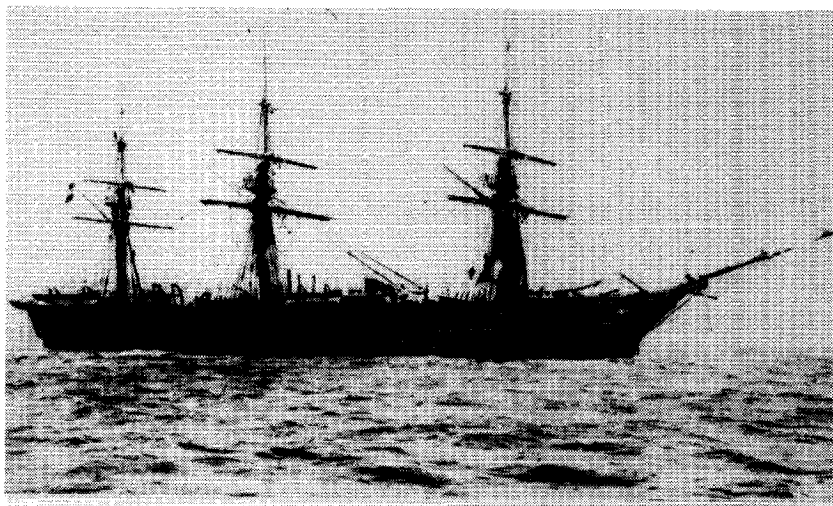
'It was in 1880, and I was about to sail on the 'Emma' round the Cape to the Dutch East Indies. I did not like it in the navy. It was an office forced on me by my guardians and I wanted to quit.

I wanted to study chemistry and mathematical physics under Van 't Hoff and Van der Waals, about whom I had heard much even as early as that. I remember, as if it had happened yesterday, that I hesitatingly rang the bell of an upstairs flat, difficult to find, on the Binnen-Amstel at the Blauwbrug in the vicinity of the Oude Mannen- en Vrouwenhuis (Old Men and Women's Home). It was evening and my heart was pounding terribly. After waiting a few moments, the door opened and presently I was standing in a small room facing the great man of the asymmetric carbon atom. I gave a short account of my adventures and told him that I wanted to leave the navy. I asked him what subjects I would have to study to sit my kandidaatsexamen if I quit in the Dutch East Indies and returned to Holland, and whether he would advise me to do so. Well, he did not advise me not to, for he saw clearly enough that I was very earnest about it and that I knew more about it than others of my profession. I still hear his words, spoken with sudden emphasis and slowly metered, his face assuming a particularly solemn professorial expression: 'By then you must be acquainted with the contents of Wüllner, Lehrbuch der Experimentalphysik, that is to say know everything there is in it, and further to have studied

Richter, Anorganische Chemie and Richter, Organische Chemie...'. It sounded like a sentence, as if my life depended on the fulfilment of that requirement. I left, completely impressed by the overwhelming greatness of the demi-god I had stood face-to-face with for a few minutes, and for days I heard the words being scanned in my ear: Wüllner, Lehrbuch der Experimentalphysik, Richter: Anorganische Chemie and Richter, Organische Chemie...'.<sup>22</sup>

On 2 March 1881, at six o'clock in the afternoon, the 'Emma' anchored off Rio de Janeiro. Although the trip had gone well, signs of scurvy were found among the crew.<sup>23</sup> On 12 March 1881 the voyage continued and the 'Emma' proved to be a well balanced ship. On the morning of 19 May, at 9 o'clock, the 'Emma' steamed into the Strait of Sunda and anchored at Batavia late in the afternoon of 20 May 1881.<sup>24</sup>

It was probably while on the Atlantic, on the way to Rio de Janeiro, that Van Laar petitioned the King for an honourable discharge from the naval service, subject to the training fee of Dfl. 900,- being refunded.<sup>25</sup>



*H.M.S. Koningin Emma der Nederlanden.*<sup>27</sup>

This petition was considered at the Ministry of Naval Affairs on 31st March 1881 and it was decided to contact his aunt Miss P.J.B. Rost van Tonningen in Haarlem. He had also become of age.<sup>26</sup> Apparently no objection was raised and Van Laar, having paid his own expenses, returned home on 20 June 1881 as a passenger on a French mailboat.<sup>28</sup> His discharge followed on 31 August.<sup>29</sup> At the commencement of the

academic year 1881/1882 he took up physics, chemistry and mathematics in the Faculty of Mathematics and Natural Sciences at the University of Amsterdam, thus following his vocation.<sup>30,31</sup> At the beginning of November 1881 he became friendly with the chemical student and writer Ch.M. van Deventer (1860-1931).<sup>32</sup> They saw a lot of each other during this time and Van Deventer showed that he could be very taciturn at times. Through him Van Laar came into contact with men such as the writers of the Eighteen Eighties, Willem Kloos (1859-1938) and Albert Verwey (1865-1937), the painter and photographer Willem Witsen (1860-1923) and many others. Later, in 1890, Van Eeden found him 'a thoroughly good-hearted chap' and the writer L. van Deyszel (1864-1952), with whom Van Laar had contact from 1890 until 1905, called him 'goodness itself, who wouldn't hurt a fly, perfectly ordinary, and yet quite unusual'.<sup>33,34</sup> In 1931 Van Deyszel said that finally, but much too late, Van Laar was officially recognized as Professor Van 't Hoff's pupil.<sup>35</sup> Van Laar and Van Deventer attended concerts at the Paleis voor Volksvlijt (Palace of Industry) and the Ronde Lutherse Kerk (Round Lutheran Church). At the end of the month they occasionally ate in the people's kitchen, where the cutlery was fastened to chains.<sup>36</sup> Sometimes, in the middle of the night, Van Deventer dragged himself off to 'Bis-Nihil', a café on the Nes, for a 'hot brandy grog with a slice of lemon'.<sup>37</sup> He liked the lectures given by Van 't Hoff and admired the enthusiasm with which everything was presented.<sup>38</sup> However the lectures of J.D. van der Waals, testifying to great scientific seriousness, were of particularly deep significance to Van Laar and would be crucial for the rest of his life:

'Those given by Van der Waals were masterpieces of clarity and exactness. Thermodynamics and kinetic gas theory. But what kind of thermodynamics! Such teaching one never forgets'.<sup>39</sup>

He attended these lectures together with his friend Van Deventer and Van 't Hoff's brother, H.J. van 't Hoff (1859-1939).<sup>40</sup> Later he would regard himself as a pupil of Van der Waals, and Van der Waals, for his part, regarded Van Laar as one of his pupils.<sup>41,42</sup>

However, Van Laar was not allowed take any examinations because his secondary education was insufficient.<sup>43</sup> In 1883 Van der Waals wrote to the Inspector of Secondary Schools, recommending that he be appointed to a vacant position:

'That his career promised to be a fine and glorious one'.<sup>44</sup>

Thus, under Section 89 of the Secondary Education Act 1863, he became a mathematics teacher at the Rijks Hoogere Burgerschool in Middelburg, with an annual salary of Dfl. 1,600.-.<sup>45,46</sup> In



*Rijks Hoogere Burgerschool in Middelburg.*<sup>47</sup>

the school year 1892/1893 he also had a temporary appointment as a natural history teacher at the Openbare meisjes M.U.L.O. (State School for Advanced Elementary Education for Girls) there, with an extra annual salary of Dfl. 400.-. Later his salary would be fixed at Dfl. 2,000.-.<sup>48</sup>



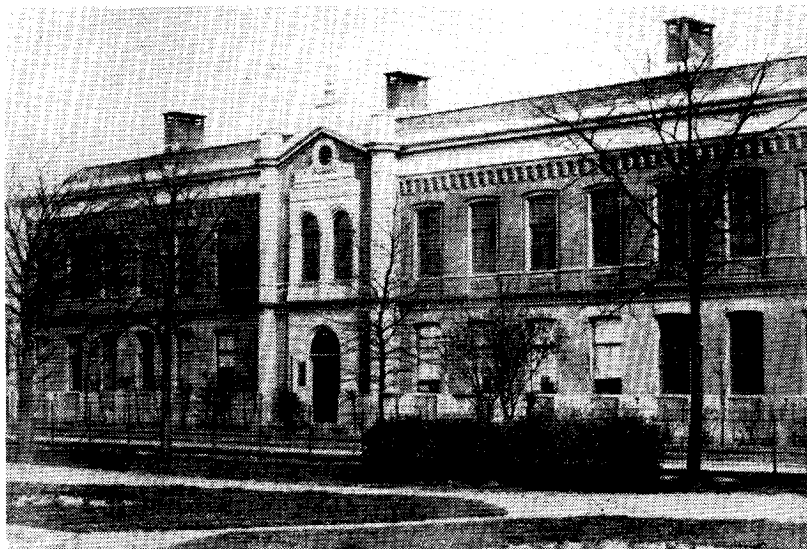
*Van Laar in 1885.*<sup>49</sup>

On 7 April 1885, in Meppel, he married Woutera Hendrika Timona ten Brink (1861-1912).<sup>50</sup> He had three sons and two daughters from this marriage, but the second son died in Middelburg at the age of three.<sup>51</sup> In his Middelburg days Van Laar tried in vain to contribute to 'De Nieuwe Gids'.<sup>52</sup> From 1888, Van Laar was entitled to elect members of parliament,

provincial state representatives and town councillors.<sup>53</sup> He felt lonely in Middelburg.<sup>54</sup>

On 1 September 1895, at the suggestion of Lorentz, he left Middelburg and became a teacher at the Rijks Hoogere Burgerschool in Utrecht.<sup>55</sup> He also hoped to be accepted as an unsalaried lecturer (privaatdocent) of mathematical chemistry at the university there.<sup>56</sup> The change of working environment and the fact that he could not become an unsalaried lecturer because he had not taken his doctor's degree were probably so difficult to bear that in 1896 he was compelled to stop working.

'Since J.J. van Laar had also become seriously ill, he was given leave until 15th July 1896 by letter dated 20th April 1896, nr. 60, his teaching duties being entrusted to Mr. G.L. 't Hooft from 1st May to 15th July 1896, by ministerial letter dated 28th April 1896, nr. 2543, Department O. After Mr. Van Laar had resumed his duties, an increasing nervous disorder compelled him to apply for an honorary discharge from his position by letter dated 4th December 1896'.<sup>57</sup>



*Rijks Hoogere Burgerschool in Utrecht.*<sup>58</sup>

He accompanied this application with a claim for a pension.<sup>59</sup> He was granted the discharge on 1 February 1897 and his pension was fixed at Dfl. 589,-.<sup>60</sup>

### 3. Unsalariated university lecturer and research assistant.

After moving to Utrecht and having had some rest, he contacted Professors H.W. Bakhuis Roozeboom (1854-1907) and Van der Waals in Amsterdam. In 1898 he was admitted as an unsalariated lecturer of mathematical chemistry at the University of Amsterdam.<sup>61,62</sup> The biography he wrote on Van der Waals in 1899 shows his admiration for his teacher.<sup>63</sup> However, contacts with Van der Waals were difficult and on 18 August 1899, he wrote to Lorentz:

'But I have imagined you to be against me since '96 (wrongly, I fortunately see now). And this worried me terribly since another person whom I esteem highly, I mean Prof. Van der Waals, is totally impossible in normal (scientific) contact. Never have I had any help or support from him when I was having difficulties with scientific work. Among one of the less pleasant characteristics of Prof. Van der Waals is certainly the fact that he does not very much appreciate the work of other people (I do not mean my work, but work of much greater men, men with excellent reputations). A is a third rate scientist, B is fourth rate etc. Putting himself only for one moment in their place is not his strongest point. This accounts for the fact that he never gives any encouragement to others. He can sometimes be extremely cold. Therefore I am glad that you are willing not to withhold your suggestions and considerations on this work'.<sup>64</sup>

It is common knowledge that Van der Waals could make a very unfriendly impression and because of his brusque way with people he was difficult to get along with. He did not, therefore, have many friends.<sup>65</sup> It was typical of Van der Waals that from 1870 until 1910 he did not allow his photo to be taken.<sup>66</sup> It is certain that Van Laar held Van der Waals in high esteem, maybe even admired him. This does not only show in his biography about Van der Waals, but also in the following quotation:

'And to conclude, that I highly esteem the man (Van der Waals, v.E.) as a scientist - whoever should doubt that, is referred to the biography on this scholar, which I wrote in 'Mannen en Vrouwen van Betekenis van 1900', which was also translated into German'.<sup>67</sup>

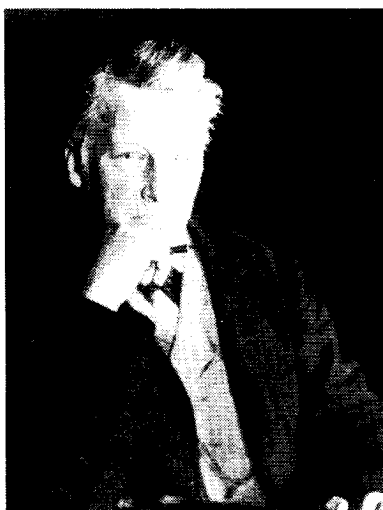
One of Van Laar's characteristics was that he was always in a hurry. For instance when Van 't Hoff recommended Van Laar to W. Ostwald (1853-1932), Van 't Hoff wrote:

'Ich bekomme von Van Laar zwei Postkarten, worin er darauf dringt dass seine Referate wie möglich etwas früher in der Zeitschrift (für physikalische Chemie, v.E.) erscheinen; die betreffenden Autoren beklagten sich schon über diese Verspätung. Möchten Sie in dieser Hinsicht etwas thun können für meine Landsleute, so würde das auch mir sehr freuen'.<sup>68</sup>

On 6 July 1899, Ostwald answered with a postcard from Leipzig:

'Trotzdem hat er mir eben einen so groben Brief geschrieben, dass ich alle Verkehr mit ihm abbrechen muss.....'.<sup>69</sup>

That this indeed happened, and that he antagonized Ostwald is evident from the printed statement Van Laar wrote on 11 July 1899.



*J.H. van 't Hoff.*<sup>70</sup>



*W. Ostwald.*<sup>71</sup>

L. S.

De ondergeteekende ziet zich verplicht mede te deelen dat *Referaten*, door hem sinds 1898 op verzoek van Prof. OSTWALD voor het „*Zeitschrift für Physikalische Chemie*“ geleverd, vooral sinds 1899, aanhoudend zeer laat worden geplaatst.

Zoo zijn referaten over verschillende Verhandelingen van WIND, LOBRY de BRUYN, BREMER, MEYERS, DE VISSER, v. EVERDINGEN, HAGA, ZEEMAN, JULIUS, HARTMAN, KRAMERS, door ondergeteekende den 13<sup>en</sup> Februari 1899 ingezonden, niettegenstaande herhaalde en stellige beloften van plaatsing: eerst na 6 weken, toen in het Meinummer, daarna (*uiterlijk*) in het Juninummer, *heden nog altijd niet gepubliceerd!*

Een volgende serie referaten, ingezonden 21 Mei over Verhandelingen van ARONSTEIN, ABERSON, SPRING, v. D. WAALS, VERSCHAFFELT, v. D. LEE, KAMERLINGH ONNES, SCHREINEMAKERS, COHEN zijn nog niet eens in proef gegeven!

Op zijn zeer rechtmatige reclame hierover, toen in het Heft dat 1 Juli verscheen de referaten van 13 Febr. (in Maart reeds in proef gecorrigeerd) *wederom niet geplaatst waren*, kreeg ondergeteekende eerst *geen antwoord*, daarna slechts: *Ich verzichte auf weitere Referate und weiteren Verkehr*, W. OSTWALD.

De beoordeeling eener dergelijke handelwijze en de kwalificatie daarvan gaarne aan anderen overlatende,

hoogachtend,

*Uw. Dw.*

J. J. VAN LAAR.

UTRECHT, 11 Juli 1899.

Buys-Ballotstraat 6<sup>de</sup>.



It appears that in 1901 Van Laar lectured in Utrecht after all and in the same year he applied for a teaching post at the H.B.S. for girls in Amsterdam.<sup>73,74</sup> He was an enthusiastic teacher and took his unsalaried lectureship very seriously.<sup>75</sup> On 18 August 1899, he wrote to Lorentz about his contacts with Van der Waals:

‘In this respect - sans comparaison ailleurs - Van der Waals is very useful to me, he who so repeatedly returns to the old deductions, sharpens them, and constantly criticizes his own work. I am one who is in this respect often hard to please, I always see weak points. I once had quite an amusing conversation with Van der Waals on this subject, who at the time was so amazed that I immediately mentioned two or three weak points in his theory of Capillarity, when he asked me, or rather suggested it, adding that no one had ever brought that to his attention’.<sup>76</sup>

It is certain that in 1901 Van Laar met opposition from Van der Waals. To Lorentz he wrote:

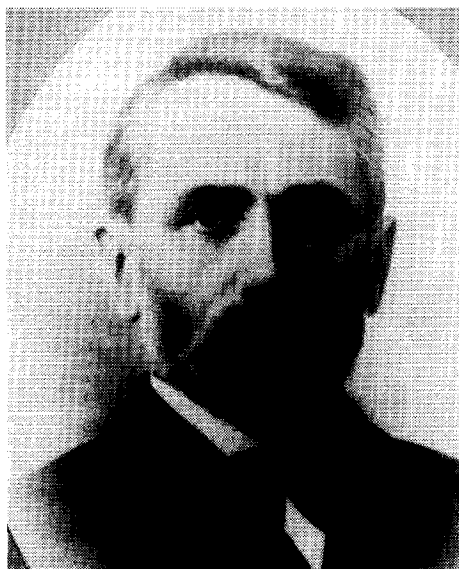
‘I would like to see what is at the bottom of all this, and ask who hates me so much that they have always succeeded in doing me wrong, I would like to mention names but my pen will not let me. I feel that there are two people who have always opposed me - well, I will name them: Onnes and Van der Waals. I do not know why, but I feel that it is true’.<sup>77</sup>

Around 1902 Van der Waals must have realized that Van Laar’s lectures in mathematical chemistry had started to create a threat to his own lectures on thermodynamics given for future chemists because, on 27 September 1902, at a meeting of the Faculty, the following happened:

‘(...) Mr. Roozeboom clarifies the lectureship which is on the agenda. Because of Mr. Cohen’s move to Utrecht, Mr. Roozeboom is forced to take on the lectures given by Cohen. He would however be permanently relieved of this task when Van Laar, a unsalaried lecturer at this university, could provide the lectures hitherto given by Cohen. Part of the money intended for Mr. Cohen could be given to Van Laar and he could be given the title of lecturer. The last point is disputed, in view of the consequences which might result from this step, and these are clarified by Van der Waals. Mr. Sissingh (Experimental Physics Professor, v.E.) asks whether Van Laar could be given the title of research assistant of theoretical chemistry; the

proposal is seconded by Mr. de Bruyn.(...) As far as the case of Van Laar is concerned it is decided that Mr. Roozeboom will inquire into the possibilities of appointing him research assistant of theoretical chemistry'.<sup>78</sup>

Van Laar was opposed. The reason was clarified by Van der Waals. In 1903 Van Laar was appointed research assistant to Bakhuis Roozeboom. His task was to give a lecture of one hour a week on the subject of his studies and to advise Bakhuis Roozeboom on mathematical matters. In the same period Van der Waals tried to prevent Van Laar from offering his articles to the Royal Academy of Science. He did not succeed and Bakhuis Roozeboom avoided contact with Van der Waals after this.<sup>79</sup> Lorentz and F.A.H. Schreinemaker (1864-1945) submitted Van Laar's papers.



*H.W. Bakhuis Roozeboom.*<sup>80</sup>

Whatever the reason, contact between Van Laar and Van der Waals left much to be desired. At the same time it is remarkable that this was not the case in Van Laar's working relations with Bakhuis Roozeboom, for in October 1906, Bakhuis Roozeboom, together with Holleman, again tried to obtain a lecturership in mathematical chemistry for Van Laar. At the Faculty meeting of 23 October 1906, he tabled a second proposal:

'By this nomination of Mr. Aten as lecturer, one of the youngest trainees at our University, they however believe that with regard to an older unsalaried lecturer, in casu, Mr. Van Laar, a wrong would be

done, that is why they, through Mr. Bakhuis Roozeboom, suggest nominating Mr. Van Laar, in recognition of his merits for a lectureship as well.

Mr. Van der Waals thereupon given the floor, feels the lectureship of Mr. Van Laar to be highly unlikely, because he is of the opinion that this lectureship comprises the same subjects which he teaches, and that thus, a proposal to appoint a lecturer would have to come from him. After lengthy discussion, in which Mr. Roozeboom opposes Mr. Van der Waals' views, Mr. Roozeboom retracts his proposal about the lectureship of Mr. Van Laar. The proposed lectureship of Mr. Aten is not opposed and it is decided to address this proposal to the Mayor and Aldermen'.<sup>82</sup>

Van der Waals opposed Van Laar's appointment again, despite the fact that Bakhuis Roozeboom challenged him. The proposal to offer a lectureship to Van Laar was withdrawn.

At the end of December 1906, an unsalaried lecturer in crystallography, F.M. Jaeger (1877-1945) heard that A.H.W. Aten (1877-1950) had been nominated as lecturer and wrote about this to his colleague Van Laar. Van Laar could hardly believe it and wrote to Lorentz on 2 January 1907.

Dear Professor,

I am sorry to have to write you about a sad matter. On New Year's Day I was 'surprised' by a letter from Dr.F.M. Jaeger, an unsalaried lecturer of crystallography in Amsterdam (Zaandam), in which he voices his indignation about the future appointment -(unreadable) and to me until this moment unknown - of the only recently promoted student *Aten*, as *lecturer in Electrochemistry(!)*-at the moment he is research assistant to Prof. B.R.. Never has he done anything on electrochemistry, *nor published anything on the subject*. He was one of my *very bright* students and in collaboration and under the influence of Prof. Bakhuis Roozeboom he wrote one or two articles (on a different subject: the theory of phase equilibria).

Everyone could have known that I have, over the last five years, practiced electrochemistry with special fondness and have written a *textbook* on it, which was finished in 1901 but which, due to lack of time, will only be published this spring. They *know* this in Amsterdam. Also that I published *three articles* from that book in the 'Koninklijke Akademie voor Wetenschappen' (at the time they were

still submitted by Van der Waals) and translated into German. Also in my six 'Vorträge', the sixth was for a large part devoted to this.

I repeatedly gave successful lectures on electrochemistry, which belong to the best attended and most closely listened to of all my lectures. And now, one of my *former students* who has not achieved anything yet, which would entitle him to the title of lecturer, is appointed, *passing me by*, the teacher who has so many former claims, and who believes he could claim the title, if not more. This disgraceful fact is the straw that breaks the camel's back and spontaneously brings forth heartfelt protest from Jaeger, who calls this a slap in the face for all unsalaried lecturers, and in my face especially.

It is so bad that I *cannot* believe it yet, but it seems to be the sad truth (also that Van der Waals tried to force Kohnstamm as lecturer of theoretical chemistry upon B.R.) Jaeger wrote that this scandalous act forced him to take steps, that all unsalaried lecturers: Jaeger, Blanksma and I *together* hand in our *resignation* as a protest against this action.

It is a sad decision for me, because it leaves my family without means of support. Because I will have Dfl. 600.- left of my *pension*, without private tuition or *extra income*. I have already suffered poverty this year, because there was no private tuition after the holiday. (The lack of my *doctor's degree hurts* me very much because I am regarded as a simple old fashioned former teacher, without qualifications. And worse, there was (unreadable) no space in two consecutive editions for my latest, edited article, which you submitted, about the longitudinal-plaits (including calculations) so that this article cannot be published before March or April. That means missing two or three hundred guilders, which I had *counted* on, and which forced me to borrow money again. All this depresses me, I cannot think of a way out. Who on earth can maintain four grown-up children (The eldest is 21, the youngest 13) and get by on Dfl. 1.600.-?)

And that at *my* age, after all I have done, and yet, if Aten is appointed I will have to take this step. Because *now*, I will no longer work as a *research assistant*, who, please note, knows no more about the subject he is going to teach than the first student who will listen to him.

the time of *Smits'* appointment as lecturer, that I have been refused a *doctor's title* (at *every* university in the Netherlands) that, in a word, I have been passed over everywhere and always, in the most hurtful way possible.

But *now* it is over. I will draft a letter of resignation, with a full explanatory memorandum, and we will have it published in the daily newspapers. And Van der Waals will not be spared. Because the fact that he, and no one else does this to me, out of *hate*, because I work in *his* field, is an *open* secret, *everybody* knows this.

But even worse is the fact that the Faculty shows so much slavish subordination, and allows Van der Waals to force them (in chemistry) into deciding who will be lecturer. What is worse is - something that has never been allowed at any university in this or in any other country, that professors of *chemistry* allow physics colleagues to lay down the law and are powerless to act against it.

This injustice is outrageous.

And my *family* has been a victim of this for the past ten years.

We suffer poverty, *undeserved* poverty. That is the worst, and only because of one man who cannot be stopped. These are scandalous situations which have to be made *public*, everywhere, now that the worst is about to happen.

The students, mostly private students, have given me much sympathy - you and Prof. B.R. excluded, who did more for me than anyone else - the students often showed this in the most unambiguous way by staying away from lectures given by Smit, who replaced me at the time.

But these are the facts!

I had to open my heart to you. The new year started sadly with yesterday's blow. I postponed writing to you until I had calmed down - more than 24 hours. But writing brings back all the old bitterness and I end.

Now lack of food and hunger await my wife and children. Because of this I can not and must not put up with the humiliation that awaits

me. And with me, all the other unsalaried lecturers will resign.

Do you know something that might save us, a way out?

Forgive my poor handwriting, I am too upset, I must *force* myself to keep calm, and my hand is shaking.

With kind greetings, awaiting your answer, I remain faithfully,

Yours obediently,

J.J. Van Laar.<sup>83</sup>

1) In preceding years, many honorary degrees had been awarded in Utrecht and Leiden, but I am not worthy of one. Easton, a (unreadable) in India, (unreadable). And again and again I am forgotten.

After a short illness Bakhuis Roozeboom died on 7 February 1907. This was a great loss to the University of Amsterdam and Van Laar wrote a valedictory article in 'Chemisch Weekblad' of 16 February 1907.<sup>84,85</sup> His plans for resignation etc. came to nothing because with the death of Bakhuis Roozeboom a new situation had arisen.

It will be seen in the next chapter that Van Laar's scientific development in the period from 1898 until 1906 was great. Neither Van der Waals nor Bakhuis Roozeboom would have thought that Van Laar would expand mathematical chemistry (today's chemical thermodynamics and theory of phase equilibria) into an independent subject.

#### **4. Appointment of Bakhuis Roozeboom's successor**

On 8 February 1907 Mrs. Bakhuis Roozeboom reported her husband's death to the College van Curatoren (Board of Governors).<sup>86</sup> On 13 February 1907 the Board of Governors requested that the Faculty put forward names to fill the vacancy.<sup>87</sup> The minutes of the Faculty meeting of 18 February 1907 show that Schreinemakers, Professor of Inorganic and Physical Chemistry in Leiden was considered, but he let it be known at the beginning of March 1907 that he would rather stay in Leiden.<sup>88</sup> At the Faculty meeting of 9 March 1907 it was decided to appoint a committee to consider the candidates. Van der Waals, Korteweg and A.F. Holleman (1859-1953), a physicist, a mathematician and only one chemist, took seats on the committee, the latter being the Faculty secretary. The meeting also

discussed some matters regarding examinations, and it was decided



*A.F. Holleman.<sup>89</sup>*

that the lectures which were formerly given by Bakhuis Roozeboom would be continued. Holleman would take steps to make this possible.<sup>90</sup> The result was that lecturer Aten would take over the lectures on inorganic chemistry and that research assistant Van Laar would temporarily assume responsibility for the lectures on the theory of phase equilibria.<sup>91,92</sup>



*Bakhuis Roozeboom and his family.<sup>93</sup>*

Now that Schreinemakers had proved to be unavailable, the Faculty meeting of 18 March 1907 decided to nominate in first place A. Smits, (1870-1948), Professor of Inorganic and Physical Chemistry in Delft and in second place Jaeger, unsalaried lecturer on crystallography at the University of Amsterdam and teacher at the Dutch secondary school (H.B.S.) in Zaandam.<sup>94</sup> The nomination was sent to the Board of Governors on 20 March 1907.<sup>95</sup> In April 1907 a petition and an explanatory memorandum from outside the Faculty, signed by 25 doctors of chemistry, research assistants at the chemical laboratory, candidates and Ph.D. students, including Aten, but not Van Laar, was sent to the Board of Governors.<sup>96</sup> The petition included a request not to nominate Smits as Bakhuis Roozeboom's successor. The Board of Governors handed this petition over to the Faculty.<sup>97</sup> The meeting of 29 May 1907 decided to disallow the petition.<sup>98</sup> Thereupon, a second petition was sent to the Board of Governors in June, which was signed by 12 students, candidates, Ph.D. students and doctors of chemistry. This petition proposed to nominate Smits as Professor.<sup>99</sup> The petition was noted at the meeting of 27 June 1907.<sup>100</sup>

The nomination of the Faculty of 20 March 1907 was discussed twice by the Board of Governors. The first discussion was at the meeting on 3 June 1907 when it was decided that the Chairman (also Burgomaster of Amsterdam v.E.) would informally inquire whether Smits would accept a possible appointment. If he would not, Jaeger would be recommended.<sup>101</sup> The second time the matter was considered was at a meeting on 1 June 1907 when the Chairman reported that Holleman had informally heard that Smits was willing to come to Amsterdam.<sup>102</sup> Governor Blooker had asked Van 't Hoff, E. Cohen (1894-1944), P. van Romburgh (1855-1945), J. Bosscha (1831-1911) and J.P. Kuenen (1866-1922) about Smits and Lorentz and C. Hoitsema (1867-1958) also sent letters to Blooker.<sup>103</sup> Apparently these letters were not sufficiently positive and it was decided not to adopt the nomination of the Faculty.<sup>104</sup> On 3 July 1907 the Board of Governors let it be known to the Faculty that they had made one more unsuccessful effort to encourage Schreinemakers to join the University at Amsterdam.<sup>105</sup> And that further:

'Although we would now very much appreciate it if the great traditions of the vacant chair could be continued and held high, we do in the present circumstances not consider it wise to adopt the nomination in the aforementioned letter or, to choose between the two mentioned persons. We therefore have the honour of inviting you to further consider whether other persons, possibly from



abroad, could be considered to fill this said vacancy'.<sup>106</sup>

The letter from the Board of Governors of 3 July 1907 was discussed at the Faculty meeting of 9 July 1907 and it appears that Holleman had in the meantime seen the Burgomaster (the Burgomaster was also President of the Board of Governors, v.E.). He agreed with the Burgomaster to travel personally to Leipzig and Berlin to ask Professors Nernst and Ostwald about the vacancy.<sup>107</sup> Van der Waals reacted negatively:

'Mr. Van der Waals deplores the course matters have taken; he believes that maintaining traditions with regard to the vacant seat, that is the continuation of the physical chemistry direction, as it was developed in the Netherlands, is very desirable. This would not be possible with the appointment of a German physical chemist, because the practice of physical chemistry there still supports the view of diluted solutions, which has here been acknowledged as untenable. Thus, Mr. Van der Waals opposes the nomination of a foreigner; but would like to maintain the present nomination, if need be, with the addition of some younger scientists of talent, for instance Mr. Boeke and Mr. Büchner.

The secretary says that he is well aware, now that the Board of Governors does not wish to adopt our nomination, that another direction will have to be taken; he wholeheartedly agrees with Mr. Van der Waals on his assessment of German physical chemists with regard to the study of osmotic pressure and related aspects; but remarks that this does not concern a chair of physical chemistry only, but rather a chair of inorganic and physical chemistry, which in addition includes subjects other than osmotic pressure and that there are perhaps persons in Germany who could be of such significance in the field of inorganic or physical chemistry that they could perhaps be nominated to fill the vacancy'.<sup>108</sup>

After that, Holleman travelled to Berlin and Zürich and met Nernst, E. Fischer (1852-1919) and Ostwald. Three people came to the fore, R. Abegg (1869-1910), P. Walden (1863-1957) and A. Werner (1866-1919).<sup>109</sup> These are still famous names today, especially Werner who could more or less be called the founding father of the chemistry of complex compounds. These names were discussed at the Faculty meeting of 31 July 1907 and it was decided to maintain the original nomination: No.1 Smits and No.2 Jaeger; also added were No.3 Walden, and No.4 Jorissen.<sup>110</sup> The Faculty notified the Board of Governors of this in a letter on 31 July 1907.<sup>111</sup> This letter was also discussed twice by the Board of Governors, on 1 August

and 2 September 1907. On 1 August 1907 it was decided to bring the documents into circulation and await further information on Walden.<sup>112</sup> On 2 September 1907 it was decided to recommend: No.1 Smits and No.2 Jaeger to the City Council.<sup>113,114</sup> (As the University of Amsterdam was a municipal university, the Town Council had to make the nominations, v.E.) The minutes of the Board of Governors reads:

'A letter from the Faculty has been received in which they explain that Van 't Hoff and Bakhuis Roozeboom founded a school, which is well known and famous, even abroad, as a result of which many foreign students come to study here for a period of time. The Faculty feels it advisable to maintain this tradition. That will not be the case if a foreigner is appointed to succeed Bakhuis Roozeboom. In view of this, the Faculty maintains its views and expresses the opinion that no one than Prof. Smits should be considered to fill the vacant chair'.<sup>115</sup>

On 25 September 1907 the City Council decided to appoint Smits as Professor of Inorganic and Physical Chemistry at the University of Amsterdam.<sup>116</sup> The vote was 25 votes in favour of Smits and 9 in favour of Jaeger. He accepted the post on 1 December 1907.<sup>117</sup> On 9 December 1907 he gave his inaugural lecture: 'De chemie in hare oude en nieuwe banen' (Chemistry on old and new paths). He remained professor until 1940.<sup>118</sup>

Smits was well known at the University of Amsterdam. He was an unsalaried lecturer there, lecturing on technical and physical chemistry from 1901 until 1904, and from 1904 until 1906 he lectured on technical chemistry. In 1906 he was appointed Professor of Inorganic and Physical Chemistry at the College of Technology in Delft.<sup>119</sup>

## 5. Curator (Governor) Blooker

C.F.J. Blooker (1852-1912), Alderman of Poverty Relief and Education, and member of the Board of Governors, played an important part in filling the vacancy created by Bakhuis Roozeboom's death, and Van der Waals' vacancy (see paragraph 7) as well as in the creation of Van Laar's lectureship. Blooker was a medical practitioner specialising in internal diseases.<sup>120</sup> He had lived in Voorburg since 1906 and was a Member of Parliament.<sup>121</sup> The minutes of the Board of Governors show that he was often the central person who collected information and met with staff. It

is certain that Van Laar had contact with him during his period in Amsterdam. Letters from Van Laar to Lorentz, minutes from the Board of Governors' meetings, two letters from the Faculty archives and Van Laar's first letter of resignation of 6 November 1911 show that Blooker was well informed about Van Laar's situation. In 1907 he proved to be equally well informed about the working relations between Van Laar and Bakhuis Roozeboom and about Van der Waals' attitude towards Van Laar. Blooker believed that Van Laar ought to show more resistance and it was also he who took Van Laar's situation to heart and through the Board of Governors put pressure on the Faculty to sort out Van Laar's position.<sup>122</sup>



*C.F.J. Blooker.*<sup>123</sup>

## 6. Lecturer

The views of Van der Waals on Smits filling the vacancy left by Bakhuis Roozeboom and his negative opinion of Van Laar were the major factors which led to the appointment of Van Laar as lecturer in mathematics and not in thermodynamics in 1908. A reconstruction of the events follows below.

The already nervous and haunted research assistant Van Laar reacted very emotionally to the death of Bakhuis Roozeboom. Some days after his death, Holleman and research assistant E.H. Büchner (1880-1967) locked away papers in Bakhuis Roozeboom's study, among them notes by Van Laar. The intention was to leave them there until Mrs. Bakhuis Roozeboom and the publisher had decided what to do next.<sup>124</sup> In a letter

Van Laar accused Smits of using Mrs. Bakhuis Roozeboom's grief to obtain her husband's notes. Among other things, Smits was supposed to have taken the notes. Smits wrote about this:

'It is a long list of crimes which has reached him from different sides, for which I am blamed, and which can only be believed by the brains of a nervous patient like Van Laar'.<sup>125</sup>

Van Laar had overreacted! (v.E.).

As was mentioned before, Holleman asked the Faculty meeting of 9 March 1907 whether, with regard to Bakhuis Roozeboom's vacancy, it was desirable to continue Bakhuis Roozeboom's lectures. The meeting answered affirmatively and Holleman was instructed to consult the Burgomaster as President of the Board of Governors on the question of whether the Faculty could charge authorized persons with this task autonomously, or whether the Board of Governors or perhaps the Council should be consulted. Apparently this matter was directly dealt with by the Burgomaster and aldermen, because in a letter of 20 February 1907 to the Burgomaster and aldermen, Holleman recommended the appointment of Van Laar:

'I have the honour of proposing the following, which would without doubt have come from my colleague Bakhuis Roozeboom, but which, because of his deeply mourned and unexpected death was left unfinished. The proposal concerns a raise in salary of Dfl. 1,000.- for the research assistant at the laboratory of inorganic and physical chemistry, Mr. J.J. Van Laar.

Said gentleman lives in very special circumstances. For many years he has been an unsalaried lecturer at this University and in that rôle he lectures on mathematical chemistry, which was highly appreciated by Prof. Bakhuis Roozeboom and the students. He also often supports advanced students in their theoretical studies, and often assisted Bakhuis Roozeboom in solving mathematical-chemical problems, which resulted from his research. Thus in reality he functions as a lecturer, but without title or salary. I believe, and Prof. Bakhuis Roozeboom was of the same opinion, that Van Laar is entitled to this position and we are trying to convince the Faculty of this opinion, which is however blocked by fierce opposition from some of its members. But, since Mr. Van Laar is in a very difficult financial situation, the late Bakhuis Roozeboom and I felt that I should try to change that situation at least, so that a man like Van Laar, who is also

regarded abroad as a valuable scientist, will not have to live in a truly poor situation any longer.

Together with the late Bakhuis Roozeboom I therefore have the honour of offering the abovementioned proposal for your kind consideration'.<sup>126</sup>

A stronger plea is hardly conceivable! With reference to this letter Blooker contacted Holleman. On 6 March 1907 he wrote to Holleman with reference to the letter above.

'This can be resolved, if he is instructed to take over part of Bakhuis Roozeboom's work'.<sup>127</sup>

And on 10 March 1911:

'Let Mr. Van Laar start his lectures on the theory of phase equilibria as soon as possible'.<sup>128</sup>

Subsequently Blooker voiced his surprise at the fact that the lectureship had not been given to Van Laar because it was blocked by only one member of the Faculty. Did the Faculty have an opinion or not? Blooker mentioned that he had noticed that this case put Van Laar's career in a very sad light. Van Laar had, in effect, been cast into poverty by one man. Holleman hurried to answer on 11 March 1907 that the Faculty could have an opinion because the two people who were able to assess Van Laar's merits (Van der Waals and Bakhuis Roozeboom, v.E.) had held diametrically opposed opinions.<sup>129</sup> From 12 March 1907 onwards Van Laar temporarily gave Bakhuis Roozeboom's lectures on the theory of phase equilibria and he received an allowance of Dfl. 1,000.- for the year 1907.<sup>130,131</sup>

Van Laar did not rest because three petitions were drafted, in which a statement was included suggesting that the creation of a chair of theoretical chemistry be considered. This would be independent from the chair Bakhuis Roozeboom had formerly held, and Van Laar would be invited to fill it. The first petition was addressed to the Board of Governors on 11 March 1907 and was sent by the 'Society of Mathematics and Natural Sciences Students' in Amsterdam.<sup>132</sup> The second petition was also addressed to the Board of Governors and was sent on 5 April 1907 by twenty seven of Bakhuis Roozeboom's former students.<sup>133</sup> The third was addressed to members of the Town Council and sent in July 1907 by twenty ex-research assistants from the laboratory.<sup>134</sup>

The Board of Governors' meeting of 3 April 1907 decided to send the first petition of 11 March to the Faculty for advice.<sup>135</sup> This happened in the letter of 25 March 1907.<sup>136</sup> The petition was discussed at the Faculty meeting on 17 April 1907:

'The matter under discussion is the request of the Board of Governors for a report and advice on the petition of department III of the students of the Faculty, containing the wish, that in addition to the filling of Bakhuis Roozeboom's vacancy, a chair of physical and mathematical chemistry be created and that it be filled by Mr. J.J. Van Laar, at this time an unsalaried lecturer at this University. At the request of the chairman, Van der Waals gives his opinion that the time at which this request is made is in his view improper because he feels it could better wait until the successor of the late Bakhuis Roozeboom is appointed, so that he will have the opportunity to express his opinion on the matter. After some discussion it is decided to answer the Board of Governors along these lines'.<sup>137</sup>

This happened. It was the third time that Van der Waals' actions had caused a decision on van Laar's position to be postponed. In keeping with Van der Waals' views it was decided to reply to the Board of Governors saying that this matter could only be dealt with after the appointment of Bakhuis Roozeboom's successor. On 18 April 1907 the letter was sent.<sup>138</sup> The Board of Governors' meeting of 6 May 1907 dealt with the letter as received correspondence without further comment.<sup>139</sup> The Board of Governors adopted the advice offered.

It should be noted that there is a difference between the situation in 1902 and that in 1906. In 1906 an associate professorship instead of a lectureship was at stake.

A second incident occurred. On 19 August 1907 Van Laar wrote to Holleman that he thought Lorentz's advice on Smits to be a bit odd because Lorentz had held a different opinion before the holidays.<sup>140</sup> Holleman must have written to Lorentz immediately because on 23 August 1907 Lorentz wrote that he could not say anything about Smits because he was not familiar with his work, that he was surprised at the misunderstanding and that Van Laar must have acquired the information about Smits on the advice of his friends.<sup>141</sup> On 24 August 1907 Holleman sent Van Laar's letter to Lorentz.<sup>142</sup> On 26 August 1907 Lorentz wrote that Van Laar should not have written to Holleman 'That I was of a

different opinion before the holidays', because he had never given Van Laar his opinion on Smits.<sup>143</sup> Apparently Lorentz requested an explanation from Van Laar on 26 August.



*H.A. Lorentz*

*H.A. Lorentz.*<sup>144</sup>

On 27 August 1907 Van Laar wrote the following to Lorentz:

'Consequently I wrote to Prof. Holleman that you used to be of a different opinion on this matter, by which I meant:

'You have always been interested in me and it will give you pleasure when my position is finally, after a long time, arranged. Well, the appointment of Smits makes such impossible (I should know) and thus Prof. Lorentz will never assist in advancing this appointment'.<sup>145</sup>

With this, Lorentz regarded the matter closed.<sup>146</sup>

In the meantime the procedures to fill the vacancy created by Bakhuis Roozeboom's death continued and it became clear that Smits would be appointed. He was appointed by order of the City Council on 25 September 1907.

During this time a third incident occurred. A writing error was made in the document prolonging Van Laar's appointment as research assistant. His appointment said organic chemistry department instead of inorganic

chemistry department.<sup>147</sup> This would lead Van Laar to think that Smits had tried to 'banish' him, which would be a misconception.<sup>148</sup> The mistake caused much misunderstanding and writing of letters. Van Laar was asked to see Holleman, who informed him that his position after Smits' appointment would seem to be difficult. Van Laar concluded that if Smits were to be appointed he would have to look for another job. This caused suspicion: 'As one treats a drunken labourer who lives an immoral life', Van Laar is to have said. Van Laar apologized for this remark.<sup>149</sup> Smits deplored the mistakes which were made as well as Holleman's view. Smits had always liked Van Laar and would help him whenever the occasion arose. He was convinced that Van Laar would come to think better of it and the same, Smits believed, was true of Aten.<sup>150,151</sup>

After the vacancy was filled, the Board of Governors asked the Faculty to give their opinion on 18 October 1907 so that the petition submitted by the students of the Faculty could be dealt with.<sup>152</sup> At a meeting on 23 October 1907 the matter was again discussed and Smits was present.

'The letter of the Board of Governors is discussed, requesting advice on a petition submitted by ex-students and students, directed to their Board in which the wish is expressed to appoint Mr. Van Laar Professor of Mathematical Chemistry at this University (see minutes of 733rd. meeting)

Invited by the chairman, Holleman says that Mr. Van der Waals assesses Mr. Van Laar's capabilities negatively and the subject to which Mr. Van Laar would be appointed is already taught by Mr. Van der Waals himself. He feels perfectly able to do so and does not require any assistance, and certainly no assistance from Mr. Van Laar. Thus, he maintains his original position (see minutes of the 722nd. meeting) and advises against positive advice on the students' request, as well as nominating Van Laar for a lectureship. Mr. Sissingh argues postponement until the vacancy of Van der Waals is under discussion, because he would have to resign at the end of this course, because of reaching retirement age. The matter of teaching thermodynamics (because that in fact is the subject Van Laar is teaching) could also be resolved at that point in time. A second argument in favour of postponement is the fact that Mr. Smits is not yet in office.

Mr. Smits would like to help Van Laar but does agree to the proposal made by Mr. Sissingh.

Mr. Korteweg also objects to appointing Van Laar as lecturer, but, on the other hand, feels that in connection with our latest letter, this



matter could not be postponed any longer. This would also create the impression that we were, at the end of this course, willing to consider Van Laar's position. It would also give too much honour to the students' petition if we were unable to answer at this moment. He proposes to advise negatively on the matter.

Mr. Hugo de Vries proposes to answer simply that the students' letter does not induce us to make proposals about Van Laar. The meeting adds to this proposal by saying that the Faculty finds that the account the petition gives of Van Laar's scientific merits to be overdone. The thus amended proposal is accepted with one vote against (by Mr. Hugo de Vries).<sup>153</sup>

For the fourth time it can be seen that Van der Waals' opinion, now expressed by Holleman, was heard at the meeting (Van der Waals was not present). The Faculty pleaded postponement until the Van der Waals' vacancy was under discussion at the end of the course. On 24 October 1907 this was put in writing to the Board of Governors.<sup>154</sup> The Board of Governors accepted the letter without further discussion because Mr. Blooker was not present at the meeting.<sup>155</sup> At the meeting on 6 January 1908 Blooker brought up Van Laar's position.<sup>156</sup> It was decided to ask the Faculty whether it would not be advisable to have mathematical chemistry taught and whether, in order to sort out Van Laar's position, an appointment of lecturer should be arranged.<sup>157</sup> The letter was sent on 7 January 1907.<sup>158</sup> It was asked whether a lectureship in mathematical chemistry was advisable, so that the tuition of this subject was permanently strengthened.

The letter was discussed at the Faculty meeting on 22 January 1908. The complete minutes of this meeting follow.

'Not present were Van der Waals, Weber, Hugo de Vries and Smits. The minutes of the 742nd. meeting of 23 October are read and approved after a minor change.

The purpose of the meeting is to consider a reply which is to be sent to the Board of Governors concerning their question about Mr. Van Laar's position. The Faculty's advice is sought on the question of whether said person should be commissioned with a lectureship in mathematical chemistry.

The problem in this matter is, on the one hand that Van Laar for a large part teaches the same subject as Van der Waals, be it in a different form, and that the latter is a pronounced opponent to assistance by Van Laar; and also that Van Laar teaches electro-

chemistry, and that this subject is already represented by lecturer Aten. In other words, Van Laar is really superfluous; on the other hand, Van Laar's present social position is officially only research assistant to Smits and is salaried as such. This is the salary on which Van Laar must live. This position could be defended in Bakhuis Roozeboom's lifetime, but is now, in the unanimous opinion of the Faculty untenable.

Mr. Korteweg proposes a way out of this difficult situation. He puts two views to the fore. 1. that in this matter the faculty will have to sail on Van der Waals' compass, whose opinion on Van Laar's qualities is negative; and 2. that the fact is nevertheless that Van Laar's lectures have, over the years, been well attended and that he is apparently appreciated by the candidates, so that in the name of academic freedom Van Laar should be given the opportunity to continue lecturing on mathematical chemistry.

Mr. Korteweg reads an answer to the Board of Governors which he drafted, to the effect that Van Laar be nominated to be appointed lecturer in mathematics with the expressed intention of having him lecture for candidates who wish to continue in chemistry. There is a need at this University for such a person. It is not the intention to dissuade Mr. Van Laar from continuing to lecture on mathematical chemistry. In this way the academic freedom of education could be maintained. Mr. Sissingh feels scruples about this, but not against proposing Van Laar as lecturer of mathematics. The problem is the second part of Korteweg's proposal. Mr. Sissingh feels that there is something unnatural, something that is forced on the Faculty. There is in fact no need to appoint a lecturer who also teaches mathematical chemistry; were it not that the Faculty feels for Van Laar and recognizes that his position is untenable, there would never have been the possibility of a lectureship. Mr. Van der Waals will continue to regard this appointment as placing an unwanted person next to him; and with reason, since Van Laar is in fact teaching part of mathematical physics with which Van der Waals is charged. Mr. Sissingh proposes appointing a committee from the Faculty meeting to consider the matter further.

After some debate Mr. Sluiter proposes to give up the idea of proposing Van Laar as lecturer of mathematics and only to answer on the question which was put to us by the Board of Governors, that is, whether we believe Van Laar fit to be a lecturer of mathematical chemistry and to answer this question in the negative.

Mr. Korteweg feels that the choice is indeed only between these two proposals and advises taking a vote. However this does not happen,

but after further debate, in which Mr. Zeeman and Mr. Hugo de Vries take part, it is decided to make it a committee matter. Korteweg, Sissingh and Holleman are appointed to this committee and it is commissioned to write to the Board of Governors in such a way that they are dissuaded from appointing Mr. Van Laar as lecturer of mathematical chemistry at this time, but that the future possibility is left open. The solution to the matter will be found when Van der Waals' situation is sorted out'.<sup>159</sup>

It was for the fifth time, now formulated by Korteweg, that Van der Waals' opinion was sounded out. Korteweg offered the Faculty a compromise with which all parties concerned, the Board of Governors, Van der Waals and the other members of the Faculty could agree. At the Faculty meeting on 11 March 1908, the letter which had been drafted by the committee was read. Mr. Korteweg further explained the 'mathematical matter'. Mr. Hugo de Vries declared that he was fully 'homogeneous' with the proposal (the content was similar to the minutes of the meeting of 23 October 1907).<sup>160</sup> The letter was sent to the Board of Governors on the same day.<sup>161</sup> The Faculty's advice was discussed at the meeting of the Board of Governors on 6 April 1908. It was proposed that the Chairman contact Van Laar.<sup>162</sup> At the meeting of the Board of Governors on 4 May 1908 the Chairman reported that he had met with Van Laar and that Van Laar was willing to act as lecturer of mathematics.<sup>163</sup> The Board of Governors once again asked Korteweg about the proper names of the subjects to be taught by Van Laar: 'Mathematics, more particularly for students of chemistry and biology'.<sup>164</sup> A proposal to the City Council was submitted in which the yearly salary was fixed at Dfl.2,000.-.<sup>165</sup> At a closed meeting on 10 June 1908 this proposal was discussed and the City Council agreed with 34 votes in favour and 2 against and 2 unmarked.<sup>166</sup> On 16 September 1908 Van Laar was appointed lecturer.<sup>167</sup>

Van Laar's appointment to the position of lecturer can be summarized as follows:

1. Van der Waals assessed Van Laar's capabilities negatively.
2. Korteweg drafted a compromise which could be changed in structure after Van der Waals's retirement and if Van Laar agreed.
3. The Faculty committee as well as the Faculty agreed with this compromise.
4. The Board of Governors also agreed.
5. The vote at the City Council was clearly positive.



*D.J. Korteweg.*<sup>168</sup>

Van Laar's reaction in his letter of 15 June 1908 to Lorentz was the following:

Dear Professor Lorentz,

You have perhaps seen that I have been made 'lecturer' of mathematics in Amsterdam and that I have been commissioned to teach the first and second (year) students of chemistry and biology. (only differential and integral calculus and differential equations) Just as much as that category of students needs. That means that the desirable division of a part of mathematical tuition has occurred so that the students no longer have too much differential calculus before their candidate degree but, conversely, nothing of integral calculus and the simplest differential equations. I intend to use mainly your excellent textbook on infinitesimal calculus, as well as Nernst's and Schoenflies'. On different subjects I can give those applications which the auditors will often come across in their studies. Thus, this is a pleasant task and I am glad to have been given an *independent* post, although the salary of Dfl. 2,000.- of which Dfl.105.- goes towards pensions and Dfl. 125.- towards taxes of the City of Amsterdam, is not much. As far as I am concerned there are some drawbacks to the way in which this matter has been decided, without any involvement on my part, which makes the taste of the fruit which is offered somewhat bitter.

Apparently one has had (unreadable) - and I will later give some evidence of that - to drive me out of chemistry and thermodynamics entirely, and thus keep the *candidates* away from me. My ten year period as unsalaried lecturer with some successful lectures has come to an end, and I can only continue along cunning clandestine paths, against the intentions of the Faculty. I could name it: 'Capita selecta in the field of applied mathematics', and even then I run the risk that the students no longer attend because, and that is an open secret - Kohnstamm has been appointed as successor of Van der Waals (Thermodynamics) and also in *chemistry*, and will take my place. I have been sidetracked, to have his express train pass even faster. That the Faculty regards this arrangement as final is evident from Holleman's letter and from the discussion at the closed meeting of the council which lasted two and a half hours and in which only this case was deliberated. The feeling is so general that congratulations on my appointment, which I received from different sides, are mostly messages of condolence. It was also said at the council that I could *never* be nominated for thermodynamics because I had *not worked on experiments!!!* (Is Van der Waals unsuitable for thermodynamics? Is the teaching of so many professors unsound?) So this is the latest bromide. First they have said for years on end that I was *incompetent*, that my work was *without any value*. When that no longer cut wood it was that I was no physicist (or chemist) but *mathematician*. And now that this has lost its strength they say that I am *no experimentalist!!!*

Secondly, that the Faculty's advice said (This in answer to Mr. Worst's question as to why I had not at least been appointed associate professor) that my lectures *were clear and lucid* but that they lacked depth, and were superficial, so that I could be given the title of lecturer, but not the title of professor!

If that is the case, I should say that I do not deserve the title of lecturer.

Who, by the way, can assess that? Van der Waals, who has *never* taken any notice of me, or *Holleman* (whose advice this apparently is) who has never attended any of my lectures *nor is able* to judge them??

Of those who could assess them, many have often assured me of the opposite. Besides, at my lectures I deal with just the content of my books (added to or reduced according to the intellects and needs of

my students, expanded with numerous and always varied examples). If my lectures lack depth and are superficial, (how then are Prof. Holleman's lectures??) then *my books* too suffer these same negative characteristics. Well, that too has been asserted by these gentlemen. Which of my colleagues (Van der Waals did not attend the Faculty meeting, neither did Smits) can assess my electrochemistry, and my '6 Vorträge'? I have read nothing but favourable reports on both and the most favourable were even on my Electrochemistry, by my opponent Abegg! who calls it in one of the latest editions of 'Zeitschrift für Elektrochemie', a beautiful book 'In which the writer who has never worked experimentally, shows to have an unusual command of the experimental material', and concludes by calling it 'Das wichtigste Produkt der Holländischen Theoretische Schule, that he can recommend to more advanced students'. In 'Natur Centralblatt' it was also discussed favourably, and against that Holleman's advice to others: Van Laar's lectures (books) lack depth and are superficial. That is something that *cannot* be fought. Ignorance can be fought with conviction, but malice, only (unreadable) with me (unreadable) never!!

Thus there is nothing to be expected from the Faculty, as some members have assured me that the Council can only urge my appointment on thermodynamics (at the succession of Van der Waals in September), when a petition to that effect or any other means of pressure is brought to bear from outside (from the authorities, not from the students). I completed my studies in June 1883 at the University in Amsterdam and after twenty-five years we still have not yet surpassed the shallowness and superficiality of my writing. So be it, but it is enough to lose all heart. Soon I will be walking in the high mountains and I expect to feel better. At the moment I feel exhausted and broken, and I do feel the need, also because of pressing domestic concerns, for rest and solitude. Would you show this letter to Prof. Schreinemakers? Writing tires me too much to write everything down again. Greetings always faithfully,

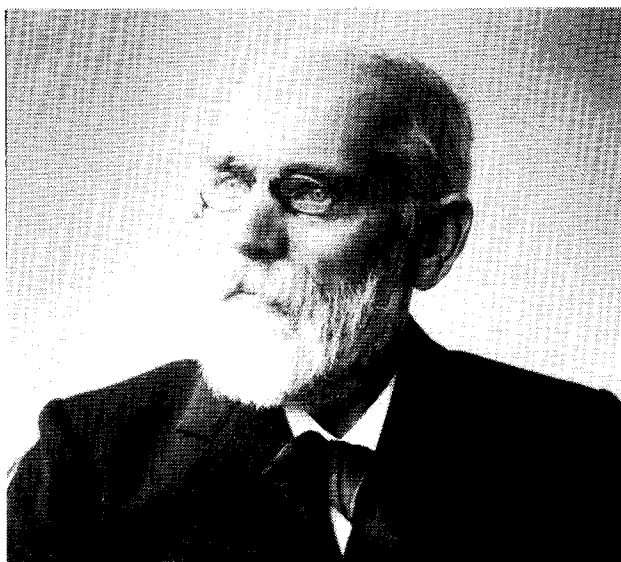
Yours obediently

J.J. Van Laar.<sup>169</sup>

## 7. Appointment of Van der Waals' successor

On 21 March 1908 Van der Waals offered his resignation to the City Council.<sup>170</sup> The Board of Governors' meeting decided to ask the Faculty the way in which the tuition of physics should be arranged after Van der Waals' resignation.<sup>171</sup> At the Faculty meeting of 27 May 1908 the ad hoc committee which had been formed and which consisted of Van der Waals, Korteweg, Zeeman and Sissingh reported. The following was proposed.

1. To nominate the Professor of Physics from Groningen, son of Van der Waals, J.D. Van der Waals Jr. (1873-1971) as Professor of Theoretical Physics, (with the exception of thermodynamics) Hydrodynamics and Theory of Probabilities.
2. To nominate Kohnstamm, research assistant to Van der Waals Sr. as Associate Professor of Applied Thermodynamics.
3. To convert Zeeman's associate professorship into a regular professorship, at which time Zeeman would become Director of the physics laboratory.
4. In the case that J.D. Van der Waals Jr. proved to be unavailable, the lecturer of mathematical physics from Groningen, L.S. Ornstein (1880-1941) would be considered.<sup>172</sup>



*J.D. van der Waals.*<sup>175</sup>

The Board of Governors were notified of this in the letter of 29 May 1908. Blooker, on behalf of the Board of Governors, contacted Korteweg

who wrote to him on 10 and 12 June 1908.<sup>174</sup> Korteweg among other matters explained that Van der Waals' school of thought could be divided into two parts:

1. Theoretical physics, which included general theoretical thermodynamics.
2. Applied or experimental thermodynamics. The latter also included Van der Waals' last great creation: the theory of mixtures. Kohnstamm was Van der Waals' right-hand man in this area and had the practical as well as the theoretical experience to continue Van der Waals' work.

Van Laar was mentioned in Korteweg's letter of 10 June 1908:

'v. Laar does not bring *relief*, but does bring improvement, because the chemists could have a more suitable course'.

At the meeting of 15 June 1908 Blooker mentioned his correspondence with Korteweg and it was decided to contact Bosscha to hear his views.<sup>176</sup> Information provided by Bosscha was available at the meeting on 6 July 1908. The Board of Governors did not immediately agree to the appointment of an Associate Professor of Thermodynamics. They would have liked to see the appointed professor charged with theoretical physics in its entirety and they would have liked to consult further with somebody.<sup>177</sup> In a secret letter of 7 July 1908 the Faculty was thus notified.<sup>178</sup> In July Van der Waals Sr. visited the Burgomaster, (also Chairman of the Board of Governors) and he wrote to him on 15 July 1908.<sup>179</sup> In this letter he explained that thermodynamics was an experimental subject and that:

'Not to teach that subject would be a significant diminution of our University, not only for students of mathematics and physics but mainly for students of chemistry, who would have to miss the basis for further specialist studies'.

At the meeting of the Board of Governors on 30 July 1908 the proposal of the Faculty meeting was accepted and on 3 August 1908 sent to the Council, with a copy to the Faculty.<sup>180,181</sup> At the City Council meeting of 1 September 1908 the proposal was accepted by 23 votes, with one in favour of Van Laar.<sup>182</sup> It is curious that without Van Laar's name having been mentioned there was one vote in favour of him. Kohnstamm was appointed Associate Professor of Physics and charged with teaching applied thermodynamics. In the letter of recommendation from the Faculty it is clearly stated that the latter also included the tuition of chemists.<sup>183</sup>



In 1908 the continuation of Van der Waals' school of thought nearly became a reality: Van Laar was lecturer of mathematics, and chemical thermodynamics fell to Professor of Physics Kohnstamm.

After nomination in the Council Van der Waals Sr. was granted honourable discharge on 16 September 1908.<sup>184</sup>

## 8. End of Van Laar's lectureship

In 1909 Van Laar was forced to separate from his wife. His wife moved to Amsterdam with his youngest daughter and Van Laar moved to Haarlem.<sup>185</sup> In 1910 the City of Amsterdam reminded Van Laar that a municipal official was expected to live in Amsterdam.<sup>186</sup> He informed the Burgomaster and aldermen that his 'unstable state of health, especially as far as my nervous condition is concerned' did not allow that.<sup>187</sup> Van Laar was granted a dispensation.<sup>188</sup> In the same year he became a member of the scientific society 'De Hollandsche Maatschappij der Wetenschappen' in Haarlem.<sup>189</sup>

Due to the fact that his subject was not acknowledged by the Faculty, Van Laar entered a state of mental exhaustion and complete despondency in 1910.<sup>190</sup>

On 9 June 1910 he requested that the Council improve his position by raising his salary and by appointing him Associate Professor of Mathematical Chemistry.<sup>191</sup> The Council requested a report and advice from the Board of Governors on 13 June 1910.<sup>192</sup> On 17 June 1910 the letter was discussed at the meeting of the Board of Governors and it was decided to ask the Faculty for advice. A letter was sent on 22 June 1910 and the matter was considered at a Faculty meeting on 7 July 1910.<sup>193,194,195</sup> A prolonged debate ensued in which the most important points were discussed. The advice on the requested raise of salary was negative because his salary was no lower than that of others. The advice on the appointment of associate professor was also negative, because the proposal should have come from the Faculty and because it would have meant that next to Kohnstamm there would have been a second professor teaching practically the same subject.<sup>196</sup> The letter was ready on 9 July 1910, but Holleman forgot to send it.<sup>197</sup> About Van Laar's scientific merits the Faculty remarked:

'(...) that it is true that his many writings have achieved some fame, but that this fame does, in our opinion, not include great admiration,

neither here in our country nor abroad'.<sup>198</sup>

Holleman sent the letter on 19 July 1910.<sup>199</sup> The Faculty's advice was discussed at the meeting of the Board of Governors on 12 September 1910.<sup>200</sup> According to Blooker's advice it was decided to inform the Burgomaster and aldermen that there was no need for a chair of mathematical chemistry and that Van Laar's salary was not regarded as too low.<sup>201</sup> On 16 October Van Laar informed Blooker that he had not received an answer to his request of 9 June 1910 and that, on the advice of Lorentz and Bosscha, he had requested a three month medical leave because of mental exhaustion. He did not know what his position was.<sup>202</sup>

He indeed requested a three month medical leave on 10 October 1910 and he was allowed to take it.<sup>203,204</sup> A City Council decision of 1 November informed him that there were no reasons for the requested improvement of his salary.<sup>205</sup> However his medical condition had in the meantime deteriorated so much that he had had to consult specialists on nervous and mental disorders.<sup>206</sup> On 22 December 1910 he requested a continuation of his leave until 1 October 1911, which he was granted on 11 January 1911.<sup>207,208</sup> On 9 March 1911 Van Laar left to recuperate in Switzerland.<sup>209</sup>

On 15 September 1911 he wrote to the Burgomaster and aldermen and gave them a metaphorical choice. He requested that the Council either improve his position financially or discharge him for reasons of health.<sup>210</sup> His letter was discussed at the meeting of the Board of Governors on 16 October 1911.<sup>211</sup> The minutes show that Blooker once again asked for Lorentz's advice. He is said to have said:

'No doubt Van Laar is a very clever man but he is inclined to overestimate his own abilities'.<sup>212</sup>

It was decided to inform the Burgomaster and aldermen that Van Laar's letter did not give grounds for any such remarks.<sup>213</sup> This was written to the Burgomaster and aldermen on 27 October 1911.<sup>214</sup> His request was denied on 1 November 1911 in the following words:

'Herewith we have the honour of informing you that your letter dd. 15 September last, does not provide us with any reasons to retract our decision, of which you were informed in our letter dd. 1 November 1910, no. 15964/4161. 0'.<sup>215</sup>

November 1911 for an honourable discharge on medical grounds, with claims to pension, preferably as from 1 January 1912.<sup>216</sup>

Totally unexpectedly, Smits informed Van Laar that he was trying to obtain Dfl. 1,000.- for lectures on electrochemistry which were to be given by Van Laar.<sup>217</sup> At this, on 16 November 1911 Van Laar asked the City Council to cancel his request for the honourable discharge of 6 November 1911 and requested instead a continuation of leave until 1 January 1912.<sup>218</sup> Van Laar's request for discharge and Smits' request for the electrochemistry lectures to be given by Van Laar were discussed at the meeting of the Board of Governors on 8 January 1912.<sup>219</sup> Blooker informed the meeting that he had written to Van Laar and had used harsh words and he ended his letter stating that as of this moment he would do nothing more for Van Laar. Blooker had seriously started to doubt Van Laar's reliability and felt less inclined to trust Van Laar's words against Van der Waals Sr. and Jr., Kohnstamm and Smits. Smits in the meantime had explained his request to the Chairman. It was denied because the impression had arisen that there were some professors who would not like to see Van Laar leave because his tuition of mathematics was facilitating their own work. It was decided to advise the Council negatively on the request for resignation and negatively on the proposal by Smits.

It is to be noted that Van Laar on his side had started to doubt Blooker's sincerity, because in his letter to Lorentz of 19 December 1911 he wrote:

'So it is true, what my friends used to write about the total unreliability of Blooker'.<sup>220</sup>

Remarkable also is the surprise Smits voiced in his letter to the Burgomaster and/or aldermen of education of 28 December 1911:

'What caused Mr. Blooker to suddenly change his position towards Van Laar is totally beyond me'.<sup>221</sup>

The second and final letter of resignation of 10 December in which the first letter of 6 November 1911 served as explanation, consisted of an elaborate motivation with three annexes. It shows that Van Laar discussed his position with Blooker in 1907, but that Blooker wanted to postpone improving his position until Van der Waals had left, so that 'Van der Waals would not be hurt'. Two professors who died in 1911, Bosscha and J. M. van Bemmelen (1830-1911), probably knew about this for Van Laar wrote:

'Often caring Faculty members advised me cordially to 'reconcile myself to the situation'. They did not want to hurt the professor in question, who had already threatened to resign if he could not have his way, or so they said. Everything would work out when this professor had resigned.... (How well they meant, will become clear later) A recently deceased famous professor of an advanced age could never hold back his indignation when this honourable motive 'not to hurt' was mentioned. Should a life, a career be offered to that? *Let* him feel some sorrow; he fully deserves it! Let him resign. And he could be all aflame, when there was someone else who could, *against all evidence* (he stressed these words) *still* believe in the Professor's honourable intentions. Another no less famous professor, also recently deceased at an advanced age, said the following: "The way in which said Professor has treated Mr. Van Laar is an unwashable stain on his character".<sup>222</sup>

Information about Blooker's views are to be found in a letter from Van Laar to Lorentz:

'But, you will ask, what was in Blooker's letter? It said:

1. That my illness was of a suspect nature, including some hateful remarks on the subject.
2. That I had profited long enough of the 'generosity' of Amsterdam (by leave) which required nothing in return! (Imagine, what rudeness, just *because* I no longer wanted to profit of that generosity any longer after one year, I wanted to *resign* on 1 October. As if there were not many others who have had leave because of illness. In (unreadable) Houwing, more than a year, I even believe two years and he received more than Dfl. 6,000.-! And my friend, Van Deventer, who has already been on leave for three years with 2/3 times Dfl. 10,800.- = Dfl.7,200.- salary of leave. So what rudeness, these assertions by Blooker!)
3. That he had seen you and that I had not taken your advice (his inspiration?) with some spiteful remarks about the form of my petition. But further on he says: 'Have I *provided you* a lectureship of Dfl. 2,000.- at the time, I cannot go any further now'.<sup>223</sup>

After receiving Blooker's letter, Van Laar definitely offered his resignation for medical reasons, which he was granted on 1 April 1912.<sup>224,225</sup>

## 9. Appointment of Wind's successor

At the end of Van Laar's lectureship, he was approached for the vacancy which arose because of the death of the Professor of Physics from Utrecht C.H. Wind (1867-1911), who died 7 August 1911. In filling this vacancy, the efforts of W.H. Julius (1860-1925), Professor of Experimental Physics, were crucially important. After A. Einstein (1879-1955) had been offered the position but had declined it, P. Debye (1884-1966), W.A. Keesom (1876-1956) and Van Laar were mentioned.<sup>226</sup> Van Laar, who for health reasons lived in Clarence, demurred:

'Confidentially, I inform you that I indeed had the chance in Utrecht, next to two other persons (well-known to you), which I of course knew because I was approached for the acceptance of the professorship, which I accepted after much struggle, for I felt I was not up to the full task. How the matter would have been resolved, or will be resolved, I do not know'.<sup>227</sup>

Debye was appointed. From the correspondence on Einstein's vacancy the assessment of Van Laar was saved:

'Van Laar beherrscht die Gibbs-Planck'schen thermodynamischen Theorien vorzüglich und ist unbedingt ideenreich. Aber die physikalischen Früchte seiner vielen Denkarbeit sind eigentlich doch ziemlich mager. Es fehlt ihm nach meiner Meinung der unmittelbare Blick für das Reale; er sieht absolut nur durch die Brille der klassischen Thermodynamik. Auch ist seine Art und Weise zu argumentieren nicht immer einwandfrei. (...) Intressensphäre eine gar zu eng begrenzte (...). Aus diesen Gründen würde ich diesen übrigens klar denkenden und scharfsinnigen Mann nicht zum Lehrer der theoretischen Physik an einer Universität machen'.<sup>228</sup>

When Debye was appointed Professor in Göttingen in 1914 a new vacancy arose and he also gave his opinion on Van Laar on that occasion:

'In deinem Brief sagst Du nichts von van Laar. Ich könnte es zwar nicht verantworten mich für ihn intensiv zu verwenden. wo es sich von die Besetzung einer Professor für das ganze Gebiet der theoretischen Physik handelt. Trotzdem bedenke ich dass er Gutes geleistet hat und tut es mir sehr Leid seines Nahmen ganz vergessen zu sehen'.<sup>229</sup>

On 12 April 1912, Van Laar's first wife died of tuberculosis and he returned to the Netherlands.<sup>230,231</sup> For a short time he lived in Baarn, where Maartje Schagen (1864-1934) kept house for him. Two years later, in 1914, in Amsterdam, she became his second wife.<sup>232</sup>

## 10. Doctor Honoris Causa

In 1914 the University of Groningen awarded a number of honorary degrees to mark the tricentenary of its founding. The minutes of 24 January 1914 of the Faculty of Mathematics and Physics show that Van Laar's name did not occur on the original list of those to be awarded honorary degrees. Jaeger nominated Van Laar at the meeting of 5 February 1914.

'A lengthy discussion arises on the nomination made by Jaeger of a candidate from our country, J.J. van Laar to (crossed out, v.E). The decision is reserved to give Mr. Haga the opportunity to inquire in writing of Prof. Lorentz'.<sup>233</sup>

And the minutes of 10 February 1914:

'Mr. Haga reads the letter by Prof. Lorentz on the scientific merits of Mr. J.J. Van Laar. As a result of this, it is decided to nominate Mr. Van Laar for an honorary degree'.<sup>234</sup>

On 1 July 1914 Van Laar was promoted to Doctor Honoris Causa. Queen Wilhelmina and Prince Consort Hendrik attended the graduation ceremony in the 'Nieuwe Kerk' in Groningen. In the letter Van Laar addressed to the Rector Magnificus and the Senate, and also in the letter to the Faculty of Natural Sciences both of which were written following the invitation to come to Groningen, he regarded the promotion as a ray of light in his life and the first official recognition....<sup>235,236</sup> In the letter of 13 June 1914 to the editor of 'Chemisch Weekblad', W.P. Jorissen (1869-1959), Van Laar proved to be very pleased with his promotion:

'I would wish that, they, too had been lacking something, so that I could congratulate them on obtaining it! Lorentz and others are also very pleased; I also received a very kind letter from Kruyt, in which he even spoke of divine justice!'<sup>237</sup>

### 13. Concluding Remarks

The preceding pages show that Van Laar, because of his guardians' decision to force him to become a marine cadet, did not follow a normal pattern of education. When he was just twenty years old he was forced to make an important decision on whether to resign from the navy. At this age a serious decision such as this could have caused a rift within his family. Without sufficient preparatory education he studied at the University of Amsterdam, under Professors Van 't Hoff and Van der Waals in particular. The social value of his education was meagre and because of not possessing a doctoral degree and with that the impossibility of being allowed promotion, his scientific career would be hampered. It is curious that, as far as is known, Van Laar in his student years in Amsterdam never contacted the Director of a H.B.S. (secondary school) or the Rector of a gymnasium to investigate the possibilities of obtaining certificates to allow him to take university exams after all. Time and again he was put to the test and only with great difficulty found academic recognition. His life's ambition was to obtain a professorship.

Although he studied with passion, article 89 of the Act of Secondary Education of 1863 determined his occupation: a teacher of mathematics. It may be assumed that Van Laar knew this when he started his studies.

Consequently Van Laar begins to appear as a man of principles, enterprising, self-willed, nervous and often mistrustful and somewhat hasty. His nervousness was especially marked when there were tensions, for example changes of job and opposition in his scientific career. In 1910 he voiced his nervousness as follows: 'unstable condition of health, especially as far as my nervous condition is concerned'. He was often short tempered and his haste caused many people to turn away from him. His exaggerated concern during his Swiss period about the non-arrival of his post was characteristic.

According to H.R. Kruyt (1882-1959), Van Laar was a very lively person of great talent. He was of a cheerful, humorous disposition, but at times rather naive. The many disillusionments in his life made him nervous and mistrustful.<sup>238</sup> According to Cohen, many of his friends broke off relations as a result of this irritability, which often went hand in hand with fierce outbursts of fury. Cohen called him a sharp and enthusiastic researcher.<sup>239</sup> Letters to Lorentz show that Van Laar was for years unable to find peace with his own development.

In 1898 he was appointed unsalaried lecturer of mathematical chemistry in Amsterdam and he was an enthusiastic teacher. After some years in Amsterdam Bakhuis Roozeboom recognized his qualities but curiously these were denied by Van der Waals who openly opposed him. Van der Waals' influence at the Faculty in Amsterdam was strong. When Bakhuis Roozeboom, together with Holleman, pleaded for a lectureship in mathematical chemistry for Van Laar in 1906, Bakhuis Roozeboom was forced to retract the proposal because it should have come from Van der Waals, because the subjects which he taught were involved.

In 1902 Van der Waals turned sixty-five and the minutes of the Faculty show that from 1902 until he left in 1908 he occupied himself with the succession of his professorship. He tried to maintain the characteristics, merits and traditions which had arisen during his period in office. An active policy with clearly defined aims is not discernable, but Van der Waals kept guard over the theory of phase equilibria as a subject of study at the University of Amsterdam when the vacancy created by Bakhuis Roozeboom's death occurred. Van Laar filled in for of Bakhuis Roozeboom's lectures but it was due to Van der Waals' pressure that Smits finally became Professor of Inorganic and Physical Chemistry. German candidates were thus passed over. Especially after the death of Bakhuis Roozeboom in 1907, Van Laar's merits were judged very divergently, possibly because the Faculty was strongly influenced by Van der Waals.

1. When Van Laar gave the lectures of Bakhuis Roozeboom the faculty's opinion (letter by Holleman of 20 February 1907) was extremely positive. Later when his lectureship was discussed it was not. (Letter of the Faculty to the Board of Governors of 24 October 1907).
2. In Van der Waals' view Van Laar was not able enough. However Lorentz thought he was a bright and assertive man who suffered from overestimating his own capabilities. In 1914 Lorentz, in his advice on the honorary degrees which were to be awarded in Groningen, was very positive about his scientific achievements. Einstein believed him to be a 'scharfsinniger Mann'. Debye would have been sorry if he had been completely forgotten. It was clear that Van der Waals' and the Faculty's assessment was wrong.
3. Van Laar was a chemist, and could not be appointed lecturer of mathematical chemistry, of which chemical thermodynamics was a part in Amsterdam. This post traditionally had to be filled by a physicist. In Utrecht he was nominated with others to fill Wind's position; a



situation diametrically opposed to that in Amsterdam.

Closer analysis shows that opposition and contradictions in Amsterdam stem from Van der Waals' policy, and in Van Laar's opinion were caused by feelings of envy. Van der Waals felt threatened because Van Laar was working in the same field. Van der Waals' succession was arranged according to his own wishes. Van der Waals' son, J.D. van der Waals Jr. succeeded him and Kohnstamm then taught thermodynamics for chemists as well as for physicists. Van der Waals personally saw to this and Van Laar did not have a chance. Creating a limited lectureship of mathematics for chemists for Van Laar was also part of the tradition of the Faculty and defended by Van der Waals (chemical thermodynamics is a part of physics).

It may be said that Van Laar's introduction of mathematical chemistry in Amsterdam was way ahead of its time. This later had great significance for the theory of phases. At the expense of his scientific career he smoothed the way for chemical thermodynamics to become part of the chemical discipline. This situation continued until Kohnstamm left Amsterdam in 1927, when, although with some opposition by Van der Waals Jr., a place was created for chemical thermodynamics beside the lectures in thermodynamics by the lecturer and physicist A.M.J.F. Michels (1889-1969). From that moment onwards thermodynamics was taught by the chemist J.M. Bijvoet (1892-1980). It was no longer a point of discussion as long as the adjective 'chemical' was retained.

Scheffer's remark in the introduction to his book: 'Toepassingen van de Thermodynamica op Chemische processen,' Delft, Waltman (1945) also refers to this:

'It was therefore natural that elementary tuition of thermodynamics is certainly best taken care of in the hands of physicists (while) the application of this subject is in good hands with the chemists'.<sup>240</sup>

## References

1. J.J. van Laar (1818-1873) was in the Royal Armed Forces from 1834 until 1870. In 1838 he was appointed veterinary surgeon, third class, in 1846 second class and in 1857 first class. He received four golden clasps for honourable and protracted effective service as officer in the Netherlands Armed forces. (List of name and rank of officers in the Royal Netherlands Army and the army of the Netherlands Indies 1838-1871, ARAG).
2. Register of Residents Zierikzee (Streekarchivaat Schouwen-Duiveland and Sint Philipsland in Zierikzee).
3. W.P. Jorissen, Dr.J.J. van Laar, 11 Juli 1860-11 Juli 1920, *Chemisch Weekblad* 17 (1920) 362-367.
4. Register of Residents Haarlem (GAH).
5. *Ibid.*, 3.
6. Information (GAH).
7. Letter F. van Eeden to L. van Deyssel of 16 August 1895, included in 'De Briefwisseling tussen Frederik van Eeden en Lodewijk van Deyssel', by H.W. van Tricht and H.G.M. Prick, The Hague: Nijhoff (1981) p.283: 'Did I so much belittle Van Laar at the time? He makes me feel forced, when I talk to him, that is all. Once when we were schoolboys I punched him in the stomach, the results of which were probably longer painful for my conscience than for his stomach'.
8. *Ibid.*, 3.
9. O.H. Dijkstra, Willem Martinus Logeman, *Jaarboek Haarlem 1974*, Haarlem: Schuyt & Co (1975) 139-159.
10. J.J. van Laar, *De Dwaalwegen der Wetenschap*, *Chemisch Weekblad* 24 (1927) 302-311, p.310.
11. *Ibid.*, W.F. Koppeschaar, *Leerboek der Chemie en van Eenige Harer Toepassingen*, Three volumes, Leiden: Sijthoff (1877).
12. Testament J.J. van Laar (1818-1873), 5 March 1873 (GAH); *Ibid.*, 3 and information: Archives Royal Household, The Hague.
13. Photograph GAH.
14. Resolution 31 March 1881, No. 26 (Archives Department of Naval Affairs 2.12.01, Nr.2537, ARAG).
15. Record of Service No.715 J.J. van Laar (Register Officers, Archives Department of Naval Affairs 2.12.06, No.8, ARAG).
16. M.J.C. Klaassen, *Adelborstopleiding te Delft-Medemblik-Breda*, Koninklijke Marine (1979) 145.
17. *Jaarboek van de Koninklijke Nederlandsche Zeemacht 1879-1880*, 's-Gravenhage: Van Cleef (1881) 217-234.
18. *Ibid.*, 15.
19. *Ibid.*, 17, p.289-297.
20. A.J. Vermeulen, *De Schepen van de Koninklijke Marine en die der Gouvernementsmarine 1814-1962*, *Uitgave van de Koninklijke Marine* (1962) 60.
21. *Jaarboek van de Koninklijke Nederlandsche Zeemacht 1880-1881*, 's-Gravenhage: Van

- Cleef (1881) 295-312.
22. J.J. van Laar, Prof.J.H. van 't Hoff, *Amsterdammer, Weekblad voor Nederland*, 5 March 1911, p.6.
  23. *Ibid.*, 21, p.299.
  24. *Ibid.*, 21, p.311.
  25. *Ibid.*, 15.
  26. *Ibid.*, 3.
  27. Photograph (MMH).
  28. *Ibid.*, 15.
  29. *Ibid.*, 15.
  30. On 20 September 1881 Van Laar was registered at the Binnen Amstelstraat 182 in Amsterdam (Register of Residents, GAA).
  31. Petition to the City Council of Amsterdam of 15 September 1911: 'That, had he at the time not left the Royal Navy to complete his studies of his favourite subjects of mathematical physics and theoretical chemistry at the University in Amsterdam, to serve science, for which he felt the calling - (...)' (ASAO.5191, No.657, GAA).
  32. J.J. van Laar, *Enige Herinneringen aan Ch.M. van Deventer*, *Chemisch Weekblad* 28 (1931) 547-550.
  33. Letter F. van Eeden to L. van Deyssel, 14 April 1890, included in H.W. van Tricht en H.G.M. Prick, *De Briefwisseling tussen Frederik van Eeden en Lodewijk van Deyssel*, The Hague: Nijhoff (1981) p.67.
  34. Letter L. van Deyssel to F. van Eeden, 27 July 1890, included in H.W. van Tricht en H.G.M. Prick, *De Briefwisseling tussen Frederik van Eeden en Lodewijk van Deyssel*, The Hague: Nijhoff (1981) 74.
  35. Lodewijk van Deyssel, *Gedenkschriften*, Uitgegeven door H.G.M. Prick. Zwolle: Tjeenk Willink (1962) 397.
  36. *Ibid.*, 32, 547.
  37. *Ibid.*, 32, 547.
  38. *Ibid.*, 32, 549.
  39. J.J. van Laar, *Het bestaansrecht der theoretische en toegepaste thermodynamica naast de moderne atoomtheorie*, *Chemisch Weekblad* 35 (1938) 351-363, p.352.
  40. *Ibid.*
  41. Letter J.J. van Laar to H.A. Lorentz, 6 May 1901 (AL. 2.21.203, No.45, ARAG).
  42. J.D. van der Waals, *Over de Moeilijkheden, welke waren te Overwinnen bij het Opstellen van de Toestandsvergelijking*, *Chemisch Weekblad* 8 (1911) 69-82.
  43. His name does not occur in the book of exams of the Faculty of the University of Amsterdam (AF.1020, No.611, 612).
  44. Van Laar's first letter of resignation to Burgomaster and aldermen of 6 November 1911 (ASAO.5191, No.657).
  45. Article 89 of the Law on secondary education of 1863:  
 'They who, though not possessing a certificate of engineer, who serve or served the country in that position, are, under the conditions stated art.82 below, qualified to

teach technical sciences, of which the knowledge to fill the post of engineer is required. Under the same conditions those, who have completed a training of engineer and officer of land- and sea forces at a state institution are authorized to teach technical sciences, which they have been taught during that course'. In Utrecht as well as in Middelburg the column 'qualification' of the yearly report of the 'Staats Hogere Burgerschool' of Van Laar is filled in with 'Art.89'.

46. Letter L. van Deyszel to F. van Eeden, 17 April 1890, included in H.W. van Tricht and H.G.M. Prick, 'De Briefwisseling tussen Frederik van Eeden en Lodewijk van Deyszel'. The Hague: Nijhoff (1981) p.68: 'Yes, good old Van Laar came to see me, he started by telling me that he was rather skinned, because up to now he had only earned Dfl. 1,600.- and Dfl. 400.- in extra earnings, that this year it should have been Dfl.2,000.- and Dfl. 400.- for the first time. It was also funny to hear, because he did nothing else but repeat, verbatim, what he had read in the last five volumes of the N.G.. One cannot be more of an N.G.-man. During the walk we took together, he walked next to me, thin, high and meagre, shivering like an old poodle, who had just stepped out of the 'Nieuwe Gids', and constantly marking N.Gids quotations by exclamation marks of his admiring chatter while laughing enthusiastically. He was very taken with my son. I would be myself, if the possession of such a child in my position had not been comparable to a heavy sack of gold round the neck of a drowning man'.
47. Photograph (GAM).
48. Ibid.
49. Photograph (Mrs.E.W. van Laar, Amsterdam).
50. Information Register of Residents Meppel.
51. Herman Dignus van Laar 10 juli 1889 - 27 September 1892, funeral card (Archive L. van Deyszel, H.G.M. Prick Maastricht).
52. K.A.P. Reijnders, Couperus bij van Deyszel, Dissertation, Amsterdam: Athenaeum-Polak & Van Genneep (1968) 106-107.
53. Ibid., 48.
54. In a letter of J.J. van Laar to W. Kloos, 8 May 1886, 'Please, do me a favour, and let me soon hear from you. I am so lonely here in Middelburg. There is no one to speak with. I would so much like to be in Amsterdam so that I could discuss everything together with your lot...'(Archive De Nieuwe Gids 69E2 KB and published in G.H. 's-Gravensande, De Geschiedenis van de Nieuwe Gids, Arnhem: van Lochem (1956) 88).
55. Letter J.J. van Laar to H.A. Lorentz, 18 August 1899: '(....) I add that it was you who at the time of the publication of my 'Thermodynamics' wrote so kindly to me, and that it was you who helped me to get away from Middelburg in 1895'. (AL.2.21.203, No.45 ARAG).
56. Letter J.J. van Laar to H.A. Lorentz, 28 August 1895: 'And now I would like to confer with you on the lectureship in Utrecht. Because I wanted to follow the path of calmness and modesty, and you will be able to inform me about how to go about it. Should I ask for admission as lecturer without cost to the state, or how is it done? Etc. My intention was this, that I start as lecturer without cost to the state with one lecture a week on

theoretical (mathematical chemistry, and that perhaps next year a state appointment could ensue which ensured me of for instance Dfl. 1,000.- a year, and for which I could, apart from the H.B.S. (secondary school) to which I would hold on, teach for a few hours a week. Thus, I would obtain an income of Dfl. 2,000.- + Dfl. 1,000.- = Dfl. 3,000.-, on which I could live with my wife and four children. Of course, the first year would be a financial disaster because of (temporarily) missing private tuition, but that would be all right if the future were good. And to that I fully trust. How is the collection of tuition fees arranged when one lectures without cost to the state's treasury?' (AL.2.21.203, No.45 ARAG).

57. Verslag van den toestand der Gemeente Utrecht in 1896 (Bibl.No. XXXIV E9 p.24, GAU).
58. Photograph (GAU).
59. Letter Director Dr.H.F. Jonkman of the Rijks H.B.S. in Utrecht, 5 December 1896, to the Superintendent Prof.Dr.W.B.J. van Eyk (Archive Rijks H.B.S. No.12, GAU).
60. Letter Minister of Home Affairs, 7 January 1897 (Archive Rijks H.B.S. No.42, GAU) and The Register of Residents of the City of Utrecht state 'teacher' as profession, added later is: retired Dfl 589,-' (GAU).
61. Letter J.J. van Laar to H.A. Lorentz, 10 July 1898 (AL.2.21.203, No.45, ARAG).
62. Faculty Minutes, 22 March 1899 (AF.1020, No.2, GAA).
63. J.J. van Laar, J.D. van der Waals, In: J. Kalff, *Mannen en Vrouwen van Betekenis in onze Dagen* (1900).
64. Letter J.J. van Laar to H.A. Lorentz, 18 August 1899 (AL.2.21.203, No.45, ARAG).
65. A.J. Kox, Johannes D. van der Waals (1837-1923), In: *Van Stevin tot Lorentz*, Amsterdam: Intermediair (1980) 153.
66. *Ibid.*, 63, p.87.
67. First letter of resignation: J.J. van Laar to City Council of Amsterdam, 6 November 1911 p.10 (ASAO 5191, No.657 GAA).
68. Postcard J.H. van 't Hoff to W. Ostwald, 5 July 1899, included in: *Aus dem Wissenschaftlichen Briefwechsel Wilhelm Ostwalds*. Berlin: Akademie-Verlag (1969).
69. Postcard W. Ostwald to J.H. van 't Hoff, 17 July 1899, Fragment included in: *Aus dem Wissenschaftlichen Briefwechsel Wilhelm Ostwalds*, Berlin: Akademie-Verlag (1969).
70. Photograph (Prof.Dr.G. Frens, T.U. Delft).
71. Photograph (DMM).
72. Printed statement by J.J. van Laar, which is included in a letter to H.A. Lorentz, 16 August 1899:

L.S.

The undersigned feels obliged to impart those papers, which he at the request of Prof. Ostwald, provided for 'Zeitschrift für Physikalische Chemie', especially since in 1899, they are continuously published very late. Papers about different dissertations by Wind, Lobry de Bruyn, Bremer, Meyers, de Visser, v. Everdingen, Haga, Zeeman, Julius, Hartman, Kramers, which were sent in by the undersigned on 13 February 1899, are

notwithstanding repeated and emphatic promises of publication, first after six weeks, then in the edition of May and then, (no later than) in the edition of June still not published today! A following series of papers, sent on 21 May about dissertations by Aronstein, Aberson, Spring, v.d. Waals, Verschaffelt, v.d. Lee, Kamerlingh Onnes, Schreinemakers, Cohen have not even been proofread! On regular objections to this when in the publication which was published on the first of July, the papers of 13 February (already proofread) were again not published, the undersigned was at first not answered at all, and after that only: Ich verzichte auf weitere Referate und weiteren Verkehr, W. Ostwald. Gladly leaving the assessment of such conduct and pertaining qualification to others, etc.(AL.2.21.203, No.45, ARAG).

73. Letter J.J. van Laar to H.A. Lorentz, 12 March 1901: 'After all, you are aware of the fact I have been teaching theoretical chemistry in Amsterdam for years, and also to candidates in chemistry in Utrecht since September 1901' (AL.2.21.203, No.45, ARAG).
74. Letter J.J. van Laar to H.A. Lorentz, 21 March 1901 (Archief Lorentz 2.21.203, No.45, ARAG).
75. Anonymous, J.J. van Laar, *Chemisch Weekblad* 7 (1910) 653 and F.E.C. Scheffer, Dr. J.J. van Laar 70 Jaar, *Ibid.* 27 (1930) 418-420.
76. Letter J.J. van Laar to H.A. Lorentz, 18 August 1899 (AL.2.21.203, No.45, ARAG).
77. Letter J.J. van Laar to H.A. Lorentz, 21 March 1901 (AL.2.21.203, No.45, ARAG).
78. Faculty Minutes, 27 September 1902 (AF.1020, No.3, GAA).
79. *Ibid.*, 67, p.4.
80. Letter H.W. Bakhuis Roozeboom to H.A. Lorentz, 2 December 1904 (AL.2.21.203, No.3, ARAG).
81. Photograph UMA.
82. Faculty Minutes, 23 October 1906 (AF.1020 No.3, GAA).
83. Letter J.J. van Laar to H.A. Lorentz, 2 January 1907 (AL. 2.21.203, No.45, ARAG).
84. W.P. Jorissen, en W.E. Ringer, H.W. Bakhuis Roozeboom, *Mannen en Vrouwen in onze Dagen*, Baarn: Hollandia (1907): 'A Researcher of which there are few, a magnificent teacher and outstanding tutor'.
85. J.J. van Laar, H.W. Bakhuis Roozeboom, *Een Afscheidswoord*, *Chemisch Weekblad* 4 (1907) 79-81.
86. Letter Mrs.Bakhuis Roozeboom to Board of Governors, 8 February 1907 (AC.279, No.38, GAA).
87. Letter from the Board of Governors to Faculty, 13 February 1907, No. 735 (AC.279, No.93, GAA).
88. Faculty Minutes, 18 February 1907 (AF.1020, No.4, GAA) and Undated letter (received on 5 March 1907) F.A.H. Schreinemakers to Faculty (AF.1020, No.196, GAA).
89. Photograph GAA.
90. Faculty Minutes, 6 March 1907 (AF.1020, No.4, GAA).
91. Minutes of the Board of Governors, 6 May 1907 (AC.279, No.4, GAA).
92. Minutes of the Board of Governors, 1 July 1907 (AC.279, No.4, GAA).

93. Photograph (Mrs.E.C. Bakhuis Roozeboom, Amsterdam).
93. Faculty Minutes, 18 March 1907 (AF.1020 No.4, GAA).
95. Letter Faculty to the Board of Governors, 20 March 1907 (ASAO.5191, No.5012 Hoger Onderwijs, 1907, GAA).
96. Adress: (ASAO.5191, No.5012 GAA).
97. Letter from the Board of Governors to Faculty, 22 May 1907, (AF.1020, No.196 GAA).
98. Faculty Minutes, 29 May 1907 (AF.1020, No.4, GAA).
99. Adress: (ASAO.5191, No.5012, GAA).
100. Faculty Minutes, 27 June 1907 (AF.1020, No.4, GAA).
101. Minutes of the Board of Governors, 3 June 1907 (AC.279, No.4, GAA).
102. Minutes of the Board of Governors, 1 July 1907 (AC.279, No.4, GAA).
103. Letter Secretary to the Board of Governors, 30 April 1907 (AC.279, No.93 GAA).
104. Ibid., 102.
105. Letter FA.H. Schreinemakers, 18 April 1907 (AC.279, No.39, GAA).
106. Letter from the Board of Governors to Faculty, 3 July 1907 (AF.1020, No.196, GAA).
107. Faculty Minutes, 9 July 1907 (AF.1020, No.4, GAA).
108. Ibid.
109. Faculty Minutes, 31 July 1907 (AF.1020, No.4, GAA).
110. Ibid.
111. Letter Faculty to Board of Governors, 31 July 1907 (Copy in AF.1020, No.196, GAA).
112. Minutes of the Board of Governors, 1 August 1907 (AC.279, No.4, GAA).
113. Minutes of the Board of Governors, 2 September 1907 (AC.279, No.4, GAA).
114. Letter from the Board of Governors to City Council, 6 September 1907, (ASAO.5191 No.5012, Hoger Onderwijs 1907, GAA).
115. Ibid., 113.
116. Gemeenteblad van Amsterdam Afdeling II, p.1005 (GAA).
117. Extract of book of Resolutions No.15769 A, 17 December 1907 (ASAO.5191 GAA)
118. H. Gerding, Professor Dr.A. Smits, 14 Juni 1870 - 14 Juni 1940, Chemisch Weekblad 37 (1940) 430-436.
119. Chemisch Weekblad 3 (1906) 582-583.
120. Amsterdamsche Courant, 16 November 1896.
121. Gabriël Gorris, Dorp aan de Vliet, Scheveningen: Watez (1961).
122. Letter J.J. van Laar to H.A. Lorentz, 19 December 1911:'(...) At the time Blooker verbally accused me of not, in the interest of my career, putting myself more to the fore (...)'. (AL.2.21.203, No.45 ARAG)
123. Portrait: Ibid., 120.
124. This probably concerns documents pertaining to the second or third part of: 'Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre', the second part was completed by A.H. Aten and E.H. Buchner in 1918, the third part was completed by EA.H. Schreinemakers in 1911 and 1913.
125. Letter A. Smits to A.F. Holleman, 26 February 1907 (AF.1020, No.196, GAA)
126. Letter A.F. Holleman to Burgomaster and aldermen, 20 February 1907 (ASAO.5191,

No.35, GAA).

127. Letter C.F.J. Blocker to A.F. Holleman, 6 March 1907 (AF.1020, No.196, GAA).
128. Letter C.F.J. Blocker to A.F. Holleman, 10 March 1907 (AF.1020, No.196, GAA).
129. Copy of letter: A.F. Holleman to C.F.J. Blocker, 11 March 1907 (AF.1020, No.196, GAA)
130. Letter J.J. van Laar to City Council, 13 June 1907 (ASAO.5191, No.35, GAA).
131. Extract of book of Resolutions, No.3967/814 O (ASAO.5191, No.35, GAA).
132. Adress (AC.279, No.40, GAA)
133. Adress (AC.278, No.48, GAA).
134. Adress (Copy by first letter of resignation: J.J. van Laar to City Council of Amsterdam of 6 November 1911 (ASAO.5191, No.657, GAA).
135. Minutes of the Board of Governors, 3 April 1907 (AC.279 No.4, GAA)
136. Letter from the Board of Governors to Faculty, 25 March 1907 (AF.1020, No.196, GAA).
137. Faculty Minutes, 17 April 1907 (AF.1020, No.4, GAA).
138. Letter Faculty to Board of Governors, 18 April 1907 (AC.279, No.39, GAA).
139. Minutes of the Board of Governors, 6 May 1907 (AC.279, No.4, GAA).
140. Letter J.J. van Laar to Holleman, 19 August 1907 (AF.1020, No.196, GAA).
141. Letter H.A. Lorentz to A.F. Holleman 23 August 1907 (AF.1020, No.196, GAA).
142. Copy of letter: A.F. Holleman to H.A. Lorentz, 24 August 1907 (AF.1020, No.196, GAA).
143. Letter H.A. Lorentz to A.F. Holleman, 26 August 1907 (AF.1020, No.196, GAA).
144. Photograph (MBL)
145. Letter J.J. van Laar to H.A. Lorentz, 27 August 1907 (AL. 2.21.203, No.45 ARAG).
146. Letter H.A. Lorentz to A.F. Holleman, 28 August 1907 (AF.1020, No.196, GAA).
147. Letter Secretary to A.F. Holleman, 10 August 1907 (AF.1020, No.196, GAA).
148. Letter A. Smits to A.F. Holleman, 2 September 1907 (AF.1020, No.196, GAA).
149. Minute: A.F. Holleman to A. Smits, 2 September 1907 (AF.1020, No.196, GAA).
150. Letter A. Smits to A.F. Holleman, 30 August 1907 (AF.1020, No.196, GAA).
151. Ibid.
152. Letter from the Board of Governors to Faculty, 18 October 1907 (AF.1020, No.196, GAA).
153. Faculty Minutes, 23 October 1907 (AF.1020, No.4, GAA).
154. Letter Faculty to Board of Governors, 24 October 1907 (AC.279, No. GAA)
155. Minutes of the Board of Governors, 4 November 1907 (AC.279, No.4, GAA).
156. Minutes of the Board of Governors, 6 January 1908 (AC.279, No.4, GAA).
157. Ibid.
158. Letter from the Board of Governors to Faculty, 7 January 1908 (AF.1020, No.196 GAA)
159. Faculty Minutes, 22 January 1908 (AF.1020, No.4, GAA).
160. Faculty Minutes, 11 March 1908 (AF.1020, No.4, GAA).
161. Letter Faculty to the Board of Governors, 11 March 1908 (AC.279, No.49, GAA).
162. Minutes of the Board of Governors, 6 April 1908 (AC.279, No.4, GAA).



163. Minutes of the Board of Governors, 4 May 1908 (AC.279, No.4, GAA).
164. Letter D.J. Korteweg to the Board of Governors, 11 May 1908 (AC.279, No.49, GAA).
165. Recommendation No.665, Appointment of a lecturer of mathematics to the University of the City, Gemeentebld I 1908 p.440 (GAA).
166. Minutes of closed meeting of the City Council of 10 June 1918 (City Council 5079, No.286, GAA).
167. Extract of the book of Resolutions: No. 3593 O, 19 June 1908 (GAA).
168. Photograph (GAA).
169. Letter J.J. van Laar to H.A. Lorentz, 15 June 1908 (AL. 2.21.203, No.45, ARAG).
170. E.P. van Emmerik, Het laboratorium voor Van der Waals, Laboratoriumpraktijk (1988) 278-282.
171. Minutes of the Board of Governors, 6 April 1908 (AC.279, No.4 GAA).
172. Faculty Minutes, 27 May 1908 (AF.1020, No.4, GAA).
173. Letter Faculty to the Board of Governors van 29 May 1908 (AC.279, No.41, GAA).
174. Two letters D.J. Korteweg to C.F.J. Blooker, 10 and 12 June 1908 (AC.279, No.41, GAA).
175. Photograph (Van der Waals-Laboratory of Amsterdam)
176. Minutes of the Board of Governors, 15 June 1908 (AC.279, No.4, GAA).
177. Minutes of the Board of Governors, 6 July 1908 (AC.279, No.4, GAA).
178. Letter from the Board of Governors to Faculty, 7 July 1908 (AF.1020, No.196 GAA).
179. Letter J.D. van der Waals to the Mayor, 15 July 1908 (AC.279, No.41, GAA).
180. Minutes of the Board of Governors, 30 July 1908 (AC.279, No.4, GAA).
181. Copy of letter of Board of Governors to City Council, 3 August 1908 (AF.1020, No.196, GAA).
182. Gemeentebld II p.708 en 709 (GAA).
183. Ibid., 182: 'And such an interruption of tuition would, also in the interest of education of chemistry, be particularly deplorable because especially in the field of thermodynamics, the research of the resigning Van der Waals Sr. has shown a new direction in physics and has created a characteristic school of physicists in Amsterdam'.
184. Letter City Council to the Board of Governors, 8 May 1908 Laboratoriumpraktijk, (1988) 278.
185. Letter J.J. van Laar to H.A. Lorentz, 3 July 1910. (AL.2.21.203, No.45 ARAG).
186. Minutes of a letter of Burgomaster and aldermen, 2 July 1910, (ASAO.5191, No.2864, GAA).
187. Letter J.J. van Laar to Burgomaster and aldermen, 2 July 1910 (ASAO.5191, No.2864, GAA).
188. Extract of the book of Resolutions: No.11146 21 July 1910 (ASAO.5191, No.2864 GAA).
189. J.A. Bierens de Haan, De Hollandsche Maatschappij der Wetenschappen 1752-1952, Haarlem: (1952).
190. Letter J.J. van Laar to Burgomaster and aldermen, 10 October 1910 (ASAO.5191, No.657, GAA)

191. Request Van Laar to Burgomaster and aldermen, 9 June 1910 (ASAO.5191, No.657 GAA).
192. Letter Burgomaster and aldermen to Board of Governors, 13 June 1910, (AC.279 No.46, GAA).
193. Minutes of the Board of Governors, 17 June 1910 (AC.279, No.4, GAA).
194. Letter from the Board of Governors to Faculty, 22 June 1910 (AF.1020, No.196, GAA).
195. Faculty Minutes, 7 July 1910 (AF.1020, No.4, GAA).
196. Ibid.
197. Postcard A.F. Holleman from Doorn, to Board of Governors, 13 July 1910 (AC.279, No.46, GAA).
198. Copy of letter from the Faculty to the Board of Governors, 9 July 1910 (AF.1020, No.196, GAA).
199. Letter A.F. Holleman to Board of Governors, 19 July 1910 (AC.279, No.46, GAA).
200. Minutes of the Board of Governors, 12 September 1910 (AC.279, No.4, GAA).
201. Ibid.
202. Postcard J.J. van Laar to C.F.J. Blooker, 16 October 1910 (AC.279, No.46, GAA).
203. Ibid., 187.
204. Letter Burgomaster and aldermen to J.J. van Laar, 19 October 1910 (ASAO.5191, No.657, GAA).
205. Letter Burgomaster and aldermen to J.J. van Laar, 1 November 1910 (ASAO.5191, No.657, GAA).
206. Letter J.J. van Laar to de Burgomaster and aldermen, 22 December 1910 (ASAO.5191, No.657, GAA).
207. Ibid.
208. Letter Burgomaster and aldermen to J.J. van Laar, 6 January 1911 (ASAO.5191, No.657, GAA).
209. J.J. van Laar is deleted from Register of Residents of Haarlem (GAH).
210. Letter J.J. van Laar to Burgomaster and aldermen, 15 September 1911 (ASAO.5191, No.657, GAA).
211. Minutes of the Board of Governors, 16 October 1911 (AC.279, No.4, GAA).
212. Ibid.
213. Ibid.
214. Letter from the Board of Governors to Burgomaster and aldermen van 27 October 1911, (ASAO.5191, No.657, GAA).
215. Minutes a letter of Burgomaster and aldermen to J.J. van Laar, 1 November 1911, (ASAO.5191, No.657, GAA).
216. First letter of resignation: J.J. van Laar to City Council of Amsterdam, 6 November 1911 (ASAO 5191, No.657 GAA).
217. Letter J.J. van Laar to H.A. Lorentz of 19 December 1911 (AL.2.21.203, No.45, ARAG).
218. Letter J.J. van Laar to Burgomaster and aldermen, 16 November 1911 (ASAO.5191, No.657, GAA).

219. Minutes of the Board of Governors, 8 January 1912 (AC.279, No.4, GAA).
220. *Ibid.*, 217.
221. Letter A. Smits to Burgomaster and aldermen, 28 December 1911 (ASAO.5191, No.657, GAA).
222. *Ibid.*, 216 p.3.
223. *Ibid.*, 217.
224. Letter J.J. van Laar to Burgomaster and aldermen, 10 December 1911 (ASAO.5191, No.657, GAA) and Extract of the book of Resolutions: 31 January 1912, No.657 O (ASAO.5191, No.657, GAA).
225. Extract of the book of Resolutions: 31 January 1912, (ASAO.5159, No.657, GAA)
226. H.A.M. Snelders, De bemoeienissen van Lorentz en Einstein met de Utrechtse leerstoel voor theoretische fysica, *Tijdschrift voor de Gesch. der Gen, Natuurwet. en techn.* 2 (1987) 57-71.
227. Letter J.J. van Laar to H.A. Lorentz, 19 December 1911 (AL.2.21.203, No.45 ARAG).
228. Letter A. Einstein to W.H. Julius, 18 December 1911 (Archive W.H. Julius I, UMU).
229. Letter P. Debye to W.H. Julius, 23 September 1914 (Archive W.H. Julius I, UMU).
230. Information (Mrs.L. van Laar te Amsterdam).
231. Register of Residents Amsterdam (GAA).
232. Register of Residents Baarn.
233. Minutes of Faculty in Groningen, 24 January 1914 (No.623 RAG).
234. Minutes of Faculty in Groningen, 5 February 1914 (No.623 RAG).
235. Letter J.J. van Laar to Senate in Groningen, 11 April 1914 (No.369 RAG).
236. Letter J.J. van Laar to Faculty in Groningen, 15 April 1914 (No.629 RAG).
237. Letter J.J. van Laar to W.P. Jorissen, 13 June 1914 (AKNCV).
238. H.R. Kruyt, In Memoriam J.J. van Laar, *Chemisch Weekblad* 36 (1939) 19-20.
239. E. Cohen, *Chemisch-Historische Aantekeningen XVII*, *Chemie en Chemische Industrie in Amsterdam in der loop der Eeuwen*, *Chemisch Weekblad* 37 (1940) 486-502.
240. F.E.C. Scheffer, *Toepassingen van de Thermodynamica op Chemische Processen*, Delft: Waltman (1945) 9.



# ACHIEVEMENTS

*'You should see the paper on which I made the calculations which failed!'*

## 1. Introduction

This chapter consists of three parts. After the introduction, the second part gives a global overview of Van Laar's work from 1884 until 1938. The third part describes its significance for the fields of chemical thermodynamics and phase equilibria as they are practiced today. The departure point is Van Laar's formula for the heat of mixing (1910), his discussion with Dolezalek about his theory about the formation of complexes about the same period, his equation of state, his calculation of the double point and his predictions regarding retrograde solubility of 1903.

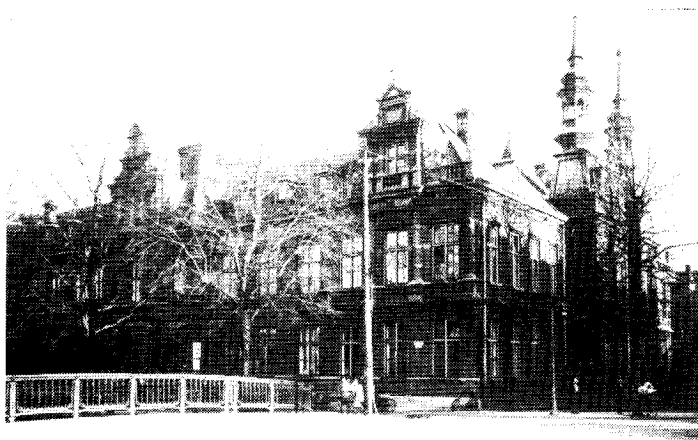
To understand Van Laar's work it is important to remember that he lived and worked in the times immediately following the initial developments in physical chemistry by Van 't Hoff and Ostwald in the 1880's. Van 't Hoff's book 'Etudes de Dynamique Chimique' was published in 1884. The interpretation of Van 't Hoff's formula for the osmotic pressure of 1887, especially in Germany, had been wrong, and deviations were incorrectly explained by a theoretical insight. For the fields of chemical thermodynamics and phase equilibria, the starting point was the work of Gibbs in 1876 which was further developed by Van der Waals, Van 't Hoff and Bakhuis Roozeboom at the University of Amsterdam. With regard to the molecular kinetics approach of the school of Van der Waals of 1873, the existence of molecules was in question until 1910 when the results of experiments by J.B. Perrin (1870-1942) about Brownian movement were made known. For Van Laar, questions about osmotic pressure and the existence of molecules were not always pleasing but he wrote about these subjects in 1927 (H.30)

## 2. Overview

### 2.1 Introduction

As a student of thermodynamics, Van Laar took his views from Gibbs and Van der Waals. His strength was to treat equilibria by equating thermodynamic potentials. Van der Waals' equation of state and the molecular kinetics approach of his school were of the utmost importance for Van Laar; it was always his starting point and he even applied it to the solid state and to liquids far below their critical point. As far as the interaction of molecules was concerned, he took, like all his contemporaries, the forces which were closely related to the Van der Waals parameter  $a$  of the equation of state as a starting point. It is remarkable that the content of his publications often directly referred to, or ran parallel to Van der Waals' work. He regarded the application of the Carnot cycle as outmoded and he rejected the pragmatic American method of introducing the 'activities' of G.N. Lewis (1875-1946).<sup>1</sup> Van Laar understood the application of mathematics very well because of his innate abilities and his naval training. Navigation had been second nature to him while at sea and he remained a real arithmetician in his scientific work. This sets him apart from his contemporary chemists in the Netherlands and abroad. When his work is studied, it appears that he discovered while calculating. He regarded his field of study, 'mathematical chemistry', as the pendant of 'mathematical physics', for which Gibbs' work served as a foundation. It included the thermodynamic theory of phase equilibria and the application of thermodynamics in chemical processes. He worked in this field of study for the whole of his life. In his publications, statistical and quantum mechanical discussions of thermodynamic questions hardly ever occur. As an author he was very able, never dull, but sometimes so sarcastic that he completely overshot the mark and became a caricature. This is one reason why many of his colleagues found him uncongenial.<sup>2</sup> His articles are often two sided in character: sometimes he created an impression of beauty, but the effect was then often nullified by the great number of detailed calculations included. This is also the reason for the lack of scientific response from the world of physics and chemistry. Many of Van Laar's articles were written on the occasion of a special event, for instance the publication of a thesis, or for engaging in a controversy, for example after the use of an incorrect formula in an article. Alongside these, there were also individual articles. He was often repetitive, as in his theoretical discussion of osmotic pressure.<sup>3,4</sup> Many articles were first published in Dutch and later in translation, in among others, 'Proceedings of the Section of Science of the Koninklijke Akademie van Wetenschappen', 'Archives Néerlandaises', and 'Zeitschrift für anorganische und allgemeine Chemie'. His most original

work must have dated from between 1903 and 1920. Within his field of study, mathematical chemistry, Van Laar wrote 6 books and about 200 articles and in 1920 and again in 1930 a survey of his work appeared in 'Chemisch Weekblad'.<sup>5</sup> Van Laar's significance is that he was one of the trailblazers for the integration of chemical thermodynamics in the Netherlands: not only was he a missionary, but also a pioneer! He was somewhat aggressive, like a schoolmaster; exasperated, he would explain a certain problem once again, or mercilessly point out mistakes. His first publication in 1892 is a good example of this; in a note he wrote that the article was written originally with reference to an inaccuracy by Arrhenius. Perhaps



*Chemistry Laboratory of Van 't Hoff in the 1890's.*<sup>6</sup>

the greatest charm his work nevertheless possesses is found in the fact that he was able to communicate his never failing enthusiasm to the reader. A.E. Korvezee (1899-1978) mentioned that Van Laar wanted to convince his reader of his ideas, and wanted to have them accepted.<sup>7</sup> He is today certainly not forgotten; in professional circles of thermodynamics and chemical engineering fields his work is still highly appreciated, though not much read anymore.

In his publications, Van Laar discussed the following subjects: electrolyte solutions, osmotic pressure, equilibria in galvanic cells, the development of phase theory following the theory by Van der Waals for binary mixtures, melting point lines, spinodal and plait point lines, the constants of  $a$  and  $b$  in Van der Waals' equation of state, the solid state, reaction rates, Nernst's heat theorem, and other subjects.

An outline of his work upto 1914 is given in a letter which he wrote to Jorissen on 13 June 1914 on the occasion of his honorary degree in Groningen.<sup>8</sup> Jorissen used the letter to give an overview of Van Laar's work to mark his 'promotion' in 1914 and his sixtieth birthday in 1920. This letter still exists and in the following survey it also serves as a guide and is supplemented with other material. The purpose of this part is to give, in broad terms, an outline of Van Laar's work between 1884 and 1938. It is interesting to note that some of Van Laar's original papers are in the private collection of Dr.Ir.C.J. Peters and Dr.Ir.Th.W. de Loos of the Section of Applied Thermodynamics and Phase Behaviour of the Technical University in Delft. A complete discussion of all aspects of Van Laar's work is not possible. The most relevant parts are selected and short outlined but his numerical results have been omitted. For the sake of completeness, it should be noted that much of his work has now lost its significance and meaning.

From 1906 until his death in 1938 Van Laar was an opponent of Nernst's heat theorem. This opposition will be discussed in relation to the scientific reception of the heat theorem in the Netherlands in this chapter IV. Van Laar's bibliography is included in Appendix II. The numeration which is used incidentally in the text of this part refers to this appendix. Van Laar published in the following periodicals:

- A. Verslag van de gewone vergaderingen der wis- en natuurkunde afdeeling, Koninklijke Akademie van Wetenschappen, henceforward to be called *Vers.K.Ned.Akad.Wet.*;
- B. The English translation of *Vers.K.Ned.Akad.Wet.* in Proceedings of the Section of Science of the Koninklijke Akademie van Wetenschappen, henceforward to be called *Proc.K.Ned.Akad.Wet.*, of which also the translations are mentioned which appeared in *Zeitschrift für anorganische und allgemeine Chemie (Z.Anorg.Allg.Chem.)*; *Archives Néerlandaises (Arch.Neerl.Sci.Exactes Nat.)* and *Journal de Chimie Physique (J.Chim.Phys.)*;
- C. Archives du Musée Teyler, henceforward to be called *Arch.Mus. Teyler*;
- D. *Zeitschrift für physikalische Chemie*, henceforward to be called *Z.Phys.Chem.*;
- E. *Zeitschrift für anorganische und allgemeine Chemie*, henceforward to be called *Z.Anorg.Allg.Chem.*
- F. *Journal de Chimie Physique*, henceforward to be called *J.Chim.Phys.*;
- G. *Recueil des Travaux Chimiques des Pays-Bas*, henceforward to be



called *Rec. Trav. Chim. Pays-Bas*;

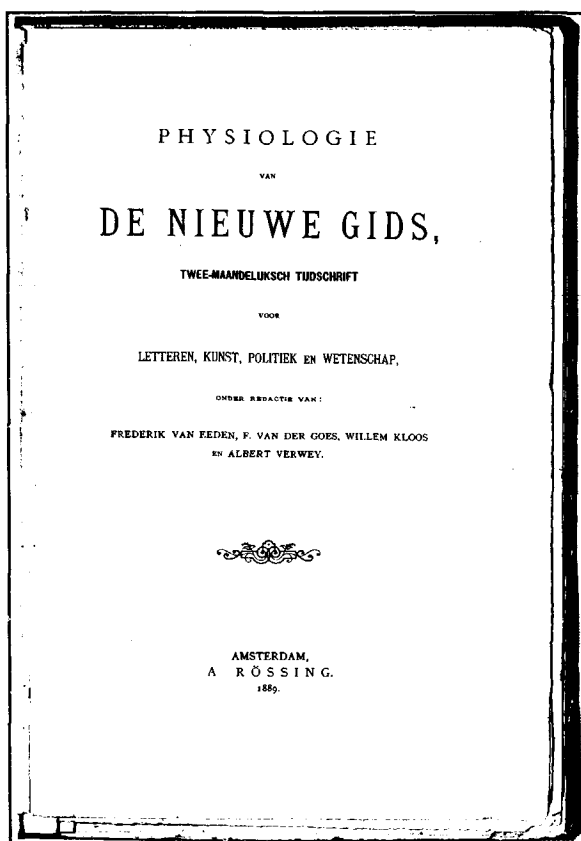
H. Chemisch Weekblad henceforward to be called *Chem. Weekbl.*;

J. Other periodicals: Tijdschrift de Beweging, De Amsterdammer, De Nieuwe Gids, Festschrift Boltzmann, Transactions of the Faraday Society, Physica, Zeitschrift für technische Physik, Zeitschrift für Physik.

To facilitate the reading of this text, the original English titles from Proc.K.Ned.Akad.Wet. are used for articles published in Vers.K.Ned.Akad.Wet.

## 2.2 Period 1884-1892

In the period between 1884 and 1892 Van Laar wrote six books and was occupied with pure mathematics, among other subjects. In 1887 he wrote 'Het systeem der Wetenschappen' (The system of the Sciences) followed by an elaborate bibliography, as well as 'Algemene Beschouwingen over Middelbaar en Universitair Onderwijs' (General Reflections about Grammar and University Education, I.1). In this booklet he divided the system of sciences into an abstract and a concrete part and warned about overloading the curriculum. The conclusion of this essay shows that Van Laar was antimilitarist. After his 'Register op de Ideën van Multatuli' (Register of the Ideas of Multatuli, I.2) was published in 1887 he wrote a textbook in two parts 'Leerboek der Algebra' (Textbook of Algebra), the first part of which appeared in 1889 and the second part in 1890 (I.5). Characteristic of his thought process is the connection between specific parts of arithmetic and algebra. His aim was to work didactically and more efficiently. His intention had been to produce two further parts about higher algebra but they were never published. Two supplementary books with problems did appear and they resulted in a conflict with the Dutch mathematician J. Versluys (1845-1920) who accused Van Laar of plagiarism. Van Laar was said to have used Versluys' question book, but in his letter of defence 'Plagiaat of niet' (Plagiarism or not, I.3) of 1889, Van Laar showed that the problem concerned only a small matter which had happened by mistake, and also that Versluys had himself translated and copied complete passages from the French textbook 'Traité d'Arithmétique' in his 'Leerboek der Rekenkunde' (Textbook of Arithmetic). In 1889 his anonymous brochure 'Physiologie van de Nieuwe Gids' (Physiology of the Nieuwe Gids, I.4) appeared, and was a critical appraisal of the work of some of the authors of the literary magazine 'De Nieuwe Gids' which had started in 1885. Today this essay is considered as 'a discursive, catalogued book with some praise, some criticism and some expression of the authors own opinion'.<sup>9</sup> Since there were, according to Van Laar, no good textbooks



*Title page of Van Laar's 'Physiologie etc.' at 1887*

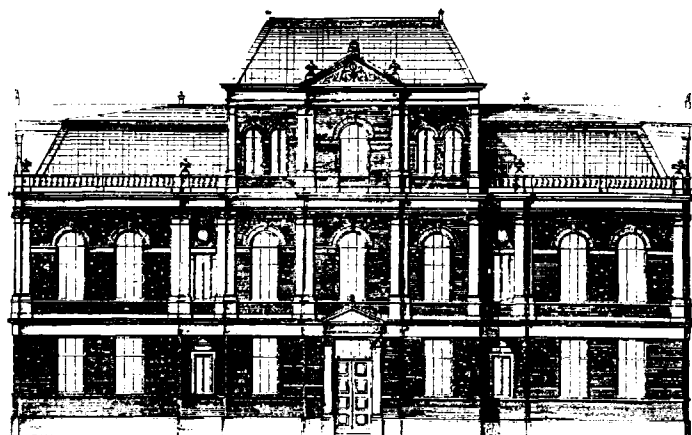
on trigonometry, he published his 'Leerboek der Boldriehoeksmeting' (Textbook of Spherical Trigonometry, I.6) in 1892. This included an extensive chapter on trigonometric applications in the art of navigation at sea. In 1892 he also started to write about mathematical chemistry.

### 2.3 Period 1892-1900

This period saw the beginning of Van Laar's mathematical dissertations about problems in chemistry and physics. In his first publication in 1892 in Z.Phys.Chem.: 'Zur Thermodynamik der elektrolytischen Dissoziation' (D.1) he proved the validity of Van 't Hoff's formula for solutions and vapours:  $d \log K / dT = Q / RT^2$  and he took the formula of Gibbs' free energy  $G$  as a starting point. In this formula  $K$  is the equilibrium constant and  $Q$  the heat effect of dissociation. In his two extensive articles, also in Z.Phys.Chem.: 'Ueber die genauen Formeln für den osmotischen Druck etc. etc.' (D.9,11) of 1894 and 1895, he discussed by equalization of

thermodynamic potentials a number of equilibrium problems, among them osmotic pressure. In 1898 Van Laar published, also in Arch.Mus. Teyler, 'Théorie générale des dissolutions' (C.1). The content of the article is an extension and repetition of earlier articles on the same subject. In this article thermodynamics was applied to totally arbitrary systems, following the methods of Gibbs, the German physicist M. Planck (1858-1947) and the French physicist P. Duhem (1861-1916). It was not therefore only applied to dilute systems as the formula of Van 't Hoff for the osmotic pressure  $\pi = RTc$  ( $c=n/v$ , the molar concentration of the solute). Van Laar had applied an extended formula with a logarithmic term (see also the remark at the end of part 2.4). Van Laar did this mainly because in Germany at the time these formulas were still assumed and many mistakes were being made by their interpretation. He engaged in many controversies with Cornelius, Arrhenius, Noyes, Nernst and Schükarew about the relations between the heat of a solution and solubility, dissociation heat etc. and he was finally proved correct on the matter.<sup>10</sup> In 1900, in his publication in Arch.Mus.Teyler: 'Sur la loi de dilution chez les électrolytes fortement dissociées' (C.4) he assumed almost full dissociation for strong electrolytes and explained that the molecular conductivity is connected with the degree of dissociation and proportional to  $c^{1/2}$  ( $c$  is concentration).<sup>11</sup> He never elaborated on this idea; later in 1923 Debye and Hückel found for the equivalent conductivity the same proportion.<sup>12</sup> In his publication of 1895 Van Laar was probably the first to remark that the deviations from the dilution law of Ostwald, even at greater dilutions of strong electrolytes, were caused by electrostatic forces between the ions.<sup>13</sup> In 1893 his first scientific book appeared: 'Die Thermodynamik in der Chemie' with an introduction of Van 't Hoff (I.7), it was an elaboration of Van der Waals' lectures.<sup>14</sup> In this book he applied Gibbs' thermodynamics on vapours and chemical problems. This work brought him into contact with Lorentz, with whom he remained in touch until Lorentz's death in 1928.<sup>15</sup> In 1899 two articles appeared, one in the 'Festschrift' for Van 't Hoff and the other in 'Livre jubilaire dédié à H.A. Lorentz'. In the first article, also published in Z.Phys.Chem.: 'Ueber die teilweise Assoziation der Flüssigkeitsmoleküle' (D.17) he gave, by assuming the existence of associated double molecules  $(H_2O)_2$  a thermodynamic explanation for the maximal density of water at 4 °C. In the second article, also published in Z.Phys.Chem., 'Ueber die Ableitungen des thermodynamischen Potentials nach T und p bei zusammengesetzten Komponenten' (D.22), he again provided the general evidence for the Van 't Hoff's formula  $d \log K / dT = Q / RT^2$  also for combined components. In 1898 he solved a difficult mathematical problem about the heating of a cylinder, by following the Fourier method

and combining it with Bessel functions: 'Sur le chauffage d'un cylindre, etc.' (C.2). The solution of this problem appeared in the same year in Arch.Mus.Teyler. During the period 1891-1902 the article 'Quelques remarques sur la solution d'un problème de la 'Geometria situs' (C.6) was written and it answered the question 'De combien de manières peut on replier, sur un seul, une bande de n timbres poste?': a combinational problem. In 1899 he wrote a biography of Van der Waals in 'Mannen en Vrouwen van Betekenis' (Men and Women of Importance, I.8), which he also translated into German.



*Physics Laboratory of Van der Waals.*<sup>16</sup>

## 2.4 Period 1900-1909

Three books by Van Laar appeared during these years. The first was 'Lehrbuch der Mathematischen Chemie', with an introduction by Bakhuis Roozeboom in 1901 (I.9) in which he described the thermodynamic introduction of the chemical equilibria in gases and solutions and other equilibria problems combined with some applications. 'Sechs Vorträge über das Thermodynamische Potential' (I.11) was the second in 1906 and was called a 'small masterpiece' by Korvezee in her inaugural lecture in 1954.<sup>17</sup> It is a translation of Van Laar's articles in Chem.Weekbl.: 'Iets over den thermodynamischen potentiaal en zyne toepassingen op scheikundige evenwichtsproblemen' (About the thermodynamic potential and its applications to problems in chemical equilibria, H.4) of 1905 and was at the time translated into Russian and Italian. It is a simple treatise of the chemical thermodynamics of Gibbs and is probably his best read book. With reference to his 'Lehrbuch der Mathematischen Chemie' and his lectures he wrote the third book: 'Lehrbuch der theoretischen Elektro-

chemie auf thermodynamischer Grundlage' (I.12) in 1907. He had already published sections from this book in Vers.K.Ned.Akad.Wet. (A.2,4,5) and 'Sechs Vorträge' and the contents are especially theoretical. His publications from this period can be divided into five groups.

*I. Articles on Van der Waals' equation of state.*

During Van der Waals' time the change of  $a$  and  $b$  as functions of temperature and volume in his equation of state was the subject of much discussion and research. Van Laar wrote two articles in Vers.K.Ned.Akad.Wet.: 'Calculation of the second correction to the quantity  $b$  of the equation of state of Van der Waals' (A.1), with an elaborate translation in Arch.Mus.Teyler in 1899 (C.3) and 'Quelques remarques sur l'équation d'état' in Arch.Mus.Teyler in 1905 (C.10). This concerned the so-called 'theory of distant spheres'. In a infinitely diluted gas, the limiting value  $b_g$  of the volume correction term  $b$  is equal to four times the volume  $m$  of the molecules  $b_g = 4m$ ,  $b_g$  is the value of  $b$  when  $v$  is infinite. About the question of 'how'  $b$  became smaller if the volume became smaller, Van der Waals in 1896 and 1898 found the following expression for the volume correction term:

$$b = b_g(1 - \alpha b_g/v + \beta(b_g/v)^2 \dots). \quad (1)$$

In 1896 Van der Waals calculated  $\alpha = 0.513$ . After much work Van Laar in 1899 found  $\beta = 0.0958$ . Later in the 1950's these calculations were repeated by Van Hove and the results were identical.<sup>18</sup> In his 1905 (C.10) article Van Laar, with the help of experimental data found in literature, made some additional calculations which he later, in 1912-1914, used for relations and at the critical point (A.26,27). In 1903 he calculated some values for the  $b$ -quantities of hydrogen (A.7). In 1904 he published in Festschrift Ludwig Boltzmann: 'Ueber die spezifische Wärme in flüssigen Zustände bei niedrigen Temperaturen' (J.1). In this article he deduced a general expression for the specific heat  $C_v$ .

*II. Articles about spinodal and plait point curves of mixtures.*

Van Laar believed that these articles were among his best work and they are considered publications of revelational significance.<sup>19</sup> After Van der Waals had unfolded his theory on binary mixtures in 1889 and 1900, Van Laar expanded on this matter in eight papers, five in Vers.K.Ned.Akad.Wet. and three in Arch.Mus.Teyler. In the first article in 1905: 'An exact expression for the course of spinodal curves and their plait points for all temperatures, in the case of mixtures of normal substances' (A.15), by assuming that Van der Waals'  $a$  and  $b$  were independent of  $v$  and  $T$ , Van

Laar was the first to deduce with the help of the empirical relation of Berthelot  $a_{1,2} = \sqrt{a_1 a_2}$ , the equation for the  $v,x$ -projections of the spinodal.

$$RT = \frac{2}{3} \left[ x(1-x)(\alpha v - \beta \sqrt{a})^2 + a(v-b)^2 \right] \quad (2)$$

and for the plait point line:

$$(\alpha v - \beta \sqrt{a})^2 [(1-2x)v - 3x(1-x)\beta] + \\ + \sqrt{a}(v-b)^2 \left[ 3(\alpha x - \beta \sqrt{a})(\alpha v - 2\beta \sqrt{a}) + \frac{a(v-b)(v-3b)}{x(1-x)} \right] = 0 \quad (3)$$

when:  $\alpha = \sqrt{a_2} - \sqrt{a_1}$  en  $b = b_2 - b_1$

Unlike Van der Waals, Van Laar did not start from the Helmholtz free energy, but from the Gibbs free energy. From Van Laar's letter to Lorentz on 20 March 1905 it becomes clear that Lorentz wrote the following to Van Laar:

'This belongs of course to the things of which people will immediately say 'I could have done that'.

The letter shows that Van Laar had had to produce some painstaking work to find the two equations:

'You should see all the paper on which I made the calculations which failed!'<sup>20</sup>

In the second article in 1905: 'On the shape of the plaitpoint-curve for mixtures of normal substances' (A.16) he investigated lines for different cases under the conditions  $b_1 = b_2$  and  $T_{c,1}/T_{c,2} = P_{c,1}/P_{c,2}$  ( $c$  is critical). He concluded that the plait point curve contained a double point (this is a critical double point) when  $b_1 = b_2$  and  $a_1/a_2 = T_{c,1}/T_{c,2} = 2.887$ . He explained this with the help of diagrams. P.H.E. Meijer refers to this double point and called it the 'Van Laar point' in 1989, see part 3.6 of this chapter. In the third article: 'The molecular rise of the lower critical temperature of a binary mixture of normal components' (A.18) of 1905 he discussed the general case and found that for the case of critical pressures of both components being the same, the following formula for the molecular rise of the lower critical temperature of a dilute solution  $\Delta = T_{c,2}/T_{c,1} (T_{c,2}/T_{c,1} - 1)$ . The fourth article was published in Arch.Mus.

Teyler (C.11) and Van Laar discussed the double point again with some extensions. In the fifth article in *Vers.K.Ned.Akad.Wet.* (A.19), he discussed the conditions for a minimum critical temperature and that for a maximum vapour pressure at higher temperatures. The sixth article in *Arch.Mus.* Teyler (C.13) is an extension of his fifth article and in the seventh article in *Vers.K.Ned.Akad.Wet.* (A.19) he discussed the longitudinal plait. In his eighth article in *Arch.Mus.* Teyler (C.14) he discussed it again. A short survey about these articles can be found in his seventh article in *Vers.K.Ned.Akad.Wet.* (A.19).<sup>21</sup> These eight articles do not stand alone but are inherent in the work of Kamerlingh Onnes, Korteweg and Van der Waals.<sup>22</sup> According to Van Laar's letter to Jorissen and remarks in his articles, two entirely different types of critical (plait point) phenomena which originally were considered not to be associated now appeared related.

### *III. Articles about electromotive equilibria in metals, amalgams, alloys and liquids (1902-1907).*

These articles began with a discussion in *Vers.K.Ned.Akad.Wet.* in 1902: 'On the asymmetry of the electro-capillary curve' (A.2) and presented a close examination of the relation between surface tension and the potential difference between the capillary mercury surface and the electrolytic solution of Lippmann's capillar-electrometer. Using thermodynamics Van Laar deduced a formula for the relation between the surface tension and the potential difference across the meniscus of the capillary. His most important conclusion is that in this way the curve is asymmetrical and that this electrometer was unsuitable for measuring the potential differences between metal and electrolyte. In his second article in *Vers.K.Ned.Akad.Wet.*: 'On the potential-difference, which occurs at the surface of contact of two different non-miscible liquids, in which a dissolved electrolyte has distributed itself' (A.4) of 1903, he showed that this mentioned potential difference always occurred and he deduced for this a formula which is equivalent to the formula of Nernst. In his third discussion in *Vers.K.Ned.Akad.Wet.* (not translated into English): 'Over het electromotorisch gedrag van amalgamen en legeringen' (About electromotive behaviour of amalgams and alloys, A.5) in 1903 he discussed the potential difference of miscible metals with one single electrolyte. He concluded this with his discussion in *Z.Phys.Chem.*: 'Ueber den Dissoziationsgrad gesättigter Lösungen eines Electrolyten in verschiedenen Lösungsmitteln und Lösungen, welche im Teilungsgleichgewicht stehen' in 1907 (D.34) and 'Ueber die Löslichkeit von Electrolyten' in 1907 (D.35), in which he provided a theoretical explanation of the relations that the degree of dissociation for different saturated electrolytical solutions are equal, which already was found by Walden, for the solubility of the electrolyte

$N(C_2H_5)_4I$  in different solvents.

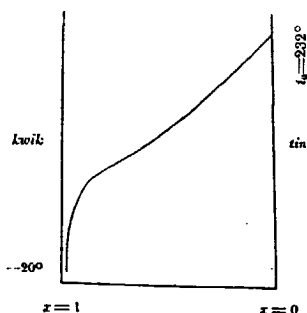
*IV. Articles about the melting curve (1903-1909).*

Bakhuis Roozeboom used these articles in his book : 'Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre' Heft 2, Teil 1, published in 1904. Van Laar's discussion : 'Ueber den Verlauf der Schmelzkurven bei festen Lösungen (oder isomorphen Gemischen) in einem speziellen Fall' (D.31) in Z.Phys.Chem. encouraged the American physicist P.W. Bridgman (1882-1961) to perform experiments which confirmed Van Laar's formulas.<sup>23</sup> Van Laar's work in this field started with publications on the course of melting curves in 1903 and 1904 in Vers.K.Ned.Akad.Wet. These are discussed below.

In 1902 W.J. van Heteren was 'promoted' under the supervision of Bakhuis Roozeboom on 'Onderzoekingen over Tinamalgamen' (Investigations on Tin amalgam). The experimentally determined melting curve in that research was theoretically discussed by Van Laar in Vers.K.Ned.Akad. Wet.: 'The course of the meltingpoint-lines of solid alloys or amalgams' (A.3). In it he deduced two approximation formulas for the melting curve of the mixture of tin and mercury. The first formula started from the thermodynamic potential of solid tin and tin in liquid amalgam and had the following result:

$$T = \frac{T_0}{1 + \frac{RT_0}{q} x}, \quad (4)$$

To is the melting point of pure tin, q the heat of fusion of solid tin at the transition into amalgam and x the mole fraction. Equation (4) represents





the experimentally deduced melting point line qualitatively correctly. In the same article Van Laar deduces a stricter relation. For the thermodynamic potentials he takes  $\mu = e - cT$  for solid tin, and  $\mu_1 = e_1 - c_1T - (\alpha x^2 + \beta x^3 + \gamma x^4) + RT \log(1-x)$  for tin in liquid amalgam. After equalization of the thermodynamic potentials the result is:

$$T = T_0 \frac{1 - (\alpha x^2 + \beta x^3 + \gamma x^4)}{1 - \frac{RT_0}{q} \cdot \log(1-x)} \quad (5)$$

With the Redlich-Kister expression (1948) this formula is still in use.<sup>25</sup> In the second article: 'The meltingpoint-line of tin-amalgams' (A.6) of 1903, he did the same, however now with a corrected term for expressing the thermodynamic potential taken from Van der Waals' equation of state, he formulated the following expression for the melting curve:

$$T = T_0 \frac{1 + \frac{1}{q_0} \frac{\alpha_1 x^2}{(1+rx)^2}}{1 - \frac{RT_0}{q_0} \log(1-x)} \quad (6)$$

When  $T_0$  is the melting point,  $q_0$  the heat of fusion of pure component and  $\alpha_1$  is an expression in the Van der Waals' parameters  $a$  and  $b$ . This formula fits very well and is included in Bakhuis Roozeboom's book.<sup>26</sup> In the third article: 'The course of the meltingpoint-line of alloys' (A.8), also written in 1903, Van Laar tested these formulas on a number of alloys. In the following series of three articles in *Vers.K.Ned.Akad.Wet.* from 1903 and 1904 the melting curves were drawn through the eutectic point and a number of types were theoretically deduced (A.9.10.11). In another article in *Vers.K.Ned.Akad.Wet.*: 'On the course of melting-point curves for compounds which are partially dissociated in the liquid phase, the proportion of the products of dissociation being arbitrary' (A.20) of 1906 in *Vers.K.Ned.Akad.Wet.*, together with the already mentioned article: 'Ueber den Verlauf der Schmelzkurven bei festen Lösungen (oder Isomorphen Gemischen) in einem speziellen Fall' (D.31) Van Laar discussed melting curves which are close together. In his letter he noticed that these occur in feldspars and are important in mineralogy.<sup>27</sup> These theoretical discussions were issued again in 1908 and published in *Z.Phys.Chem.* under the title: 'Die Schmelz- oder Erstarrungskurven bei binären systemen, wenn die feste Phase ein Gemisch (amorphe feste Lösung oder Mischkrystalle) der beiden Komponenten ist' (D.39). In the earlier mentioned letter to Jorissen, Van Laar pointed to the significance

of his 1906 article in *Vers.K.Ned.Akad.Wet.* (A.20).

#### *V. Articles on reaction velocity.*

The two articles which appeared in *Chem.Weekbl.* in 1908 must be mentioned: 'Over reactiesnelheden I and II' (On reaction velocity, H.9). Although later, with reference to an article in *Rec.Trav.Chim.Pays-Bas* by Scheffer and W.F. Brandsma (1894-1964) in 1929 Van Laar would acknowledge the content of these articles as false in: 'Iets over reactiesnelheden' (About reaction velocity, H34) in *Chem.Weekbl.*, they are still interesting because he tried to express in reaction rates of the difference thermodynamic potentials between products and reactants.<sup>28</sup> In 1908 he established the following formula:

$$v = h(\mu_1 - \mu_2)C_1 \quad (7)$$

$v$  is the reaction velocity,  $(\mu_1 - \mu_2)$  is the difference between the thermodynamic potentials of the first and second system, factor  $h$  is the function of temperature and medium and  $C_1$  is the product of the concentrations or power of the reacting substances. In 1948 I. Prigogine proved this formula to be correct close to the equilibrium. In fact he was working here in the field of irreversible thermodynamics.<sup>29</sup>

In 1904 Van Laar gave a speech to the 'Bataafsche Genootschap' in Rotterdam: 'Over niet verdunde oplossingen' (On non-dilute solutions, H.1) which was published in *Chem.Weekbl.* and *Sechs Vorträge* in 1905. In this speech he pleaded for the general thermodynamic treatment of solutions and use of the formula for thermodynamic potential with correction terms for the non-dilute solutions of Van der Waals:

$$\mu = f(T) + RT\log(1-x) + \alpha x^2. \quad (8)$$

For dilute solutions  $\log(1-x)=-x$  and  $\alpha x^2=0$  becomes  $\mu = f(T)-RTx$ . For the application of this equation to the osmotic pressure he argued throughout his life because some chemists supposed solutions to follow the gas laws, see A.17,21; C.1; D.11,40,44; H.1,4,30; J.5, with P. Ehrenfest (1880-1933) in *Vers.K.Ned.Akad.Wet.*, Van Laar's own short account in his last book in 1935 (A.35) and the detailed study by H.A.M. Snelders, *The Dutch Physical Chemist J.J. van Laar (1860-1938) versus J.H. Van 't Hoff's 'Osmotic School' in 1986 (Ref.4).*<sup>30</sup>

### **2.5 Period 1909-1914**

Before entering a discussion on this period, it is interesting to note a new

idea which Van Laar developed. He started to take associating molecules into consideration in his discussions.<sup>31</sup> Van Laar's thermodynamic explanation for the maximum density of water at 4°C in 1899 was his first result (D.17), which is already mentioned in part 2.3. It is also important that Van der Waals, after 1906, assumed that molecules were able to associate into larger complexes.<sup>32</sup> Van Laar's basic idea boiled down to the fact that association increased when gas condensed into liquid and solid substances. In the period from 1909 to 1914 three fields of study can be distinguished.

*I. Articles about association and the solid state (1909-1911).*

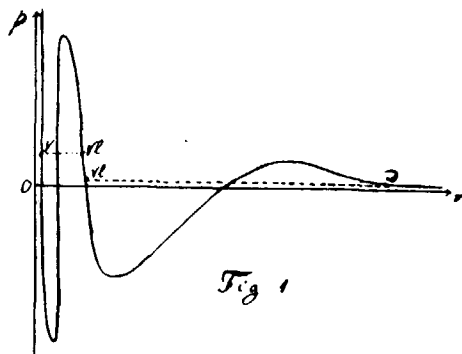
The first article on this subject appeared in Arch.Mus.Teyler: 'Théorie générale de l'association de molécules semblables et de la combinaison de molécules différentes' (C.15) in 1909. Van Laar departed from the idea of two variables: the degree of dissociation  $\beta$  and the change of  $b$  in Van der Waals' equation of state. To explain his theory he discussed water, which



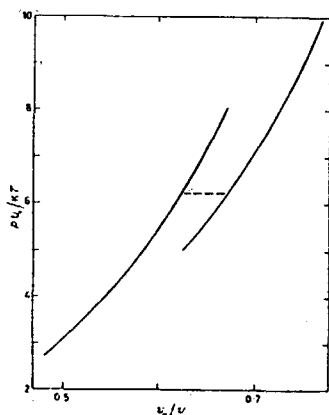
*Study of Bakhuis Roozeboom.*<sup>33</sup>

according to him occurred as a double molecule  $(H_2O)_2$  and dissociated into two simple molecules  $H_2O$ . The change of  $b$  was equal to  $-b_1+2b_2$ ;  $b_1$  was valid for the double molecule and  $b_2$  for the simple molecule of water. By equating the thermodynamic potentials at equilibrium he deduced the relation between the degree of dissociation  $\beta$  and the change of  $b$ . The change in  $b$  could be either negative or positive; negative if the volume of

the associated molecules was larger than two simple molecules, positive when the volume of the associated molecules was smaller than two simple molecules. He called it a fundamental article, and thought it among the best he wrote.<sup>34</sup> While writing it, Van Laar discovered that Van der Waals' isotherm, in the theory which he published in the first of seven articles in *Vers.K.Ned.Akad.Wet.*: 'On the solid state' (A.24), followed a different course. Van Laar succeeded in proving, following thermodynamic principles, that when two simple molecules united into a so-called double molecule, that at very high pressures and regardless of the phase, Van der Waals' isotherms bent once again, to rise permanently after a



*Van der Waals' isotherm with the solid state  
by Van Laar in 1909.<sup>35</sup>*



*Equation of state of rigid spheres,  
as calculated on computers.*

new minimum, to an infinite value of pressure. One of the conditions for this was that a new phase had to occur: the solid phase. B.J. Alder and T.E. Wainwright got more or less a comparable result with computer simulations of rigid spheres, the so-called Kirkwood transition, in 1957.<sup>36</sup> Van Laar assumed that Van der Waals' equation of state is valid for the solid state. This solid phase was characterized by a new specific volume and a corresponding associated state. The specific volume  $v$  as well as the value of  $b$  would change because of the assumption of association. When this was applied to the liquid and solid phase, Van Laar believed the changes in  $v$  and  $b$  could be both positive, both negative or opposite. An interesting aspect of his theory is the course of the melting curve near absolute zero temperature and in this case the changes in  $v$  and  $b$  are negative. These dissertations were cited by Bridgman 1912.<sup>37</sup> The melting curve then recedes, has a maximum in the proximity of absolute zero temperature and ends at  $T = 0$  with a finite pressure. Bakhuis Roozeboom had already predicted this.<sup>38</sup> It proved to be valid for helium and in 1926 and 1927 provided a source of discussion with the physicist from Leiden W.H. Keesom (1876-1956) who first obtained solid helium. This discussion is reviewed in part 3 of chapter 4.

## *II. The variability of the quantity $b$ in Van der Waals' equation of state.*

In 1901 Van der Waals had already written an approximation formula for the  $b(v)$ . In Van Laar's article: 'On the course of the value of  $b$  for hydrogen, in connection with a recent formula of Van der Waals' (A.7) in 1903, he worked out this equation for hydrogen and calculated  $v_k$ ,  $b_g$ ,  $b_k$  and  $b_o$  ( $b_o$  is the smallest value for  $b$  at high pressures). In 1911, Van Laar believed that he had deduced a better one in relation to his own theory of 'association' in the solid state. Van Laar was convinced of the fact that this association coincided with a change in the volume of the molecules, thus also of  $b$ . In 1911 and 1912 four articles appeared in *Vers.K.Ned.Akad. Wet.*: 'The variability of the quantity  $b$  in Van der Waals' equation of state, also in connection with the critical quantities' (A.26) and two complementary articles (A.27,28), in which he discussed and calculated some relations holding for the critical point. Later, in 1920, in his two articles in *Rec.Trav.Chim.Pays-Bas*: 'Quelques remarques sur la tension de la vapeur et la chaleur de vaporisation, précédées d'une étude sur la dépendance des grandeurs  $a$  et  $b$  de la température et du volume' (G.1), he developed the following formula:

$$b = b_g/[1 + (b_g - b_o)/v]. \quad (9)$$

In this equation  $b = b_o$  is the smallest value of  $b$  at high pressures and  $b = b_g$

as  $v = \infty$ . If this formula and the parallel one for  $a$  ( $a = a_g/(v+c)$ ,  $a = a_g$  if  $v = \infty$ ,  $v$  is volume and  $c$  is a constant) are substituted in Van der Waals' equation of state, the so-called Van Laar equation of state emerges, see part 3.5.

### III. Formula for the heat of mixing.

In his article in Z.Phys.Chem.: 'Ueber Dampfsparnungen von binären Gemischen' (D.42) of 1910, a formula for the heat of mixing was deduced with the help of Van der Waals' state equation and Berthelot's relation:

$$\text{when } r = (b_2 - b_1) / b_1 \text{ and } \alpha = \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b_1^3}$$

For both components the partial excess Gibbs' energies are:

$$w_1 = \frac{\partial W}{\partial n_1} = W - x \frac{\partial W}{\partial x} = \frac{ax^2}{(1+rx)^2} \tag{10}$$

$$w_2 = \frac{\partial W}{\partial n_2} = W + (1-x) \frac{\partial W}{\partial x} = \frac{a(1-x)^2}{(1+r)(1+rx)^2}$$

which are identical to the activity coefficients of Lewis  $RT \ln \gamma_1$  and  $RT \ln \gamma_2$ . Later, in 1931, the American chemist G. Scatchard (1892) gave this equation its general form and is discussed in part 3.2 of this chapter. In 1914, Van Laar and J. Dolezalek (1873-1920) were engaged in a heated discussion about Van Laar's different insight into the theory of binary mixtures. The discussion is reviewed in part 3.3 of this chapter.

### 2.6 Period 1914-1920

Information about this period of Van Laar's work comes from an article Jorissen wrote in Chem.Weekbl. in 1920. In 1913 and 1914 Van Laar wrote four articles 'A new relation between the critical quantities, and on the unity of all the substances in their thermic behaviour' (A.31) with a summary in his fourth article. With the help of the rectilinear diameter he deduced  $b_c/b_o = 2\gamma$  ( $b_c$  is  $b$  at the critical point,  $b_o$  is  $b$  if  $b = v_o$  and  $\gamma$  is the slope of the rectilinear diameter), and complicated formulas for  $b(v)$  and  $b(T)$  which are inherent in the work of Van der Waals and Kamerlingh Onnes. In 1915 some articles about earlier discussed subjects were written, among others, about the association and critical quantities and about osmotic pressure (A.32,33,34,35). Central to this period is Van Laar's discovery that  $\sqrt{a}$  of a molecule is additive, that is, composed of  $\sqrt{a}$  of the component atoms. Especially interesting are the six articles in Vers.K.

Ned.Akad.Wet. which appeared during 1916-1917: 'On the additivity on the values of  $b$  and  $\sqrt{a}$  of the equation of state, and on the fundamental values of these quantities for different elements, in connection with the periodic system' (A.36). In the first article he discussed the addition of the values of  $b$  and  $\sqrt{a}$  in the equation of state. The additive property of the value  $b$ , when elements were compounded into molecules, was already known by Van der Waals and others. Van Laar found that the addition of  $b$  and  $\sqrt{a}$  was related to the periodic system. He ascertained that Van der Waals' forces of the central atom were not present in cases in which a central atom was involved and was surrounded by other atoms or atom groups in a molecule. At  $0^{\circ}\text{C}$  and 1 Atm the fundamental value of  $b_k \cdot 10^5$  ( $b_k$  in  $\text{cm}^3$ ) for the elements which were grouped in periods (horizontal rows) of the periodic system decreased from left to right by 15 units. In the columns,  $b_k \cdot 10^5$  increased from top to bottom by 55 units. The values of  $\sqrt{a_k} \cdot 10^2$  ( $a_k$  in Atm) appeared to increase in a ratio of 1:3:5:7:9:11 from row to row. In the following five articles he discussed a number of groups within the periodic system: the hydrogen-helium group, the halogen, oxygen and nitrogen groups, the carbon and titanium groups and alkali metals.



*Van Laar and probably his second wife with a couple in Switzerland near his house 'Les Arolles' in Tour de Peilz.<sup>39</sup>*

Subsequently, he showed in his article: 'On the heat of dissociation of diatomic gases in connection with the increased valency attractions  $\sqrt{A}$  of free atoms' (A.40) in 1918 that the specific attraction  $\sqrt{A}$  in isolated atoms was much greater than that of  $\sqrt{a}$  in similar atoms, when these were united into molecules. The difference, it appeared, remained the same on average. With the difference of  $\sqrt{a}$  and  $\sqrt{A}$  he calculated the heat of the dissociation of two atomic gases such as  $H_2$ ,  $N_2$ ,  $O_2$ ,  $Cl_2$ ,  $Br_2$  etc. The calculated values appeared to correspond well with the experimentally found values. In 1932 this addition was theoretically deduced by A.E. van Arkel (1893-1976) in Leiden.<sup>40</sup>

In 1918 four more articles appeared in *Vers.K.Ned.Akad.Wet.* under the title: 'On the course of the values of the  $a$  and  $b$  for hydrogen at different temperatures and volumes' (A.39). Van Laar had already written on this subject in 1903 (A.7) and in these articles he mainly added a theoretical explanation about the increase of Van der Waals' parameter  $a$  at reducing temperatures up to a certain maximum value, after which the attraction reduced at very low temperatures. In the years 1918-1919 five essays appeared in *Chem.Weekbl.*: 'Beschouwingen over eenige theoretische en empirische betrekkingen in verband met de oppervlakteenergie, den moleculairdruk, de verdampingswarmte, den dampdruk en de dichtheden der coëxisterende fasen' (Views on some theoretical and empirical relations for the surface energy, molecularpressure, heat of evaporation, vapour pressure and density of co-existing phases, H.16). In 1919 and 1921 three articles were published in *Vers.K.Ned.Akad.Wet.*: 'On the equation of state for arbitrary temperatures and volumes. Analogy with Planck's formula' (A.41). By studying negative electrons which ran round the positive nucleus of an atom, Van Laar concluded that the working forces between two molecules was a periodically functioning affinity and repulsion force of which the resultant on averaging was not zero.

## 2.7. Period 1920-1938

That this really was the start of a new era for Van Laar is shown by two new associations. The first was with the Swiss chemist P.A. Guye (1862-1922) of the University of Geneva who was also editor of '*J.Chim.Phys.*' and the second with the German chemist R. Lorenz (1863-1929) at the University of Frankfurt, who was editor of '*Zeitschrift für anorganische und allgemeine Chemie*'. Although Van Laar sometimes complained about the Lorenz's cooperation, they must have worked well together, because in 1927 Lorenz dedicated his book: 'Das Gesetz der chemischen Massenwirkung, seine thermodynamische Begründung und Erweiterung' to Van Laar:



DEM MEISTER  
DES  
THERMODYNAMISCHEN POTENTIALS

J. J. VAN LAAR

IN TREUER FREUNDSCHAFT

ZUGEEIGNET

In 1924 Van Laar's fifth book appeared: 'Die Zustandsgleichung von Gasen und Flüssigkeiten mit besonderer Berücksichtigung der Veränderlichkeit der Werte von  $a$  und  $b$  des Kritischen Zustandes und der Theorie der Dampfspannungskurven' (I.15), in which he gave a complete review of his articles published in Vers.K.Ned.Akad.Wet. from 1914 onwards. He discussed the equation of state, the critical state and relations about vapour pressures. In this book he deduced an equation of state on page 91, see 3.5. In 1935 his sixth and last book, published by Noordhoff, appeared in Groningen: 'Die Thermodynamik einheitlicher Stoffe und binäre Gemische, mit Anwendungen auf verschiedene physikalische-chemische Probleme' (I.16). This book is referred to again in Chapter III. His article in Nieuwe Gids entitled 'De Hodler-tentoonstelling te Bern' (The Hodler Exhibition in Bern, J.4) is interesting because it shows Van Laar's interest in art and music. F. Hodler (1853-1918) was a well-known Swiss painter and sculpter, who had lived in Geneva. Van Laar's physical chemical work up to 1930 can be divided into six groups.

*I. Two articles in 1922 and 1923 in Vers.K.Ned.Akad.Wet.: 'On the heat of mixing of normal associating liquids' (A.43).*

In the first article he deduced again his formula for the heat of mixing and he also discussed the points he had neglected in the original of 1910 (E.40). He made improvements regarding the volume contractions for mixtures of normal components and deduced a more complete formula. In the second article he did the same for associated components and tested his results with a fairly positive outcome, using experimental data from literature.

*II. Five articles, in collaboration with Lorenz, about various subjects, which appeared in 1925 and 1926 in Z.Anorg.Allg.Chem.*

In the first article: 'Untersuchung über das Verhältnis Schmelzpunkt-kritische Temperatur' (E.4) they deduced a formula for  $T_m/T_k$  ( $T_m$  is melting temperature,  $T_k$  is critical temperature) with results from Van Laar's book 'Die Zustandsgleichung ...' and found the values for ideal and

normal substances. In the second and fourth articles: 'Ableitung der Grundgleichungen zum Massenwirkungsgesetz für kondensierte und heterogene Systeme' (E.5) and 'Erweiterung der neuen Grundgleichungen des Massenwirkungsgesetzes auf den Fall eines Zusatzes zu den Komponenten einer Phase' (E.10) they deduced with the equations of state of Boyle and Van der Waals, basic equations for the thermodynamic potential. In the third article 'Berechnung von Mischungswärmen kondensierter Systeme' (E.6) they deduced a formula for condensed systems such as metals and salts, see part 3.2. In the fifth article 'Theorie der galvanischen Stromerzeugung kondensierter Systeme' (E.11) they gave formulas for the electromotive force with equalization of thermodynamic potentials. Among these articles, (E.5) and (E.6) are the most important. The content of these articles was later included in Lorenz's book.

*III. An article in Vers.K.Ned.Akad.Wet. in 1924: 'On the equation of state of liquids and solid bodies at high and at low temperatures'.*

In this article (A.44) Van Laar returned to his equation of state:

$$p + a/v^2 = [RT/(v-b_0)] \cdot [1 + (b_g - b_0)/v] \quad (11)$$

with  $b_g$  the value of  $b$  when  $v = \infty$ ,  $b_0$  the value of  $b$  when  $v = v_0$  (molar volume at 0 K and 1 Atm), in which he, with the help of experimental data from literature, confirmed for some liquids at normal temperatures which were approximately  $1/2T_k$ . Subsequently, he deduced thermodynamically a equation for  $cv$  which was valid for solid substances, liquids and gases.

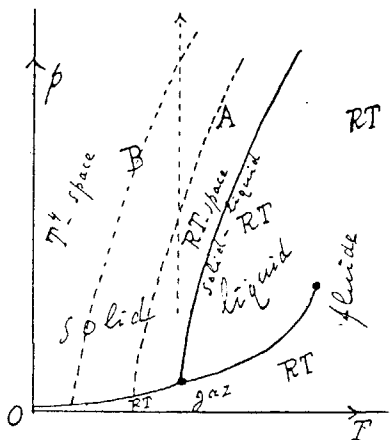
*IV. Three articles in Vers.K.Ned.Akad.Wet. in 1926 about the equations of state of solid substances.*

In the first article: 'On the equation of state of solid substances (metals) in connection with their compressibility and with the pressure and temperature coefficient of this quantity' (A.46), Van Laar assumed for metals at normal and higher temperatures a variation on Van der Waals' equation of state:

$$(p + a/v^2)(v - b) = (\lambda + RT) \quad (12)$$

$\lambda$  is a term that for solids is related to the repulsive forces of the molecules and  $b(v)$ . In the second article: 'On the equation of state of solid substances in connection with the general expression for the energy' (A.47), he gave, with the help of Debye's theory, an overview of his ideas about energy in the equation of state at higher and very lower temperatures. In the case of

very lower temperatures the equation of state changed form:  $RT$  was replaced by  $PT^4$  ( $P$  is a constant). In the third article: 'On the equation of state of solid substances in connection with the general expression for the energy and entropy, simple derivation of the so-called entropy constant' (A.48), he gave a general discussion about the energy which are combined in the figure below. He also gave for the integrated form of  $dS = dQ/T$  a deduction of the so-called entropy constant.



*Energy spaces for pure substances  
by Van Laar.<sup>41</sup>*

*V. His articles about helium of 1926, 1927 and 1936 (A.49,50,52,56,57).*

After helium had been successfully brought into a solid state in 1926, W.H. Keesom (1876-1956) used the experimentally found melting curve in relation to Nernst's heat theorem. This caused the controversy, described in Chapter IV, Obstinacy, between Van Laar and Keesom, which Lorentz resolved by mediation in 1927.

*VI. From 1930 until 1938 Van Laar published about 15 more articles on various subjects.*

Van Laar wrote in *Zeitschrift für Physik* about the equation of state of solid substances at higher temperatures (J.9), and in *Vers.K.Ned.Akad. Wet.* some articles about the equation of state of gases and liquids (B.54). In *Chem.Weekbl.* several more polemical articles appeared which in part repeated what he had written before. It is curious that Van Laar, in the 1930's, changed his opinion on the Debye-Hückel's theorie. In 1924 in his article 'Einiges über die Theorie der starken Electrolyte und ihre Geschichte' (E.2) he still appeared to be in favour of this theory; the correction factor

of I.C. Ghosh (1894-1959) had not to be  $c^{1/3}$  but  $c^{1/2}$ ,  $c$  is concentration of the electrolyte. However, by 1936 in his publication in Chem.Weekbl.: 'De tegenwoordige opvattingen omtrent den toestand van electrolyten in waterige oplossingen' (Modern conceptions about the state of electrolytes in aqueous solutions, H.48), he stated the opposite and did the same in his final book (I.16).

## 2.8 Concluding remarks

From this brief overview, Van Laar's versatility and above all his relentless concern with Van der Waals' equation of state are apparent. Some observations about his work appear below.

It was the American chemist E.W. Washburn (1881-1934) who wrote highly about Van Laar's ideas of solutions in 1910.

'(...) Van Laar mit viel Wärme und grossem Eifer die Verwendung der Methode des thermodynamischen Potentials und Einführung der Konzentration der Lösung in Gleichungen mittels des Ausdruckes  $\ln(1 - N^s)$  ( $N^s$  is mole fraction of solvent, v.E.) in Stelle der Annahme, dass die Lösung verdünnt sei, befürwortet. (...) Wenn es jemand einfallen sollte, sich darüber zu wundern, wehalb die Theorie in der chemischen Welt nicht in allgemeiner Gebrauch gekommen ist, so braucht er nur einen flüchtigen Blick auf einige van Laarschen Abhandlungen, insbesondere die frühern, zu werfen, und der Grund wird dann mehr oder minder offenkundig sein'.<sup>42</sup>

And in the same year E. Jänecke in Germany:

'Für das tiefere Verständnis sind auch einige holländische Arbeiten mehr theoretischer Natur von Wichtigkeit, besonders die neuen Untersuchungen von Van Laar'.<sup>43</sup>

Van Laar considered this period between 1903 and 1910 his best. Indeed it can be said that his position as a scientific assistant to Bakhuis Roozeboom and the influence of Lorentz had great significance. Van Laar's deduction of the melting point line, spinodal and binodal curves remains unchanged and his formula for the heat of mixing is still mentioned in the literature today. All his articles demonstrate a great insight. In 1927 Lorenz showed in his book that the equation of Duhem-Margules and Van der Waals' vapour pressure formulas were identical. He pointed this out to Van Laar:

(...) geht aus von der Aufstellung der molaren thermodynamischen Potentiale für kondensierete Phasen, wobei eine Zustandsgleichung zugrunde gelegt wird. Fast ausschliesslich wird die van der Waalsche verwendet. Diese Methode hat ihren Uesprung bei van der Waals selbst und fand ihren Hauptvertreter in van Laar.<sup>44</sup>

Even during Van Laar's lifetime, in 1937, an article about this by the German physical chemist P. Drossbach: 'Ueber die Theorie binärer Gemische von Van Laar' appeared in *Z.Anorg.Allg.Chem.*

'Da die Van Laar'schen Arbeiten so meiner Ueberzeugung nach ihre Bedeutung auch in der Zukunft behalten (....).<sup>45</sup>

Van Laar was a real theoretician and arithmetician. He was in love with his subject and ahead of his time with his ideas. The lengthy bibliography which is included under Appendix II shows that he must have spent his whole life working, studying and writing articles which are still held in high regard. The next section will describe the relevance of his work today. Everyone who has studied Van Laar's work is very enthusiastic about his scientific contributions. In 1988, Rowlinson ended the first part of his book about Van der Waals' thesis as follows:

'A final note records his thanks to Van Laar for his work of translation and with help in dealing with new developments of both theory and experiment which, he says, have still not come to an end'.<sup>46</sup>

### 3. Significance

#### 3.1 Introduction

Bakhuis Roozeboom was the founder of the theory of phase equilibria in the Netherlands.<sup>47</sup> With Gibbs' phase rule he wanted to classify and describe the known systems with one, two and three components. An account of his studies is to be found in his books which were completed after his death by Buchner, Schreinemakers and Aten. In the theory of phase equilibria, binary systems hold a key position. After Van der Waals' theories about binary mixtures of 1889 and 1900, Van Laar was the one who finally discussed the binary mixtures quantitatively and thermodynamically. He was thus a co-founder of the theory of phase equilibria. An overview of Van Laar's work in this field is to be found in 'Z.Phys. Chemie' from 1907 until 1910 (D.39,42).<sup>48</sup> Although his findings had been published at an earlier stage in *Vers.K.Ned.Akad.Wet.* and translated

into English in Proc.K.Ned.Akad.Wet., present day literature refers to these German articles.

The previous section presented an outline of Van Laar's work in chronological order. This section looks at the subjects which have proved to be of lasting significance to pure and applied thermodynamics and phase equilibria. Six subjects are discussed here. The first is Van Laar's equation and the development of his 1910 formula for the heat of mixing in connection with Lewis' activity coefficients. This formula is still known today. The second subject is the heated arguments between Van Laar and Dolezalek in 1910 and 1913 about the association of molecules. Harris and Prausnitz studied this subject again in 1963 and it appears that a tautology was at issue here. Van Laar's treatment was more physical and Dolezalek's of a more chemical nature. The third part discusses Van Laar's dilated model, the so-called improved Van Laar model, developed for mixtures if one of the components is near the critical point at relatively high pressures by Chueh in the 1960's. The fourth subject to be considered the so-called Van Laar equation of state, which is the Van der Waals equation of state with the a and b deduced by Van Laar in 1920. The fifth subject discussed is Meijer's Van Laar point in the classification of fluid phase equilibria by Van Konynenburg and Scott in 1968. They paid attention to computer calculations of critical lines and to phase equilibria with the theory of binary mixtures by Van der Waals. It originated in Van Laar's formula for spinodal and plait point curves of 1905. The sixth and last subject to be considered is retrograde solubility, a phenomenon Van Laar drew attention to in 1908 and which was experimentally observed in 1926.

### 3.2 Van Laar Equation

As mentioned in part 2.5, Van Laar deduced the formula for the heat of mixing (*Mischungswärme*) in his article in Z.Phys.Chem.: 'Ueber Dampfspannung von binären Gemischen' of 1910 (D.42). With the help of Van der Waals' mixing rules  $a_{\text{mix}}=x_1^2a_1+2x_1x_2a_{12}+x_2^2a_2$  and  $b_{\text{mix}}=x_1b_1+x_2b_2$ , Berthelot's relation for geometric averages  $a_{12}=.a_1a_2$ ,  $v^E=0$  (volume change by mixing is zero) and  $U^E=H^E=G^E$  by approximation  $-a/b$  for not associated liquid mixtures; it is written in mole fractions:

$$G^E = \frac{x(1-x)V_A V_B}{xV_A + (1-x)V_B} \left[ \frac{\sqrt{a_A}}{V_A} - \frac{\sqrt{a_B}}{V_B} \right]^2 \quad (1)$$

means that in mixing, heat is extracted from the mixture and it becomes colder. It is at zero (ideal solution) when  $\sqrt{a_1/b_1} = \sqrt{a_2/b_2}$ , which is only possible when both components have equal critical pressures. By partially differentiating this equation with respect to composition, the result is by definition Van Laar's two equations for the activity coefficients as a function of temperature, composition and properties of the pure components  $(a_1, b_1)$  and  $(a_2, b_2)$ .<sup>49</sup>

When however Van Laar's differential heat of mixing, described in section 2.5, is equated with the above mentioned given differentiation, it is apparent that they are equal. Van Laar found two terms that he likewise defined as correction terms for the molecular thermodynamic potentials for a binary mixture with the help of the parameters  $a$  and  $b$  of van der Waals (see Sechs Vorträge p.84-87). The terms for the molecular thermodynamic potentials were as follows:

$$\mu_1 = \mu_1^0 + \frac{\alpha x_2}{(1 + r x_2)^2} + RT \ln c_1 \quad (2)$$

$$\mu_2 = \mu_2^0 + \frac{\alpha x_1}{(1 + r)(1 + r x_2)} + RT \ln c_2 \quad (3)$$

when  $\alpha$  and  $r$  are expressions related to the parameters  $a$  and  $b$  of der Waals. When (2) and (3) are equated with Lewis' terms (4) and (5):

$$\mu_1 = \mu_1^0 + RT \ln(\gamma_1 c_1) \quad (4)$$

$$\text{and } \mu_2 = \mu_2^0 + RT \ln(\gamma_2 c_2) \quad (5)$$

then Van Laar's correction terms appear to be Lewis' activity coefficients.<sup>50</sup>

In Van Laar's last book of 1935 : 'Die Thermodynamik Einheitlicher Stoffe und Binäre Gemische...' (I.16) and his final publication in 'Chemisch Weckblad' of 1938: 'Het Bestaansrecht der Theoretische en Toegepaste Thermodynamica naast de Moderne Atoomtheorie' (H.47) give an insight in his ideas to Lewis' activity coefficients. On page 168 of his book he writes the following:

'Activitäten' zu reden, was nur ein Wort ist für eine Sache, von welcher der exacte Begriff den genannten Forschern (Lewis and Randall, v.E.) offenbar fehlt'. (The discussion about 'activity' which is only a word for something and about which the previously mentioned scientists (Lewis

and Randall, v.E.) apparently missed the correct meaning).

And in his publication Van Laar calls 'activity':

'para-thermodynamic'.

Van Laar would have turned in his grave, twice! Unfortunately he was very strict in his views and in his article of 1910 he after all deduced the two formulas which are equivalent to Lewis' activities! Now activity is called a thermodynamic auxiliary function and has proved very useful in chemical engineering.<sup>51</sup>

For the sake of completeness, it should be mentioned that there are four known expressions for Van Laar's formulas for the heat of mixing. The first is from Van Laar in 1910 and is already mentioned as formula (1), the second is by Hildebrand from 1919, the third is from Van Laar and Lorenz in 1925 (E.6), and the fourth is by Hildebrand-Scatchard from 1931.

While it is difficult to determine the Van der Waals constant  $a$ , Hildebrand changed the formula in 1919 and substituted for  $a$  the specific cohesion  $U/V = a/V^2$  to Van der Waals' equation of state.<sup>52</sup>

$$\frac{x(1-x)V_A V_B}{x V_A + (1-x) V_B} \left[ \left( \frac{U_A}{V_A} \right)^{1/2} - \left( \frac{U_B}{V_B} \right)^{1/2} \right]^2 \quad (7)$$

In 1925, in cooperation with Lorenz (E.6), the difficult-to-determine Van der Waals constant  $b$  was substituted by the molecular volume  $V$ , which is approximately  $4b$ . Equation (1) becomes:<sup>53</sup>

$$\frac{x_1 x_2 v_1 v_2}{(x_1 v_1 + x_2 v_2)} \left[ \frac{a_1^{1/2}}{v_1} - \frac{a_2^{1/2}}{v_2} \right]^2 \quad (8)$$

In the Netherlands this formula was critically discussed in a thesis by Staverman in 1938. He concluded that it is difficult to grasp what Van Laar's assumptions were.<sup>54</sup> Seen from a thermodynamic point of view, the assumptions are  $V^E = 0$  and  $S^E = 0$ . In 1931, Scatchard and Hildebrand used of Van Laar's theory about Van der Waals' equation of state, which led to the regular solution theory. Their formula is written with volume fractions.<sup>55</sup>



$$V_{\text{mix}} \varphi_A \varphi_B \left[ \left( \frac{U_A}{V_A} \right)^{\frac{1}{2}} - \left( \frac{U_B}{V_B} \right)^{\frac{1}{2}} \right]^2 \quad (9)$$

$V_{\text{mix}} = x_A V_A + x_B V_B$  the molecular volume of mixture.

### 3.3 Van Laar versus Dolezalek

In his article 'Zur Theorie der binären Gemische und konzentrierte Lösungen' of 1908 Dolezalek tried to explain the positive and negative deviation of the partial pressures of a binary mixture as compared to Raoult's law  $y_i P = x_i P_{i,\text{sat}}$ ,  $x_i$  and  $y_i$  is the mole fraction of solute,  $P_{i,\text{sat}}$  is the saturated vapor pressure of pure species and  $P$  is the vapour pressure of a solution, by assuming the partial association of the molecules of the mixture.<sup>56</sup> For the two components A and B, he assumed that complexes AB,  $A_2$  and  $B_2$  are formed with regard to the ideal state and that the partial pressures are determined by the mole fractions of the complexes in the solution. In 1909, after calculations with experimental data, W. Bein believed that he could prove Dolezalek's theory.<sup>57</sup> In 1909 T.S. Patterson thought that the theory contained a serious error.<sup>58</sup> He felt that the argument Dolezalek put forward, that volume contraction was a measure for the formation of complexes, was false. Dolezalek's second article: 'Über Dampfspannung von binären Gemische und konzentrierte Lösungen II' in 1910, gave a few examples of his theory with calculations.<sup>59</sup> These are the two publications to which Van Laar reacted so vehemently (D.42,45).<sup>60,61,62</sup> In Van Laar's article of 1910, 'Ueber Dampfspannungen von binären Gemischen' he deduced not only the well-known formula for the heat of mixing, but also showed that the deviations of Raoult's law found their origins in Van der Waals' theory for binary mixtures. In other words, an explanation for the deviations of Raoult's law results from the cohesive forces of molecules! As early as 1915 F.H. Campbell pointed out that Van Laar and Dolezalek's treatments were in fact complementary.<sup>63</sup> Later this was confirmed and repeated by J.H. Hildebrand in 1916 and C.W. Porter in 1921.<sup>64</sup> In this respect it is interesting that in 1969 H.G. Harris and J.M. Prausnitz again pointed to the difference in opinion between Van Laar and Dolezalek.<sup>65</sup> They differentiated between association ( $nB = B_n$ ) and solvation ( $nA + mB = A_n B_m$ ) and said that Dolezalek with his theory was the first to form the basis for the 'chemical theory of solutions'. About this discussion between Van Laar and Dolezalek, they remark:

'The borderline between chemical and physical forces is arbitrary and in many cases designation of mixture as 'chemical' or 'physical'

is only a matter of taste or convenience'.

In this respect it might be seen as typical of Van Laar who, after the death of Dolezalek in 1920, is reported to have said:

'Right, again someone who did not understand anything about it, has died'.<sup>66</sup>

With regards to the above mentioned controversy, it has to be noted that its basis is not just a question of tautology, it goes much further. The explanation by Dolezalek is actually very simple. When his formulas did not balance, he had recourse to association. Van Laar's approach was much more fundamental and is based on the force between particles and therefore won on points. From his postcard to Jorissen of 22 November 1917, it is obvious that Van Laar was convinced that Van der Waals was in complete agreement with him on this point.

### 3.4 Dilated Van Laar Model

When Van Laar's equation is applied to systems with a temperature above the critical temperature of the most volatile component, in particular in the area of the critical region of the least volatile component, the result is unsatisfactory. This was reported by Muirbrook in 1964.<sup>67</sup> At the beginning of the 1960's, the American researcher Chueh tried to adapt Van Laar's model.<sup>68,69</sup>

In 1946 Wohl evaluated and expanded the thermodynamics of the binary and ternary liquid systems.<sup>70</sup> His equation for binary mixtures is as follows:

$$G^E = \frac{RT (q_1 x_1) \cdot (q_2 x_2) \cdot 2a_{12}}{q_1 x_1 + q_2 x_2} \quad (7)$$

Here  $x_1$ ,  $x_2$  are the mole fractions and  $q$  is a measure for the sphere of influence of the molecules amongst each other. The difference with Van Laar's original equation (1) is that the constant  $b$  (from Van der Waals' equation of state) is replaced by  $q$  and that the quadratic term  $(\sqrt{a_A/V_A} - \sqrt{a_B/V_B})^2$  is replaced by  $2a_{12}$ , in which  $a_{12}$  represents the interaction energy between molecules 1 and 2 of the mixture. Wohl's equation is related to Van Laar's because this results after differentiation in equivalent formulas for the activity coefficient. Chueh, Muirbrook and Prausnitz adapted Wohl's equation in 1965 for experimental circumstances close to the

critical point by adapting  $q_1$  and  $q_2$ .

$$q_1 = v_{c1} \left[ 1 + \eta_{2(1)} \Phi_2^2 \right] \text{ and } q_2 = v_{c2} \left[ 1 + \eta_{2(1)} \Phi_2^2 \right] \quad (8)$$

$v_{c1}$  and  $v_{c2}$  are the critical volume of the pure component,

$$\Phi_2 = \frac{x_2 v_{c2}}{x_1 v_{c1} + x_2 v_{c2}}$$

and  $\eta_{2(1)}$  the so-called dilation constant. Substitution in Wohl's equation (7) after differentiation results in formulas for the activity coefficient for both components for a number of mixtures. These were studied in the early 1960's and reflected experimental results.<sup>71</sup> At the moment, the diluted Van Laar model is, as far as could be determined, no longer applied. This development has been replaced by a description of gas and liquid phases with one equation of state.

### 3.5 Van Laar's equation of state

As a result of Van Laar's 1920 formula for  $b(v) = b_g / (1 + (b_g - b_o)/v)$ , see section 2.5 of this chapter, he derived another formula in 1924 for  $a(v) = a_g / (1 + c/v)$ ,  $a_g$  being the value of  $a$  when  $v = \infty$ ,  $c = (a_g - a_o) \cdot b_o / a_o$ ,  $a_o$  and  $b_o$  are the smallest value of  $a$  and  $b$ .<sup>72</sup> Substitution in Van der Waals' equation of state gives the following:

$$\left( p + \frac{a_g}{v^2(1 + c/v)} \right) \left( v - \frac{b_g}{1 + (b_g - b_o)/v} \right) = RT$$

and after rearrangement:

$$\frac{pv}{RT} = 1 + \frac{b_g}{v - b_o'} - \frac{a_g : RT}{v + c}$$

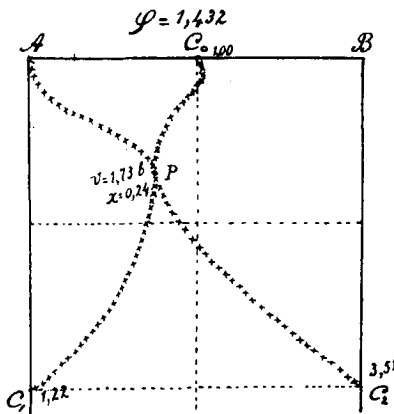
with  $b_o$  ( $b_o$  is the smallest value of  $b$  by  $v = 0$  or  $p = \infty$ ),  $b_g$  and  $c$ , in principle, as temperature dependent parameters.<sup>73</sup> This equation gives a good agreement with experiment.<sup>74</sup> Also note that the attractive term in this equation agrees with the attractive term in the cubic equation of state proposed by O. Redlich and J.N.S. Kwong in 1949 and modified by G. Soave in 1972.<sup>75</sup> However, more striking is the resemblance between Van Laar's equation of state and a cubic equation of state recently derived from a generalized Van der Waals theory by T. Sako, A.H. Wu and J.M. Prausnitz in 1989.<sup>76</sup>

$$p = \frac{RT(v - b + bc)}{v(v - b)} - \frac{a}{v(v + b)}$$

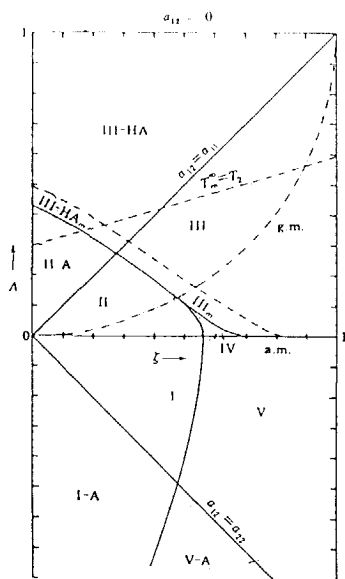
In this equation  $b$  is the volume parameter,  $a$  the temperature dependent energy parameter and  $c$  the total number of external degrees of freedom. For  $c = 1$  this equation reduces to the Redlich-Kwong equation of state. It is remarkable that the almost forgotten Van Laar equation of state was deduced in a more or less heuristic way, whereas the later equation has a background in statistical mechanics.

### 3.6 Van Laar Point

With the re-emergence of Van der Waals' equation of state in the 1960's, other related work was regarded in a different light.<sup>77</sup> This was also the case with Van Laar's equation for the spinodal and critical lines (Van Laar wrote: plait point lines) of 1905, described in part 2.4. With this equation calculated, and with the aid of Van der Waals' equation of state, Van Laar discovered that there was a double point.<sup>78</sup> Assuming that the co-volumes of both components are equal ( $b_1=b_2$ ) and assuming the validity of the empirical relation of Berthelot  $a_{12} = \sqrt{a_1 a_2}$ , he simplified the equations for the projections on the  $v, x$  plane of the spinodal and critical lines (plait point line) into two new equations. He thus discovered, after solving the seventh power equation, the double point. Van Laar calculated more plait point lines for different temperatures in the  $v, x$ -projection. In order to do this, he found the solution of the equation of fifth power and found the double point at  $\sqrt{a_1}/(\sqrt{a_2}-\sqrt{a_1}) = 1,43$  at  $v = 1,73b$  and  $x = 0,24$ . When the two corresponding critical lines are projected on the  $v, x$  plane, the result is Van Laar's figure as illustrated below.



In Van Konynenburg's dissertation 'Critical Lines and Phase Equilibria in Binary mixtures' of 1968, phase equilibria are calculated for all possible cases on the basis of Van der Waals' theory by computer.<sup>80</sup> Two new parameters for the difference of the molecules of kind 1 and 2 are introduced:  $\zeta$  is a measure for the dissimilarity and  $\Lambda$  is a measure for the affinity. By placing  $\zeta$  and  $\Lambda$  in a Cartesian coordinate system, a parameter space results in which four areas can be detected I, II, III and IV.<sup>81</sup> In this figure Meijer called the point of intersection of the double point curve with the geometric mean



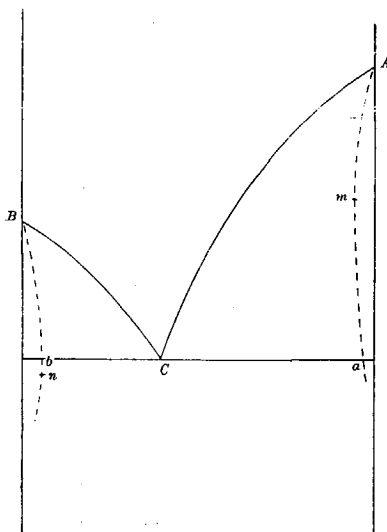
*The parameter space according to Van Konynenburg and Scott where the dotted line is the geometric average.*

curve, the 'Van Laar Point'. He studied this point in 1988 and discovered that it is not only a double critical endpoint but also a tri-critical point.<sup>82</sup>

### 3.7 Retrograde solubility

In his publications in 1903 in Reports Vers.K.Ned.Akad.Wet.: 'On the possible course of the melting point curve for binary mixtures of isomorphous substances' (A.9,10), expanded in Archives du Musée Teyler, 1904, (C.8) and later at Bakhuis Roozeboom's request included in 'Zeitschrift für physikalische Chemie' in 1908 (D.39), Van Laar predicted the form of the melting point lines (solidus) and found that the solubility of mixed crystal phases could show a turning point. Beside this point

solubility is retrograde.<sup>83</sup> In these articles Van Laar deduced, among others, a formula for  $T=f(x')$  in which  $x$  is the mole fraction and the prime refers to the solid state. He showed that these melting point lines (solidi) have a turning point, and with an example he calculated that these maxima



*Retrograde solidus by Van Laar in 1903.*<sup>84</sup>

were close to the vertical axis. In his 1908 article, he called these maxima: 'Merkwüdig'! During his research into the alloys of cadmium and zinc in 1926, Jenkins found the experimental confirmation of Van Laar's predictions.<sup>85</sup>

### 3.8 Concluding remarks

From this discussion of six modern topics, it will be obvious that Van Laar's significance is important, especially for the technological applications of physical chemistry. His name and work are still known but Van Laar himself would hardly have expected it. His field of interest has, apart from becoming a fundamental field of study, also become an applied science. If these concluding remarks are combined with those of chapter II, it is fair to say that the opinion of the Faculty of Mathematics and Sciences at the University of Amsterdam about Van Laar was incorrect and that Van Laar's work was in fact underestimated.

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# OBSTINACY

*'Immediately after Nernst's first publication on the subject I voiced my objections.'*

## 1. Introduction

That Van Laar could be positive as well stubborn and that he was not always appreciated by his contemporaries is shown by his opposition to the heat theorem and his intervention at the publication of solidification of helium of Keesom in 1926. This is discussed in parts two and three. His opposition to the heat theorem has been placed in a broader scientific context which shows that originally he was not alone and that his opposition could be related to a difference of opinion about the application of thermodynamics at the time.

## 2. Nernst's Heat Theorem

### 2.1. Introduction

The present day formulation of the heat theorem by Nernst nowadays called the Third Law of thermodynamics is as follows:

'By the standard methods of statistical thermodynamics it is possible to derive for certain entropy changes a general formula which cannot be derived from the zeroth, first, or second laws of classical thermodynamics'.<sup>1</sup>

In which the zeroth law reads: 'When two systems A and B are in thermal equilibrium with a third system C, then A and B are also in thermal equilibrium'. A more direct formulation is:

'For an arbitrary system in equilibrium  $S_{T \rightarrow 0} = 0$  is valid. The addition in "equilibrium" is necessary for all systems and also excludes mixtures, which at  $T = 0$ , because of their greater enthalpy, are unstable with regard to the demixing in stoichiometric compounds'.<sup>2</sup>

Nernst did not formulate the heat theorem this way in 1906 and 1907. At the time he was primarily interested in the position of the equilibrium of homogeneous gas reactions. Consequently, the title of his publication was: 'Ueber die Berechnung chemischer Gleichgewichte aus thermischen Messungen'. In this article he mentioned his 'neue Hypothese' for the first time. Later it would develop into the heat theorem, the Third Law of Thermodynamics. In the application of his 'neue Hypothese' he started from the equation of the maximum work or free energy for a closed system. Free energy was defined by  $F = U - TS$ . Since the entropy was  $S = -(dF/dT)_V$ , substitution resulted in the Gibbs-Helmholtz' equation:

$$F = U + T(dF/dT)_V.$$

This equation was identical to the equation of maximum work:

$$A_{\max} = U + T(dA/dT).$$

In 1906, during Nernst's time, the internal energy  $U$  was written as heat  $Q$ . Here the symbol  $U$  is maintained. In this expression,  $A_{\max}$  is the maximum work in an isothermal process in a closed system. The factor  $(dA/dT)$  is called the temperature coefficient of the maximum work.

Some opinions about Nernst are described first and then follows an investigation into the formation of his thermodynamic views. To show how Nernst's heat theorem was received in the Netherlands, observations are included on the theorem in the light of the first two original publications of 1906 and 1907.

A description of the reception the heat theorem received in the Netherlands and the reactions of Van Laar, Scheffer, Kohnstamm together with Ornstein, Kruyt, and others are also included. Van der Waals reacted indirectly to the theorem but Kohnstamm and Ornstein did not accept it in any form. Van Laar was particularly critical of Nernst's deduction; the criticism mainly touching on the way in which Nernst applied his heat theorem for the calculation of the equilibrium constant of homogeneous gas reactions. Kruyt criticized the treatment of the transition of rhombic into monoclinic sulphur.

The primary aim of this chapter is to investigate whether these reactions echo the tradition, policy and culture of the Faculty in Amsterdam, which were described in Chapter I. By doing so it will show whether Van Laar's objections were his own private concern or whether they had cultural components of the Faculty. The material studied will also show whether Van Laar's views on the heat theorem developed over the years.

## 2.2. Nernst

Walther Nernst (1864-1941) was the third son of a judge. He studied in Zürich, Berlin, Graz and Würzburg and studied with Ostwald among others. It was primarily the theoretical physicist L. Boltzmann (1844-1906) who made a great impression on him with his atomistic interpretation of natural processes.<sup>3</sup> In 1891 he became professor in the new Institut für physikalische Chemie und Elektrochemie in Göttingen and in 1905 he succeeded H.H. Landolt (1831-1910) in Berlin. In 1920 he was awarded the Nobel Prize for Chemistry and in the fields of theoretical and experimental physics as well as chemical physics he ranked among the most prominent scientists. During the time of his 'Wärmesatz' he was held in high regard because of his theory about the galvanic cell. His book 'Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik', was first published in 1893, and the fifteenth edition had appeared by 1926. With his softspoken but penetrating voice he was a great teacher. He was a curious man: authoritarian, clever in business but no great mathematician.<sup>4,5</sup>



*W. Nernst (1864-1941).<sup>6</sup>*

Letters from Kohnstamm and Van Laar to Lorentz give an idea of how he was regarded in academic circles. Kohnstamm expressed his opinion (one probably shared by others in the Faculty at the University of Amsterdam) in an undated letter, - probably 1912 - to Lorentz:

'As for the matter of the theory of mixtures on the other hand, with which I was especially engaged, I have seen him and his school do so much damage, in the way of premature generalizations and because they are set on the idea that one has to develop simple theories on all subjects, that I indeed regret to see, how even the problem of chemical equilibrium which Boltzmann investigated with great sagacity and delicacy is now, with his authorization, decided on too rashly.

I write you this because this is closely related to your reproach that I would, above everything else, be combatting the heat theorem. In principle I am of course totally impartial as to whether two substances have equal or different entropy and when we succeed in expanding our knowledge of this area I will be very pleased. However the way in which Nernst, and many others, have tackled the problem is no expansion, but a danger to our knowledge and I am indeed sorry to see that he has succeeded in diverting the attention from the points in question. Of course, I also feel a certain kind of admiration for the clever way in which he used Planck's and Einstein's results on specific heat and created the impression that there is a close correlation between that theory and the original theorem of heat, which at the time had nothing to do with it. But my admiration is (unreadable) only of the kind I have for a clever director, not for a scientific genius. I of course exclude from these remarks, his experimental work which I have also praised in my article'.<sup>7</sup>

Van Laar was also negative in his letter to Lorentz on 18 August 1899.

'I know that they will not be unfounded, like the nonsensical objections of Noyes, Nernst etc. who never mastered higher mathematics (perhaps not even essential maths). Fortunately there is no example in our country of such insufferable superficiality. One who has just taken his degree here is certainly at a higher level than most Germans. But let me not make the same mistake - which I have just criticized - as Van der Waals'.<sup>8</sup>

The mistake Van der Waals made was that he classed the scientists by rank. It is certain that Van der Waals sometimes doubted the praises that



were bestowed on him from abroad because the mathematical knowledge there was considered to be substandard. He believed the thermodynamic knowledge in the Netherlands to be superior to that in Germany.<sup>9</sup> He did not want a German to fill the vacancy left by Bakhuis Roozeboom while the treatment of osmotic pressure in Germany was inadequate!

The origin of the heat theorem suddenly came to Nernst as the solution to a problem he had long been deliberating.<sup>10</sup> He thought of it while lecturing in 1905 and formulated it for the first time in 1906 as 'neue Hypothese'.<sup>11,12</sup> The hall in which Nernst lectured and had his brain wave survived the ravages of the World War II and in 1964 a plaque was mounted there to mark the centenary of Nernst's birth.

IM JAHRE 1905 ENTDECKTE  
**WALTHER NERNST**  
IM VERLAUF SEINER IN DIESEM  
SAALE GEHALTENEN VORLESUNG  
DEN 3. HAUPTSATZ  
DER THERMODYNAMIK.  
DIE HUMBOLDT-UNIVERSITÄT  
GAB 1964, IM JAHRE  
DES 100. GEBURTSTAGES  
DES GROSSEN GELEHRTEN,  
DIESEM HÖRSAAL DEN NAMEN  
**WALTHER-NERNST-  
HÖRSAAL**

*Plaque in the Institute of Physical Chemistry in Berlin.*<sup>13</sup>

As for thermodynamics, Nernst combined the first and second laws into the formula for the maximum work. He argued as follows:

If a reservoir of heat of the absolute temperature  $T + dT$  quasi-statically transfers an amount of heat  $Q$  to a second reservoir of heat with absolute temperature  $T$ , it is, according to experimental experience, possible to obtain a maximal amount of work  $dA$  which is equal to  $Q(dT/T)$ . If the difference in internal energy  $U_2 - U_1$  is abbreviated to  $U$ , and the difference between the external work  $A_2 - A_1$  abbreviated to  $A$ , then, the heat  $Q$  from the first law equals  $A - U$ , or,  $dA = (A - U)dT/T$ . He rewrote the formula for the maximum work  $A_{\max} = U + T(dA/dT)$ , the equation of Helmholtz, in which the differential quotient  $dA/dT$  equals the entropy  $S$

of Clausius.<sup>14</sup> Under the maximum work it is understood that the work in a chemical reaction which can have a maximal effect on its surroundings, provided that the process proceeds isothermally. In 1913 Nernst, through Planck, became aware of the deduction which is based on the definition of free energy as was described in the introduction.<sup>15</sup>

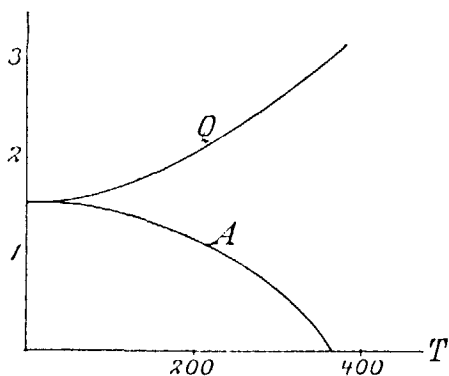
This also shows the difference between the schools of thought of Van der Waals in Amsterdam and Nernst in Berlin. In Amsterdam, Van der Waals based his work on the views of Gibbs, while Nernst on the other hand worked with the ideas of H.L.F. Helmholtz (1821-1894) and combined the first and second laws into the formula for the maximum work. In Amsterdam this might well have been regarded as old fashioned and would have been a reason for considering Nernst in a poor light.

### 2.3. Nernst's Heat Theorem 1906 and 1907

In 1906 and 1907 Nernst published two articles, the first being submitted on 23 December 1905 and published in 1906.<sup>16</sup> The second was submitted on 6 December 1906 and published in 1907.<sup>17</sup> In both articles his thoughts were called 'neue thermodynamische Hypothese'. The first article was mainly about the calculation of the chemical equilibrium from thermal measurements and the second gave a calculation of among other things, the transition temperature of sulphur and the electromotive force of the Clark cell. These two publications formed the basis of principles for the heat theorem. The theorem was formulated much more accurately due to Planck's work and in 1911 was completely confirmed by the  $T^3$ -law for specific heat by Debye. In 1917 and again in 1924 Nernst gave a full discussion on the topic comprising all the similar publications on the theorem available in books.<sup>18</sup>

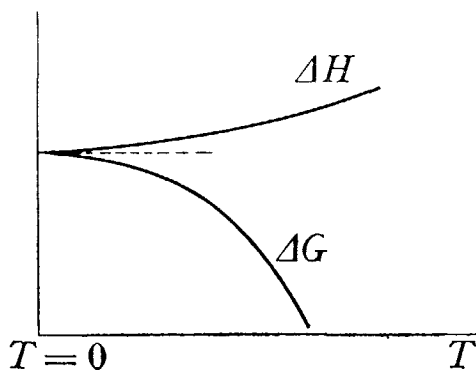
Nernst observed that in the electrical cell, the maximum work  $A$  was never equal to the change in internal energy  $U$  (Nernst wrote  $Q$ ). Neither could  $A$  be calculated by integration of the formula for the maximum work because the constant factor in the integration could not be determined. However Nernst observed that in electrical cells with only solid matter and/or highly concentrated solutions  $A$  and  $U$  at room temperature differed very little. This gave Nernst the sudden idea that at lower temperatures the difference between  $A$  and  $U$  would be further reduced. In this way he formulated the hypothesis that at absolute zero the difference had to be nought. According to Nernst,  $A$  and  $U$  would approach each other asymptotically at absolute zero (neue Hypothese), or:

He illustrated this in his second publication with the following diagram.



*The heat of reaction  $Q$  (or  $U$ ) and the maximum work  $A$  as function of the temperature according to Nernst in 1907.<sup>19</sup>*

For the sake of completeness it is noted that Nernst's symmetrical representation of  $U$  and  $A$  is incorrect. At that time he did not know the  $T^3$  law. The correct diagram is as below.



*The course of the enthalpy and free enthalpy as a function of  $T$  at constant pressure.<sup>20</sup>*

The importance of Nernst's theory is:

1. For condensed systems (pure liquids and solids) the maximum work (free energy) and the heat of reaction (internal energy) are equal at absolute zero temperature. The incorrect 'Principe du Travail Maximum' by Berthelot becomes true at absolute zero temperature. The term

$T(dA/dT)$  in the formula for the maximum work may be regarded as a correction on the 'Principe'.

2. The differential quotient of the maximum work and of the heat of reaction at absolute zero temperature are both equal to zero.

In connection with the unattainability of the absolute zero temperature, the views of Nernst cannot be directly tested experimentally and other methods have to be applied. He gave calculations in the two publications mentioned.

To understand the reception of the heat theorem by Van Laar and others in the Netherlands, it is sufficient to present Nernst's computations for the homogeneous gas reaction, the transition temperature of sulphur and the calculation of the electromotive force of the Clark cell.

#### a. Homogeneous gas reaction

With the 'neue Hypothese',  $\lim dA/dT = \lim dU/dT = 0$  for  $T = 0$ , it is possible to calculate the equilibrium constant for the homogeneous gas reaction.



This was discussed in Nernst's first publication. Without actually saying so, he assumed the condensed substances which took part in the reaction to be quasi-statically transformed into saturated vapours. The reaction took place in the gas phase after which the products of the reaction were again condensed quasi-statically. The volume of the condensed phase was neglected here with respect to the volume of the saturated vapour. To be able to apply the 'neue Hypothese' as a limit, he had to find an expression for the maximum work  $A$ . He achieved this by applying a formula for the maximum work for diluted solutions:

$$A = RT[\ln K - \ln(c_1^{v_1} c_2^{v_2} \dots)/(c_3^{v_3} \dots)]. \quad (2)$$

$\ln K$  is found in the Van 't Hoff's formula and  $\ln(c_1^{v_1} c_2^{v_2} \dots)/(c_3^{v_3} \dots)$  in the formula by Clapeyron by replacing the concentrations by partial-pressures. This worked as follows. For the equilibrium constant  $K$  of reaction (1) the equation of Van 't Hoff applied:

$$d \ln K / dT = U / RT^2. \quad (3)$$

to the following power series:  $U = U_o + \alpha T + \beta T^2 + \gamma T^3 \dots$  (Later this was replaced by Einstein and Debye by the  $T^3$ -law of specific heat, v.E). Here  $U_o$  was the heat of reaction at  $T = 0$ . By substitution of these series in equation (3) it follows that, after integration, an expression for the equilibrium constant is obtained.

$$\ln K = -U_o/RT + (\alpha/R)\ln T + \beta T/R + \gamma T^2/2R + \dots + J \quad (4)$$

J was the undetermined integration constant. For Nernst the next step was to find J. Hereto he had substituted the concentrations  $c_i$  in the second term  $\ln(c_1^{v_1} c_2^{v_2} \dots)/(c_3^{v_3} \dots)$  of formula (2) by  $p_i/RT$  and applied for each component the equation of Clapeyron  $(1/p) dp = (L/RT^2) dT$  in order to find  $p_i$ . L was the heat of evaporation of component i. Again he assumed on empirical grounds that the evaporation heat L could also be developed in a power series:  $L_i = L_{i,o} + a_i T + b_i T^2 + \dots$  Substitution of this in Clapeyron's equation followed after integration of one component i in the vapour pressure formula:

$$\ln p_i = -L_{i,o}/RT + (a_i/R)\ln T + (b_i/R)T + \dots + j_i \quad (5)$$

By converting to Brigg's logarithm, Nernst found through experimentation that  $a_i/R = 1,75$ . (Later, this proved to be a rough estimate and would lead to much discussion and strong opposition for Van Laar, v.E). By using the values of  $\ln K$  and  $\ln p_i$  found so far in the formula for the maximum work (2) the result was:

$$A_{\max} = -(U_o - \sum v_i L_{i,o}) + (\alpha - \sum v_i a_i) T \ln T + (\beta - \sum v_i b_i) T^2 + RT(J - \sum v_i j_i) \quad (6)$$

By applying the 'neue Hypothese' as a limit proposition, (6) was differentiated to T, and neglecting the quadratic term:

$$(dA/dT)_{T=0} = (\alpha - \sum v_i a_i) (1 + \ln T)_{T=0} + R(J - \sum v_i j_i) \quad (7)$$

Substitution of (6) and (7) in the formula for maximum work  $A_{\max} = U + T(dA/dT)$  resulted in an expression for U which differentiated to T and neglecting the terms of higher powers resulted in the following expression:

$$(dU/dT)_{T=0} = -(\alpha - \sum v_i a_i).$$

Because  $(dU/dT)_{T=0}$  according the limit proposition  $\lim dA/dT = \lim dU/dT$  is equal to zero,  $-(\alpha - \sum v_i a_i)$  also equals zero. After substitution of

this in the expression (7) it followed that  $R(J - \sum v_j j_i) = 0$ , or:

$$J - \sum v_j j_i, \text{ (Nernst writes } J = \sum v_j j_i \text{)}. \quad (8)$$

Nernst said:

‘Denn die zunächst völlig unbestimmte Integrationskonstante J ist dadurch auf eine Summe von Integrationkonstante j zurückgeführt, die jeder einzelnen Substanz eigentümlich sind und durch an jeder einzelnen Substanz auszuführende Messungen ermittelt werden können’.<sup>21</sup>

It can be seen that the limiting proposition of Nernst’s results in equalizing the integration constant resulted from the integration equation (3) and that the sum of the integration constants resulted from the integration of Clapeyron’s equations for each component.

After this interesting discovery Nernst continued with the calculation of the integration constant J. To do this he wrote the integration constant in another form by introducing the so called: ‘chemical constants’.

Because the equilibrium constant K was expressed in partial pressures, and he worked not with Napierian’s but with Brigg’s logarithm, the  $j_i$  and J were converted. Nernst introduced the chemical constant  $c_i$ , and wrote c, which was equal to:

$$c = (j + \ln R)/2,302. \quad (9)$$

Now the chemical constant could be calculated and it was possible to find the unknown integration constant J because

$$C = (J + \sum v \ln R)/2,302 \text{ and } C = \sum c. \quad (10)$$

In his first publication he calculated the chemical constants for ten gases. Subsequently he used the vapour pressure formula for the saturated vapour of Van der Waals’  $\log p_v/p = f(T_v/T - 1)$  of 1880 (Law of Corresponding States), and experience showed that the chemical constant was equal to  $C = 1,1f$ . With this empirical connection he calculated another 13 chemical constants.<sup>22</sup> By ignoring the quadratic term  $\gamma T^2/2R$  in expression (4) for the equilibrium constant, and rewriting this with the help of the formula for the chemical constant, the following formula resulted:

$$\log K' = -U_o/4,571T + \sum v_1,75 \log T + (\sum v_b)T/4,571 + \sum v_c. \quad (11)$$

With formula (11) Nernst tested the theorem on the dissociation of H<sub>2</sub> and CO<sub>2</sub> and the formation of NO<sub>2</sub>, HCl and NH<sub>3</sub>OH.<sup>23</sup> He did not calculate the equilibrium constant but entered a chosen equilibrium constant as 100 times the dissociation constant and then calculated the matching temperature. Again and again the calculated values corresponded with the experimental data.

Later, in 1912, a very young physicist from Amsterdam, Hugo Martin Tetrode (1895-1931) deduced a formula for monoatomic gases for the chemical constant.<sup>24,25</sup> The seventeen year old physicist did this with the help of the statistical theory of Boltzmann. An identical formula was deduced at the same time by the German physical chemist O. Sackur (1880-1914).<sup>26</sup>

### b. Transition point of sulphur

In his second article Nernst considered condensed systems; this simpler and more straightforward development of A and U (or Q) in the power series in the coefficient of the terms with T had to be zero as a consequence of the above limiting proposition:

$$\lim dA/dT = \lim dU/dT \text{ for } T=0.$$

If higher terms are neglected the result is:

$$U = U_o + \beta T^2 \text{ and } A = A_o - \beta T^2. \quad (12)$$

The values at T = 0 are equal to U<sub>o</sub> = A<sub>o</sub> according to the heat theorem.

The first example chosen was the transition of rhombic to monoclinic solid sulphur.<sup>28</sup> For the calculation of the two unknown parameters U<sub>o</sub> and A<sub>o</sub> and β, Nernst used experimental data for U from Brönsted and Tammann at two different temperatures. The result was U<sub>o</sub> = A<sub>o</sub> = 1,55 cal/g and b = 1,14·10<sup>-5</sup> cal/g·grade. At the transition temperature T<sub>e</sub>, the maximum work (free energy) of both modifications in equilibrium was equal, thus Δ = 0 (A was in reality ΔA, the difference between both modifications). Then T<sub>e</sub><sup>2</sup> = 1,55/1,14·10<sup>5</sup> or T<sub>e</sub> = 368.8 K equal to 95.8°C, Nernst took 94.4°C. The careful experimental determination by L.T. Reicher (1857-1943) under the supervision of Van 't Hoff in Amsterdam gave 95.6°C.<sup>29</sup> This correspondence was too good to be true given the very rough treatment by Nernst, based on a linear dependence of specific heats on T

and also on the imprecise thermal data used.

This apparently excellent correspondence was one of the points of criticism by the opponents of Nernst's heat theorem, for example Van Laar and Kruyt.

Nernst was well aware of the lack in accuracy of his reasoning. In the last sentence of his second publication he stressed the need for measurements of specific heat down to the boiling point of hydrogen. Helium was first liquified two years later.

### c. Electromotive force

Even in his first two publications Nernst mentioned the fact that the electromotive force could be deduced from thermal quantities.<sup>30,31</sup> If the formula for maximum work was applied to the produced electrical energy of a galvanic cell, then  $A = n \cdot F \cdot E$ ;  $n$  was the number of electrochemical equivalents that took part in the reaction,  $F = 96540$  Coulombs and  $E$  was the electrical energy. Because 1 Voltequivalent = 23046 cal. the formula reads as follows:

$$E_T = U/(23046 \cdot n) + T(dE/dT) \quad (13)$$

and shows at  $T = 0$  the connection between electrical energy  $E_T$ , the heat of reaction  $U$  and the temperature coefficient  $dE/dT$ . Although Nernst did not make the distinction,  $U$  was not the energy, but the enthalpy, because the measurements of  $E_T$  were taken at constant pressure. However, in reactions between condensed phases, the difference could be ignored. Nernst took the Clark cell as an example. The reaction which produced electrical current in this device was  $Zn + H_8SO_4 + 7H_2O = ZnSO_4 \cdot 7H_2O + 2Hg$ . In order to have to deal with the reactions of only pure compounds, Nernst studied the Clark element at the cryohydratic temperature of 266 K ( $-7^\circ C$ ) where ice is present in the solution. At this temperature  $E_T = 1,4624$  V from which Nernst estimated in his second publication  $A = 67405$  cal/mole with  $n = 2$ . The heat effect was measured at 290 K ( $17^\circ C$ ) but the measured value had to be corrected to 66600 cal/mol for the heat of melting of ice at  $17^\circ C$  from the experimental value at  $0^\circ C$  and the difference of the specific heat of water and ice. Nernst satisfied himself by stating that at temperatures far above zero the difference between  $A$  and  $U$  for such condensed systems was already very small. This made it possible to calculate the EMF of a galvanic element in which only pure substances were involved in the reaction equation for the production of electric energy. No mixtures or solutions were introduced



unless ice was present. Indeed the difference between A and U for a normal Clark element at 291 K was far greater than calculated above.

## 2.4. Addition by Planck in 1911

In 1911 the theorem of heat was changed significantly by M. Planck (1858-1947). In the third edition of his textbook 'Thermodynamik' in 1911, Planck included a chapter about the 'Absoluter Wert der Entropie. Theorem von NERNS'T'.<sup>32</sup> In this chapter he discussed the heat theorem. Initially in Nernst's views, the reaction entropies of transition of solid and liquid substances, that is also the differences between the entropies of the components, would become zero at the limit of the absolute temperature going to zero:

$$\begin{aligned} \text{Lim } (S_2 - S_1) &= 0 \text{ for } T = 0 \\ \text{and also } \text{Lim } dF/dT &= \text{Lim } dU/dT = 0 \text{ for } T = 0. \end{aligned}$$

The additional postulate made by Planck was:

$$\text{Lim } S_i = 0 \text{ for } T = 0 \tag{14}$$

for all pure solids and liquids. Planck, contrary to Nernst, explicitly excluded solutions at 0 K, which would still have had a positive entropy (but which could not exist if the equilibrium was thought to be maintained on cooling).

## 2.5. Van Laar

### a. 1906 and 1909

In November 1906 Van Laar was the first to react to the heat theorem. Later, in 1927, he wrote the following in 'Chemisch Weekblad' (H.30):

'Immediately after Nernst's first publication on the subject I voiced my objections. The article, intended for publication in 'Z. Elektrochem.' had already been printed and corrected when the editor Abegg kindly but urgently requested me to retract the article because Nernst had 'energisch' (energetically v.E.) protested against publication. The corrected version of the article which was written on 10 November 1906 has been in my drawer ever since... The article is free for everyone to see, perhaps some university might one day ask for it, to include it as a curiosity in a list! Anyway, my fight is not a recent one but ever since the start in 1906 I have been a declared opponent of the heat theorem'.<sup>33</sup>

The article of 1906 which is mentioned here has been lost.<sup>34</sup> In his book 'Sechs Vorträge über das thermodynamische Potential' of the same year, Van Laar made a short note about Nernst's deduction of the formula about the equilibrium constant of homogeneous gas reactions. Van Laar pointed out that Nernst's formula (11) was the same as Gibbs' equation for ideal gas mixtures of 1876. Van Laar preferred the Gibbs equation.<sup>35</sup> In Van Laar's publication: 'Die Schmelz- oder Erstarrungskurven bei binären Systemen, wenn die feste Phase ein Gemisch der beiden Komponenten ist, und eine Verbindung auftritt' (D.39) from 1909 he deduced with reference to his first publication of 1892: 'Zur Thermodynamik der elektrolytischen Dissoziation' (D.1) corresponding the Gibbs method a general expression for  $K$  and  $d \log K/dT$ . He considered Nernst's method to have an insufficiently theoretical foundation because it took an empirical formula as its starting point.  $\lim dA/dT = \lim dU/dT$  for  $T=0$  was therefore, he believed, also untenable.

#### **b. 1918, 1924, 1926 and 1927**

In 1918 he wrote in 'Chemisch Weekblad': 'Over de dissociatiewarmte van tweeatomige gassen in verband met de verhoogde waarde van de  $\sqrt{A}$  der vrije atomen' (H.17).<sup>36</sup> At the end of the publication he noted that equation (11) had no bearing on the heat theorem.

'This theorem only says something - and that provides its strength - with regard to the approaching of zero of the entropy of specific heat, etc. at  $T = 0$  in condensed systems, which makes it possible to relate the constants  $C$  etc. of the separate gas components with the corresponding constants of the vapour pressure equations. But as long as these constants cannot be calculated by an independent method, and we are thus forced to determine these from a few vapour pressure measurements, and this at very low temperatures, thus far, nothing has been gained (...)

Furthermore he pointed out that it had only recently become possible to determine the chemical constant statistically.

Consequently, in 1924, Van Laar wrote in the preface to his book 'Die Zustandgleichung von Gasen und Flüssigkeiten' that he did not use the heat theorem because at very low temperatures it automatically came into its own in the so-called 'quantum area'. Debye and Einstein had shown that at very low temperatures specific heat became zero at absolute zero temperature.<sup>37</sup> According to Van Laar the heat theorem should not be applied at higher temperatures because classic thermodynamics was

sufficiently adequate. In this book he also made objections to the 1,75 in the vapour pressure formula (5). His views became fully known in 1926 and 1927.

In 1926 Van Laar toured the Netherlands and gave several lectures at different chemical societies and at the Technological Society in Delft. He lectured on the 'Dwaalwegen der Wetenschap' and about Nernst's heat theorem and its consequences. An account of his lecture about the heat theorem of 1926 and his own account of his lecture in 1927 were preserved (H.30).<sup>38</sup> In this report he called Nernst's heat theorem a serious mistake but admitted that Nernst intuitively found a qualitative solution to the problem but that he had not proved anything. Only Debye's quantum theory could clarify the matter. Van Laar explained this as follows:

According to Debye the inner energy was equal to:

$$U = U_0 + AT^4 + \dots + P. \quad (15)$$

In the presence of external forces, P referred to the potential energy. (P could be omitted at atmospheric pressures for condensed systems, v.E.). The specific heat then became  $C_V = (dU/dT)_V = 4AT^3$ , and the entropy at low temperatures:

$$\begin{aligned} \Delta S &= \int_0^T dQ/T = \int_0^T (C_V/T) dT = \int_0^T (4AT^3/T) dT = \int_0^T 4AT^2 dT \\ &= 4/3 \cdot AT^3. \end{aligned} \quad (16)$$

The constant of integration was zero because  $S = 0$  at  $T = 0$ . This approach to zero of the third power of the entropy at absolute zero was, according to Van Laar, the real content of the heat theorem. The theorem could only be valid when this essential condition was met. Helmholtz's free energy  $F = U - TS$  became for low temperatures:

$$\begin{aligned} F &= U_0 + AT^4 + P - T \cdot 4/3 \cdot AT^3 \\ &= U_0 + P - 1/3 \cdot AT^4. \end{aligned} \quad (17)$$

When the equations (15) and (17) were compared, the U and F lines would not be in a symmetrical position with respect to each other. Nernst actually sketched this in his book of 1921.<sup>39</sup> This diagram was the same as the original symmetrical diagram based on his equations  $U = U_0 + \beta T^2$  and  $A = A_0 - \beta T^2$ . According to Van Laar, Nernst made three mistakes:

1. He neglected the potential energy P by using an abbreviated formula. (This was not straightforward because for condensed systems  $U = H$  and  $F = G, v.E$ ).
2. He used  $U = U_0 + \beta T^2$  instead of  $U = U_0 + AT^4 + \dots + P$ . (In 1906 Nernst could not have known the difference, v.E).
3. The formula which were valid at lower temperatures were also valid at higher temperatures, even at 4000°! (I have never read such an argument in Nernst papers, v.E).

As for the transition temperature of sulphur, Van Laar believed that Nernst chose the constant of integration in a way that it fitted the transition temperature fairly accurately, in this case at 96° (This is not true since Nernst accounted  $U_0$  and  $b$  at two temperatures, v.E). Finally Van Laar showed that the factor 1,75 in formula (11) was not correct.

Van Laar's own report appeared one year later, in 1927, in 'Chemisch Weekblad' (H.30). His account was somewhat expanded and further explained his lecture about the heat theorem.<sup>40</sup>

'There was Nernst with his incredible solution pressure, of billions and milliards of atmospheres 'die nie ein Sterblicher gemessen hat, auch wahrscheinlich nie gemessen wird', as Jahn expressed it in his battle with Nernst'.

He ended the article as follows:

'And now we approach the second part of this lecture in which Nernst's heat theorem, which was one of the greatest sources of scientific iniquities, is discussed'.

That the article was a success may be demonstrated by a postcard of 6 April 1927 to Jorissen:

'On Monday I received several letters of congratulations from Dutchmen paying homage to my article!!!<sup>41</sup>

He sent Jorissen the following postcard on 23 April 1927 with the second article:

first, but it is best to type set and publish it in one go. I do not think that I have ever discussed the matter so clearly, so completely, and such a clearly structured way, and I have tried to achieve 'Gemein Verstandlichkeit' at least as far as possible with such a difficult subject. Of course the reader gets a lesson in thermodynamics, unfortunately there are no textbooks which can do that nowadays.<sup>42</sup>

If the subjectivity of the article is disregarded, it shows that his objections were the same as those he stated in his lecture. He deduced the vapour curve formula and showed that  $c_3'$  and  $c_2'$  were the specific heats along the vapour curve and were not equal to the specific heats at constant volume or constant pressure.

Thereupon he stressed the fact that according to his evidence of 1926 helium did not degenerate at lower temperatures. This issue is referred to again in the next chapter.

During 1926 and 1927 a polemic arose between Van Laar and Keesom. Correspondence of the time shows Keesom's opinion on the article because on 22 June 1927 Keesom wrote to Lorentz:

'In the first place, Van Laar asserts much which, to put it mildly, is open to discussion. I even believe, that the question on the validity of Nernst's heat theorem will not have to be solved in the way that Van Laar handles the question'.

And about the article in 'Chemisch Weekblad':

'Concluding I feel that Van Laar has gone too far in his opposition to Nernst and has far surpassed the limits of propriety'.

and further:

'In which among other matters Nernst is charged with unlimited superficiality. In my view it would be well for you to look at the article. I believe it to be very sad that something like this appears in a serious Dutch magazine ('Chemisch Weekblad'.v.E.) and I further feel that there is nothing to be gained by this for Dutch science, but possibly much to be lost'.<sup>43</sup>

In 1930, when Van Laar celebrated his seventieth birthday, 'Chemisch Weekblad' devoted a whole issue to him. J.E. Verschaffelt wrote about

Van Laar as a physicist and his opinion about Van Laar and the heat theorem is as follows:

'It is curious that he never made use of the so-called heat theorem or the third law; he pointed out that such a theorem is only significant in the area of the quanta, that is, at very low temperatures, while all the determinations with respect to the vapour pressure are outside that area, even for solid matter. It is therefore understandable that Van Laar took issue with the authors so vigorously, authors who have misused the theorem, by applying it to liquids at, for instance, relatively high temperatures in which a noticeable influence of the quanta could not be discerned and classic thermodynamics still applies to the full. Therefore he is proud to have written a heat theorem-free book that is based solely on classic thermodynamics'.<sup>44</sup>

## 2.6. Other views

### a. Scheffer 1910

In 1910 Scheffer began giving his lectures as an unsalaried lecturer with a public lecture about 'Over Snelheden en Evenwichten en hun Onderling Verband'.<sup>45</sup> In this lecture he too discussed Nernst's heat theorem, and reached the following five conclusions:

1. The substitution which Nernst applied with the series  $U = U_0 + \alpha T + \beta T^2 + \gamma T^3 \dots$  in the equation by Van 't Hoff, leads in principle to the same equation as Gibbs' 1876 equation for ideal gas mixtures. Like Van Laar, Scheffer preferred Gibbs' equation.
2. Though the specific heats of solids normally decrease with decreasing temperatures this was not necessarily true for the algebraic sum.
3. About  $J = \sum v_j$ , he said that this was in concurrence with Gibbs' equation which was mentioned earlier. The constant of integration could not be determined, neither could it be determined directly with the help of Gibbs' equation. However, if the theorem was right, it could be done indirectly through the vapour pressure determination of pure matter.
4. With regards to the application of the abbreviated series  $A = U_0 - \beta T^2$  and  $U = U_0 + \beta T^2$  in relation to the transition temperature of sulphur, he found that these sometimes resulted in curiously accurate results.

5. About the heat theorem in general, Scheffer said that the applications were close to the truth.

One year later, in his article about gas equilibria, Scheffer wrote in *Vers.K.Ned.Akad.Wet.* that the entropy constants were to be found in Nernst's constant of integration J.<sup>46</sup>

#### **b. Van der Waals 1910**

In his lecture in 1910, Scheffer intimated that he had asked J.D. van der Waals Sr. about the physical theories which supported Nernst's assumptions. Van der Waals had answered that, in his opinion, there was insufficient support to be found in physics to back Nernst's views, but that every effort to calculate the constant of integration of the chemical equilibrium, even by a 'find' like this, should be welcomed. It should be noted that at the time Van der Waals apparently did not think of Einstein's theory of 1907 about specific heat which states that the specific heat of all solid matter approaches zero at absolute zero temperature.

#### **c. Lorentz 1910**

Lorentz's theoretical evidence on the theorem is dated 1910. It was worked out in his notebook from 1910-1911 and was finally published in 'Chemisch Weekblad' on 12 July 1913.<sup>47</sup> He believed that the heat theorem boiled down to the fact that the entropies of two condensed phases which contained one single component and between which transition was possible at continually decreasing temperatures, became more and more equal and became equal at absolute zero temperature. He stressed the fact that as early as 1912 Nernst had provided the theoretical evidence with the principle that in experiments in which there were only finite changes, it was impossible to reach absolute zero temperature. With this principle and Einstein's theoretical discussions,  $\lim(T \rightarrow 0) c_v / T = 0$  was demonstrated. Later this was confirmed by experiments. Based on the first and second law, Lorentz deduced that  $dv/dT = c_v (dv/dp) / T (dv/dT)$  and showed with  $\lim(T \rightarrow 0) c_v / T = 0$  that he was in conflict with Nernst's heat theorem when at absolute zero temperature  $dv/dT$  maintained a finite value. In other words,  $dv/dT$  had to become zero at absolute zero temperature. After that he basically did the same in the case of two phases with one component each and by equating the thermodynamic potentials he came to the same result. He thus believed the heat theorem to be proven.

#### **d. Kohnstamm and Ornstein 1910**

Kohnstamm and Ornstein's attacks on the heat theorem of December

1910 were based on Scheffer's lecture of the same years.<sup>48</sup> A letter dated 22 December 1910 from Ornstein to Lorentz shows that Kohnstamm urged him to combine his observations with Ornstein's. Ornstein objected, but agreed after Kohnstamm's insistence.<sup>49</sup> They began from a fictitious case and chose a reaction in which the number of molecules before and after the reaction remained the same. Furthermore, for all elements taking part in the reaction as well as for the products, Van der Waals' equation of state with  $a$  and  $b$  are constant was valid. Their discussion consists of two parts. In the first part they found an expression for the entropy difference between products and reactants for this fictitious case:

$$\eta_2 - \eta_1 = \sum \nu MR \log(v_2 - b_2) - \sum \nu MR \log(v_1 - b_1) + \int_1^T \frac{\sum \nu c_{2v\infty}}{T} dT - \int_1^T \frac{\sum \nu c_{1v\infty}}{T} dT + \sum \nu H. \quad (18)$$

$\nu_i$  is stoichiometric coefficient,  $M$  is the molecular mass of reactants and products,  $c$  is the specific heat,  $R$  the gasconstant,  $T$  the absolute temperature,  $v$  the volume and  $b$  the constant of Van der Waals.  $\sum \nu H$  is the sum of entropy constants.

Since it was assumed in advance that in this fictitious case Van der Waals' equation of state was valid,  $T = 0$  also meant  $v = b$ . Because the way in which they wanted  $v$  to approach  $b$  could not be determined, neither could  $S_1$  or  $S_2$  be found at  $T=0$ . This meant that the value of the entropy difference  $S_1 - S_2$  at absolute zero temperature was undetermined. This matter, so they said, was hidden by Nernst because his reaction took place in the phase of saturated vapour and he later condensed the products into liquid. Kohnstamm and Ornstein then showed that the expression  $d(S_1 - S_2)/dT$ , which was equal to the temperature coefficient ( $dA/dT$ ) in the equation of maximum work, did not become zero at  $T = 0$ , but became infinite. With this they believed to have sufficiently refuted the heat theorem. Nernst should not have asked the question about how matter behaved at absolute zero temperature, but should have asked how he could have found something about the entropy constants at absolute zero temperature. (The error in their argument is that they assumed gases persist as such in the limit of  $T = 0$ , Nernst however applied his theorem on condensed systems at  $T = 0$  only, v.E).



In the second part they applied Boltzmann's kinetic gas theory. This discussion was provided by Ornstein. In 1908, under the supervision of Lorentz, Ornstein was awarded a doctor's degree on the dissertation 'Toepassingen van de Statistische Mechanica bij Gibbs' (Applications of the statistical mechanics of Gibbs), in which he found an expression for the entropy. In the article with Kohnstamm he calculated the average entropy difference between products and reactants for the reaction  $\text{H}_2 + \text{I}_2 = 2\text{HI}$ . Ornstein found an analogous expression with a rest term of unknown value  $\log w$  which was equal to the sum of the entropy constants  $\sum \nu H$ . According to Kohnstamm and Ornstein this reduces the heat theorem to the thesis that Boltzmann's 'chemical volume'  $w$  was a characteristic value. (This discussion confirms the earlier conclusion but the error is the same as in the first part of their work: the heat theorem is applicable only to condensed systems at  $T = 0$ , v.E).

Finally, they pointed out that the choice of specific heat in the formula (18) for the calculation of the entropy difference was so large that the value of  $\sum \nu H$  could be changed within very broad limits without contravening the experiments. (This criticism is correct with respect to the results used in the proof that Nernst gave, but it does not disprove the heat theorem, v.E). The heat theorem was, therefore, not accepted by the two authors.

Lorentz's archives show that Lorentz and Nernst corresponded about the heat theorem from 2 May 1911 until 24 April 1912. Eight letters by Nernst have been preserved and in his letter to Lorentz of 2 May 1911 he pointed out that the article by Kohnstamm and Ornstein was of polemic character and apparently based on a misunderstanding:

'Vor kurzer Zeit ist in den Verhandlungen Ihrer Akademie eine Arbeit über mein Wärmethorem erschienen, die rein polemisch ist, jedoch auf offenbaren Missverständnissen beruht.

Aus der sehr konfusen Darstellung glaube ich folgenden Kern herauschälen zu können: Die Autoren (Kohnstamm und Ornstein) gehen von der Formel von van der Waals aus, nehmen dieselbe als bis zu den tiefsten Temperaturen gültig an, finden, dass man da nicht zu meinen Wärmesatz gelangt und halten ihn so für erledigt. Nun habe ich auch längst darauf hingewiesen, dass mein Wärmesatz mit der Theorie der Energiequanten von Planck und Einstein in engster Beziehung steht: dann ist es natürlich selbstverständlich dass die Formel von Van der Waals, die ja übrigens bei tiefen Temperaturen

schon längst als ganz unbrauchbar erkannt worden ist, mit meinem Wärmesatz nicht harmonieren kann.<sup>50</sup>

Nernst criticized the fact that Kohnstamm and Ornstein based their discussion on Van der Waals' formula, assuming that this would also be valid at low temperatures. He correctly believed this was not true. His heat theorem was closely related to Planck and Einstein's theory of 'energy quanta' and in the letter he included two papers on the quantum theory, probably articles by Planck and Einstein.

A second letter by Nernst, of 15 May 1911, shows that Lorentz requested Nernst to change the tone of his remarks and Nernst agreed to do this:

Einliegend übersende ich die Notiz, meinen Wärmesatz betreffend: Ich habe nach Möglichkeit die form gemildert: freilich bleibt die Zurückweisung des Angriffs etwas scharf, aber daran wird sich schwer etwas ändern lassen, weil eben der ganze Angriff von missverständlichen Voraussetzungen ausgeht und die Autoren sicherlich besser daran getan hätten, einen Sache nicht anzufassen, deren Verständnis offenbar ein wenig ihre Kräfte übersteigt.

Ich übersende gleichzeitig eine Darstellung meines Wärmesatzes die ich vor einem Jahre gegeben habe und, wenn sie sich vollständig sachlich mit allen meinen anderen Arbeiten deckt, doch vielleicht etwas klarer ist, als meinen früheren Darstellungen.

Darin findet sich auch besonders deutlich betont, dass bei tiefen Temperaturen das Kräftepotential  $A$  (von Helmholtz kurz 'Ergal' genannt) sich doch unmöglich ändern kann, wenn man die Quantentheorie als zutreffend annehmen darf; denn im Sinne dieser Theorie behalten ja doch gerade die einzelnen Atome bei festen und flüssigen Körpern auch noch ein wenig oberhalb des absoluten Nullpunkts ihre Stellung unverändert bei;  $\lim dA/dT = 0$  ist ja aber der *gesamte* Inhalt meines Satzes.

Eine zweite Notiz, die ich beilege und soeben erscheinen ist, bringt vielleicht eine der schlagendsten Bestätigungen der Quantentheorie, freilich auch zugleich eine gelinde Modifikation derselben; unser Erklärungsversuch der neuen Formel kann übrigens, wie ich mich bei einem Gedankenaustausch mit Planck und Einstein überzeugte, nur verstanden werden, wenn man die kürzlich in der Zeitschrift für Elektrochemie von mir gegebene und Ihnen kürzlich übersandte

Darstellung der Quantentheorie zu Hilfe nimmt; an sich unterliegt natürlich der Versuch einer Zerlegung des Energieinhalts in einen kinetischen und einen zweiten potentiellen Bestandteil gewissen Bedenken.<sup>52</sup>

In the same month, May 1911, Nernst visited the Netherlands but did not have the opportunity to visit Kohnstamm.<sup>51</sup>

In a third letter, of 25 May 1911, it becomes clear that Nernst regretted not having discussed the 'Grenzübergang' (transition temperature) properly. He wrote:

(...) Ingefolgedessen muss ich mich sehr kurz fassen, wenn ich nun mehr auf Ihre so klaren und überzeugenden Äusserungen, meinen Wärmesatz betreffend, eingehe: ich bedaure natürlich noch täglich, dass ich nicht vom Anfang an die Frage des Grenzüberganges eingehender behandelt habe. Aber die Sache lag doch, wenn man Sie etwas anders ansieht, wiederum so einfach, dass Bedenken kaum entstehen konnten.

Dass letzte Glied ist nämlich in Ihrer Gleichung (4)

$$A - U = T(dA/dT)_p + (a_1v_1 - a_2v_2)pT$$

gegen A und U *absolut* zu vernachlässigen.

*Erstens* sind der Natur der Sache nach *alle* meine bisherigen praktischen Anwendungen so, dass man sich am einfachsten die Verwandlung oder Reaction *unter dem Dampfdruck* vor sich gehend denkt: beim Schwefel setzt man z.B.  $A = RT \ln p_1/p_2$  ( $p_1$  und  $p_2$  Dampfdrucke der beiden Modifactionen) und ähnlich in allen Fällen. Nun wird der Dampfdruck (bei  $T = 20^\circ$  für Schwefel sicher kleiner als  $10^{-30}$  Atmosphären und man sieht leicht, dass beim Grenzübergang  $(a_1v_1 - a_2v_2)pT$  kein Billionstel von A oder U sein kann; eine solche Genauigkeit aber möchte ich meinem Satze überhaupt nicht zuschreiben.

*Zweitens* habe ich gezeigt (Planck hat sich dem später angeschlossen), dass

$$\lim a_1 = \lim a_2 = 0 \text{ (für } T = 0)$$

sein muss, wenn mein Satz richtig ist; der Beweis findet sich S. 236 der Abhandlung die ich gleichseitig übersende, und ich habe diese Stelle auch in dem Manuscript, das Sie haben, S 2 zitiert.

*Drittens*, und dass ist vielleicht die allgemeinsten Behandlung, kann (unreadable) die Umwandlung bei constanten Volum sich abspielend und dann die umgewandelte Substanz auf das dem betreffenden Druck entsprechende Volumm gebracht sich denken; diese Möglichkeit erwähnen Sie ja auch in Ihren freundlich Schreiben. Da nun auf beide Vorgänge mein Theorem ohne Weiteres anwendbar ist, so darf er auch auf die Umwandlung bei constantem Druck ohne Weiteres angewandt werden.

Alle diese Dinge sind mir natürlich seit Jahren bekannt und so geläufig, dass ich sie, gewiss mit Unrecht, als fast selbstverständlich angesehen habe; es wäre gewiss richtiger gewesen, sie einmal gründlich zu besprechen, anstatt (sie) nur, wie ich es in meinen Arbeiten gethan habe, kurz im streifen. Aber trotzdem muss ich gegenüber Kohnstamm und Ornstein betonen, dass ich bei meinem Rechnungen keine unerlaubte Vernachlässigung oder gar einem logischen Fehler begangen habe, und sie hätten dies einsehen müssen, wenn sie nicht so völlig oberflächlich und unüberlegt an die Fragen herangegangen wären.

Wenn ich (unreadable) noch einmal mein Manuscript, von dem ich eine Copie hier habe, durchsehe, so gebe ich vollkommen zu, dass ich auch dort mich ausführlicher hätte äussern können; aber ich finde keine Wendung erheblich zu ändern - ich habe die oben mit *drittens* bezeichnete Grenzmethod S. 2 angedeutet - und Kleinigkeiten kann ich vielleicht im Manuscript noch bei der Correctur ändern. Ich glaube, ich bin berechtigt zu betonen, dass K. und O. Unrecht haben, wenn sie der Grenzübergang bei constanten Volum finden einzig erlaubten handeln (unreadable), und das ist ja der Inhalt der beiden ersten Seiten.

Ich sehe soeben noch in Ihrem Briefe, dass die Wendung in der Einladung betr. Constanz den spez. Wärme der Gase besser geändert werden muss; es wird dies natürlich geschehen und ich weiss auch, dass Boltzmann eine Darstellung gibt, nach der änderungen möglich wären. Trotzdem glaube ich zeigen zu können, dass nach Boltzmann z.B. das starre  $O_2$  = Molekül (—) seine spez. Wärme eigentlich mit der Temperatur nicht

ändern dürfte, wenn man aus seinen Grundannahmen die letzten Konsequenzen zieht. Aber das sind natürlich mehr Fragen für den 'Conseil' und gehören nicht auf die 'Einladung'.

Mit vielen Grüßen und (unreadable)  
Dank für Ihr ausführliches schreiben. Ihr ergebener  
W. Nernst.<sup>53</sup>

N.B. Es würde mir natürlich eine sehr grosse Freude sein, wenn Sie sich noch weiter mit meinem Satz beschäftigen und mir gelegentlich darüber schreiben wollten. d.O.

\*)Ich muss um Entschuldigung bitten, dass ich Ihnen jetzt soviel Abhandlungen ins Haus sende! d.O.

In May 1911 Lorentz and Zeeman submitted Nernst's publication to Vers.K.Ned.Akad.Wet.<sup>54</sup> In it, Nernst explained that his 'neue Hypothese'  $\lim dA/dT = \lim dU/dT = 0$  at  $T = 0$  was not clear to either Kohnstamm or Ornstein. With the help of the transition between rhombic and monoclinic sulphur, he explained it again. Then he showed that Van der Waals' equation could not be reconciled with his heat theorem at very low temperatures, but that this did not mean that the heat theorem was false. Furthermore, experiments by G.A. Tammann (1861-1938) showed that super-cooled liquids assumed a glassy state and that Van der Waals' equation was no longer valid.

In his fourth letter, of 31 May 1911, Nernst thanked Lorentz for his trouble and in his fifth letter, on 30 June 1911, he mentioned the fact that his article had been submitted to the Akademie, not by Van der Waals, but among others by Zeeman.<sup>55</sup> According to Nernst, this implied that Van der Waals did not seriously object to the attack by Kohnstamm and Ornstein.<sup>56</sup>

The long letter from Kohnstamm to Lorentz of 28 June 1928 shows that Lorentz was forced to discuss the theorem because of certain circumstances and that he sent his ideas to Kohnstamm on 12 June 1911.<sup>57</sup> This was probably Lorentz's same attempt to find evidence that was written in his notebook and that he later published in 'Chemisch Weekblad' on 12 June 1913. The content of Kohnstamm's letter is rather confused and was at the time, and still is, debatable. In the meantime, the first Solvay conference took place and apparently Nernst, Einstein and Lorentz discussed the heat theorem there. Thus Nernst's letter of 25 December

1911 to Lorentz is very interesting and is reproduced in full:

Hochverehrte Herr College!

Ihre freundlichen Zeilen vom 19 d.M. beantworte ich erst Heute, weil ich noch inzwischen mit Collegen Warburg über das Projekt gerne sprechen wollte, was Heute geschehen ist. Einen besseren Vorschlag, als der in Ihrem Briefe entwickelt ist, wird man unter den gegebenen Umständen gewiss nicht machen können; ob das kleine Institut in Brüssel viel der Physik wird leisten können, kann ja fraglich sein, aber jedenfalls wird man es versuchen müssen, um so mehr, als Herr Solvay mit Recht darauf Wert legt.

Warburg und ich können also Sie nur bitten, ganz in der Weise vorzugehen, die Ihnen als der geeignete Weg erscheint.

Darf ich zwei kleine wissenschaftliche Bemerkungen zufügen? 1) Die Gleichung

$$(I) A_v - U_v = T(dA/dT)_v$$

ist meiner Meinung nach zweckmässig für homogene Gasreactionen, aber bisher wohl kaum auf andere prozesse, wie Umwandlung, galv. Elemente u.dgl. angewendet worden. Hier operiert man besser und hat es wohl ausschliesslich bisher getan mit der Form

$$(II) A_p - U_p = T(dA/dT)_p;$$

z.B. hat man den Temperaturcoefficienten  $dE/dT$  des Clark-Elementen u.s.w. doch immer nur bei constanten *Druck* bestimmt,  $U$  ist doch ebenfals nur bei constanten Druck (z.B. für  $H_2O$  (fast) -  $H_2O$  (fl!)  $Ag + J = AgJ$  etc) bekannt. Es ist mir allerdings aufgefallen dass man bisher (I) theoretisch abgeleitet, mit (II) aber ausschliesslich oder fast ausschliesslich in den charakterizierten Füller operiert hat. Es ist aber leicht zu zeigen, dass (II) vollkommen exact gilt. Nach meinem Wärmesatz gilt sowohl

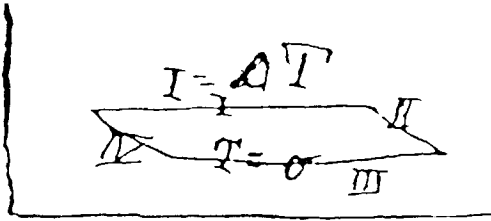
$$\lim (dA/dT)_v = 0 \text{ wie } \lim (dA/dT)_p = 0,$$

aber *prüfen lässt sich zur Zeit nur die zweite Beziehung.*

nach (unreadable) sein!

Ich möchte nachträglich vermuten, dass bei einer Unterredung in Brüssel Sie die Form (I), ich aber als Experimentator die bisher (z.B. auch bei der Umwandlung  $S_m - S_{rh}$ ) allein benutzte Form (II) im Auge gehabt haben u. dass wir deshalb nicht sofort einig wurden.

2) Wenn man als erfahrungsthatsache annimmt, dass die spez. Wärmen festen Körper bei sehr tiefen Temperaturen verschwinden, so kann man leicht durch Rechnung finden, dass es möglich sein muss, den absoluten Nullpunkt durch Distillation fester Körper, durch den reversibelen Umsatz (unreadable) exact zu erreichen.



(original sketch from Nernst's letter)

Dann aber könnte man durch einen Kreisprozess (I u. III isotherm, II u. IV adiabatisch) einem Reservoir von der niedrigen aber *endlichen* Temperatur  $dT$  beliebig viel Wärme entziehen, um sie in (unreadable) Arbeit umzusetzen, *falls nicht mein Wärmesatz gelten würde.*

Mit anderen Worten: es genügt, dass die spez. Wärmen beim Absoluten Nullpunkt verschwinden (sogar nur von ersten Ordnung null werden!), um meinen Wärmesatz *exakt* zu beweisen.

Ich habe das betr. Manuskript, das ich denn nicht unserem Akademie vorlegen werde, Planck gezeigt, und er war überrascht von dem Resultat, aber ganz überzeugt. Die Sache liegt jetzt so einfach und klar, wenn man die Rechnung durchführt, dass Raum für einen Zweifel, soweit ich sehe, gar nicht übrig bleibt. Sie werden aber gewiss auch ohne Rechnung sofort den obigen Kreisprozess durchschauen u., wie ich denke, ebenfalls zustimmen.

In Brüssel glaubte ich noch, die spez. Wärme müsste von höherer Ordnung verschwinden, um meinen Wärmesatz ableiten zu können;

Sie u. Einstein bestritten dies. Nun aber glaube ich bewiesen zu haben, dass ich nicht nur Recht hatte, sondern sogar zu wenig behauptet habe. Natürlich empfinde ich einige Genugthuung, dass mein naturwissenschaftliche Instinkt zwei solchen Theoretikern, wie Sie u. Einstein, gegenüber stand gehalten hat - vorausgesetzt natürlich, dass Sie nicht doch in meinen Beweis eine Lücke finden werden, was ich allerdings nicht glauben möchte.

Mit vielen Grüßen und Wünschen zum neuen Jahre, Ihr ergebener  
W. Nernst.<sup>58</sup>

On 30 December 1911 Kohnstamm and Ornstein reacted to Nernst's publication in *Vers.K.Ned.Akad.Wet.*<sup>59</sup> They announced that because of additions by Planck there had been an important change in their views on the theorem and that using Van der Waals' law was not an essential element in their discussion. They said that the heat theorem was not one single theorem, but consisted of the three following, separate theorems:

1. The specific heat at constant pressure becomes zero at absolute zero temperature, in accordance with  $\lim C_p \log T = 0$ .
2. At absolute zero temperature the entropy of a solid matter becomes independent from the pressure, or  $(dS/dp)_T = 0$ . In other words, constant pressure is no binding condition for the occurrence of the reaction. Because  $(dS/dp)_T = - (dv/dT)_p$  is valid, the expansion coefficient of all matter will have to approach the limit zero.
3. The entropy difference maintains a finite value when mixed crystals or amorphous solid solutions are present in the products or reactants of the reaction. If that is not the case, the entropy difference becomes zero.

Both authors stressed that their original discussion was related to the last point, but that a change in the emphasis to the first two points was noticeable. Then they repeated their discussion but without mathematical evidence. They failed to see how their objections would be less urgent and very much doubted whether any conclusions could be drawn on the basis of experimental data on the entropy difference of a chemical reaction which took place at absolute zero temperature. This was demonstrated by the dissociation of carbon dioxide and water. For both reactions they showed that the constant of integration in the formula for equilibrium constants could be found with data on specific heat. Since these data



varied in technical literature, the values which were found for the constant of integration varied as well. Their conclusion was that the value of the constant of integration was determined by the extrapolation of the specific heat. This, in principle, is also true for the vapour pressure formula. They believed the relation between integration constant  $I$  ( $J$  in Nernst) and chemical constant  $C$ , as well as the application of 1,1f to find the chemical constants with the help of Van der Waals' vapour pressure equation to be dubious.

All in all they maintained their initial conclusion and reached a 'non liquet' on the heat theorem.

They believed that evidence for the heat theorem had to be found in the statistical theory on the entropy and entropy difference of a chemical reaction as the function of the reaction temperature.

In a letter dated 30 March, 1912 to Lorentz, Nernst reacted to the second discussion by Kohnstamm and Ornstein. The letter shows that Lorentz, Einstein and Nernst discussed the heat theorem in Brussels at the Solvay conference. Concerning Kohnstamm and Ornstein's discussion, Nernst wrote:

'Nun haben inzwischen Kohnstamm und Ornstein ja noch einmal in Ihrer Akademie hierzu sich geäußert. Wenn die Autoren am Schluss ihrer Abhandlung behaupten, 'man müsste chemische Reaktionen in der nächsten Nähe des absoluten Nullpunk(t) es untersuchen, um meinen Wärmesatz exact zu prüfen', so zeigen sie, dass sie immer noch nicht begriffen haben, warum es sich eigentlich handelt; denn es ist doch ganz klar, dass man nur die spezifischen Wärmen bis hinreichen tiefer Temperatur und zwar nicht einmal bis zum absoluten Nullpunkt, sondern nur bis zu denjenigen Temperaturen, bei welchen die Wärmetönung des Prozesses nach dem Gesetz von der Erhaltung der Energie sich als unabhängig von der Temperatur herausstellt, zu messen braucht, um meinem Wärmesatz völlig exact zu prüfen, wie ja auch Planck kürzlich ausgeführt hat und wofür das Buch von Pollitzer zahlreiche Belege bringt. Aber auch sonst enthält die letzte Abhandlung der genannten Autoren so zahlreiche handgreifliche Missverständnisse, dass ich in der Tat nicht umhin kann, zu bedauern, dass Ihre so hochangesehene Akademie derartig unreife Betrachtungen zum Abdruck hat bringen können. Noch einmal zu erwiedern, scheint mir unter solchen Umständen überflüssig; denn eine wissenschaftliche Polemik hat ja doch nur einen Sinn, wenn

man bei dem Gegner ein gewisses Verständnis der strittigen Frage voraussetzen darf; da andererseits ein Stillschweigen meinerseits unrichtig gedeutet werden könnte, so frage ich ganz ergebenst an, ob Sie die grosse Freundlichkeit haben wollen, meine obige Auffassung in einer Sitzung Ihrer Akademie zum Ausdruck zu bringen und ob es (was weniger richtig wäre) angängig ist, dass ein entsprechender kurzer Vermerk in Ihren Sitzungsprotokollen aufgenommen wird'.<sup>60</sup>

On 24 April 1912 Nernst wrote to Lorentz:

'Sehr habe ich mich gefreut, dass der Beweis meines Wärmesatzes bei Ihnen keinen Widerspruch findet; vielleicht hätte ich noch deutlicher betonen sollen, dass ich die Hypothese weisse, *dass bei  $T=0$  die gewöhnliche Potentialtheorie gilt*, d.h. dass A und U nicht etwa asymptotisch gleich werden, sondern einfach *identisch* sind; gibt man dieser Hypothese zu, so ist mein Beweis, wie ich denke, völlig streng. Nach Ihren freunl. Zeilen vom 22 d. M. scheint es mir das Einfachste, die neue Arbeit K + O auf sich beruhen zu lassen'.<sup>61</sup>

Apparently Nernst believed the acceptance of his evidence by Lorentz to be of such great importance that he put the second article by Kohnstamm and Ornstein to one side.

In 1911 Ornstein proved that entropy and probability were related and in September 1911 he provided the requested statistical evidence for the heat theorem: For two co-existenced solid phases at absolute zero temperature the solid state is  $S_1 - S_2 = 0$ .<sup>62,63</sup>

By this time Lorentz had written to Kohnstamm once again. Kohnstamm probably answered this letter in January 1912 (the letter is undated).<sup>64</sup> His letter shows that on the advice of Lorentz  $c_p = 0$  was replaced by  $c_p \log T = 0$  with  $\lim T = 0$ . Although Kohnstamm was thoroughly convinced that nothing he could write would have any effect, he defended his views again and rejected Lorentz's evidence.

However, Kohnstamm gradually accepted the heat theorem and in 1927 the third edition of the textbook 'Lehrbuch der Thermodynamik' of 1908 by Van der Waals and Kohnstamm was published. The title was changed to 'Lehrbuch der Thermostatik' and Kohnstamm stresses in the preface that the conversations about the heat theorem with P. Ehrenfest (1880-1933) and J.D van der Waals Jr. (1873-1971) were very instructive. He

gave a contemporary discussion but did not openly react to the earlier criticisms of 1910 and 1911.<sup>65</sup>

#### **e. Cohen 1911**

Cohen wrote five articles about the thermodynamics of standard cells. Three appeared in 'Zeitschrift für Physikalische Chemie' and the other two came out in 'Chemisch Weekblad'.<sup>66</sup> In 1911 he criticized the work of F. Pollitzer, who had calculated the electromotive force for the series Hg-HgCl-PbCl<sub>2</sub>-Pb with the help of the heat theorem.<sup>67</sup> He found 82770 calories for the forming heat of PbCl<sub>2</sub> and suspected that this was a few thousand calories short. He determined the electromotive force at 234 K at 0.4636 volts. Cohen stated that the experimentally determined value of the heat of formation for PbCl<sub>2</sub> was false.<sup>68</sup> The value which was found for the electromotive force was of no use because it was found by extrapolation and was not experimentally determined. In 'Chemisch Weekblad' he wrote that the value had to be 0.5216 volts and that the difference between this value and Pollitzer's calculated value was wrong because Pollitzer used a lead amalgam electrode instead of an electrode of pure lead. When Pollitzer's values are corrected in this respect, the correct values are found.<sup>69</sup> However, Nernst felt that Pollitzer's ideas were correct and he did not believe that Cohen offered any material evidence.<sup>70</sup>

#### **f. Kruyt 1913**

It is well known that the element sulphur occurs in a great many forms including in crystalline and rhombic sulphur. In the Netherlands, Kruyt was the first to investigate the allotropy of sulphur experimentally. These experiments took place in Utrecht and Groningen between 1908 and 1913. His results were published in four articles in 'Zeitschrift für physikalische Chemie', and a fifth article appeared in Vers.K.Ned.Akad. Wet.<sup>71,72</sup> Next, he discussed the relation between the three triple points of sulphur in 'Chemisch Weekblad'.<sup>73</sup> In the meantime, an English translation of Kohnstamm and Ornstein's second article was published in Vers.K. Ned.Akad.Wet. In his fourth article Kruyt took up this point and discussed the transition temperature of monoclinic and rhombic sulphur in relation to Nernst's heat theorem. Kruyt started with the following remark about Kohnstamm and Ornstein:

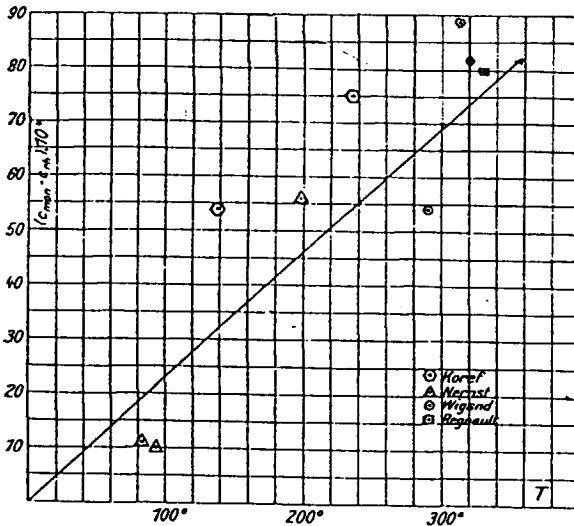
'Uebrigens möchte ich darauf hinweisen, dass, wenn ihr (K. en O.) Ausgangspunkt richtig gewesen wäre, mir dennoch die Tragweite ihrer Bemerkung nicht klar ist. Nernst verwendet Zahlenwerte, die sich auf den reinen, kristallinischen Schwefel beziehen (auf Schwefel, der wenigstens annähernd als "reiner" Schwefel zu bezeichnen ist).

Er werd somit bei der berechnung auch die Umwandlungs temperatur des reinen S $\lambda$  finden. Welchen einfluss hätte es nun, wenn diese Temperatur im pseudobinären System, weit vom Gleichgewichte entfernt, wohl einmal 10° tiefer liegen könnte? Will man jene Zahl Finden, muss man selbverständlich ganz andere Konstanten benutzen'.

In 1910 Nernst's second report about the investigation into specific heat at lower temperatures appeared.<sup>74</sup> The report discussed among other subjects the transition temperature of sulphur and related this to Kirchhoff's equation, and suspected a linear relation:

$$dU/dT = c_{\text{mon.}} - c_{\text{rh.}} = aT$$

Nernst gave a review of the experimental results of Nernst, Koref, Wignand and Regnault. Kruyt discussed this review and combined the results in the following graphical representation by Nernst. Nernst chose  $a = 2.3 \cdot 10^{-5} \text{ cal/T}^2$ . Kruyt sketched this curve and concluded that it did not present the experimental results of Nernst's publication adequately.



$$dU/dT = (c_{\text{mon}} - c_{\text{rh}}) \cdot 10^{-5}$$

In the rest of the discussion he omitted one of the values (Wignand's at  $T = 290^\circ$ ) and with the equation  $U = U_0 + bT^2$  he calculated the value of the transition temperature  $T$  for sulphur just as Nernst had done. By combining the values for  $U$  and  $b$ , which he discovered elsewhere, he

found the transition temperatures of 63°, 72° and 9°C. Kruyt did not consider these temperatures to be in satisfactory correspondence with the values he had found: 95.9(± 0.1)°C.

#### **g. After 1920**

In 1921 W.H. van de Sande Bakhuyzen (1888-1946) was awarded a doctor's degree under the supervision of Schreinemakers on the thesis: 'Het Warmtetheorema van Nernst'. He discussed thermodynamics and dealt with the applications on condensed systems and the theorem for gases and solutions. About the transition temperature of sulphur he said:

'Summarizing we may say that the allotropy of sulphur does not support Nernst's heat theorem, because the mistake of the calculated transition temperature is certainly within the experimental errors in the determination of specific heats. This calculation cannot be called unsatisfactory for Nernst's theorem'.<sup>75</sup>

In the thesis there is no other criticism of the heat theorem.

In 1927 the textbook 'Thermodynamica' by M. de Haas.<sup>76</sup> (1866-1951) was published. In the widely used book, he discussed the heat theorem in a way which closely follows Nernst's publications. However, he discussed the equilibria with the help of Gibbs' method for equation of thermodynamic potentials.

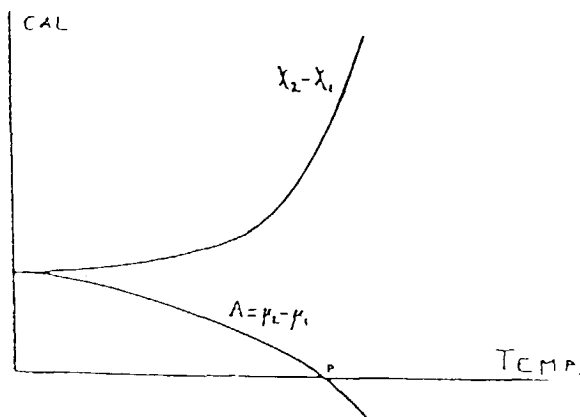
In 1930 D. MacGillavry (1902-1987) who was working under the supervision of J.M. Bijvoet (1892-1980) published a discussion in 'Receuil des Travaux Chimiques des Pays Bas' about the heat theorem which was based on Lorentz's evidence from 1913.<sup>77</sup> He showed that absolute zero temperature could not be reached. Furthermore he stated that Nernst's heat theorem was correct for physical as well as chemical equilibria consisting of pure matter. The specific heat in them reduced as fast with temperature as Lorentz had assumed in his hypothesis.

In 1932 Bijvoet, together with H. Verweel (1901-1937), discussed the heat theorem in an in-depth article in 'Chemisch Weekblad'.<sup>78</sup> They assumed that the energy difference as well as the entropy difference at standard conditions determined the position of the equilibrium of a chemical reaction. In combination with Boltzmann's formula  $S = k \ln W$ ,  $W$  is probability, applied at absolute zero temperature for crystals:  $W$  is equal to 1, or  $S_{T=0} = 0$ . A general section followed in which they found the transition temperature of sulphur directly with the help of the equation of

the thermodynamic potentials  $A = \mu_2 - \mu_1 = 0$  for the transition of phase 1 to phase 2:  $H_2 - H_1 = T(S_2 - S_1)$ ,  $H$  is enthalpy. By substituting the formula  $S_T = \int_0^T (C_p/T)dT$  in place of  $S$ , the following expression was determined:

$$(S_2 - S_1) = T \left( \int_0^T (C_{p,2}/T)dT - \int_0^T (C_{p,1}/T)dT \right). \quad (19)$$

With this equation inserted in  $(H_2 - H_1) = T(S_2 - S_1)$  the following diagram results.



*Diagram by Bijvoet and Verweel  
where  $\chi_2 - \chi_1$  is  $H_2 - H_1$ .*

The reaction heat  $U$  was now replaced in the original diagram made by Nernst in his second publication in 1907 by the enthalpy difference  $H_2 - H_1$  and the maximum work  $A$  by the difference of thermodynamic potentials,  $\chi_2 - \chi_1$ .

### 2.7 Concluding remarks

Consideration of the content of the undated letter by Kohnstamm to Lorentz indicates that it is not surprising that Nernst did not enjoy a good reputation in Amsterdam.

Nernst's discussions of 1906 are interesting. He must have had a great intuitive insight into the application of the formula for maximum work on the chemical reaction. His first publication of 1906 is primarily about the calculation of the chemical equilibrium from thermal measurements of gas reactions. In it he applied his heat theorem as a limit statement  $\text{Lim}(dA/dT)_{T=0} = \text{Lim}(dQ/dT)_{T=0} = 0$  for the first time. Despite the fact

that he discussed gas reactions in his publication, his heat theorem is about solid pure matter. It is clear that he was not aware of Gibbs' method: the equalizing of thermodynamic potentials in the discussion of equilibrium problems. Van der Waals in Amsterdam was however aware of the method. This clearly shows the difference in Nernst's opinion on the one hand and Van der Waals' on the other. Despite Nernst's more primitive discussion and Planck's formulation in 1911, Nernst's assertions of 1906 remain correct. Several years later, in 1912, Debye showed that in the proximity of absolute zero temperature the specific heat of a solid matter is proportional to the third power of absolute zero temperature ( $T^3$ -law). This proved the heat theorem and Planck's formulation and both are still published in modern textbooks. The reasoning of Nernst's heat theorem in 1906 and 1907 is indeed doubtful, as Van Laar and Kruyt had earlier shown. This reflects Nernst's way of working. He applied the heat theorem and tried to prove it with all the methods at hand, even if these methods were not always sound.

In the Netherlands, people who were influenced by Van der Waals' school of thermodynamic felt objections to the heat theorem. This resistance slowly subsided. And this would certainly have been the case after 1927 because of the discussion of the theorem in the second edition of the first book by Van der Waals and Kohnstamm. It must be noted that in 1911 Kohnstamm and Ornstein rejected the principle itself, for others it was mainly the argument that was open to discussion. An interesting fact is that the seventeen year old Tétrode, on his own, deduced a formula for the chemical constant in 1912.

By applying an intersubjective weighting and by dividing the nature of the reception into 5 categories: acceptance (++) , partial acceptance (+) , neutral (+-) , partial rejection (-) , and rejection (--) and combining year and university, the reception of Nernst's heat theorem can be mapped out as follows:

## OVERVIEW

year	name and age	Univ.	++	+	+-	-	--
1906	Van Laar (46)	Am					x
1910	Scheffer (27)	Am			x		
1910	V.d. Waals (73)	Am			x		
1910	Lorentz (57)	Lei	x				
1911	Kohnstamm (36)	Am					x
1911	Ornstein (32)	Lei/Gr					x
1911	Cohen (42)	Am/Utr				x	
1912	Ornstein (33)	Lei/Gr			x		
1913	Kruyt (31)	Am/Utr				x	
1918	Van Laar (58)	Am/Cla					x
1921	Sande B. ((33)	Lei	x				
1926	Van Laar (66)	Am/Cla					x
1927	Kohnstamm (52)	Am	x				
1927	De Haas (66)	Delft	x				
1927	MacGillavry (25)	Am	x				
1932	Bijvoet (40)	Am/Utr	x				

Am: Amsterdam, Utr: Utrecht, Gr: Groningen Lei: Leiden and  
Cl: Clarence.

If this table is related to tradition as it was defended by Van der Waals in Amsterdam in 1907 (see Chapter II) although not unreservedly (Scheffer's reaction for instance was benevolent), it may be said that the tradition and culture at the University of Amsterdam is discernable in the opposition which has been described. Policy and the upholding of tradition are related to people.

The reception in Leiden was positive. This was perhaps due to Lorentz's reasonable attitude towards a new scientific theory and towards ideas from outside the Netherlands. He was able to recognize the scientific value of Nernst's work.

It is certain that Van Laar remained negative, as is shown in his article of 1927 'Dwaalwegen der Wetenschap' (H.30). He assumed that the theorem was only of value for the area of quanta that is at very low temperatures, while in fact all determinations with regard to vapour pressure, even for solid substances were outside this area. This is Van Laar's curious and



repeated misunderstanding, for the heat theorem is perfectly applicable as the count off point of entropy in accordance with Planck's formulation. Perhaps there was some 'emigration effect' at play here caused by his scientific isolation in Switzerland. After he left the University of Amsterdam in 1911, his attitude towards persons and ideas remained unchanged for the rest of his life.

### 3. Solidification of Helium

#### 3.1 Introduction

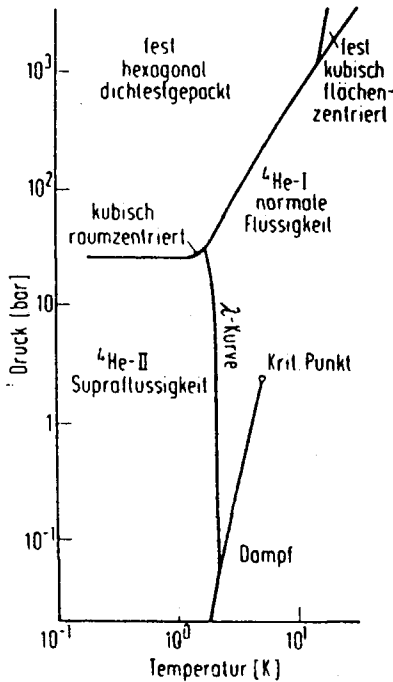
The inert gas helium was discovered in 1868 as an absorption line in the solar atmosphere. Naturally occurring, it is essentially all  $^4\text{He}$ . Especially after the appointment of H. Kamerlingh Onnes (1853-1926) as Professor in Leiden in 1882, helium became a subject of study and experiment. In 1909 helium was obtained in liquid form and the boiling point under atmospheric pressure was determined to be 4.215 K.<sup>79</sup> On 25 June 1926 his successor, W.H. Keesom (1876-1956), succeeded in solidifying helium at 25.3 atm. and 1.19 K.<sup>80</sup>

The p-T diagram differs from all other elements in that there is no sublimation curve. Between the solid and gas phases, a liquid area remains until the lowest temperatures. Instead of a triple point there is a lambda-curve which separates two different liquid areas. These are named I and II. The remarkable point is that the change from liquid phase I to super fluid liquid phase II is not marked by a change of density or the production of heat.

Helium II is the only substance which occurs in a stable liquid modification at 0 K. Experiments have shown He II to have the same entropy as was found for solid helium. The equation

$$(dp/dT)_v = 0 = (dS/dV)_T \quad (1)$$

shows that both phases have the same entropy.<sup>81</sup>



*The p-T-diagram of helium.<sup>82</sup>*

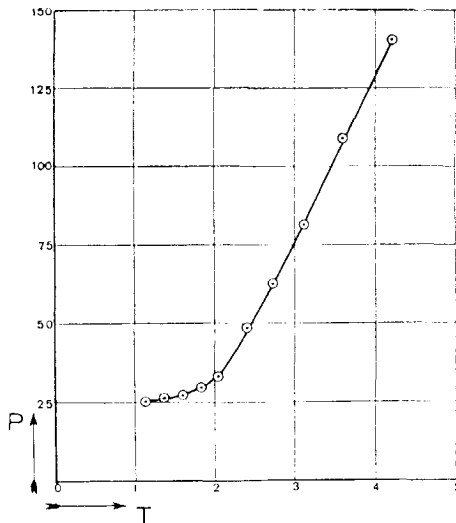
'Helium', the book by Keesom which was published in 1942, describes all aspects of this element in detail. On pages 204-205 there is a paragraph which says the following about the p-T diagram and Nernst's heat theorem:

'It must, however, not be forgotten, as Van Laar pointed out, that it is not an experimentally proved fact that  $dp/dT$  along the melting pressure curve of Helium becomes zero at  $T = 0$ , though the experimental data do not point to the probability of the alternative curve, viz. a bending of the curve at the lower temperatures after having passed through a minimum'.<sup>83</sup>

The quotation above shows that Van Laar was concerned with the course of the melting curve of helium. A discussion did indeed take place and Lorentz mediated between Keesom on the one hand and Van Laar on the other. The heat theorem was a very important aspect in this discussion. The matter will be clarified later.

### 3.2 Solidification by Keesom (1926)

Keesom reported on the solidification of helium in *Vers.K.Ned.Akad.Wet.* of 25 September 1926. Efforts had been made in 1909 and 1910 to solidify helium by reducing the gas pressure at pressures of 2.2 mm Hg and 1.4 K,



*The melting curve of helium (Keesom, 1926).*

and at at 0.2 mM Hg and 1.15 K respectively, but without success. Kamerlingh Onnes tried again in 1921 and he reached 0.013 mM Hg and 0.82 K, but the helium remained liquid. Keesom tried once again in 1926, now however, at a higher pressure in the solid. The results of the observations of this experiment are shown in the diagram.

Keesom's conclusions were as follows:

1. 'The melting curve shows an important peculiarity: it bends at the lowest temperatures so as to become more and more parallel to the T-axis. (This is now ascertained down to very low temperatures, ref. 4 and 22 v.E) It shows no tendency at all to meet the vapour pressure curve in a triple-point.
2. There is no sublimation curve; evaporation of the solid into gaseous state will not be possible at those temperatures, the solid will always melt first'.

The passage in question finishes as follows:

'The approaching to zero of  $dp/dT$  of the melting curve indicates according to the equation of Clapeyron, that the heat of fusion approaches in a higher power of  $T$  to zero than  $T (v_{liq} - v_{sol})$ . This is in agreement with the heat theorem of Nernst, when this is applied to the change liquid-solid helium, and perhaps forms, as Ehrenfest

remarked, one of the most elementary confirmations of it'.

The well-known equation of Clapeyron reads as follows:

$$dp/dT = Q/T(v_{liq} - v_{sol}) = (S_{liq} - S_{sol})/(v_{liq} - v_{sol}) \quad (2)$$

### 3.3 Van Laar's reaction (1926 and 1927)

Van Laar reacted as follows:

1. An essay in the 'Nieuwe Rotterdamsche Courant' of 21 July 1926, with a translation on 26 July 1926 in the 'Journal de Genève' and on 31 July 1926 in 'Chemisch Weekblad'.<sup>84</sup>
2. A communication in Vers.K.Ned.Akad.Wet. on 29 January 1927 (A.50).<sup>85</sup>
3. A postcard to Lorentz on 30 January 1927.<sup>86</sup>

The article in 'Nieuwe Rotterdamsche Courant' called 'Eenige theoretische beschouwingen naar aanleiding van het vastworden van helium' (Some theoretical observations on the solidification of helium) is an account of his answer to the American physicist Bridgman at his home in Switzerland. Van Laar assumes the validity of the Van der Waals equation of state  $(p + a/v^2)(v-b)$  in which  $p$  is the 'outer pressure' and  $a/v^2$  is the 'inner pressure',  $b$  the volume correction, and the numerator  $a$  in the fraction  $a/v^2$  is in direct relation to the forces of mutual attraction between molecules. To quote Van Laar:

'(...) The mentioned attractive force of the helium molecules is not only smaller than in any other compound or element, but, something special also happens with the attractive force at lower temperatures, in which helium is liquid (below 5° absolute). At decreasing temperatures the attractive force increases (at the melting point it is usually 1 1/2 times greater than at the critical temperature), only to decrease somewhat at very low temperatures. This means that in nearly all substances there in an area where the  $a$  parameter increases with decreasing temperature, so that the inner pressure gradually increases, and thus helps the lowering of the temperature by reducing the volume, i.e. increasing the density.

Hydrogen reaches this decreasing area of  $a$ , but this does not have fatal results. With helium however, the reduction of  $a$  has already taken place above critical temperatures and  $a$  will, at temperatures of for instance 2° certainly not be 1 1/2 times greater than at the critical

temperature, but, on the contrary, the other way around, about 1 1/2 times smaller! This results in the fact that in helium the inner pressure does not increase at decreasing temperatures, but decreases, so that helium, instead of gaining a greater density, like any normal substance would, at a certain temperature (approximately 2° absolute) shows a maximum density, and assumes lesser density with further reduction of temperatures. Because the reduced pressure obstructs further reduction of temperatures by increasing the density (...)'.

In the meantime Van Laar included these thoughts in a polemical article which he asked Lorentz to publish in 'Vers.K.Ned.Akad.Wet.' (the letter concerning this publication is not present in the Lorentz archives v.E). Van Laar adjusted the article at Lorentz's request and it was included in Vers.K.Ned.Akad.Wet. of 29 January 1927. There were two subjects:

1. The theoretical discussion by Keesom in which he says that the melting curve which was found in experiments  $(dp/dT)_{\text{coex}}$  would reach 0 when T reached T=0.
2. When the heat of melting Q with a higher power would reach from T to T=0, then  $T(v_2 - v_1)$  would be in accordance with Nernst's heat theorem! (Probably Van Laar read subject 2 in Keesom's report in a way other than was intended. It refers to the approach to zero of  $dp/dT$ , as a result of which  $(S_{\text{liq}} - S_{\text{sol}})/(v_{\text{liq}} - v_{\text{sol}})$  also becomes zero when the temperature is reduced to zero. In other words, it does not refer to  $T(v_2 - v_1)$ , v.E)

The relevant passages from 'Vers.K.Ned.Akad.Wet.' in which Van Laar considers the article by Keesom read thus:

'No theorem whatever, neither that of Nernst nor any other theorem decrees or can decree (I am sorry, I shall have to disillusion Prof. Keesom on this point), that in Clapeyron's equation

$$(dp/dt)_{\text{coex.}} = Q/T(v_2 - v_1)$$

the melting heat  $Q = E_2 - E_1$  (the index 2 refers everywhere to the liquid, and 1 to the solid phase) would have to approach T<sup>4</sup> at T=0. No more than the heat of evaporation or the heat of sublimation. Nernst's theorem (would it not be better to speak of Debye's T<sup>4</sup>-law at very low temperatures for the Energy of solid substances, for so far as it depends on the temperature?) says that according to the

equation of state valid then, viz.<sup>1)</sup>

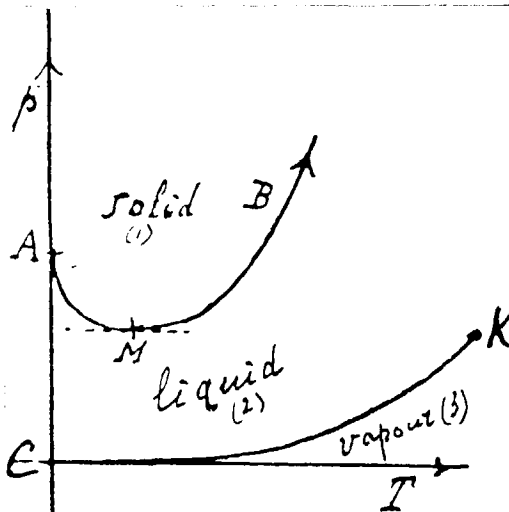
$$p + a/v^2 = (\lambda/v + PT^4...)/(v - b)$$

the quantity  $(dp/dt)_v$  will approach 0 in one single phase (i.e. the solid phase), but not that for reason this would be the case with  $(dp/dt)_{\text{coex.}}$ ! (...) And the same thing applies to the melting heat  $Q$ , which can become = 0, but not only at  $T=0$ . For this quantity is not only determined by the difference of the thermic Energies, as Nernst and others believe, but also by the much more important difference of the potential Energies. The latter is often overlooked.'

1)  $\lambda/v$  refers to static repulsive forces of the lattice.

Van Laar gave a further explanation of the course of the melting curve in the proximity of  $T = 0$  as in his fourth article 'On the Solid State' of 1910 in 'Vers.K.Ned.Akad.Wet.' (A.24) and in his two articles in 'Chemisch Weekblad' of 1910 and 1912 (H.11,12).<sup>87</sup> According to Van Laar's theory about the solid state, he claimed that in helium the pressure  $p$  would, at about 1 K, pass through a minimum ( $dp/dT=0$ ) at which the heat of melting is  $Q = 0$ . However, according to Van Laar, at  $T = 0$  K, it would be  $Q = aT \log T$  and it becomes:

$$dp/dT)_{\text{coex.}, T=0} = -Q_0/T(v_2-v_1) = -\infty. \quad (3)$$



Van Laar concluded as follows:

‘(...) We see accordingly that here the theorem of heat (or rather the  $T^4$ -law of DEBIJÉ) does not play any essential part, and that the fact, that  $dp/dt$  becomes 0 at  $+ 1^\circ$  abs., by no means implies that  $dp/dt$  would also have to disappear at  $T = 0$ , which (...) is not required by any theorem. If Prof. Keesom should succeed in descending to still lower temperatures, he will very probably be able to observe after the minimum at  $1^\circ,2$  abs. a change of the sign of  $dp/dt$  of the melting point line (from M to A). This would at the same time be an interesting confirmation of my theory’.

He believed he could draw these conclusions from Keesom’s observations. Next, Van Laar wrote to Lorentz on 30 January 1927:

‘A few days ago I was glad to receive your kind letter, for which I thank you very much. As well as for tendering the article. I gladly accept the mitigations you have suggested; they do of course not deduct from the content of the article. I am glad that you feel the same. About the matter of the heat of melting, I sent it to Keesom, together with the letters to you and a copy accompanied with a letter. Later I received a (unreadable) short answer, in which he advised me to retract the article, because I was totally wrong and certainly, everybody knew who was on the side of truth!! I answered that I would certainly not consider retracting the article since I was completely convinced of my assertions. I also explained the matter to him once again and wrote that while it was true that the entropy  $S$  of a solid body disappears at  $T=0$  (which really is the content of Heat Theorem, but that does not mean *Energy!*  $Q = E_2 - E_1$ ) as I demonstrated by taking into account the potential energy. But again I received the answer that he even more strongly urges my retraction of the article, because I was with  $S = 0$  at  $T = 0$  completely on his side and thus  $E(Q)$  had to be 0. As I showed in my article that this is *Not* true, so Keesom showed he had not even read the material I sent him!! Not (unreadable) whether a message from you would arrive in time. Ask Schreinemakers for Keesom’s copy, to tender it in your name. (You had said so in your postcard before you left.) But there is no need for it anymore! He too (S), Verschaffelt and (unreadable) are completely on my side. Only Keesom in Holland and de Haas from Delft still take Nernst’s foolish excesses of heat theorem as gospel truth. It is worse than in Germany.

In the meantime Lorentz had left for Pasadena (U.S.A.). He had given Van Laar permission to report during his absence to the Royal Academy of Science through Schreinemakers. Van Laar did this and in 'Vers.K.Ned.Akad.Wet.' of 26 March 1926 he wrote: 'About evaporation-sublimation- and heat of melting, respectively -pressures, also in the proximity of the absolute zero; also in connection with the so-called Nernst's heat theorem' (A.51), in which he among other aspects dealt with the equilibrium solid - liquid and deduced for the heat of melting his so-called  $T \log T$  formula for very low temperatures. He did this in accordance with his theory about the solid state.<sup>89</sup>

$$p = \alpha T \log T - \beta T + \gamma \text{ atm} \quad (4)$$

with  $\alpha = 58.4$ ;  $\beta = 28.6$  and  $\gamma = 54.1$ . He applied this to the area below 2°K. and with another formula  $p = -16.4 + 14,54T + 5,40T^2$  atm. above 2°K. he did indeed find a minimum! (At 1,14 K, just below the 1,2 K from Keesom Van Laar obtained his results with formula (4) with three adjustable parameters applied to only four points v.E.)

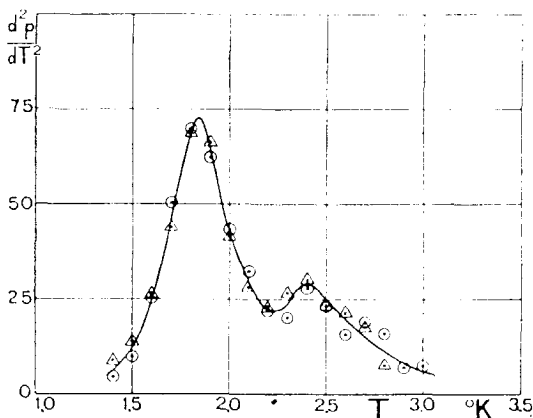
### 3.4 Reply by Keesom

In 'Vers.K.Ned.Akad.Wet.' of 26 March 1927 Keesom reacted to Van Laar's controversial article with a thorough and sharply worded argument entitled: 'The melting curve of helium and the heat theorem of Nernst'.<sup>90</sup> In the first place it compelled Keesom to explain his opinion somewhat more fully and secondly to make some remarks about Van Laar's claims.

Keesom believed that the course of the melting curve, i.e. a minimum at approximately 1 K, and then rising at decreasing temperatures to touch the p-axis at 0 K was not impossible because experimental data were lacking. However, he did not believe it to be likely. He expected the melting curve to run parallel to the T-axis.

To reach an objective judgement, Keesom asked two of his co-workers independently to draw a smooth curve which was as far as possible in accordance with the observations, and to read the pressure for each 0.1 degree between 1.2 to 3.0 K and to determine the values of the two inferences ( $d^2p/dT^2$ ). The result is shown in the diagram on the next page.





*The second differential quotient.*

According to Van Laar the curve would have to bend sharply upward on the left hand side. This is not the case and it is clear that the experiment did not provide any reason to find this likely. Next, the  $T \log T$  formula by Van Laar was tested, and again no reasons were found for a melting curve with a minimum. Keesom either expected the melting curve to run parallel to the  $T$ -axis, or for it to maintain a slight inclination.

Keesom again remarked that both possibilities with regard to Nernst's heat theorem had to be distinguished.

'Let us then in the first place consider the case that for the melting-curve should approach to 0 at  $T = 0$ . If we write the equation of Clapeyron in the form:

$$dp/dT = (S_{liq} - S_{sol}) / (v_{liq} - v_{sol})$$

then it follows that for  $T = 0$ ,  $S_{liq}$  should be =  $S_{sol}$  and so the entropies of the zero-point for the solid and liquid phase would be equal for helium. This then would be in strict correspondence with the heat-theorem of Nernst'.

If the melting curve on approaching  $T = 0$  still maintained a small inclination, Keesom explained that in this case  $S = 0$  at  $T = 0$  was not true, but nearly true.

The continuation of Keesom's reaction consisted of five points, as summarized below.

1. As long as no experimental data were known, nothing could be said and nature would not have to obey Van Laar's very personal theory of the solid state.
2. Nernst's heat theorem could not be equated with the  $T^4$ -law by Debye.
3. The thermodynamic sophism was false (Van Laar thought that Planck's passage: 'Beim Nullpunkt der absoluten Temperatur besitzt die Entropie eines jeden chemisch homogenen festen oder flüssigen Körpers den Wert Null' was proven incorrect and he called it: 'thermodynamic sophism').<sup>91</sup>
4. The equation of state for the solid state by Van Laar was dubious.
5. Van Laar may not know that the specific heat at constant volume of liquid helium at 0 K remained finite. In experiments at 2.5 K a value nearing zero is expected.

However, Van Laar continued the polemic. In his letter to Lorentz of 24 May 1927 he wrote:

'I find Keesom's article in the latest edition of the 'Akademie verslagen' not at all convincing, and furthermore, there are many misconceptions about me, so that I have to write something to contradict it. Although I am about to leave for a week in Paris (...) May I bother you again to submit this article the coming Saturday? (...) Do you not also believe that Keesom is too easy on himself: He himself says that we know nothing (experimentally) yet he bases his argument on what is experimentally known, in my view inadmissible decisions with regard to what is not known'<sup>92</sup>

Apparently Lorentz wrote him a letter, because on 17 June 1927 Van Laar answered:

'I received your letter. I would now very much like to know whether you have found the time to read my article, and if so, if it can be submitted, changed or not. You must have noticed -and only on that would I like to make one further remark - that most of Keesom's arguments (mentioned in my article) are totally beside the point. He completely ignores the premise, that liquid helium does not degenerate<sup>1</sup> (neither do other liquids) which, by the way, Onnes has already shown for gaseous He (and H<sub>2</sub>) But K. is up to his ears in the

heat theorem and everything must be made to fit'.<sup>93</sup>

1) As I believe to have shown in my article on He

This must have been the reason for Lorentz's intervention between Keesom and Van laar. Apparently Lorentz did not want to submit Van Laar's article.

### **3.5 Mediation by Lorentz (1926 and 1927)**

It was probably on 21 June 1927 that Lorentz started his reconciliation process by writing to both Keesom and Van Laar. Both gentlemen immediately agreed to mediation. Keesom answered Lorentz on 22 June 1927.<sup>94</sup>

'I am very grateful for your letter of yesterday and gladly agree to your proposals. Thus, pending Van Laar's reaction I will not publish my remarks on Van Laar from our latest meeting. I will gladly go even further, I will postpone translating my 'zittingsverslag' 36, p.256 to see what can be deleted after Van Laar's response. This has the less pleasant consequence that it will take a bit longer before an answer to Van Laar's attacks, which has already appeared, is published in the 'Proceedings'; however, I hope that the secretary will be willing to publish Van Laar's statement in the 'Proceedings' as soon as the text is known.

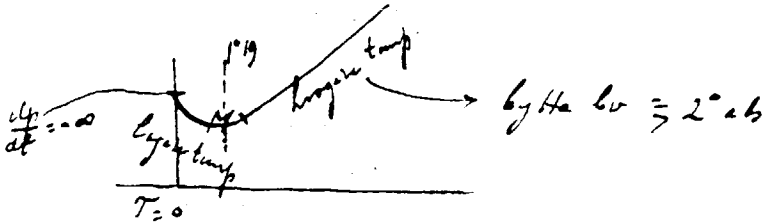
Now, about the time scheme you propose for a statement by Van Laar. I would like to say the following:

I wholeheartedly agree with your remarks in points 1 and 2 as well as with the first half of point 3: 'that this means that nothing has been said on the general validity of the Heat Theorem'. As for the latter half of point 3: Of course Van Laar must decide for himself whether he wants to maintain his objections to Nernst's Heat Theorem and as far as that is concerned I can not find fault with it: however, I would not like to be put in a position in which I was in any way responsible for such a statement, which was as it were put in my mouth. I believe that Van Laar goes too far in disputing the theorem. In the first place, Van Laar states much which, to put it mildly, is open to discussion. I even believe that the question of the validity of the theorem of Nernst will not be solved in the way that Van Laar deals with the question. (...).'

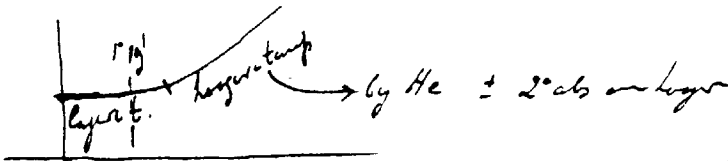
Van Laar answered Lorentz with a long letter on 25 June 1927.<sup>95</sup>

'(...) We are discussing the equilibrium liquid-solid. The solid phase degenerates with the familiar  $T^4$  law the liquid phase I believe<sup>1</sup> does *not* (nor does K. Onnes).

This results in:



If the liquid phase degenerates, then this would follow:

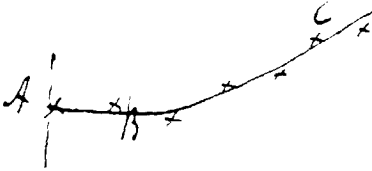


Thus this matter is still unresolved, as long as the tests (Keesom's) do not go further than  $1^\circ.19$ , and the curve stops at the dotted line ( $1^\circ.19$ ). The problem is that Keesom says, and that is what I mainly object to, *that* from



he can deduce: *No minimum* at M, (so  $dp/dt$  is temporarily zero) but already  $dp/dt$  *definitely* = 0. I say *he cannot know* that as long as the tests have not been continued for temperatures below  $1^\circ.19$ , so that his assertions can be confirmed. In order to prove this, he uses the second differential quotient and concludes the improbability of my minimum!

This is what I call mathematical heresy. When one has determined several points in order to discuss a curve, then one should draw the curve through the points as accurately as possible:



However if one deduces the second differential quotient from crosses (experimental values) the result is of course very odd.



And it is impossible (as Keesom does, see his first diagram) to deduce from that below A!! *This* is my main objection.

1) I believe to have *proven* this in my latest articles on helium.

Van Laar's second objection was Keesom's calculations with his TlogT-formula above 2 K. The TlogT-formula is then no longer valid. His third objection was Keesom's remark that he could know nothing about the degeneration of liquid helium while the equation of state was unknown.

Apparently Van Laar wrote to Keesom too, because Keesom replied with the following to Van Laar on 25 July 1927. Keesom sent a copy to Lorentz.<sup>96</sup>

'I received your copies and noted in one of your remarks on your 'akademiemedelingen' that you wish to draw attention to p.16 below; I assume you mean remark 1.

Although I believe it to be better not to enter a personal discussion at the moment:

1° Because of your correspondence of some months ago I feel you do not give proper attention to my arguments, but mainly 2° because Professor Lorentz has taken the matter between us in hand and thus it would not be right for us to exchange opinions personally without informing him. I would like to make an exception on this specific

point and I would like only to draw your attention to this 'slip' in case you would want to raise this point somewhere, and without expecting an answer on your part, I would like to point out that your arguments in said remark lack all force of proof.

I believe I am right when I deduce from the passage in your 'Akademiestuk' p.1 below and p.2 above: 'but that liquids and gases (Unless at very high pressures) remain in the RT area until the lowest temperatures, that is do not degenerate', as well as from the last sentence of remark I p. 16: 'Thus, in reality the reduction follows another law, in casu the  $T \log T$  law, which is valid, when the liquid helium does not degenerate'. You are, like me, of the opinion that under degenerate we must understand: deviate from the classic laws.

To give an example: as soon as a diluted monoatomic gas the s.h. becomes less than  $3/2R$  at constant volume, we would call the gas degenerated.

Well then, it is clear that your assertion: 'liquid helium is not degenerated' could only be defended by proving that liquid helium conforms to classic laws, but not by proving, as you do, as far as that is the case, that liquid helium does not conform to a specific law (the  $T^3$  law). That proof would only be valid as outside: 'liquid helium is not degenerated' and liquid helium conforms to the  $T^3$ -law' a 'tertium non datur'.

And that I have further sufficiently shown that the melting curve does not conform to the  $T \log T$  law in the 'Mededelingen'.

In his letter Keesom refers to Van Laar's article: 'On the heats, resp. pressures of evaporation, sublimation and melting, also in the neighbourhood of the absolute zero; in connection with Nernst's so-called heat-theorem' (B.51). He made the following remark:

'If liquid helium were degenerated between  $1^\circ.19$  and  $1^\circ.83$ , something which we, based on several facts, believe to be very unlikely (...)  $dp/dt$  would reduce proportionally with  $T^3$  at reduction of temperatures. Now, between  $1^\circ.19$  and  $1^\circ.42$  and  $1^\circ.42$  and  $1^\circ.60$  etc. the quantities  $dp/dt$  are in proportion of  $0.8/0.23 : 1.3//0.18 : 2.4/0.23$ , ie as  $3.2 : 7.2 : 10.5$  or as  $1 : 2.25 : 3.3$ , while the third powers of  $2.22 : 3.44 : 5.04$  of  $1 : 1.55 : 2.3$ . In reality the reduction conforms to another law, in casu the  $T \log T$  law, which is valid when liquid helium does not degenerate'.<sup>97</sup>

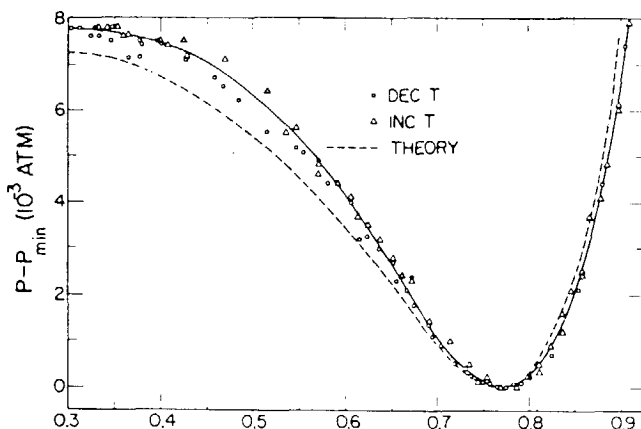
Finally Lorentz wrote for Van Laar the article 'The Melting-Point Line of Helium and Nernst's Theorem of Heat' (B.52) with the intention of submitting it, together with Schreinemakers, as a communication in the Vers.K.Ned.Akad.Wet.<sup>98</sup>

Although no letters about the content of the debate have been found, it must be assumed that Van Laar and Keesom agreed.

Then two other dissertations by Van Laar followed in the Vers.K.Ned. Akad.Wet.<sup>99</sup> The first was in 1932 on the equation of the melting curve, in which the melting curve conformed entirely to Van Laar's prediction and the second in 1936 about the course of the thermal and caloric quantities of the melting curves of helium. In his last book, Van Laar appears to have dropped his theoretically predicted melting curve below 1,2 K. It is worth noting that Van Laar in his first article from 1916: 'Ueber den Verlauf von einigen thermischen und kalorischen Gröszen längs den beiden Schmelzkurven des heliums' (B.56) uses an empirical formula for the melting curve with two optional parameters  $p = 24,396 + 0,45536 \cdot T^4$ . No mention is made of a minimum or of the equation of state. He seems to agree with Keesom without saying so. 'A small concession' on Van Laar's part perhaps?

### 3.6 Recent experimental data

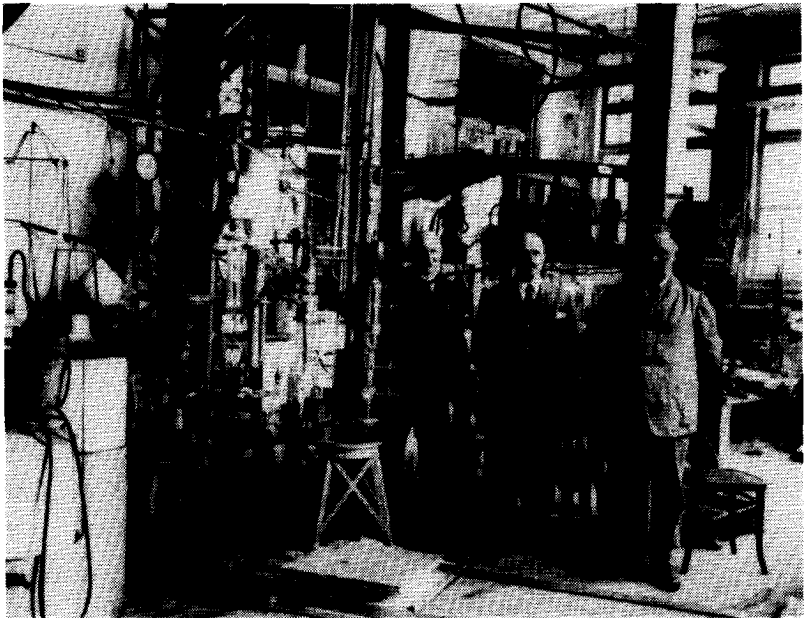
When E.R. Grilly's very accurate experimental data of 1973 is studied, it appears that the melting curve of helium shows a very small minimum. The position of that minimum is at  $24,985 \pm 0,005$  atm and  $0,775 \pm 0,012$  K,



*The melting curve of <sup>4</sup>He close to the minimum. The drawn line represents Grilly's measurements.*

the depth is only  $8 \cdot 10^{-3}$  atm.<sup>100</sup> L. Goldstein had already predicted this in 1960 and the effect can apparently be attributed to the fact that the entropy of the solid state is raised somewhat above that of He II.

The minimum which is found has nothing to do with Van Laar's minimum at 25,3 atm and 1,14 K, after which the melting curve rises again quickly until 54.1 atm at  $t = 0$ . Van Laar calculated this minimum with the formula  $p = \alpha T \log T - \beta T + \gamma$  (below 2 K) with three variables. These three variables are chosen in such a way that only four of Keesom's points are below 2 K.



*Laboratory for Physics in Leiden with from left to right Kamerling Onnes, unknown and Keesom.<sup>101</sup>*

### 3.7 Concluding remarks

This chapter focuses on Van Laar's reaction to the melting curve of helium as was first found experimentally in 1926 by Keesom. The explanation of the course of the melting curve was grist to the mill for Van Laar. It sheds doubt on his theory about the solid phase during the period from 1909-1911. However, there is a third possibility which is one that did not occur to Van Laar: the occurrence of helium I and helium II where the entropy value is the same. Van Laar indeed predicted a minimum in the melting curve but he did so in a dubious way, based on his weak theory of the solid state, but also on a rise to 5 atm at 0 K. Keesom carefully admitted that it



was not possible to be sure about the curve beyond the last experimental point but felt that a horizontal, or almost horizontal melting curve was possible. It is a pity that Van Laar was not very flexible and could not easily accept the ideas of others, and that Lorentz had to intervene in the dispute.

After this controversy there was a period of about ten years during which Van Laar abandoned his theory, and one would have expected him then to have accepted the heat theorem as it was clearly proven by Keesom. However, this assumption proves to be false because the article in 'Chemisch Weekblad': Het bestaansrecht der theoretische en toegepaste thermodynamica naast de moderne atoomtheorie (H.47) includes the following passage:

'I would rather not say too much on Nernst (The Third Law) because at the start of my scientific career and in several later articles for the 'Koninklijke Akademie' of Amsterdam I was at variance with him. It was Debye who, after Einstein, had the great merit of laying down the gradual reduction of energy of solid matters at very low temperatures in the so-called  $T^4$  law as the ideal law, in contrast to the assertions of Nernst and his many followers who still, without a thought, apply the so-called 'heat theorem' on solid bodies close to the melting point. (We recall the calculation of the transition point of Sulphur!) and even on liquids! on which the heat theorem is no longer valid (think of the infamous  $+1.75 \log T$  in the vapour pressure formula). Yet the number of blind is starting to reduce rapidly.<sup>102</sup>

Unfortunately, Van Laar remained in opposition to the heat theorem and did not develop his views on it.

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## LIFE IN SWITZERLAND

*'Until 1937 I was still 'young' (I was called a 'young man'!) - and now ...  
I won't say the word. It only happens to ships!'*

### 1. Introduction

This chapter deals with some of the important events in the life of Van Laar in Switzerland from 1914 until 1938. It is concerned with his experiences during the World War I, his recognition in the field of thermodynamics, his last book and the autumn of his life in Tavel-sur-Clarens.

### 2. World War I and after

The outbreak of World War I followed soon after Van Laar's arrival home in Switzerland from the presentation of his Doctor Honoris Causa in Groningen. For Van Laar and his second wife M. van Laar-Schagen (1860-1934) the war years were difficult. They were forced to practice great thrift and they suffered from cold and a lack of food. Travel to Holland was dangerous and became all but impossible after 1915. On a postcard to Jorissen on 30 December 1914 Van Laar wrote:

*'(...) All the best to you and your family in 1915, also on behalf of my wife. May this year bring peace, for this war is really too barbaric and too horrible'.<sup>1</sup>*

Through the kind offices of Kruyt, he worked as a correspondent for the

Newspaper 'De Telegraaf' for some months.<sup>2</sup> From 1913 until 1930 he was also a regular contributor to the 'Tables annuelles internationales de constantes et données numériques de chimie'. Among other things he was responsible for the chapter entitled: 'La thermodynamique des gaz'. The student (and later Professor) at the University of Lausanne, Ch. Haenny says of that period:

'J'ai apprécié à cette occasion l'originalité et le soin qu'il apportait à la rédaction de son manuscrit'.<sup>3</sup>

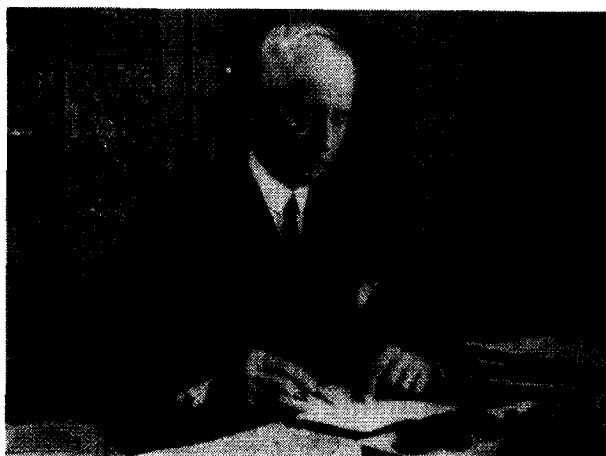
Van Laar found the work very trying, but it earned him some money. His letter to Lorentz of 23 December 1916 ended with:

'(...) We sigh under the terrible recent acts of war. The people in Holland surely, too. Fortunately the peace of Germany is forthcoming'.<sup>4</sup>

Food was scarce and on 2 May 1918 he wrote to Jorissen:

'(..) We feel -especially my wife- still very tired and have grown very thin, malnutrition, especially a lack of fats and sugar. (...) Food starts to run out here, like in Holland and still two to three more years of war to go!!'<sup>5</sup>

However, by November 1918 the end of the war was in sight and Van Laar wrote to Jorissen on 19 November 1918:





‘(...) What do you say to that? The Great Event, ‘The’ Monster Defeated, in the Great Victory of the Allied Forces! What uproar in Holland and here, too, but they have soon put a stop to the attempted Bolshevik Revolution. May Holland in God’s name make Wijnkoop and Jetje Holst look silly! Luckily Troelstra in (unreadable), as I read in De Telegraaf. What turbulent times, even worse than during the war. Let us hope it will all be temporary. Wilhelm von Hohenzollern + wife + son + lots of generals now in Holland... What should be done with them?’<sup>7</sup>

The war made Van Laar a little more patient but during the winter of 1918/1919 he had difficulty writing because of paralysis in his hand.<sup>8,9</sup> What was worse was the fact he had become increasingly concerned, to the point of exaggeration, about whether or not the mail he was sending reached its destination. When mail from Van Laar arrived at the office of the *Chemisch Weekblad*, Jorissen used to say: ‘Send a postcard immediately, or he’ll send another letter’.<sup>10</sup> This problem comes across most clearly in his letter to Lorentz of 17 February 1919:

‘What I felt coming has happened. I had not slept for weeks here and finally I caught influenza, with high fever etcetera etcetera. Fortunately I am now recovering, but I am still confined to my room. That fever is very enervating. But now I pray you, please break your persistent and, to me, absolutely puzzling silence, so that I may sleep quietly again. On January 3rd I sent you -so in good enough time- my piece for the January meeting. Not until much later did you reply with the enclosed postcard - the only thing I have received so far.1) Not until three weeks later did I know that the piece had arrived safely. Letters, newspapers etcetera take four to five days. To all postcards etcetera I receive a reply within ten days. That is why I could not understand why your letter of safe arrival had me waiting for so long and I made enquiries of the postal services. (...)’

1)I am sending you this one only so that you know which postcard I have received and that I have never received any other letters or postcards you may have written.<sup>11</sup>

In 1919 Van Laar came into contact with P. Dutoit (1873-1944), Professor of Physics and Chemistry at the University of Lausanne. Van Laar gave a course on thermodynamics and he sent word to Lorentz that in the spring of 1919 he would be giving a number of lectures ‘On the Solid State’ and ‘Van der Waals State Equation’. In the meantime Van Laar longed increas-

ingly to see his children and in 1920 reunion finally came.<sup>12</sup> Together with his wife he went to the small Dutch town of Meppel, where they stayed for a while with his youngest daughter who had since married. All the children were present, except for his youngest son who was in the Dutch East Indies. Van Laar got to meet his two year old grandchild for the first time and was delighted.<sup>13</sup> After this visit, the couple returned to the Netherlands every three or four years in order to visit family and friends.<sup>14</sup>

In that same year, in honour of Van Laar's sixtieth birthday, 'Chemisch Weekblad' produced a feature article on his life and work written by Jorissen.<sup>15</sup> Sometimes Van Laar's work on 'Tables Annuelles' involved visiting Paris, where he stayed with his eldest daughter Geertruida Johanna (1888-1972).<sup>16</sup> There he used to seize the opportunity to visit museums and to go to the cinema.<sup>17</sup> In 1926 the American physicist Bridgman was on holiday in Europe and he visited Van Laar in Clarens.<sup>18</sup> In the spring of the same year Van Laar and his wife met Schreinemakers and his wife and they dined together and went for a ride.<sup>19</sup> On 19 August 1926 Van Laar politely asked the Minister of Education to include him in the honours list.<sup>20</sup> As Van Laar made the request himself, the civil servant dealing with his request did not think he stood much of a chance, although one point has to be admitted to: Van Laar was not in a work situation where others could make such a request on his behalf.<sup>21</sup> In 1927 he moved - within Tavel-sur-Clarens - from the 'Maison Brayères' to the 'Maison les Tilleuls'.<sup>22</sup> Towards the end of the 1920's Jorissen arranged for him to receive an additional pension of Dfl. 1200,- a year.<sup>23,24</sup>

When Lorentz died in 1928, Van Laar wrote a short piece in 'Chemisch Weekblad':

'(...)Personally speaking, I owe a lot to Lorentz; not only did he (with Schreinemakers) bring almost all my academic pieces safely into port, but he also - as many have experienced - always showed great interest in my work and life'.<sup>25</sup>

Lorentz saw Van Laar as a colleague and found him a fighter.<sup>26,27</sup> Van Laar, for his part, always had great confidence in Lorentz.<sup>28</sup>

### **3. The Bakhuis Roozeboom-Medal**

For his studies of the theory of homogeneous and heterogeneous equilibria Van Laar received the Bakhuis Roozeboom Medal in the

Trippenhuis in Amsterdam on Saturday 26 October 1929.<sup>29,30</sup> It was presented by Schreinemakers and he and Van Laar



*Presentation of the Bakhuis Roozeboom medal.<sup>31</sup>*

(holding the medal) can be seen standing beside the portrait of Bakhuis Roozeboom with Bakhuis Roozeboom's eldest son, Willem (1897-1984) on the other side. Behind the committee table are the Chairman F.A.F.C. Went (1863-1935) and the Secretary B. Brouwer (1881-1949). In the first row are Van Laar's youngest son, Willem Marinus (1891-1978) and his youngest daughter, Nelly Emilie (1894-1982); next to her Mrs. M. van Laar-Schagen (1860-1934); the empty seat was reserved for Van Laar; next to that seat is Bakhuis Roozeboom's second son, Wouter Bakhuis Roozeboom (1898-1942) and at the corner Willem's fiancée, now Mrs. F.C. Bakhuis Roozeboom-Drost. In the second row are the wife of Van Laar's youngest son, Alida Wilhelmina ter Horst (1895-1985), his eldest son Johannes Jacobus (1886-1967) and his wife Greet Van Laar-Pals (1892-1976). In the third row are Lector Büchner from Amsterdam and Professor Scheffer from Delft. At the head of the table on the left is physicist Zeeman from Amsterdam and the first and second people at the same table are Professors Cohen and Kruyt from Utrecht.

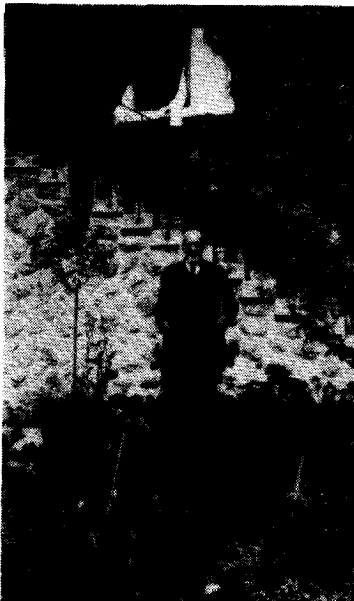
After Van Laar and his wife had been ushered in, Schreinemakers spoke. First he paid tribute to Bakhuis Roozeboom and then he addressed Van Laar and said:

'(...)as more and more systems were tested in experiments, and much of what used to be confused and unclear could be unravelled by means of the new image, a new task began to emerge, that is, to determine more closely the position of points, curves and planes of the diagrams of a theoretical point of view, and in this manner, to come to a more quantitative concurrence between theory and experiment. It is to your merit to have done just this for so many a problem, by applying your 'strict' thermodynamics and Van der Waals' state equation. Bakhuis Roozeboom often told me what support he had found in this, and hoped to find for his further work. Unfortunately, this was not to be (...)'.

He said that Van Laar's spirit had always stayed young, and:

'(...) I wish with all my heart that you may keep this privilege for many years to come'.

The medal was presented and Van Laar gave a short speech of thanks in which he said, among other things, that he greatly admired Van der Waals during the time he spent as his student from 1881 to 1884. Then all present were given the opportunity to congratulate him.



*J.J. Van Laar in front of his house 'Maison les Tilleuls' in Tavel-sur-Clarens.<sup>32</sup>*

Also in 1929 Professor J.J. Blanksma (1875-1950) from Leiden tried unsuccessfully to obtain the Nobel Prize in Chemistry for Van Laar.<sup>33</sup>

#### **4. Correspondent of the Royal Academy of Sciences and Royal Distinction**

After being recommended by Schreinemakers and others to the Committee for Correspondents of the Royal Academy of Science, Van Laar was admitted as a Correspondent on 10 May 1930.<sup>34,35</sup> In the summer of 1930 'Chemisch Weekblad' had a special issue on Van Laar with contributions on Van Laar's scientific opinions by Scheffer and Verschaffelt. Van Deventer composed a short poem and Jorissen contributed a piece about Van Laar's work. Van Laar's bibliography by then numbered 191 titles.<sup>36</sup> In 1931, at the suggestion of the Managing Director of the Koninklijke Gist en Spiritus Fabriek in Delft, F.G. Waller (1860-1935), and Schreinemakers, he received the Royal Honour of Knight of the Order of the Netherlands Lion, with the inscription: 'Well-known for his scientific writings, he enjoys high esteem in the scientific world'.<sup>37,38,39</sup>

In 1931 his former student friend Van Deventer died and even though they had been on bad terms for years, this did not stop Van Laar for writing a long piece in memory of his friend in 'Chemisch Weekblad'.<sup>40,41</sup> After an illness of some months his second wife died on 11 April 1934.

In Switzerland Van Laar led a simple life, rising early and devoting his mornings to writing letters and studying. In the afternoons he walked and in the evenings he wrote and studied. He loved music and paintings and took a great interest in plants, knowing their Latin names by heart.<sup>42</sup>

#### **5. Last Book**

From 19 December 1931 to 25 January 1936 Van Laar worked on his life's work and last book: 'Die Thermodynamik Einheitlicher Stoffe und Binäre Gemische, mit Anwendungen auf verschiedene Physikalisch-Chemische Probleme'.<sup>43</sup> The manuscript must have been finished in the winter of 1934/1935 and numbers 235 written pages in quarto, and five pages in quarto containing 50 figures. On account of the uncertain times in Germany, Van Laar was forced to find a publisher for his book in Holland.<sup>44</sup> Through Ornstein's agency he came into contact with the publisher J. Noordhoff (1870-1942) in Groningen.<sup>45</sup> In his letters to Noordhoff, Ornstein called

him 'our very first thermodynamics expert', and expected the book to be 'exceptionally good'.<sup>46</sup> Noordhoff wanted to publish it on favourable terms, that is to say, the selling price of the book would be fixed in a way that the expenses would be covered after selling the first 300 copies, for which Van Laar received no fee.<sup>47</sup> The contract was signed in early April 1935.<sup>48</sup> The mathematician P. Wijdenes (1872-1972) from Amsterdam took care of the figures.<sup>49</sup> From the correspondence between Noordhoff and Van Laar it appears that it was mainly due to Noordhoff's kind yet businesslike approach that the collaboration was problem-free. Van Laar



*Van Laar at 71.*<sup>50</sup>

was unable to sleep after learning that Noordhoff had sent the manuscript to Wijdenes.<sup>51,52</sup> Although he needed it, Wijdenes was requested to send it back and he wrote to Noordhoff:

'Never mind! When one is 75, one does not sleep much anyway. We at 42 neither, do we? (...) He is a troublesome old man! Always has been, and always known to be one'.<sup>53</sup>

Van Laar's handwriting was not easily legible and this presented some problems. Initially the plan had been to produce a typewritten copy of the manuscript, but it appeared that this was not really necessary. Noordhoff, for instance, wrote on 6 May 1935:

'Yesterday I received your postcard of May 3. Fortunately it was a Sunday, so that I had plenty of time to decipher your postcard under a magnifying glass'.<sup>54</sup>

By late May 1935 the expenses were higher than had been expected and this led to some delay.<sup>55</sup> All problems, however, were solved and in the spring of 1936 the book appeared.<sup>56</sup> It numbered 379 pages, was 25 by 17.5 centimetres and was set in Scotch Roman; the letter on the binding was set in Futura. On the title page of his own copy Van Laar wrote:

'Dedicated to the Memory of my sweet wife, who always stood by me in life and work for 25 years by her great devotion and who has not lived to see the completion of this book'.<sup>57</sup>

Van Laar dedicated his own copy posthumously to his late wife. The book consisted of two parts. The first part numbered 145 pages and the second part 230 pages. The contents mainly leaned on Gibbs and Van der Waals



*Title page of Van Laar's last book and lifework.*

and the treatment was highly mathematical. Using documented gas

pressures and the crucial data inferred from those, he discussed mainly gaseous and liquid systems, giving many numerical examples. In the first part he discussed simple substances and gave an explanation of Van der Waals' equation with variables  $a$  and  $b$  as a function of temperature and volume. After that he discussed thermodynamic quantities such as specific heat at a constant volume and pressure and their differences. This section closed with explanations of heterogeneous equilibria such as: liquid-gaseous, solid-gaseous and solid-liquid. In the second part he discussed binary systems and with the thermodynamic potential as a starting point, a number of equilibria were treated as for heterogeneous states as well as heterogeneous forms. It is remarkable that nothing was said about the heat theorem, about his prediction for the course of the melting-point line of helium or about his theory on the solid state. Does this mean that Van Laar had secretly accepted the heat theorem? The book puts forward many of Van Laar's theories which have been developed over the years. It is, indeed, the work of a lifetime and not just a mere textbook.

Five letters and postcards on the book have been saved and eight book reviews have been found. The first letter of 22 March 1936 comes from Iwanowo-Oblastnoi in Russia and was written by J.J. Saslawsky.<sup>58</sup> In it, Saslawsky considers Van Laar the greatest theoretical chemist of his time and compares him with Debye of 30, 35 years earlier, who found evidence for the influence of the positive or negative force of ions. The second postcard comes from thermodynamics expert De Haas from Delft and was dated 27 March 1936.<sup>59</sup> M. de Haas thought the book was wonderful and considers it a kind of sequel to his own book of 1927. He had no doubt as to the success of the book; it would doubtlessly meet a need. It couldn't be missed in any library! The third letter comes from L. Frank from Kofu in Japan and was dated 2 April 1936.<sup>60</sup> Frank gave the book a place of honour in his bookcase and would proudly show it to all his friends! He was certain the book would become a manual, not only because of the complete overview given, but also because it was a thorough and critical piece of writing. He was surprised to find that Van Laar preferred the Indian physicist Ghosh's calculation to Debye's. He asks his opinion on a number of things and closes his letter by stating that many did not know Van Laar's equation. The fourth letter comes from Amsterdam and was written on 27 March 1936 by Bijvoet and reads as follows:

'I was mightily pleased to leaf through your beautiful book. Naturally quiet study should soon follow, yet I wanted to express my thanks for propagating thermodynamics in its classic form, in connection with a strong state equation: the work of Gibbs-Van der Waals-Van Laar! It



must have given you great satisfaction to have written this work'.<sup>61</sup>

The fifth reaction comes from Belgium, from M. Lecat (1884-1951). The postcard is dated 5 July 1936 and he calls the book a 'magistral ouvrage'.<sup>62</sup>

The tone of the eight book reviews is generally one of praise. According to Jorissen of the *Nieuwe Rotterdamsche Courant*, the theoretical part intentionally did not say anything about what Van Laar called 'Ersatztheorien' and 'Parathermodynamics'.<sup>63</sup> The physicist C.A. Crommelin (1878-1965) from Leiden thought the book was not easy.<sup>64</sup> D. MacGillavry, Bridgman and Ketelaar all remarked that in the discussion on strong electrolytes the treatment seemed to prefer Ghosh's theory to Debye-Hückel's theory.<sup>65</sup> The book was never a financial success.<sup>66</sup>

## 6. Autumn of his life

After his wife's death in 1934, his house was kept until his own death by a Dutch lady, Mrs. Koker. He only felt really at home in his study and had relatively few outings, although he took walks in the surrounding areas.<sup>67</sup> Sudden thoughts were jotted down on his cuffs, or were written in the sand with his cane.<sup>68</sup> His interest in music continued undiminished; in 1935 he heard all of Beethoven's string quartets in seven concerts given by the Rosé Quartet. According to Van Laar, Beethoven's later string quartets and sonatas were the highest and the deepest ever to have been composed.<sup>69</sup>



*Van Laar and Mrs. Koker (?) botanizing in an alpine pasture.*<sup>71</sup>

On April 21 1938 he became an honorary member of the Nederlandsche Chemische Vereeniging. The Chairman, C.A. Lobry de Bruyn (1889) said:

'Nor was Dr.J.J. van Laar able to be here, because of his age and ill health. In his many writings, Dr. Van Laar has done very important work for physical chemistry through the mathematical treatment of Gibbs' classic work, which first made this work accessible to many, and his dissertations on the thermodynamic potential, and on Van der Waals' equation of state. Anyone, as I myself, who has had the privilege of hearing his fascinating lectures at the University of Amsterdam, will doubtlessly have good memories of his striking personality. I consider it paying off a debt of honour, to show, in the evening of his life, this hard worker, who has justly been called in an American magazine, the Nestor of Dutch physicist-chemists, our gratitude and appreciation by giving him this honorary membership'.<sup>70</sup>

It was decided to send a telegram and Van Laar sent his thanks by postcard, and wrote about his illness:



'(...) I am not allowed to go out yet - far too cold - only, weather permitting, a few steps in the garden (...)'.<sup>72</sup>

Van Laar had become ill and wrote in one of his last postcards to Jorissen:

'(...) You can see from all this, dear Jorissen, that the old Van Laar is played out. From now on I must live on a lower heart level and always take the greatest care and precaution. Until 1937 I was still 'young' (I was called a 'young man')! - and now ... I won't say the word. It only happens to ships! Best wishes, (...)'.<sup>74</sup>

Johannes Jacobus van Laar never wanted to become a sailor, but was always one in some ways! On 22 October 1938 he wrote a letter to his youngest son saying that everything was a tremendous effort for him.<sup>75</sup>



*Maison 'Les Tilleuls'*.<sup>76</sup>

He died on 9 December 1938 at Maison 'Les Tilleuls' in Tavel-sur-Clarens, in his second mother country. His death was reported in some of the Dutch daily papers.<sup>77</sup>

After his children and neighbours had paid their last respects, Van Laar was laid to rest in the 'Cimétière de Clarens'. In the funeral register he

was registered as 'homme de lettres'.<sup>79</sup> There were 21 letters of condolence but for this book only the letters from Keesom, Debye, Jaeger, Ornstein, Kruyt and Verschaffelt are of importance.<sup>80</sup> The letters from Debye, Jaeger and Kruyt were short and formal. Keesom wrote on 13 December 1938 from Utrecht:

Heden bereikte ons bericht uit Zwitserland, dat onze lieve Vader, Behuwd- en Grootvader

**DR. J. J. VAN LAAR,**

Oud-Lector a/d. Amsterdamsche Universiteit,  
Ridder in de Orde van den Nederlandschen Leeuw,  
enz., enz.,  
in den ouderdom van 78 jaar, kalm is Ingeslapen.  
Tavel sur Clarens, 9 December 1938.

Uit aller naam:  
J. J. VAN LAAR,  
Loosdrecht.

Begraafensplechtigheid zal plaats hebben te Tavel sur Clarens.

*Obituary Notice.*<sup>78</sup>

'Let me express my sympathy at the loss of your much esteemed father. I had personally met your late father only a few times, but so much more have I seen and read of his work. I have always had the highest regard for his enthusiastic love of science and for his great energy in to his old age'.

Verschaffelt wrote on 26 December 1938 from Gent:

'With regret I received the news of the death of my old friend, your father. I thank you for your kindness in informing me. Receive, both you and your family, the assurance of my sympathy at this your sad loss'.

Ornstein's letter from Utrecht of 14 December 1938 was exceptionally kind:

'Herewith I express my deepest sympathy at the death of your honoured father. I have always had great respect for his person and his work. He was a truly great man, who has long been misunderstood, but who bore this proudly. I feel gratitude for the many signs of sympathy I received from him. Our connection began in 1908, when I received a very angry letter from him about one of the propositions of my thesis. After my answer, however, this grew into a

good friendship. When in 1911 in Utrecht I was passed over, he wrote me a letter which greatly encouraged me and after my appointment in 1914 in Utrecht he was among the first to congratulate me in his own kind fashion. His memory will, because of his work, live on for a long time; his friends, among whom I count myself, will keep it alive for as long as they live. Believe me, Yours faithfully, L.S. Ornstein'.



*L.S. Ornstein.*

The rights of the graves having expired, the tombstones of both Van Laar and his wife disappeared forever in the late 1960's.<sup>81,82</sup>

## 7. Concluding remarks

From the last chapter it appears that Van Laar received much appreciation and that he bore no grudge against Van der Waals. His insights in thermodynamics can be found in his final book published in 1935. His declining years must have been quiet.

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## RETROSPECT ON VAN LAAR'S PERSONALITY

*'Lately I am so much at the mercy of all kinds of uncertainty and disillusion that I truly do not know what to do.'*

The following discussion considers Van Laar's character and illustrates its effect on his scientific work. From the documents and letters under study it appears that Van Laar was an honest man of principle and an agnostic.<sup>1,2</sup> He had a certain naïvety; this is shown for instance when, without making any inquiries, he changed jobs and moved from Middelburg to Utrecht. His resignation both in Utrecht and in Amsterdam in 1895 and 1912 show him to have been a nervous man. Sometimes his hand shook with nervous tension.<sup>3</sup> His paranoid concern for mail reaching its destination was excessive. What is remarkable is that he never made a copy of his writings which would certainly have lessened the need for such concern. It almost seems as if he wanted to be in such a state.<sup>4</sup> His letters can rarely be called calm or balanced; one always feels a certain unrest in them. Sometimes they even made Lorentz feel a bit 'queer'.<sup>5</sup> His scientific writings were usually logically composed. The extensive mathematical treatment does not however make his work easily accessible; it must often have missed its mark. He was a fighter but his arguments were sometimes very abrasive, for example those with Nernst and Keesom. Even though he was right, readers cannot help feeling that Van Laar was selling himself short. His attacks on propositions in theses are odd.<sup>7,8</sup> Also characteristic was his tendency to interfere, unasked, in an existing controversy. It seems as if, again and again, he fought in a power struggle and started a crisis of authority. He certainly made many enemies, often unnecessarily. Today we would say that he was lacking in social skills.

Van Laar was a hard worker; he never rested and always had something to do. He produced a large number of scientific publications and they

enjoyed the admiration of colleagues such as Bijvoet, Scheffer, Schreinemakers and Verschaffelt. In a way, he was ahead of his time with his ideas. In Amsterdam he was an enthusiastic teacher and his work meant everything to him.<sup>9,10</sup> Sections of his publications have apparently been copied without due credit having been given to him.<sup>11</sup>

In his own time, Van Laar's work found little response. This is not only because his approach was very exact but also and mainly because of his aggressive and nervous attitude which offended most of his contemporaries. The Leiden professor J.P. Kuenen (1866-1922), for instance, in a letter to Lorentz of 25 April 1897 from Dundee called Van Laar's writings unreadable.<sup>12</sup> Kruyt thought that Van Laar did not make things easy for others, primarily because of the 'mathematical dress' in which everything was clad.<sup>13</sup>

Many felt resistance towards Van Laar as a person. He was unbridled in his criticism but also in his admiration. He admired people like Van der Waals and the Dutch philosopher G.J.P. Bolland (1854-1922).<sup>14</sup> He behaved and felt isolated though and on 12 March 1901 he wrote to Lorentz:

'Lately I am so much at the mercy of all kinds of uncertainty and disillusion that I truly do not know what to do. If I were alone, I'd rather live in poverty somewhere in a forgotten corner in the country asking nothing from anybody'.<sup>15,16</sup>

Typical of what could be called his 'social naivety' are his requests for promotion and decoration. These betray a lack of understanding of matters of procedure. It may be that ordering people about and his endless struggle for recognition were results of his training at the Naval Institute. In his most sensitive period as a young man, between the ages of 16 and 19, trained as a naval officer. There he was taught both to give and to take orders. In later years he did not speak favourably about his naval training.<sup>18</sup> In 1887 he declared himself to be anti- military.<sup>17</sup> His naval training may have contributed to his feelings of isolation later. The community on a ship is different from one on land; on board ship people have to get on together, on land there is no such necessity. As an orphan, the lack of possibility for identification caused by the absence of his parents may have forced him to search for an identity elsewhere. Even at the age of forty this still concerned Van Laar; in the foreword of his book *Mathematische Chemie* in 1901, he says:

Dem Gedächtnis  
meiner früh verstorbenen Eltern

gewidmet.

Navy life and a marine training are different from growing up at home and in school. His naval training put him at a distinct disadvantage in later life because it had not allowed him to take academic examinations and his scientific career could not develop in the usual way. After being rejected as medically unfit in 1896, Van Laar was emotionally and socially in bad shape but as a private teacher in Amsterdam he developed into an enthusiastic teacher and scientist. Van der Waals and Bakhuis Roozeboom had differing opinions on Van Laar's work.<sup>20</sup> It does not speak well for Van der Waals that he apparently wanted to remove Van Laar from the University of Amsterdam.<sup>21</sup> Van der Waals probably hindered him in his work as well as in his private life. This must have had an effect on Van Laar's behaviour as a colleague. On the other hand Van Laar did trespass in the area of the equation of state and in thermodynamics, which Van der Waals considered his own. In this respect Einstein's views of 1914 might prove to be clarifying (chapter II). Van Laar's resistance to the heat theorem can be explained partly by his militant character and also in part by the tradition and the culture of the Faculty in Amsterdam.

Van Laar deserves great respect for his scientific achievements considering his emotionally deprived youth and his lack of a regular university education.

### **Final conclusion**

At the start of this study, attention was mainly focused on the discrepancy between Van Laar's great merits and his clearly controversial reputation. The focus has now changed as the author's original fascination with the person has been increasingly put in perspective and a greater interest in the 'physical chemical era' has developed.

There is a great difference between the reactions of Van Laar's contemporaries, his colleagues, administrators and relative outsiders to his work and behaviour. This shows that Van Laar's lack of social skills had a great influence on his career. Though it is clear that Van Laar was greatly hampered in his career by the lack of a regular academic education, he was a self-made man with the advantages and disadvantages of this type of

person. Another conclusion is also justified. The wisdom and ability to get along with people who not only have undeniable qualities but who also show somewhat deviant or ill-adapted behaviour in the academic world is not a skill which many people possess. Some great scientists have shown that they are able to pass this test with flying colours, others show themselves to be lacking in this respect.

Recapitulating it might be said that this study of Van Laar, more than only as the subject of a biography, could be regarded as an opportunity for a retrospective view on a decisive period in the development of chemical thermodynamics, focusing on the role of the Faculty of Mathematics and Physics at the University of Amsterdam at the time.

## References

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'You consider me (and I have often given you reason enough) a fighter. Yet I can assure you that such a thing does not agree with my nature. I would have nothing rather than tranquillity. Calm and moderation. This is how I order my life. In all respects I lead a moderate life. But I have two great faults:  
1. a strong sense of justice and injustice;  
2. an irritable nature caused by suffering years of *systematic* injustice.  
These two states of mind have made me militant, particularly over the last years'.
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'If therefore sometimes my hand shook when discussing his work and describing his scientific character, this was due to the fact alone that I often - driven by a desire for impartiality and truth - hesitated before writing down any expression or judgement which might cause a misunderstanding'; In J.J. van Laar's letter to H.A. Lorentz of 2 January 1907 (AL.2.21.203 Nr.45 ARAG) the final paragraph says:  
'Forgive my bad handwriting, I have a heavy disposition, I must *force* myself to stay calm, and my hand shakes'.
4. In J.J. van Laar's letter to H.A. Lorentz of 17 February 1907 the following passage appears:  
'Would you be so kind as to return my piece to me so that it may be at my disposal again. There are no copies. The *notes* used to compose my piece have become - after so many weeks - not clear, not clear enough to start from to write the piece again without, *again*, the greatest effort and thinking' (AL.2.21.203 Nr.45 ARAG).
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13. *Ibid.*, 9.
14. Letter J.J. van Laar to G.J.P.J. Bolland of 4 May 1899 (UBL).
15. Information Mrs.L. van Laar and Mrs.E.W. van Laar, Amsterdam.

16. Letter J.J. van Laar to H.A. Lorentz of 12 March 1901 (AL.2.21.203 Nr.45 ARAG).
17. J.J. van Laar, *Het Systeem der Wetenschappen, Gevolgd door een Uitvoerige Boekenopgave, benevens Algemene Beschouwingen over Middelbaar en Universitair Onderwijs*. Amsterdam: Versluys (1887) 93.
18. J.J. van Laar, Dr.W.P. Jorissen 21 Oct. 1896 - 21 Oct. 1921. *Chemisch Weekblad* 18 (1921) 605.
19. J.J. van Laar, *Lehrbuch der Mathematische Chemie*, Leipzig: Barth (1901)
20. Minutes of meeting 31 July 1907 of the Faculty (AF.1020, Nr.4, GAA)
21. Chapter II.



# SUMMARY

This thesis deals with the life and work of the Dutch mathematical chemist, Johannes Jacobus Van Laar (1860-1938). Van Laar's mathematical chemistry includes chemical thermodynamics and phase equilibria and is founded on Gibbs' and Van der Waals' work. Van Laar's scientific achievements are described and the lasting significance of his work is highlighted.

Chapter II 'Life in the Netherlands' describes Van Laar's life up to the point of the official recognition of his work in 1914, the year he became Doctor Honoris Causa in Groningen. Special attention is paid to the controversy with J.D. van der Waals (1837-1923) which created a great deal of tension for Van Laar. It appears that this dispute can not only be seen as a result of 'incompatibilité d' humeur' but can also be interpreted as a result of Faculty policy. There was no room for Van Laar's mathematical chemistry because the physicist Ph. Kohnstamm (1875-1951) was responsible for chemical thermodynamics after 1908. Van der Waals and the Faculty regarded chemical thermodynamics as thermodynamics and thus as part of physics. This situation continued in Amsterdam certainly until 1927. The policy is further illustrated with the discussions concerning the vacancies left by H.W. Bakhuis Roozeboom (1854-1907) and Van der Waals in 1907 and 1908 respectively.

Chapter III 'Achievements' studies Van Laar's scientific contributions to mathematical chemistry. The main source of information in the 'Overview', section III.2, is Van Laar's letter of 13 June 1914 in which he describes his work during the period of 1892 until 1914, on the occasion of his honorary degree at the request of the editor of 'Chemisch Weekblad', the chemist W.P. Jorissen (1869-1959). A description of his work until 1938 follows. Appendix II includes his bibliography and gives

an indication of the large number of subjects Van Laar studied. In 'Significance', section III.3, six subjects have been selected for discussion because of their importance for chemical process design. The 'Van Laar equation' is undoubtedly the best known example.

One of the main reasons that Van Laar's contemporaries found him unfriendly and cold was his often fierce polemic style. To illustrate this, chapter IV 'Obstinacy' outlines Van Laar's opposition in section IV.2 to the 'Nernst's heat theorem' in a broader scientific context. It appears that he was not alone in his views and Kohnstamm in particular also rejected the heat theorem. The policy of the Faculty, as described in chapter II, is reflected. His inflexibility is especially marked in his treatment of the melting curve of helium as a function of temperature, which is described in section IV.3, 'Solidification of Helium'. He refused to explain the course of the melting curve with the equation of Clapeyron as a result of the heat theorem. This refusal brought Van Laar into conflict with W.H. Keesom (1876-1928). It was finally the physicist H.A. Lorentz (1853-1928) who mediated in this conflict, with Van Laar finding it difficult to admit that he was in the wrong.

Chapter V 'Life in Switzerland' describes Van Laar's recognition in 1929, 1931 and in 1938, his last book and the time he spent in Switzerland until his death in 1938.

The study concludes with chapter VI 'Retrospect', his personality is discussed and it is concluded that the main reason for his unapproachable nature is to be found in the fact that he was not permitted to take university examinations in his youth. This left him feeling bitter for much of his life.

# SAMENVATTING

In dit proefschrift wordt het leven en werk beschreven van de Nederlandse mathematisch chemicus Johannes Jacobus van Laar (1860-1938). De mathematische chemie van Van Laar omvat de chemische thermodynamica en de fasenleer en is geënt op het werk van Gibbs en Van der Waals, zijn werk is beschreven en de betekenis ervan benadrukt.

In hoofdstuk II 'Life in the Netherlands' wordt het leven van Van Laar beschreven tot zijn eerste officiële erkenning als doctor honoris causa te Groningen in 1914. Het accent ligt op zijn controversie met J.D. van der Waals (1837-1923) in de periode 1900-1908. Het blijkt dat deze controversie niet zuiver terug te voeren is tot 'incompatibilité d'humeur', maar ook gezien kan worden als vorm van beleid van de faculteit: voor Van Laar's mathematische chemie is feitelijk geen plaats. Het resultaat is dat de natuurkundige Ph. Kohnstamm (1875-1951) na 1908 de chemische thermodynamica verzorgt, waardoor Van Laar overbodig wordt. Anders gezegd: de chemische thermodynamica wordt door Van der Waals en de faculteit gezien als thermodynamica en aldus als onderdeel van de natuurkunde. Dit duurt in Amsterdam zeker voort tot 1927. Om het beleid zichtbaar te maken is de vervulling van de vacatures van H.W. Bakhuis Roozeboom (1854-1907) en van Van der Waals in 1907 en 1908 eveneens onderzocht en beschreven.

In hoofdstuk III 'Achievements' wordt een overzicht gegeven van het werk van Van Laar. Voor het 'Overview' in III.2 is gebruik gemaakt van zijn brief van 13 juni 1914, waarin hij ter gelegenheid van zijn eredoctoraat te Groningen op verzoek van de redacteur van het Chemisch Weekblad, de scheikundige W.P. Jorissen (1869-1959), zijn werk van 1892 tot 1914 beschrijft. Met deze brief als aanzet is de beschrijving van zijn werk tot circa 1938 voltooid; in Appendix II is zijn bibliografie opgenomen. Zes

onderwerpen van Van Laar die voor toegepaste thermodynamica en fasenleer nog steeds van betekenis zijn, worden behandeld in III.3 'Significance'. Het meest bekende hiervan is de naar hem genoemde vergelijking voor de mengwarmte.

Van Laar gold bij zijn tijdgenoten als weinig sympathiek, onder andere wegens zijn vaak heftige polemische stijl en soms onvoldoende contactmogelijkheden. Om dit te laten zien, wordt in hoofdstuk IV 'Obstinacy' zijn weerstand tegen het warmtetheorema geschetst. Deze weerstand wordt bovendien in een ruimer kader geplaatst. Het blijkt dan dat hij niet alleen staat; het is vooral Kohnstamm die aanvankelijk het warmtetheorema afwijst. Tevens wordt getracht aan te tonen dat het gevoerde beleid uit hoofdstuk II van de faculteit in de beoefening van de wetenschap doorklinkt. De starheid van Van Laar komt vooral tot uitdrukking bij het extrapoleren van de smeltlijn van helium als functie van de temperatuur, hetgeen beschreven wordt in IV.3 'Solidification of Helium'. Hij weigert de loop van de smeltlijn met de vergelijking van Clapeyron als gevolg van het theorema uit te leggen. Van Laar raakt hierdoor in een conflict met W.H. Keesom (1876-1956), waarin tenslotte de natuurkundige H.A. Lorentz (1853-1928) bemiddelt. Het blijkt dat Van Laar moeilijk zijn ongelijk kan bekennen.

In hoofdstuk V 'Life in Switzerland' wordt de verdere erkenning van Van Laar in 1929, 1931 en in 1938 beschreven, alsmede zijn laatste boek en zijn leven tot zijn overlijden in 1938.

De studie wordt afgesloten met hoofdstuk VI 'Retrospect' waarin wordt ingegaan op de persoonlijkheid van Van Laar. Er wordt aangegeven dat de hoofdoorzaak van zijn onvoldoende contactmogelijkheden gezocht kan worden in ervaringen in zijn jeugd en het feit dat hij geen academische examens kon doen, hetgeen hem vaak verbitterd heeft gemaakt.

## APPENDIX I

### Survey of Van Laar's life:

- 1860 Born in The Hague
- 1862 Death of his mother J. van Laar-Rost van Tonningen
- 1872 Entry to the H.B.S. (Grammar school)
- 1873 Death of his father J.J. van Laar
- 1876 Enrolled in the Royal Naval Institute
- 1881 Discharge from the Navy
- 1881 Student chemistry at the University of Amsterdam
- 1884 Teacher of mathematics in Middelburg
- 1885 Marriage to W.H.T. ten Brink in Meppel
- 1892 First publication in Z.Phys.Chem.
- 1893 'Die Thermodynamik in der Chemie'
- 1895 Teacher of mathematics in Utrecht
- 1897 Discharge from teaching profession
- 1898 Unsalaries lecturer of mathematical chemistry
- 1901 'Lehrbuch der mathematischen Chemie'
- 1903 Research assistant to Bakhuis Roozeboom
- 1906 'Sechs Vorträge'
- 1907 'Lehrbuch der theoretischen Elektrochemie'
- 1908 Lecturer of mathematics, more particularly  
for students of chemistry and biology
- 1909 Separated from his wife
- 1911 Went to Switzerland on sick leave
- 1912 Discharge as a lecturer and the death of his wife
- 1914 Doctor Honoris Causa in Groningen and  
marriage to second wife M. Schagen
- 1924 'Die Zustandsgleichung von Gasen und Flüssigkeiten'
- 1929 Bakhuis Roozeboom Medal
- 1930 Correspondent of the Royal Academy of Science
- 1931 Knight of the Order of the Netherlands Lion
- 1934 Death of his second wife
- 1935 'Die Thermodynamik einheitlicher Stoffe und binäre Gemische'
- 1938 Died in Tavel-sur-Clarens

### Places where Van Laar lived:

- 1860 The Hague
- 1863 Haarlem
- 1876 Den Helder: Royal Naval Institute
- 1880 H.M.S. 'Zilveren Kruis' and H.M.S. 'Marnix'
- 1881 H.M.S. 'Koningin Emma der Nederlanden'

- 1881 Amsterdam
- 1884 Middelburg
- 1896 Utrecht
- 1901 Amsterdam
- 1903 Hilversum
- 1909 Baarn
- 1910 Haarlem
- 1911 Fontanivent sur Clarens (Switzerland)
- 1912 Baarn (Netherlands)
- 1912 Fontanivent sur Clarens (Switzerland)
- 1918 La Tour de Peilz (Switzerland)
- 1921 Tavel sur Clarens (Switzerland)

## APPENDIX II

### BIBLIOGRAPHY OF VAN LAAR

#### I. Books:

1. *Het Systeem der Wetenschappen, gevolgd door een uitvoerige boekenopgave, benevens Algemene Beschouwingen over Middelbaar en Universitair Onderwijs*, Amsterdam: Versluys (1887).
2. *Register op de Ideën van Multatuli*, Rotterdam: Elsevier (1887).
3. *Plagiaat of Niet?*, Middelburg: Van Benthem (1889).
4. *Physiologie van de Nieuwe Gids*, Amsterdam: Rössing (1889).
5. *Leerboek der algebra, 2 delen. en bijbehorende vraagstukken 2 delen.*, Leiden: Brill (1889-1890).
6. *Leerboek der boldriehoeksmeting*, Groningen: Noordhoff (1893).
7. *Die Thermodynamik in der Chemie*, Leipzig: Barth (1893).
8. J.D. van der Waals, *Mannen en vrouwen van beteekenis in onze dagen*, Haarlem: Tjeenk Willink (1900); In German: J.D. van der Waals *Ein Lebensabriss*, Leipzig: Barth (1900).
9. *Lehrbuch der mathematischen Chemie*, Leipzig: Barth (1901).
10. *Lessen over lagere algebra*, Amsterdam: Van Looy (1904).
11. *Sechs Vorträge über das thermodynamische Potential und seine Anwendungen auf chemische und physikalische Gleichgewichtsprobleme*, Braunschweig: Vieweg (1906); Translated in to Italian by A. Bartorelli and in to Russian by D. Gardner.
12. *Lehrbuch der theoretischen Elektrochemie auf thermodynamischer Grundlage*, Leipzig: Engelman (1907).
13. *Over den Gibbs'schen Phasenregel*, Amsterdam: Versluys (1907).
14. *L'hydrogène et les gaz nobles*, Leiden: Sijthoff (1922).
15. *Die Zustandsgleichung von Gasen und Flüssigkeiten mit besonderer Berücksichtigung der Veränderlichkeit der Werte von a und b, des kritischen Zustandes und der Theorie der Dampfspanningskurven*, Leipzig: Voss (1924).

16. Die Thermodynamik einheitlicher Stoffe und binäre Gemische, mit Anwendungen auf verschiedene physikalisch-chemische Probleme, Groningen: Noordhoff (1935).

## II Publications:

The following abbreviations have been used in the text and the notes after each chapter:

- A. *Vers.K.Ned.Akad.Wet.*: Verslag van de gewone vergaderingen der wis- en natuurkunde afdeeling, Koninklijke Akademie van Wetenschappen;
- B. *Proc.K.Ned.Akad.Wet.*: The English translation of Proc.K.Ned.Akad.Wet. in Proceedings of the Section of Science of the Koninklijke Akademie van Wetenschappen;
- C. *Arch.Mus.Teyler*: Archives du Musée Teyler;
- D. *Z.Phys.Chem.*: Zeitschrift für physikalische Chemie;
- F. *Z.Anorg.Allg.Chem.*: Zeitschrift für anorganische und allgemeine Chemie;
- E. *J.Chim.Phys.*: Journal de Chimie Physique;
- G. *Rec.Trav.Chim.Pays-Bas*: Recueil des Travaux Chimiques des Pays-Bas;
- H. *Chem.Weekbl.*: Chemisch Weekblad;
- J. Other periodicals.

### A. Verslag van de gewone vergaderingen der wis- en natuurkunde afdeeling, Koninklijke Akademie van Wetenschappen (Vers.K.Ned.Akad.Wet.).

- 1. Berekening der tweede correctie op de grootheid  $b$  der toestandsvergelijking van van der Waals, 7 (1899) 350-364.
- 2. Over de asymmetrie der electro-capillaircurve, 10 (1902) 753-768.
- 3. Over het verloop der smeltlijnen van vaste legeringen of amalgamen, 11 (1902/03) 478-485.
- 4. Over het potentiaal-verschil, hetwelk ontstaat aan het scheidingsvlak van twee verschillende, niet-mengbare oplosmiddelen, waarin zich een zelfde opgeloste elektrolyt verdeeld heeft, 11 (1903) 485-492.
- 5. Over het electro-motorisch gedrag van amalgamen en legeringen, 11 (1903) 558-579.
- 6. De smeltlijn van tinamalgamen, 11 (1902/03) 576-591.
- 7. Over het verloop der waarden van  $b$  bij waterstof, in verband met een recente formule van Prof. van der Waals, 11 (1903) 713-729.
- 8. De smeltlijnen van legeringen, 12 (1903) 25-34.
- 9. Over de mogelijke vormen der smeltlijn bij binaire mengsels van isomorphe stoffen, 12 (1903/04) 169-187.
- 10. Over de gedaante van het realiseerbare gedeelte der smeltlijn bij binaire mengsels van isomorphe stoffen, 12 (1903/04) 494-509.
- 11. Over de gedaante van smeltlijnen bij binaire mengsels, wanneer de mengwarmte in de beide fasen zeer gering of  $= 0$  is, 12 (1903/04) 716-729.
- 12. Over mengwarmten bij associeerende oplosmiddelen, 13 (1904/05) 121-124.
- 13. Over eenige verschijnselen, welke kunnen optreden bij de beperkte mengbaarheid van twee vloeistoffen, waarvan de eene anomaal, speciaal water is, 13 (1904/05) 573-588.
- 14. Over de verschillende vormen en overgangen der grenslijnen bij gedeeltelijke

- mengbaarheid van twee vloeistoffen, 13 (1904/05) 660-672.
15. Een nauwkeurige uitdrukking voor het verloop der spinodale lijnen en van hunne plooiopunten voor alle temperaturen, in het geval van mengsels van normale stoffen, 13 (1904/05) 685-696.
  16. Over het verloop der plooiopuntlijnen bij mengsels van normale stoffen, 14 (1904/05) 14-29.
  17. Eenige opmerkingen naar aanleiding der laatste verhandelingen van Dr.Ph. Kohnstamm, 14 (1905/06) 30-33.
  18. De moleculaire verhooging der laagste kritische temperatuur van een binair mengsel van normale componenten, 14 (1904/05) 108-116.
  19. Over het verloop der spinodale en plooiopuntlijnen bij binaire mengsels van normale stoffen, I, 14 (1905/06) 582-594; II, 15 (1906/07) 227-236.
  20. Over het verloop der smeldlijnen bij verbindingen, welke in de vloeibare phase gedeeltelijk gedissocieerd zijn, bij willekeurige verhouding der ontledingsproducten, 14 (1905/06) 711-726.
  21. Iets over den osmotischen druk van oplossingen van niet-electrolyten, in verband met de afwijkingen van de wetten der ideale gassen, 14 (1905/06) 849-858
  22. Over het verloop der plooiopuntlijnen en der spinodale lijnen, ook voor het geval, dat de onderlinge aantrekking der moleculen van een der componenten van een binair mengsel van normale stoffen gering is, 15 (1906/07) 939-952.
  23. Iets naar aanleiding van de mededeeling van H. Kamerlingh Onnes en W.H. Keesom, 16 (1906/07) 136-137.
  24. Iets over den vasten toestand, I, 17 (1908/09) 828-844; II, Ibid. 956-972; III, 18 (1909/10) 27-40; IV, Ibid. 97-105; V, 19 (1910/11) 405-426; VI, Ibid. 675-688; VII, 20 (1911/12) 3-19.
  25. Eenige opmerkingen naar aanleiding eener verhandeling van de Heeren Timmermans en Kohnstamm over den invloed van den druk op de mengbaarheid van twee vloeistoffen, I, 18 (1909/10) 497-500; II, Ibid. 749-750.
  26. Over de veranderlijkheid der grootheid  $b$  in de toestandvergelijking van van der Waals, ook in verband met de kritische grootheden, I, 20 (1911/12) 367-387; II, Ibid. 445-459; III, Ibid. 608-624; IV, Ibid. 77-789.
  27. Over eenige bij het kritische punt geldende betrekkingen, 20 (1912) 923-933.
  28. Over de waarde van eenige differentiaalquotienten in het kritische punt, in verband met de coëxisterende fasen in de nabijheid van dat punt en met den vorm der toestandvergelijking, 20 (1911/12) 1229-1245.
  29. Over de berekening van den thermodynamischen potentiaal van mengsels, wanneer een verbinding tusschen de componenten kan optreden, 21 (1912/13) 630-636.
  30. Over eenige moeilijkheden en tegenstrijdigheden bij het opstellen der toestandsvergelijking, 21 (1912/13) 1433-1449.
  31. Een nieuwe betrekking tusschen de kritische grootheden en over de eenheid aller stoffen in hun thermisch gedrag, I, 22 (1913/14) 793-807; II, Ibid. 885-899; III, Ibid. 1093-1110; IV, Ibid. 1303-1318.



32. Eenige opmerkingen over de waarden der kritische grootheden bij associatie, 23 (1914/15) 151-159.
33. Over schijnbare thermodynamische discontinuïteiten in verband met de waarde der grootheid  $b$  bij oneindig groot volume, 23 (1914/15) 446-455.
34. De berekening der moleculaire afmetingen uit de onderstelling van den electricchen aard der quasi-elastische atoomkrachten, 23 (1914/15) 820-827.
35. Eenige opmerkingen over den osmotischen druk, 24 (1915/16) 142-149.
36. Over de additiviteit der waarden van  $b$  en  $\sqrt{a}$  der toestands- vergelijkingen over de grondwaarden dezer grootheden bij verschillende elementen, in verband met het periodiek systeem, I, 24 (1915/16) 1284-1300; II, 24 (1915/16) 1635-1657; III, 25 (1916/17) 142-150; IV, Ibid. 434-460; V, 26 (1917/18) 45-57; VI, Ibid. 305-319.
37. Over de ongeldigheid van den z.g. 'valentieregel' van Mathews, 24 (1915/16) 1300-1304.
38. Over de kritische temperatuur en druk van kwik en phosphorus, 25 (1916/17) 1498-1508.
39. Over het verloop der waarden van  $a$  en  $b$  bij waterstof bij verschillende temperaturen en volumina, I, 26 (1917/18) 844-862; II, Ibid. 1209-1226; III, Ibid. 1305-1318; IV, Ibid. 1445-1454.
40. Over de dissociatiewarmte van tweeatomige gassen in verband met de verhoogde valentieaantrekkingen  $\sqrt{a}$  der vrije atomen, 27 (1918/19) 524-536.
41. Over de toestandvergelijking voor willekeurige temperaturen en volumina. Analogie met de formule van Planck, 27 (1918/19) 995-1010; II, 29 (1920/21) 766-785; III, 30 (1921) 369-370.
42. Over de kritische grootheden van kwik in verband met de vergrooting der moleculaire attractie bij dissociatie der dubbelmoleculen I, 29 (1920) 49-63; II, Ibid. 302-318.
43. Over de mengwarmten van normale en associeerende vloeistoffen, I, 31 (1922) 363-372; II, Ibid. 527-541.
44. Over de toestandvergelijking van vloeistoffen en vast lichamen bij hooge en lage temperaturen, 33 (1924) 957-974.
45. Over de verhouding der inwendige latente verdampingswarmte tot de moleculaire oppervlakte-energie, in verband met de gewijzigde wet der overeenstemmende toestanden, 34 (1925) 803-815.
46. Over de toestandvergelijking van vaste stoffen (metalen) in verband met hunne samendrukbaarheid en met den druk- en temperatuurscoëfficiënt dezer grootheid, 34 (1925) 1303-1320.
47. Over de toestandvergelijking van vaste stoffen in verband met de algemene uitdrukking voor energie, 35 (1926) 159-176.
48. Over de toestandvergelijking van vaste stoffen in verband met een algemene uitdrukking voor de energie en de entropie. Eenvoudige afleiding der z.g. entropie-konstante, 35 (1926) 403-417.
49. Over de maximum en minimumdichtheid en verdampingswarmte van helium, 35 (1926) 899-912; II, Ibid. 991-1008.
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  52. De smeltlijn van helium en het warmtetheorema van Nernst, 36 (1927) 1083.
- B. Proceedings of the Section of Natural Science of the Royal Dutch Academy of Sciences (Numbers 53-57 are written in German and not published in Vers.K. Ned.Akad.Wet.); translations into French in Archives Néerlandaises (Arch.Neerl. Sci.Exactes Nat.) and Journal de Chimie Physique (J.Chim.Phys.), into German in Zeitschrift für anorganische und allgemeine Chemie (Z.Anorg.Allg.Chem.).**
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  2. On the asymetry of the electro-capillarycurve, I, 4 (1901/1902) 560-577; Archives (II) VII (1902) 443-459.
  3. The course of the meltingpoint-lines of solid alloys or amalgams, 5 (1902/03) 424-430; Archives (II) VIII (1903) 264-284.
  4. On the potential-difference, which occurs at the surface of contact of two different non-miscible liquids, in which a dissolved electrolyte has distributed itself, 5 (1902/1903) 431-437; Archives (II) VIII (1903) 226-234.
  5. Not translated into English; Archives (II) VIII (1903) 296-318.
  6. The meltingpoint-line of tin-amalgams, 5 (1902/03) 511-525.
  7. On the course of the value of  $b$  for hydrogen, in connection with a recent formula of Van der Waals, 5 (1902/03) 573-589; Archives (II) IX (1904) 389-417.
  8. The course of the meltingpoint-line of alloys, 6 (1903/04) 21-30;
  9. On the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances I, 6 (1903/04) 151-169.
  10. On the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances II, 6 (1903/04) 244-259.
  11. On the shape of meltingpoint-curve for binary mixtures, when the latent heat required for mixing is very small or = 0 in two phases, 6 (1903/04) 518-531.
  12. On the latent heat of mixing for associating solvents, 7 (1904/05) 174-177.
  13. On some phenomena, which can occur in case of partial miscibility of two liquids, one of them being anomalous, especially water, 7 (1904/05) 517-513.
  14. On the different forms and transformations of the boundary-curves in the case of partial miscibility of two liquids 7 (1904/05) 636-646.
  15. An exact expression for the course of spinodal curves and their plait-points for all temperatures, in the case of mixtures of normal substances, 7 (1904/05) 646-657.
  16. On the shape of the plaitpoint-curve for mixtures of normal substances, 8 (1905/06) 33-48.
  17. Some remarks on Ph. Kohnstamm's papers on the osmotic pressure, 8 (1905/06) 49-51.
  18. The molecular rise of the lower critical temperature of a binary mixture of normal components, 8 (1905/06) 144-152; Archives (II) X (1905) 373-413.

19. On the course of the spinodal and the plaitpoint lines for binary mixtures of normal substances, I, 8 (1905/06) 578-590, Archives (II) XI (1906) 224-238; II, 9 (1906/07) 226-235, Archives XII (1906) 389-399.
20. On the course of melting-point curves for compounds which are partially dissociated in the liquid phase, the proportion of the products of dissociation being arbitrary, 8 (1905/06) 699-714.
21. On the osmotic pressure of solutions of non-electrolytes, in connection with the deviations from the laws of ideal gases, 9 (1906/07) 53-63.
22. On the course of the plaitpoint line and of the spinodal lines, also for the case, that the mutual attraction of the molecules of one component of a binary mixture of normal substances is slight, 10 (1907/08) 34-46.
23. Some remarks on the last observations of H. Kamerlingh Onnes and W.H. Keesom. 10 (1907/08) 238-239.
24. On the solid state, I, 11 (1908/19) 765-780; II, 12 (1909/10) 26-42, III, Ibid. 120-132, IV, Ibid. 133-141; V, 13 (1910/11) 454-475, VI, 636-649; VII, 14 (1911/12) 84-100; Archives (II) XV (1910) 1-56, (IIIA) I (1911) 51-89, (IIIA) I (1912) 272-291.
25. Some remarks suggested by a paper by Timmermans and Kohnstamm on the influence of the pressure on the miscibility of two liquids, I, 12 (1909/10) 454-457; II, Ibid. 617-619.
26. The variability of the quantity  $b$  in Van der Waals' equation of state, also in connection with the critical quantities, 14 (1911/12) 278-297; II, 428-442; III, 563-579; IV, 711-723.
27. On some relations holding for critical point. 14 (1911/12) 771-781.
28. On the value of some differential quotients in the critical point, in connection with the coexisting phases in the neighbourhood of that point and with the form of the equation of state, 14 (1911/12) 1091-1106.
29. The calculations of the thermodynamic potential of mixtures, when a combination can take place between the components, 15 (1912/13) 614-620.
30. Some difficulties and contradictions met with in drawing up the equation of state, 16 (1913/14) 44-59.
31. A new relation between the critical quantities, and on the unity of all the substances in their thermic behaviour, I, 16 (1913/14) 808-822; II, Ibid. 924-938; III, Ibid. 1047-1064; IV, 17 (1914/15) 461-465; Only the first article in *Z.Anorg.Allg.Chem.* 104 (1918) 57-66.
32. Some remarks on the values of the critical quantities in case of association, 17 (1914/15) 598-606.
33. On apparent thermodynamic discontinuities, in connection with the value of the quantity  $b$  for infinitely large volume, 17 (1914/15) 606-615.
34. The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic atomic forces, 17 (1914/15) 877-884.
35. Some remarks on the osmotic pressure, 18 (1915/16) 184-190.
36. On the additivity on the values of  $b$  and  $\sqrt{a}$  of the equation of state, and on the fundamental values of these quantities for different elements, in connection with the

- periodical system, I, 18 (1915/16) 1220-1235, II, *Ibid.* 19 (1916/17) 2-24, III, *Ibid.* 287-295, IV, *Ibid.* 295-320; V, 20 (1917/18) 492-504, VI, 20 (1917/18) 505-519; *Z.Anorg.Allg.Chem.* I, 104 (1918) 66-76; II, *Ibid.* 81-97; III, *Ibid.* 98-104; IV *Ibid.* 105-125; V, *Ibid.* 134-143; VI, *Ibid.* 144-156; *J.Chim.Phys.* I, 14 (1916) 1-24.
37. On the validity of Mathews' so-called valency law, 18 (1915/16) 1235-1239; *Z.Anorg.Allg.Chem.* 104 (1918) 77-80.
  38. On the critical temperature and pressure of mercury and phosphorus, 20 (1917/18) 138-148; *Z.Anorg.Allg.Chem.* 104 (1918) 126-133.
  39. On the course of the values of the  $a$  and  $b$  for hydrogen at different temperatures and volumes, I, 20 (1917/18) 750-767; II, *Ibid.* 1195-1212; III, *Ibid.* 21 (1918/19) 2-15; IV, *Ibid.* 16-25.
  40. On the heat of dissociation of diatomic gasses in connection with the increased valency-attractions  $\sqrt{A}$  of free atoms, 21 (1918/19) 644-655; *J.Chim.Phys.* 16 (1919) 411-428.
  41. On the equation of state for arbitrary temperatures and volumes. Analogy with Planck's formula, I, 21 (1918/19) 1184-1199; II, 23 (1920/21) 887-906; III, 24 (1921) 294-312.
  42. On the critical quantities of mercury in connection with the increase of the molecular attraction on dissociation on the double molecules, I, 23 (1920/21) 267-281; II, *Ibid.* 282-298.
  43. On the heat of mixing of normal associating liquids, I, 25 (1922) 309-318; II, *Ibid.* 399-413.
  44. On the equation of state of liquids and solids bodies at high and at low temperatures, 27 (1924) 897-913.
  45. On the relation of the internal latent heat of evaporation to the molecular surface energy, in connection with the modified law of the corresponding states, 28 (1925) 781-793.
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  50. On the course of the meltingpoint line of helium at very low temperatures, 30 (1927) 244-248.
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  52. The meltingpoint line of helium and Nernst's theorem of heat, 30 (1927) 957.
  53. Ueber die Dampfdruckerniedrigung des Wassers durch gelöste Elektrolyte, 33 (1930)

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55. Die Gleichung der Schmelzkurve, 35 (1932) 624-635.
56. Ueber den Verlauf von einigen thermischen und kalorischen Größen längs den beiden Schmelzkurven des Heliums, 39 (1936) 612-622.
57. Ueber die Lage des Lambda-Punktes beim Helium, 39 (1936) 822-823.

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2. Sur le chauffage d'un cylindre, dont chaque partie subit une élévation de température continue par quelque procès intérieur, physique ou chimique, (2) VI (1898) 65-84.
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2. Die theoretische Berechnung der Dampfdrucke gesättigter Dämpfe, 11 (1893) 433-438.
3. Neuberechnung einiger vielfach gebrauchter Konstanten, 11 (1893) 439-455.

4. Die Bestimmung des kritischen Volumens, 11 (1893) 661-664.
5. Bemerkungen über eine Notiz von Hans Cornelius, 11 (1893) 665-667.
6. Das Verhalten der thermischen und kalorischen Grössen bei der kritischen Temperatur, 11 (1893) 721-736.
7. Ueber die Dissoziationskonstante des Wassers und der Cyanwasserstoffsäure, (1893) 742-750.
8. Die Verseifungsgeschwindigkeit des methylacetats durch Wasser und deren Minimalwert, 13 (1894) 736-756.
9. Ueber die genauen Formeln für den osmotischen Druck, für die Änderungen der Löslichkeit, für Gefrierpunkts- und Siedepunktänderungen, und für die Lösungs- und Verdünnungswärmen bei in Lösung dissoziierten Körpern, 15 (1894) 457-497.
10. Zur Berechnung von Lösungswärmen aus der Löslichkeit, 17 (1895) 545-549.
11. Ueber die genauen Formeln für den osmotischen Druck, für die Änderungen der Löslichkeit, für Gefrierpunkts- und Siedepunktänderungen, und für die Lösungs- und Verdünnungswärmen bei in Lösung dissoziierten Körpern, Zweite Abhandlung, 18 (1895) 245-282.
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13. Ueber eine Fehlerquelle bei der Bestimmung der Dissoziationswärmen von Elektrolyten, 24 (1897) 608-614.
14. Die allgemeine Gültigkeit des Verdünnungsgesetzes, 25 (1898) 79-90.
15. Zurückweisung der Einwände von A.A. Noyes gegen meine Löslichkeitsformel, 27 (1898) 337-342.
16. Nochmals die Lösungswärme. Letztes Wort zur Erwiderung des Aufsatzes von Herrn Noyes, 29 (1899) 159-161.
17. Ueber die teilweise Assoziation der Flüssigkeitsmoleküle, 31 (1899) 1-16.
18. Die Beziehungen zwischen Lösungswärme und Löslichkeit bei Elektrolyten, 33 (1900) 11-17.
22. Ueber die Ableitungen des thermodynamischen Potentials nach T und p bei zusammengesetzten Komponenten, 36 (1901) 216-224; Livre jubilaire dédié à H.A. Lorentz (1901) 484-496.
24. Ueber einen Aufsatz des Herrn Schükarew, 39 (1901) 342-344.
25. Ueber die Asymetrie der Elektrokapillarkurve, 41 (1902) 386-398.
26. Zum Begriffe der unabhängigen Bestandteile, 43 (1903) 741-744.
27. Ueber die Dampftension von flüssigen Gemischen, z.B. von Brom und Jod, bei Annahme einer teilweisen (im Grenzfall nicht-oder total- dissoziierten Verbindung), 47 (1904) 129-145.
28. Zum Begriff der unabhängigen Bestandteile, 47 (1904) 228-230.
29. Ueber das anomale Verhalten von Löslichkeitskurven, in bezug auf Hydratbildung in der flüssigen Lösung, 54 (1906) 750-758.
30. Die Gleichung einer idealen eutektischen Kurve in einem ternären System und ihre Benutzung zur Berechnung eines eventuellen Umwandlungspunktes zweier Isomeren neben Lösung, 55 (1906) 64-70.

31. Ueber dem Verlauf der Schmelzkurven bei festen Lösungen (oder isomorphen Gemischen) in einem speziellen Fall, 55 (1906) 435-441.
32. Ueber endotherme und exotherme Dissoziationsprozesse, 57 (1907) 633-639.
33. Ist es erlaubt, aus einer gefundenen anomalen Siedepunkterhöhung einer verdünnten Lösung auf den Molekularzustand des Lösungsmittels zu schliessen?, 57 (1907) 742-744.
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35. Ueber die Löslichkeit von Elektrolyten, 59 (1907) 212-217.
36. Ueber Mischungswärmen von Wasser und Alkohol. Bemerkung nach Anlass einer Ausserung von prof. Bose, 61 (1907) 255-256.
37. Ueber den Dampfdruck von trockenem und gewöhnlichem Salmiak, 62 (1908) 194-198.
38. Antwort auf die Bemerkungen von Prof. Abegg; Dampfdruck von trockenem und gewöhnlichem Salmiak, 62 (1908) 678-680.
39. Die Schmelz- oder Erstarrungskurven bei binären Systemen, wenn die feste Phase ein Gemisch (amorphe feste Lösung oder Mischkrystalle) der beiden Komponenten ist, 63 (1907) 216-253; 64 (1908) 257-297; 66 (1909) 197-237.
40. Einige Bemerkungen über den osmotischen Druck, 64 (1908) 629-632.
41. Einige theoretische betrachtungen über die elektrolytische Dissoziation von gelösten Elektrolyten, 69 (1909) 434-435.
42. Ueber Dampfspannungen von binären Gemischen, 72 (1910) 723-751.
43. Ueber 'einfache' und 'nicht einfache' Systeme der thermodynamischen Chemie, 76 (1911) 67-74.
44. Zur Theorie des osmotischen Drucks, 82 (1913) 223-224.
45. Zur Theorie der Dampfspannungen von binären Gemischen (Erwiderung an Herrn Dolezalek), 83 (1913) 599-608.
46. Ueber die van der Waals'sche Zustandsgleichung. (Anlässlich eines Aufsatzes von Herrn Berger), 116 (1925) 119-122.
47. Ueber den Wert der spezif. Wärmen  $c_1$  und  $c_2$  der Flüssigkeit und des gesättigten Dampfes längs der Grenzlinie bei der kritischen Temperatur und bei  $T = 0$ , und noch einiges über die Verdampfungswärme bei  $T = 0$ , 134 (1928) 311-327.
48. Ueber den Zusammenhang zwischen der Abweichung der Dampfdruckkurve von binären Gemischen normaler Stoffe von der geraden Linie, und der Mischungswärme in der flüssigen Phase, 137 (1928) 421-447.
49. Ueber den Einfluss eines indifferenten Gases unter Druck auf den Dampfdruck des Wassers, 145 (1929) 207-219.

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2. Finiges über die Theorie der starken Elektrolyte und ihre Geschichte, 139 (1924)

108-134.

3. Ueber die Flüssigkeitsdichte bei verschiedenen Temperaturen, 140 (1924) 52-60.
4. Untersuchung über das Verhältnis Schmelzpunkt-kritische Temperatur (mit R. Lorenz), 142 (1925) 189-192.
5. Ableitung der Grundgleichungen zum Massenwirkungsgesetz für kondensierte und heterogene Systeme (mit R. Lorenz), 145 (1925) 239-250.
6. Berechnung von Mischungswärmen kondensierter Systeme (mit R. Lorenz), 146 (1925) 42-44.
7. Ueber eine einfache Formel zur Bestimmung der kritischen Temperatur aus dem Ausdehnungskoeffizient in der flüssigen Phase und die Ursache der Nichtanwendbarkeit bei vielen geschmolzenen Salzen, 146 (1925) 263-280.
8. Ueber die aus den Dampfspannungen berechneten Werte von  $\alpha$  bei der reinen Alkalimetallen und bei den Alkalihaloiden, in bezug auf die additiven Eigenschaften dieser Grösse, 148 (1925) 235-255.
9. Ueber die kritischen Temperaturen und Drucke der Alkalihaloide aus der molekularen Oberflächenspannung und theoretische Betrachtungen über den Temperaturkoeffizient dieser Grösse, 149 (1925) 324-352.
10. Erweiterung der neuen Grundgleichungen des Massenwirkungsgesetzes auf den Fall eines Zusatzes zu den Komponenten einer Phase (mit R. Lorenz), 150 (1926) 329-334.
11. Theorie der galvanischen Stromerzeugung kondensierter Systeme (mit R. Lorenz), 151 (1926) 331-337.
12. Einiges über Dampfspannungen von einheitlichen Stoffen und von binären Gemischen. Dampfdruck von Quecksilber und Kohlenstoff, 171 (1928) 42-60.
13. Ueber die Verschiebung des Gleichgewichts von geschmolzenen Elektrolyten durch einen dritten, indifferenten Stoff, 185 (1929) 35-48.
14. Ueber die Abhängigkeit der Oberflächenspannung  $\gamma$  und der Verdampfungswärme  $\lambda$  von Dichte und Temperatur, bis an die kritische Temperatur, 180 (1929) 193-214.
15. Nochmals die Oberflächenspannung und Verdampfungswärme, Entgegnung eines Artikels von W. Herz, 185 (1929) 425-427.

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2. Sur la température et la pression critique de quelques substances, 18 (1920) 273-282.
3. Sur quelques relations entre les températures (absol.) critiques, d'ébullition et de fusion, 19 (1921) 3-8.
4. Sur la valeur limite de la chaleur latente de vaporisation au zéro absolu, 24 (1927) 115-119.

**G. Recueil des Travaux Chimiques des Pays-Bas (Rec.Trav.Chim.Pays-Bas)**

1. Quelques remarques sur la tension de la vapeur et la chaleur de vaporisation, précédées d'une étude sur la dépendance des grandeurs  $a$  et  $b$  de la température et du volume, 39



(1920) 215-242.

2. Quelques remarques sur la tension de la vapeur et la chaleur de vaporisation II, 39 (1920) 371-410.
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2. Tastbare en ontastbare begrippen (osmotische druk en thermodynamische potentiaal), 2 (1905) 143-156.
3. De nauwkeurige uitdrukking voor de z.g. moleculaire verandering der kritische temperatuur, 2 (1905) 222-229.
4. Iets over den thermodynamischen potentiaal en zijne toepassingen op scheikundige evenwichtsproblemen, 2 (1905) 283-289, 369-376, 381-389, 427-440, 520, 571-584, 653-671.
5. Iets over de vriespuntsdaling van zeewater in verband met het chloorgehalte, 2 (1905) 533-538.
6. Prof. H.W. Bakhuis Roozeboom, Een afscheidswoord, 1907, 79-81
7. Een onbegrijpelijke vergissing, 4 (1907) 401-402, 419, 464-465.
8. Aluminium en de spanningsreeks, 5 (1908) 124-127, 388-390.
9. Over reactiesnelheden, 5 (1908) 698-705, 747-764.
10. Beschouwingen over eenige fundamenteele eigenschappen van den thermodynamischen potentiaal, 6 (1909) 1027-1034.
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12. Iets over de gedaante der smeltlijn (evenwichtslijn vast-vloeibaar) en hare kritische eindpunten, in verband met de proeven van Bridgeman, 9 (1912) 744-755.
13. Een bijzonder soort polarisatie (namelijk door onmacht) in verband met zelfverdeling bij concentratiecellen, 10 (1913) 305-313.
14. Iets over hydrolyse van zouten van sterke zuren, 10 (1913) 334-345.
15. Nog eens z.g. overeenstemmende temperaturen, (1917) 808-814.
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21. Dr. W.P. Jorissen. 21 October 1896-21 October 1921, 18 (1921) 604-606.
  22. Het Natuurkundig Laboratorium der Rijks-Universiteit te Leiden in de jaren 1904 - 1922, 19 (1922) 579-583.
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  24. Iets over de theorie der sterke electrolyten, 22 (1925) 86-90.
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  26. Waarom geeft zout water zoet ijs?, 22 (1925) 339, 413-414, 23 (1925) 416-418, 551-552.
  27. Antwoord aan den Heer C.W.A. Lely, 22 (1925) 357-358.
  28. Iets over het hoogovenproces, 22 (1925) 367-370.
  29. Over grensgevallen bij faseevenwichten, 23 (1926) 416-418.
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  32. Over volledige en gedeeltelijke omhulling van atomen door andere atomen of atoomgroepen, en de daardoor veroorzaakte vluchtigheidsvergrooting, 26 (1929) 229-230.
  33. Richard Lorenz, 26 (1929) 406-407.
  34. Iets over reactiesnelheden, 26 (1929) 506-510.
  35. Eenige eenvoudige voorbeelden van faseevenwichten door toepassing van de theorie van den thermodynamischen potentiaal, 27 (1930) 66-73.
  36. Natuurphilosophische beschouwingen van een dwalende, 28 (1931) 158-159.
  37. Deductief of inductief onderwijs, 28 (1931) 393-394.
  38. Enige herinneringen aan Ch.M. van Deventer, 28 (1931) 547-550.
  39. Over de genezing van carcinoom, 28 (1931) 422-423.
  40. Nog eens osmotische druk, 28 (1931) 662-665.
  41. Antwoord aan den Heer Tellegen, 28 (1931) 676-677.
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  45. Schoolscheikunde, schoolformules en schoolwijsheid, 31 (1934) 771-772.
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  47. Een kleine rectificatie, 33 (1936) 215-216.
  48. De tegenwoordige opvattingen omtrent den toestand van electrolyten in waterige oplossingen, 33 (1936) 759-768.
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### APPENDIX III

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3. W.P. Jorissen, Dr.J.J. van Laar. 11 Juli 1860 - 11 Juli 1920., Chem.Weekbl. 17 (1920) 362-367.
4. Uitreiking der Bakhuis Roozeboom-medaille aan Dr.J.J. van Laar, Chem.Weekbl. 26 (1929) 548-550.
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20. H.A.M. Snelders, The Dutch Physical Chemist J.J. van Laar (1860-1938) Versus J.H. van 't Hoff's 'Osmotic School', *Centaurus* 29 (1986) 53-71.
21. E.P. van Emmerik, Affiniteit en reactiesnelheid bij J.J. van Laar en I. Prigogine, *Laboratoriumpraktijk* (1988) 72-74.
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## APPENDIX IV

### SHORT BIOGRAPHICAL NOTES

These biographical notes are outlines of the lives of the people with whom Van Laar had, mostly scientific, contact. The 'Biografisch Woordenboek van Nederland', the 'Winkler Prins Encyclopaedia' and other information have been used. For reference, the short note in brackets indicates the number of letters which have been found.

*Bakhuis Roozeboom, H.W. (1854-1907)* was appointed professor in Amsterdam in 1896 and succeeded J.H. van 't Hoff. He is the founder of phase theory and wrote a foreword in Van Laar's book about mathematical chemistry in 1901. Van Laar was Bakhuis Roozeboom's assistant from 1903 until 1907 and they became friends during this time.

*Bloeker, C.F.J. (1852-1912)* was a medical practitioner on internal diseases, an alderman of poverty relief and education in Amsterdam and a member of the Board of Governors of the University of Amsterdam. He believed that Van Laar should show more resistance to Van

der Waals and took Van Laar's situation to heart.

*Bolland, G.J.P.J. (1854-1922)* was originally a primary school teacher. From 1896 to 1922 he was professor of philosophy in Leiden (1x v.L.: UBL).

*Bridgman, P.W. (1882-1961)* was professor at Harvard (U.S.A.) from 1926 until 1954. His research concerned the behaviour of matter at very high pressures. Bridgman visited Van Laar in Tâvel-sur-Clarens (1x v.L.: ULH).

*Boscha, J. (1831-1911)* was a professor at the Military Academy in Breda and the Polytechnical School in Delft. He was secretary to the Hollandsche Maatschappij van Wetenschappen in Haarlem from 1885 until 1909. Thanks to his intervention, Van Laar became a member of the Hollandsche Maatschappij.

*Cohen, E.J. (1860-1944)* was a professor in Amsterdam and from 1902 until 1939 in Utrecht. Cohen wrote a short passage about Van Laar in 'Chem.Weekbl.' in 1940.

*Crommelin, C.A. (1878-1965)* studied physics in Leiden and worked in the physics laboratory there from 1903 until 1947. In 1907 he became conservator and in 1924 adjunct director and lector at the University of Leiden (1x v.L.: BML).

*Deventer, Ch. van (1860-1931)* was Van 't Hoff's assistant from 1897 until 1909 and then became a teacher in Batavia. After his period in Indonesia he worked until his retirement with Cohen in Utrecht. Besides his chemical work he was a well-known writer of essays in 'De Nieuwe Gids'. Van Laar and Van Deventer were friends from 1881 until about 1910.

*Deyssel, L. van (1864-1952)* was a writer of the cultural group of the 1880's. Van Laar visited Van Deyssel in Bergen op Zoom in 1890 (73x v.L.: H.M.G. Prick, Maastricht).

*Eeden, F.W. van (1860-1932)* studied medicine in Amsterdam and became a psychiatrist and man of letters. He attended the same Hoogere Burgeschool as Van Laar (1x v.L.: UBA).

*Ehrenfest, P. (1880-1933)* studied physics in Wenen and Göttingen. He was a professor in Leiden, succeeding Lorentz in 1910 (6x v.L. and 1x E: BML).

*Hoff, J.H. van 't (1852-1911)* and Ostwald were the founders of physical chemistry. Van 't Hoff was professor in Amsterdam from 1877 to 1896 and in Berlin from 1896 until his death. He wrote a foreword in Van Laar's first book: 'Die Thermodynamik in der Chemie' in 1893 (1x v.L.: BML).

*Holleman, A.F. (1859-1953)* was professor in Groningen from 1893 until 1905 and in Amsterdam from 1905 to 1924. He had contact with Van Laar as the faculty secretary from

1905 until 1912. He wrote minutes and made an archive of Van Laar (GAA).

*Jeager, F.M. (1877-1945)* was a teacher in Zaandam and became an unsalaried lecturer in Amsterdam in 1904. He was a colleague of Van Laar's during this time. He became a professor in Groningen from 1908 until 1943 and promoted Van Laar's Doctor Honoris Causa in 1914 (RAG).

*Jorissen, W.P. (1869-1959)* was a lecturer in Leiden from 1908 until 1940. He founded the 'Nederlandsche Chemische Vereniging' in 1903 and was editor of the 'Chem.Weekbl.' and 'Rec.Trav.Chim.Pays-Bas' (71x v.L.: AHC and 34x v.L.: BML).

*Keesom, W.H. (1876-1956)* was a research assistant in the Leiden. In 1917 he became a lecturer and in 1918 professor at the Veeartsenijkundige Hogeschool in Utrecht. In 1923 he returned to the University of Leiden and was professor of physics until 1945. In 1926 he achieved the solidification of liquid helium and discovered helium I and helium II (6x v.L.: BML and 1x K: AL).

*Kloos, W. (1860-1938)* was a writer of the cultural group of the 1880's (9x v.L.: LMG; 10x v.L. and 4x K: KB).

*Kobnstamm, Ph.A. (1875-1951)* studied physics and philosophy. In 1908 he succeeded Van der Waals as professor extraordinary of thermodynamics. After 1917 he was mainly occupied with pedagogy, of which he became professor extraordinary in 1919 in Amsterdam (5x K: AL).

*Korteweg, D.J. (1848-1941)* studied physics in Amsterdam and was the first Ph.D. student of Van der Waals. He was professor of mathematics in Amsterdam from 1891 until 1918 and during this time he had contact with Van Laar.

*Kruyt, H.R. (1882-1959)* was professor in Utrecht from 1916 until 1946. He was an assistant of Bakhuis Roozeboom's at the same time as Van Laar. He wrote a kind obituary of Van Laar in 'Chem.Weekbl.' in 1939.

*Lorentz, H.A. (1853-1928)* started his career teaching at night school in 1878 he became professor of theoretical physics in Leiden, at the age of 24. Together with A. Einstein (1879-1955) he developed the theory of relativity (72x v.L. and 5x L: AL).

*Lorenz, R. (1863-1929)* worked in Zurich and from 1910 until his retirement he was professor in chemistry in Frankfurt. He was the editor of Z.a.a.Ch. Van Laar co-operated with Lorenz in writing articles during the 1920's. Van Laar wrote an article about Lorenz in 'Chem.Weekbl.' in 1929.

Groningen in The Netherlands from 1904 until 1936 (11x v.L and 11x N: AWNG).

*Ornstein, L.S. (1880-1941)* was lecturer in Groningen from 1909 until 1914. In 1915 he became a professor in Utrecht but in 1940 he forced to retire because he was Jewish. He had a positive view of Van Laar and in AWNG there are three of Ornstein's letters about Van Laar. His letter of condolence in 1938 was exceptionally kind (Mrs.E.W. van Laar, Amsterdam).

*Ostwald, W. (1853-1932)* was a professor in Leipzig in Germany and with J.H. van 't Hoff started 'Zeitschrift für physikalische Chemie in 1887 (23x v.L and 8x O: AWL).

*Scheffer, F.E.C. (1883-1954)* started as a teacher in Amsterdam and later became a professor in Delft. In 1917 his subject was analytic chemistry but from 1920 to 1953 his interests were in inorganic chemistry and thermodynamics. He wrote about Van Laar in an article in 'Chem.Weekbl.' in 1930.

*Smits, A. (1870-1949)* succeeded Bakhuis Roozeboom and was professor in Amsterdam from 1907 until 1940. Van Laar put up a stubborn resistance to Smits' appointment as professor in 1907. This resistance is to be found in Van Laar's letters to Lorentz.

*Schreinemakers, F.A.H. (1864-1945)* was professor of chemistry in Leiden from 1901 until 1934. He knew Van Laar very well and with Lorentz played an important role in Van Laar's scientific life. His letter about Van Laar in ARAG(Arch. 2.14.20, O.K. &W. No. 345 is very interesting.

*Verschaefelt, J.E. (1870-1955)* was professor in Brussels and Gent (Belgium). He wrote an article about Van Laar in Chemische Weekblad in 1930 (1x v.L: BML).

*Verwey, A. (1865-1937)* was a writer of the cultural group of the 1880's (8x v.L: UBA).

*Waals, J.D. van der (1837-1923)* was a man with a powerful drive. He took his Ph.D. in 1873 at Leiden and was professor from 1876 to 1908 at the University of Amsterdam. Van Laar wrote a biography about Van der Waals in 1900.

*Went, F.A.F.C. (1863-1935)* was professor of botany in Utrecht from 1893 until 1933. He was chairman of the Royal Academy and for this reason wrote to Van Laar (6x v.L: BMI).

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# CURRICULUM VITAE

Everard Peter van Emmerik werd op 18 april 1938 geboren te Amsterdam. Na zijn schooltijd ging hij in 1952 werken als leerling drukker, tentenmaker en expeditieknacht. In 1954 ging hij naar zee en voer als ketelbink, matroos onder de gage en matroos. Van 1956 tot 1958 doorliep hij de Zeevaartschool van het Zeemanshuis te Amsterdam en slaagde voor het diploma derde stuurman der grote handelsvaart te 's-Gravenhage. Na een korte tijd als stuurman gevaren te hebben, beëindigde hij zijn zeemansloopbaan. Hij studeerde na zijn militaire diensttijd van 1961 tot 1964 voor de middelbare akte natuur- en scheikunde A aan het Nutseminarium voor Pedagogiek te Amsterdam. Daarna volgde het avondlyceum te Amsterdam; hij slaagde in 1967 voor het Staatsexamen II.B.S.-B 's-Gravenhage. Met een rijksstudietoelage en renteloos voorschot studeerde hij in 1971 af als chemisch technoloog aan de Universiteit van Amsterdam. Voor het aanvullend doctoraalexamen bibliotheek wetenschappen slaagde hij in 1983 eveneens aan de Universiteit van Amsterdam. Van 1961 tot 1971 was hij natuur- en scheikunde leraar te Zaandam en Amsterdam en van 1971 tot 1973 conservator van het Laboratorium voor Biochemie te Amsterdam. Van 1973 tot heden is hij werkzaam bij het Algemeen Pedagogisch Studiecentrum te Amsterdam, aanvankelijk voor het hoger beroeps- onderwijs thans als stafmedewerker.

