

# The Song of the Nightingale?

Van 't Hoff and the Analogy Between Solutions and Gases



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*It is the hour when from the boughs  
The nightingale's high note is heard*

Lord Byron

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*Figure 1: J.H. van 't Hoff*

## § 1. Introduction

From 1885 onwards, Jacobus Henricus van 't Hoff (1852-1911) published a series of articles in which he laid down the thermodynamical foundation for the phenomenon of *osmotic pressure*.<sup>1</sup> One remarkable and at the same time central feature of Van 't Hoff's theory, is the far-reaching analogy that he proved to exist between the ideal gas law and the behaviour of particles in solution. Although there is a general idea on how Van 't Hoff's theory of osmotic pressure relates to preliminary investigations of osmosis (e.g. Pfeffer, De Vries), much less attention had been paid to the history behind the analogy itself. Unfortunately, this lack of interest often contributes to the impression that Van 't Hoff was the first to have recognised the similarity between the behaviour of particles in a gaseous and solute states of matter. I will however argue that this idea is incorrect. There is a history to the analogy which goes beyond Van 't Hoff, and to tell this story will precisely be the task of this paper.

In the first part of the paper, the general background to Van 't Hoff's interest in the phenomenon of osmosis will be addressed. The second part focuses on the narrative that originated around Van 't Hoff's discovery of the law of osmotic pressure. This narrative stems from Van 't Hoff's pupil and biographer Ernst Cohen. One remarkable feature of this particular story is that it has been composed according to the ideals of romanticism. Unfortunately, romanticism is no guarantee for historical accuracy, and therefore the last part of this paper will be devoted to the establishment of a historical and thus contextualized account of Van 't Hoff's analogy. I will hereby draw upon two authors: Paul Walden and Svante Arrhenius. Both authors (and at the same time respectable chemists) gave a historical overview of Van 't Hoff's analogy around the beginning of the twentieth century. Curiously enough, their work seems to have been forgotten, since to my knowledge it has not been cited or mentioned in the literature on Van 't Hoff that appeared until the writing of this paper. A minor objective of this part will therefore be the reintroduction of those authors to the current Van 't Hoff research.

## § 2. *Wie die Theorie der Lösungen entstand*

When Van 't Hoff was invited to deliver a lecture to the *Deutsche Chemische Gesellschaft* in Berlin (January 1894), he was specifically asked to talk about the origination of his theory of solutions and his law of osmotic pressure. In this lecture, titled *Wie die Theorie der Lösungen entstand*, Van 't Hoff explained that

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<sup>1</sup> J.H. van 't Hoff, "L'équilibre chimique dans les systèmes gazeux ou dissous à l'état dilué", *Archives Néerlandaises des Sciences exactes et naturelles* **20** (1885), 239. Three of publications were published in the Swedish *Svenska Vetenskaps akad. Handlingar* **21** (1886): "Lois de l'équilibre chimique dans l'État dilué, gazeux ou dissous"; "Une propriété générale de la matière diluée" and "Conditions électriques de l'équilibre chimique." The last article: "Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen", *Zeitschrift für physikalische Chemie* **1** (1887), 481.

his initial interest in osmosis<sup>2</sup> stemmed from a particular problem he encountered while writing his *Études de dynamique chimique* (1884). It was in this title that Van 't Hoff for the first time discussed the issue of osmosis. In the last section of the book, which was devoted to the application of thermodynamics to chemical reactions, Van 't Hoff treated the topic of chemical affinity. Starting point for him were the preliminary investigations that already had been done on chemical affinity by the German chemist Eilhard Mitscherlich (1794-1863). The latter had been wondering what the magnitude was of the force that held crystal-water and Glauber's salt<sup>3</sup> together. To determine this magnitude, Mitscherlich conducted an experiment around 1844 in which he measured the vapor pressure caused by the crystal-water of Glauber's salt in a vacuum. Subsequently, he compared this value to the vapor pressure of 'normal' water, from which he concluded that the difference between the two values is caused by the force that attracts water towards the salt. This difference yielded a pressure of about 1/200 atmosphere.<sup>4</sup> Nevertheless, Mitscherlich's value of the water-attractive force was too low according to Van 't Hoff. In his Berlin lecture he says: "Dieser Werth, 1/200 Atm., kam mir unerhört klein vor, hatte ich doch den Eindruck, dass auch die schwächsten chemischen Kräfte sehr gross sind, wie es mir z.B. auch aus Helmholtz' Faraday-Lecture hervorzugehen schien".<sup>5</sup> Knowing that the chemical forces between molecules were about a thousand times as high as the value Mitscherlich obtained,<sup>6</sup> he wondered whether there was another and more direct way in which the magnitude of the water-attractive force could be measured. Van 't Hoff continues: "Mit dieser Frage auf den Lippen aus dem Laboratorium kommend, begegnete ich dann meinem Collegen de Vries und seiner Frau; der war gerade mit osmotischen Versuchen beschäftigt und machte mich mit Pfeffer's Bestimmungen bekannt".<sup>7</sup>

Hugo de Vries (1848-1935), the befriended biologist who simultaneously with Van't Hoff had been employed at the University of Amsterdam, was in that period occupied with a study of the turgor pressure in plant cells.<sup>8</sup> He had recognised osmosis as a pivotal mechanism behind the turgor pressure, and was consequently acquainted with the work of the German botanist Wilhelm Pfeffer (1845-1920) who already had been studying the phenomenon of osmosis in more depth. Pfeffer too, saw the fundamental role that osmosis played in cell mechanisms. In his *Osmotische Untersuchungen* that appeared in 1876, he states that "denn osmotische Vorgänge kommen beinahe für alle Fragen in Betracht,

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<sup>2</sup> Dutrochet coined the precursor of this name, endosmose, in 1826 "Mot derive de ενδοϛ, *dedans*, et de ωσμοϛ, *impulsion*". See Dutrochet 1826, 115. Thomas Graham simplified the name to *osmosis* in 1854. See Graham 1854. For interesting remarks on terminology, see: Modderman 1857, 4-5.

<sup>3</sup> Trivial name for sodium sulfate.

<sup>4</sup> Mitscherlich 1844, 565.

<sup>5</sup> Van 't Hoff 1894, 7.

<sup>6</sup> "[A]insi que nous le verrons plus loin, la force que le sulfate de soude exerce sur l'eau soit de plusieurs milliers de fois plus grande que celle que mentionne Mitscherlich." Van 't Hoff 1884, 180.

<sup>7</sup> Van 't Hoff 1894, 8.

<sup>8</sup> Zevenhuizen 2008, 191-193.

welche sich auf Stoffwechsel und Kraftwechsel im Organismus beziehen”,<sup>9</sup> most probably the reason why he thought it important to devote a book to the subject. It was this book that was of special interest to Van ‘t Hoff.

Van ‘t Hoff, who had been looking for a more direct way to measure the water-attractive force of Glauber’s salt, now found in Pfeffer’s work a new approach to his problem. Part of Pfeffer’s *Untersuchungen* had been an extensive description of the experimental set-up that he had used to measure the osmotic pressure of different solutions.<sup>10</sup> The set-up was composed of a porous cell, in the walls of which a semi-permeable membrane had been formed by the precipitation of copper ferrocyanide. This cell, when immersed in a solution of salt or sugar, would only allow for water to pass its walls while simultaneously the salt or sugar of the solution are kept outside.<sup>11</sup> To measure a certain osmotic pressure, Pfeffer put the desired solution in the cell, hermetically sealed the opening while sticking a glass tube through the lid. If the cell is now immersed in water, the water will enter the cell as a result of the attraction by the salt solution.<sup>12</sup> The entering water will cause the solution to rise in the tube, which will only stop when equilibrium is reached between the hydrostatic pressure in the tube, and the osmotic pressure of the solution. At this point, the osmotic pressure of the solution can be calculated by measuring the rise of the liquid column in the tube. Van ‘t Hoff recognised that the same method could be applied to measure the water-attractive force of the Glauber’s salt: “Cette méthode expérimentale conduira à connaître l’affinité du sulfate de soude pour son eau de cristallisation et celle corps quelconques susceptibles [sic] de s’hydrater”.<sup>13</sup>

Based on the experimental results of Pfeffer, Van ‘t Hoff concluded that he had been rightly assuming that the water-attractive force was much higher than the value Mitscherlich had proposed: “Dieser Druck war auffallend gross, demjenigen von Mitscherlich gegenüber”.<sup>14</sup> In fact, Pfeffer had found that a 1% sugar solution was already enough to cause an osmotic pressure of about 2/3 atmosphere, which clearly exceeds Mitscherlich’s value of about 1/200

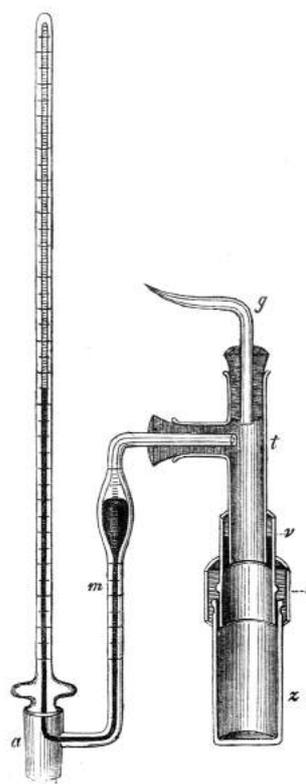


Fig. 1.

Figure 2: Pfeffer's osmometer

<sup>9</sup> Pfeffer 1876, iv.

<sup>10</sup> Idem, 3-30.

<sup>11</sup> Pfeffer gives no details about the solutions. He speaks about salt in general, and refers for example to ‘gelöste Körper’. See Pfeffer 1876, 3.

<sup>12</sup> Van ‘t Hoff 1884, 180.

<sup>13</sup> Idem, 181.

<sup>14</sup> Van ‘t Hoff 1894, 8.

atmosphere.<sup>15</sup> Nonetheless, we would be wrong in refuting the latter's results. It is always easy to state in retrospect that people have been wrong, but in this particular case the obtained pressure by Mitscherlich proved even quite useful. Van 't Hoff is eager to emphasize that the only mistake made by Mitscherlich was to assume that he had measured the attractive force of Glauber's salt for water, while in fact he had found the attractive force for its vapour. One might therefore even conceive of Pfeffer's and Mitscherlich's results as two sides of the same coin. "Die von Mitscherlich beregte Kraft ist so klein, weil es auf den verdünnteren Dampf wirkt, die von Pfeffer so gross weil sie auf das concentrirte Wasser sich bezieht."<sup>16</sup> A simple calculation by Van 't Hoff taught him that both values are related.<sup>17</sup> In his lecture he demonstrated to the audience that it is possible to arrive at Pfeffer's pressure, starting with the result of Mitscherlich. "Even an invoice could be established upon this strict relation", he humorously adds.

With the osmotic experiments of Pfeffer, Van 't Hoff had thus found a method to examine the magnitude of chemical affinity, or in this specific case the water-attractive force of Glauber's salt. This story explains sufficiently how Van 't Hoff became interested in the phenomenon of osmosis, and how his first encounter was brought about. We might nevertheless wonder what connection there is between his first interest in osmosis and the thorough account that Van 't Hoff gave of the phenomenon, just a few months later. Unfortunately, a conclusive answer cannot be given. At least to my knowledge, Van 't Hoff nowhere mentions what inspired him to derive the analogy between the behaviour of particles in a solute and a gaseous state of matter, meaning that we could only speculate on the matter. One might for example suggest that it was the relation between Pfeffer's and Mitscherlich's investigations that Van 't Hoff inspired to look further for an analogy. After all, their results proved that there is a relation between the water-attractive forces in solutions as well as in a vaporous (hence gaseous) state. From here, it is only a small step in assuming that this relation could be extended to an analogy.<sup>18</sup> Nevertheless, this only remains a suggestion as long as any supporting evidence is lacking. We will therefore suspend this discussion to the last section of the paper and proceed with the history of the analogy itself, hoping that this will shed new light on our topic.

In the next two parts I will address two different historical interpretations of the analogy that could be found in the Van 't Hoff historiography. The first being a romantic narrative as found in the Cohen biography, the second a historically contextualised account as put forward by Svante Arrhenius and Paul Walden.

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<sup>15</sup> Van 't Hoff 1894, 8.

<sup>16</sup> Idem.

<sup>17</sup> The following calculation is given by Van 't Hoff. He does however not explain the formula:  $\frac{Pfeffer}{Mitscherlich} = 1000 / \frac{P}{760} 0.08956 \frac{18}{2} (1 + \frac{1}{273} t)$ . See: Van 't Hoff 1894, 8.

<sup>18</sup> Although not explicitly, Snelders seems to hint at such an interpretation. See: Snelders 1987, 5.

### § 3. *The song of the nightingale*

How should we interpret the event called a scientific discovery, and how should the stories be interpreted that naturally accompany it? Of course, the aim of the historian is to give a historically accurate overview of his subject, but does this imply that every story should be judged on its accuracy only? In this paragraph, I will present two ways in which Van 't Hoff's discovery, and of course the surrounding narrative, could be assessed. The first follows the guidelines provided by Thomas Kuhn, the second tries to depict the story of Van 't Hoff's discovery against the background of Romanticism.

[1] – In June 1962, Thomas Kuhn published an article titled the *Historical Structure of Scientific Discovery*. The underlying thesis Kuhn puts to the fore is that to the “historian discovery is seldom a unit event attributable to some particular man, time, and place”.<sup>19</sup> It is worthwhile to take a closer look at this thesis, as Kuhn basically sets the tone for our discussion of Van 't Hoff's analogy. What Kuhn is so concerned about, is the persistent prejudice maintained by many scientists who think that scientific discoveries occur independently from history. “Rather than being seen as a complex development extended both in space and time, discovering something has usually seemed to be a unitary event, one which, like seeing something, happens to an individual at a specifiable time and place.”<sup>20</sup> It is common, but nevertheless inaccurate to perceive of scientific discoveries as if they have no context. As a result, people are inclined to approach the history of a certain discovery with simple questions like “Where?” and “When?”, while in fact the history of these discoveries is often far too complex to be caught in those terms. “That we are persistently driven to ask them nonetheless is symptomatic of a fundamental inappropriateness in our image of discovery.”<sup>21</sup>

That being said, it is even more striking that in the case of Van 't Hoff, exactly a ‘where’ and a ‘when’ can be pointed out at which Van 't Hoff discovered the analogy between solutions and the ideal gas law. Especially in the Cohen biography, every ingredient is available to transform Van 't Hoff's discovery of the analogy in what Kuhn calls a ‘unitary event’, decoupled from every historical background. The “When?” and “Where?” of the story are consequently set in a particular residence in Hilversum, during the summer of 1884. According to Kuhn we might say that the story around Van 't Hoff's discovery at least looks suspicious. That is to say that we might seriously doubt its historical accuracy.

[2] – A second way to interpret the narrative around Van 't Hoff's discovery of the analogy, is to depict it against the background of the ideals of Romantic science. Although Van 't Hoff was born rather late to be part of it – Romantic science is generally taken to end around 1840 with the emergence of positivism – nevertheless there are enough indications to believe that Van 't Hoff was a devout adherer of this movement. Why? In the first place, one cannot neglect the important role played by *imagination* in his work. A sound example is found in

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<sup>19</sup> Kuhn 1962, 760.

<sup>20</sup> Idem, 760.

<sup>21</sup> Idem, 761.

the inaugural lecture given by Van 't Hoff with his acceptance of the professorship in 1878 at the University of Amsterdam. In this speech, Van 't Hoff had demonstrated that the use of imagination is a rather important tool in the scientist's toolkit.<sup>22</sup> "Het vermogen, zich iets zoo levendig voor den geest te brengen, dat alle eigenschappen er van met even groote bepaaldheid kunnen worden erkend als door eenvoudige waarneming, zal met den naam van verbeeldingskracht worden bestempeld."<sup>23</sup> After investigating the biographies of about 200 important scholars and scientists, Van 't Hoff came to the conclusion that the role played by imagination most certainly should not be underestimated. It is not difficult to see that there is a thin line between Van 't Hoff's adoration of the *imagination* and the romantic portrayal of the *genius*, who, solely driven by his exceptional brainpower, anticipates his moment of *Eureka*. Furthermore, Van 't Hoff had been a great admirer of romantic poetry. Most of all did he love to read the works of Lord Byron, which he even took as a source of inspiration for his own poems.<sup>24</sup> This combination of hard science and poetry might be frowned upon nowadays, but this miraculous combination had nevertheless been common practice during the times of Romanticism. More than ever, poems were written about the wonders of science, and on their turn, scientists saw their professional occupation as a logical extension to the arts.<sup>25</sup> Science and poetry, it also touched the heart of Van 't Hoff.

But a third and even more striking parallel comes to mind. In his famous book *The Age of Wonder*, Richard Holmes demonstrates the power of romantic ideals to implicitly transform and shape the event of the discovery into a narrative in which the aforementioned features get the upper hand. Holmes also provides us with a fine example of this narrative-shaping romanticism. When the German-British astronomer William Herschel (1738-1822) discovered Uranus in March 1781, his discovery had been the result of five-days of doubt and uncertainty – "the hardening suspicion drawn out over five days to Saturday, 17 March that the strange body had 'proper motion', but was neither a 'nebulous star' nor a 'comet', and so was very probably a new planet".<sup>26</sup> Yet, years later, when Herschel wrote a biographical sketch to his friend James Hutton, he said to have recognized Uranus in only a few hours. The discovery had under no circumstances been an accident, since only the trained eyes of Herschel – eyes that knew what to look for – could have found Uranus. Hence, what we see is Herschel on the verge of a *Eureka* moment. A week of constant uncertainty has been converged into a single moment of intense and pure geniality.

The same pattern is also visible in the biography Cohen wrote on Van 't Hoff, (*Jacobus Henricus van 't Hoff : Sein Leben und Wirken*, 1912). The same mechanism is at work that earlier prompted Herschel to reshape his discovery into a *Eureka*. In the hands of Cohen, Van 't Hoff's discovery too is concentrated

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<sup>22</sup> After investigating the biographies of about 200 important scientists, Van 't Hoff came to the conclusion that the role played by imagination most certainly should not be underestimated.

<sup>23</sup> Van 't Hoff 1878.

<sup>24</sup> Cordfunke 2001, 82.

<sup>25</sup> A wonderful example of this attitude could be found in the person of Alexander von Humboldt. See: Walls 2009, 226.

<sup>26</sup> Holmes 2010, p.104.

into one particular time and space – a moment of divine inspiration. No wonder then, that the subtitle of Cordfunke's book on Van 't Hoff reads 'Een romantisch geleerde' [A Romantic Scholar].

From what angle do we have to interpret the story of Van 't Hoff's discovery of the analogy? Should we use the 'unmasking' strategy of Kuhn? We have indeed reason to doubt the historical accuracy of the unitary event. The main problem with this strategy is however, that it neglects the fact that the way too, in which a certain narrative has been build, sheds light on the subject. But what about the romantic approach? It is useful to know how certain narratives came into being, and how these stories are culturally embedded. The fact remains nonetheless, that Herschel's discovery had nothing to do with Eureka's, and as we will see, the same also applies to Van 't Hoff. The main problem at stake therefore is, that a balance must be found between unmasking and respecting a certain narrative. With only Kuhn, it might be tempting to reject a narrative as 'deceit' as soon as it smells like unitary events. On the other hand, judging a narrative against romantic standards only is begging for historical inaccuracy. The most pragmatic solution to this problem, I think, is to look behind the narrative while simply respecting the way it originated.

The narrative of Van 't Hoff's discovery seems to have been originated from Cohen, and it could be found as such in the biography he wrote on Van 't Hoff (*Jacobus Henricus van 't Hoff: Sein Leben und Wirken*, 1912). The particular story around the analogy has subsequently found its way to the work of H.A.M Snelders and E.H.P. Cordfunke, although it must be emphasised that both authors eliminate most of the extravagant details that could be found in Cohen.<sup>27</sup> In the rest of this paragraph, we will therefore discuss Cohen's description of Van 't Hoff's discovery in detail.

It was in the summer of 1884 that Van 't Hoff, together with his wife and children, took of to Hilversum to spend his holidays at 'Villa Heideveld'. Actually, according to Cohen, we should not so much speak of a holiday, since Van 't Hoff was spending day after day on his theory of osmotic pressure.<sup>28</sup> It was at this particular time and place that he began to suspect that there was an analogy between the phenomenon of osmotic pressure and the ideal gas law. Cohen sets the stage as follows:

Sie wurden abgefaßt in Hilversum, einer Villenstadt in der Nähe von Amsterdam, die sich der Freund [Van 't Hoff] in jenem Jahre zum Sommeraufenthalte gewählt hatte. Mit den Seinigen bewohnte er dort ein kleines Landhaus, "Heideveld", von üppigem Grün umgeben. Auf dem Rasen vor dem Hause "bei Nachtigallenklang und duftenden Reseden" brachte er seine Gedanken zu Papier, Gedanken, die dazu berufen waren, der Wissenschaft neue

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<sup>27</sup> Snelders 1987; Cordfunke 2001.

<sup>28</sup> "Eigenlijk kon van vakantie niet worden gesproken, want dag in, dag uit kon men hem bezig zien met het schrijven van eene verhandeling, welker redactie hem geheel vervulde." Cohen 1934, 2-3.

Fernblicke, ihm selbst aber den Weg zu unvergänglichem Ruhm zu eröffnen.<sup>29</sup>

A few things are remarkable about this passage. In the first place, one cannot simply neglect the several superlatives employed by Cohen to accentuate the exceptionality of the holiday in Hilversum. Cohen does not leave any opportunity unused to demonstrate the geniality of Van 't Hoff. This is especially visible a few passages further on, where Cohen paraphrases the brilliant derivation of the analogy by the words "Sapere aude, so heißt es bei Horaz".<sup>30</sup> It is very well possible that these declamations are a reference to the aforementioned inaugural lecture of Van 't Hoff in which the miraculous workings of the imagination were praised. One of the biographies Van 't Hoff investigated to make his point was that of Kant, and it is exactly in the context of the latter that these words gained a powerful meaning. In 1784, Immanuel Kant referred to Horace to explain what *enlightenment* entailed. Enlightenment, Kant writes, "is man's emergence from his self-imposed nonage. Nonage is the inability to use one's own understanding without another's guidance. This nonage is self-imposed if its cause lies not in the lack of understanding but in indecision and lack of courage to use one's own mind without another's guidance. *Dare to know! (Sapere aude.)* 'Have the courage to use your own understanding,' is therefore the motto of the enlightenment".<sup>31</sup> In this context, the words served as an encouragement to look beyond the borders of the status quo. One should think freely and unorthodox in order to reach the next level. And where, more than everywhere else, does one encounter this freedom of thought better than in the faculty of imagination? The words of Horace are surprisingly well applicable to the romantic genius, the lonely soul who is able to rise from the conventional crowd. Seen from this perspective, it is only a small step from 'dare to think' to 'dare to imagine'. Yet, regardless of whether the last suggestion is true, it remains clear that according to Cohen, the discovery of the analogy rests solely on the imaginative power and thinking of Van 't Hoff.

Secondly, Cohen directly points to the events in Hilversum as a direct cause of Van 't Hoff's *unvergänglichem Ruhm*. According to Cohen, if we want to understand the development in Van 't Hoff's career, we thus only need to consider the *Gedanken* that he had written down on that particular moment, meaning that Hilversum is where it all began. Following Kuhn we could say that this passage smells like unitary events, enriched with subtle hints of presentism. But we would nevertheless be wrong in simply refuting the passage, at least not without taking notice of its romantic overtone. Again we see the mechanism at work that concentrates time and space into one single moment, in this case the moment at which Van 't Hoff wrote down his *Gedanken* – his thoughts.

Hitherto we have only encountered some of the romantic elements in Cohen's biography, but now the narrative really gets into shape. I would like to recall the particular sentence in which Cohen wrote that Van 't Hoff, while sitting on the grass before the house, derived his analogy accompanied by the *song of a*

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<sup>29</sup> Cohen 1912, 225.

<sup>30</sup> Idem, 226.

<sup>31</sup> Kant 1784.

*nightingale*.<sup>32</sup> Nightingales have always played a remarkable role in western literature, but especially the romantic poet and the nightingale cannot be thought separately.<sup>33</sup> One only needs to remember Keats' *Ode to a Nightingale*, or Shelly's *To a Skylark*; both Coleridge and Wordsworth wrote a poem *The Nightingale*, and also Lord Byron, the inexhaustible source of inspiration for Van 't Hoff, wrote about this miraculous bird.

Is the fact that Cohen mentions the nightingale just an innocent and fancy detail, only to increase the readability of the book? Does Cohen merely winks at Van 't Hoff's obsession with poetry? Again, when we look at the context in which this bird appeared in western literature, we see that Cohen's reference to the nightingale has a deeper meaning. Through the work of many poets, from Homer to T.S. Eliot, the nightingale has been subject to a variety of symbolic connotations. Albert Chandler provides us with a few examples: "the bird symbolizes a poet or his poems; [...] the nightingale sings the praises of God; [...] the virtuosity of the song is stressed."<sup>34</sup> And Frank Doggett adds to it: "Early in the nineteenth century, the singing bird began to seem not only the master of a higher art but even to fill a role somewhat similar to that of a muse."<sup>35</sup>

The romantic nightingale is a muse, a source of inspiration for the poet. In Cohen's narrative however, the song of the nightingale is carried further, even to cover the domain of the sciences. Not only is the nightingale the 'master of higher art', but the bird also becomes the master of 'higher science'. Its song prompted Van 't Hoff to derive his analogy during a moment of divine inspiration. In other words: Van 't Hoff's derivation of the analogy had been an act of superhuman virtuosity – comparable to that of a singing nightingale!

It is not difficult to see how Cohen's story turns into a romantic narrative. Van 't Hoff has unambiguously been portrayed as a genius, which among others is



Figure 3: Villa Heideveld

stressed by Horace's words and the reference to the bird. Furthermore, Cohen's emphasize on that sole event in Hilversum, virtually decouples Van 't Hoff's discovery from time and history. Cohen focuses on the *moment*: one concentrated point of pure genius. *Eureka!* Yet, with Kuhn we might question this unitary event. Cohen's story expresses a romanticized picture of Van 't Hoff's discovery that strongly suggest that the latter was the first to have encountered the idea of an analogy between the behaviour of particles in solution and the behaviour of particles in gases. This however, was not the case. As we will see in

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<sup>32</sup> This particular passage appears to have been quoted by Cohen, indicated by the quotation marks. Unfortunately Cohen does not mention his source, and I was not able to trace the original source myself.

<sup>33</sup> Chandler 1934; Shippey 1970; Doggett 1974.

<sup>34</sup> Chandler 1934, 78.

<sup>35</sup> Doggett 1974, 550.

the next paragraph, it is more correct to depict Van 't Hoff as standing in a tradition of nineteenth-century scientists who, for several times, already had been pointing at the possible existence of the analogy.

#### § 4. Analogy in context

It was in 1885, only a few months after the Hilversum events, that Van 't Hoff published his first results in the *Archives Néerlandaises des Sciences exactes et naturelles*. The article (*L'Équilibre Chimique dans les Systèmes gazeux ou dissous à l'État dilué*) had been roughly divided between an empirical part and a theoretical part, together proving the analogy between solutions and gases. Van 't Hoff had not put much effort in the production of his own empirical data, hence the article strongly depended on the data produced by Pfeffer, De Vries, Soret, Donders and Hamburger. Nevertheless, their experimental results were enough for Van 't Hoff to show that the behaviour of solutions obeyed both Boyle's and Gay-Lussac's gas laws.<sup>36</sup> The theoretical proof, based on the thermodynamics of his *Études* and the work of Guldberg and Waage, provided the foundation for these laws when applied to solutions.<sup>37</sup> The article was soon followed by four other publications, which altogether established the existence of the analogy.<sup>38</sup> Although Van 't Hoff had explicitly introduced the analogy in his first articles, the latest seems to be the official announcement. He writes:

In the course of an investigation which aimed chiefly at the acquisition of knowledge regarding the laws that regulate chemical equilibrium in solution [*Études* and the aforementioned articles], it gradually appeared that *there is a fundamental analogy, nay almost an identity, with gases, more especially in their physical aspect, if only in solutions we consider the so-called osmotic pressure instead of the ordinary gaseous pressure.* [...] We wish to emphasise in this connection that we are not only dealing with a fanciful analogy, but with one which is fundamental; for the mechanism which according to our present conceptions produces gaseous pressure, and in solutions osmotic pressure, is essentially the same. In the first case it is due to the impacts of the gas-molecules on the containing walls, in the second to the impacts of the dissolved molecules on the semipermeable membrane. The molecules of the solvent present on

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<sup>36</sup> Boyle's law expresses that pressure at given temperature is inversely proportional to volume; Gay-Lussac found that pressure at a given volume is directly proportional to temperature.

<sup>37</sup> For a detailed, though mostly technical, commentary on this article, see: Hornix 2001.

<sup>38</sup> Three of the four publications were published in the Swedish *Svenka Vetenskaps akad. Handlingar* **21** (17, 1886): "Lois de l'équilibre chimique dans l'État dilué, gazeux ou dissous"; "Une propriété générale de la matière diluée" and "Conditions électriques de l'équilibre chimique." The last article appeared in the *Zeitschrift für physikalische Chemie* **1** (1887), called "Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen".

both sides of the membrane, since they pass freely through it, need not be taken into consideration.<sup>39</sup> [My italics.]

Contrary to what is often assumed, this passage should not be read as the *birth* of the analogy. Rather, we should regard it as its *maturation*. Indeed, throughout the nineteenth century, already many suggestions can be found that point at the existence of the analogy between solutions and gases. Nonetheless, it needs to be stressed that none of these suggestion had been as profound as Van 't Hoff would put to the fore. Many even diverge in significant aspects from the one given in 1885. In order to understand one of these differences, probably the most important, it is useful to make a distinction between being *analogous by accident* and being *analogous by identity*. In case of Van 't Hoff, the analogy seems to be one of *identity*, meaning that the behaviour of particles in gaseous and solute states of matter appear to be ontologically one and the same. Alternatively one might therefore reformulate Van 't Hoff's discovery as follows: *the analogy by identity is that ideal gas molecules and ideal solute molecules in solution obey the same equation of state.*<sup>40</sup>

Other than this formulation, the suggestions that preceded Van 't Hoff seem to have been pointing at a more accidental, not necessarily identical, resemblance between the behaviour of gases and solutions. Nevertheless, it is interesting to see that in the century preceding Van 't Hoff's discovery, serious awareness was rising that the behaviour of particles in solution was somehow similar to their behaviour in a gaseous state. Seen from this perspective, the conceptual implications of the eventual discovered law of osmotic pressure had not been entirely new. After all, people already knew that the behaviour of gases and solutions were somehow related. Another interesting implication is that these suggestions, although not fully developed, might have pointed Van 't Hoff in the right direction. At least, the hypothesis that Van 't Hoff had been familiar with some of these suggestions is very plausible.

Around 1910, Paul Walden and Svante Arrhenius published both a survey on the history of the theories of solutions.<sup>41</sup> It is noteworthy that both authors emphasise that the analogy has a history that goes beyond Van 't Hoff, and that as a consequence, he should be regarded as the chemist who brought the quest for the analogy to an end by providing it with a thermodynamical foundation. Arrhenius formulates it as follows: "the great analogy between gases and dissolved substances was admitted by a great number of leading chemists. In order to give the required force to these opinions it was necessary to apply the laws of thermodynamics to them and this was done by van 't Hoff".<sup>42</sup> At his turn, Walden agrees when he writes: "Zu gewissen Zeiten scheinen bestimmte Ideen 'in der Luft zu liegen', doch erst der große Geist [Van 't Hoff] vermag sie zu einer

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<sup>39</sup> Van 't Hoff 1887, 5-7.

<sup>40</sup> I am grateful to prof. A.P. Philipse for providing this definition.

<sup>41</sup> Arrhenius 1912; Walden 1910. Both were chemists and contemporaries to Van 't Hoff. Furthermore, Arrhenius and Van 't Hoff knew each other personally and are often regarded (together with Wilhelm Ostwald) as the fathers of physical chemistry.

<sup>42</sup> Arrhenius 1912, 81.

nutzbringenden Theorie zu gestalten”.<sup>43</sup> It is therefore worthwhile to take a closer look at both authors and their alternative account of the analogy, especially since they seem to have been forgotten in recent literature on Van ‘t Hoff.<sup>44</sup>

The first ‘leading chemist’ who is mentioned by Arrhenius and Walden, is Joseph Louis Gay-Lussac (1778-1850). The French chemist published an article in 1839, in which he explored the effects of temperature on the dissolution and chemical affinity of molecules. He writes that temperature does not affect the affinity of molecules, whereas their solubility appears to be highly dependent on it. After observing that the same applies for gaseous (evaporated) molecules, he concludes that it is inevitable that both dissolution and evaporation are analogous.

[L]es effets de l’affinité n’étant pas variables avec la température, tandis que ceux de la dissolution en dépendent essentiellement, il serait difficile de ne pas admettre que dans la dissolution, comme dans la vaporisation, le produit est essentiellement limité, à chaque degré de température, par la nombre de molécules pouvant exister dans une portion donnée du dissolvant; elles s’en séparent par la même raison que les molécules élastiques se précipitent par un abaissement de température [...] La dissolution serait donc essentiellement liée à la vaporisation, en ce sens, que l’une et l’autre sont dépendantes de la température et obéissent à ses variations. *Dès lors, elles doivent offrir toutes deux, sinon une identité d’effets complète, du moins beaucoup d’analogie.*<sup>45</sup> [My italics]

This statement of Gay-Lussac reappears almost identical in the work of the Italian chemist Bartolomeo Bizio (1791-1862).<sup>46</sup> And also Thomas Graham (1805-1869) takes the effort to introduce Gay-Lussac’s suggestion of the analogy in one of the famous Bakerian lectures, saying: “M. Gay-Lussac proceeds upon the assumed analogy of liquid to gaseous diffusion in the remarkable explanation which he suggest of the cold produced on diluting certain saline solutions, namely, that the molecules of the salt expand into the water like a compressed gas admitted into additional space”.<sup>47 48</sup> The last of the chemists referring to Gay-Lussac had probably been Rosenstiehl (1839-1916)<sup>49</sup>, a French chemist who published a note in 1870 writing that “the osmotic force is analogous to the

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<sup>43</sup> Walden 1910, 92.

<sup>44</sup> To my knowledge, the last and only references made to Walden in this context could be found in an article that appeared in 1976. The article partially dealt with Van ‘t Hoff and the reception of the analogy, but the reference to Walden seems not to be directly related to this matter. See: Dolby 1976, 300.

<sup>45</sup> Gay-Lussac 1839, 1011.

<sup>46</sup> Bizio’s ideas on the analogy appeared in 1845. Arrhenius 1912, 76; Walden 1910, 92.

<sup>47</sup> Graham 1850, 1.

<sup>48</sup> Thomas Graham is not mentioned by Arrhenius and Walden.

<sup>49</sup> Arrhenius 1912, 76-7. (Not mentioned by Walden.)



Figure 4: Gay-Lussac

elastic force of vapors. Between the fluid column, which rises in an osmometer and the piston lifted by the elastic force of a vapour there is no other difference than that of the medium in which the work is effected".<sup>50</sup> Although Rosenstiehl thought (he was however not sure) that he had encountered this idea in the work of François Arago, Arrhenius demonstrates that he probably had been confusing Arago with Gay-Lussac.

It is interesting to see that all above-mentioned chemists depart from the suggestion as initially proposed by Gay-Lussac. There are nonetheless many differences with Van 't Hoff's law of osmotic pressure. These kinds of comparisons are anachronistic, and

hence no substantial conclusions could be drawn from them. But it nevertheless shows that these chemists, despite their divergence from the later Van 't Hoff, found examples of resemblance between different cases of solute and gaseous phenomena. The first difference is that none of these chemists except for Rosentiehl, mentions the phenomenon of osmosis. Instead they refer to dissolution. (In theory, a reference to osmose had been possible since the first serious investigations of endosmose by Dutrochet in 1826, but I rather refrain from this kind of speculation.<sup>51</sup>) A second difference in these series of suggestions is that all, except for Rosentiehl, refer to particular gaseous states like evaporation (Gay-Lussac) or diffusion (Graham). Only Rosentiehl mentions a general gaseous state, like Van 't Hoff would do later. Yet despite these differences, all chemists have in common that they wrote about an actual *analogy*. The very same word would be employed by Van 't Hoff in 1885.

From the sixties and seventies onwards however, there occurs a transition in the kind of reasoning behind the analogy. Gay-Lussac is not being mentioned anymore, and the discussion of the analogy becomes more thermodynamically embedded. The first chemist who is worth mentioning in this context is August Horstmann (1842-1929).<sup>52</sup> He published a famous article in 1873 (*Theorie der Dissociation*), in which he discussed the problem of the dissociation of gaseous substances. One of the observations he made was that the disgregation<sup>53</sup> of a dissolved salt is dependent on the distance between its molecules, a phenomenon that also applies to permanent gases. He writes: "ich will bemerken, dass die Theorie auf eine Beziehung von dieser Form führen würde, wenn man annehmen wollte, dass in verdünnten Lösungen die Disgregation eines Salzes in ähnlicher Weise von der Entfernung seiner Molecüle

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<sup>50</sup> Rosenstiehl in Arrhenius 1912, 77.

<sup>51</sup> Dutrochet 1826.

<sup>52</sup> Walden 1910, 92; Arrhenius 1912, 77.

<sup>53</sup> Disgregation is a much criticised concept, initially proposed by Rudolf Clausius in 1862. It was a measure of the arrangements of atoms in a body. Despite the criticism, one could conceive of disgregation as an early formulation of the concept of entropy. See: Harman 1982, 65.

abhängt wie bei einem permanenten Gase, eine Annahme, welche auch sonst die Wahrscheinlichkeit für sich hat".<sup>54</sup> It is noteworthy that also Horstmann, like the former chemists did, departs from a rather specific phenomenon, namely the case of the disgregation of dissolved salts. Anyway, Horstmann had been the first to bring the analogy to the domain of thermodynamics.

Arrhenius continues his story with the work of the Norwegian chemists Cato M. Guldberg and Peter Waage. In 1879 they published an article (*Ueber die chemische Affinität*)<sup>55</sup> in which they drew on the aforementioned work of Horstmann. Even though they did not mention the possible existence of the analogy, the article nevertheless laid the foundation for the reappearance of the analogy in the work of Julius Thomsen (1826-1909).<sup>56</sup> In 1882, this Danish thermochemist published his magnum opus, the *Thermochemische Untersuchungen*, the first volume of which he concluded with the following remark: "Die vorliegende Untersuchung führt zu dem Schluss [...] dass die wässrigen Lösungen der Körper dieselben in einem Zustande enthalten, der ebenso wie der gasförmige Zustand die physikalischen Eigenschaften der Körper in der einfachsten Art erkennen last und eine unmittelbare Vergleichung derselben gestattet".<sup>57</sup> The last of the thermodynamically oriented analogies can be found in an article written by Tilden and Shenstone. It appeared in an issue of the *Philosophical Transactions of the Royal Society of London* in 1884, and it could therefore be safely assumed that the idea of the analogy had been brought under the attention of a wide audience. They wrote: "the solution of a solid in a liquid would accordingly be analogous to the sublimation of such a solid into a gas, and proceeds from the intermixture of molecules detached from the solid with those of the surrounding liquid."<sup>58</sup> Neither Thomsen, nor Tilden and Shenstone refer to rather particular phenomena to make their point. I.e. specific instances of solutions and gases, like dissolution, diffusion or disgregation are not being mentioned. When compared to earlier suggestions of the analogy, the suggestions of the thermodynamicists therefore appear to become gradually more general. Remarkable is that while the suggestions became more generally formulated, the word *analogy* is not mentioned anymore. Also osmosis is not being mentioned, but this seems to be a returning pattern thus far.

Thermodynamics was not the only field in which early ideas of the analogy can be traced. Curiously enough, in 1866 the German physician and physiologist Adolph Eugen Fick (1829-1901) mentions the analogy in a medical context. Fick is even one of the few (except for Rosenstiehl), who directly connects the analogy to osmosis, albeit that the solvent of the solution makes a complete and perfect analogy impossible.<sup>59</sup> In his book *Die Medizinische Physik* (1866), he describes the differences between the diffusion of gas molecules and

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<sup>54</sup> Horstmann 1903, 37.

<sup>55</sup> Guldberg, Waage 1899, 126.

<sup>56</sup> Arrhenius 1912, 78-9.

<sup>57</sup> Thomsen 1882, 449.

<sup>58</sup> Tilden, Shenstone 1884, 30.

<sup>59</sup> Remarkably, Fick is mentioned by Cohen, instead of Arrhenius and Walden. Nevertheless, Cohen does not refer to Fick for the sake of history, but merely for an experiment by Fick, which drew on the analogy between diluted solutions and diluted gases. See: Cohen 1901, 87.

the diffusion of dissolved molecules, after which he concludes: “Bis hierher ware die Betrachtung des Vorganges der des Gasaustausches ganz analog. Ganz so einfach ist er aber sicher nicht, da die Flüssigkeitsmoleküle nicht wie die Gasmoleküle ganz frei im Raume umherfliegen und nur beim Anstossen an andere oder an die Wände Wirkungen der Molekularkräfte erfahren”.<sup>60</sup> Fick indeed mentions osmosis, but he does not make an attempt to further investigate the consequences of his statement. Rather, Fick mentions the analogy with gases as a mere example to explain the phenomenon of osmosis, but from the context could be inferred that he believed his analogy to be an accidental one. One important difference with Van ‘t Hoff’s analogy could be indicated, and that is that Fick believed that the molecules of the solvent make a profound analogy impossible. About twenty years later however, Van ‘t Hoff would argue that the molecules of the solvent, need not be taken into account.<sup>61</sup>

The quotations that we have seen thus far, do not leave the domain of mere suggestions. Furthermore, none of the mentioned chemists seem to have had the intention to study the analogy in more depth. There is however one exception, which we find in the somewhat mysterious case of Isidor Traube (1860-1943). At the age of twenty-three, this young German chemist came remarkably enough to similar conclusions as Van ‘t Hoff. In 1883, two years before Van ‘t Hoff would publish his first results, Traube prepared an article (*Über die Beziehungen einiger für Lösungen und Gase annähernd geltende Gesetze*) in which he derived the analogy between solutions and gases in a much similar fashion as Van ‘t Hoff would do later.<sup>62</sup> While looking back at this episode in his life, the older Traube writes:

Ich war damals junger Assistant in Heidelberg und hatte in jener Erstlingsarbeit unter Hinweis auf die Arbeiten von Wüllner, Rüdorff, De Coppet und namentlich von Raoult auf die Analogie der Gasgesetze und Lösungsgesetze und zwar der Gesetze der idealen Gase und verdünnten Lösungen hingewiesen. Der Satz von Avogadro galt nach meinen Ausführungen für Lösungen nur dann, wenn man für Nichtleiter Aggregationen der Moleküle annahm.<sup>63</sup>

The resemblance with Van ‘t Hoff cannot be more striking: one year later Van ‘t Hoff adopted the same strategy to prove the existence of the analogy. Nevertheless, Traube never obtained himself a memorable place in the history of solutions, for the simple fact that he never published the article.<sup>64</sup> Maybe due to his young age, he had some hesitation about publishing, so he decided to send the article to the renowned chemist Lothar Meyer. He received an answer in 1884, in which the latter advised him to put the article away for a year or two, and to first gather the necessary experimental proof. An unfortunate advice after

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<sup>60</sup> Fick 1866, 37.

<sup>61</sup> Van ‘t Hoff 1887, 7.

<sup>62</sup> Edsall 1985, 390-391.

<sup>63</sup> Traube 1933, 199.

<sup>64</sup> Neither Arrhenius nor Walden mentions Traube.

all, because one year later the discovery had already been announced by Van 't Hoff.

Did Traube regret the fact that he had never published the article? Yes, but looking back, the seventy-two years old Traube acknowledges that the investigations of Van 't Hoff had been more thorough than his.<sup>65</sup> "Lothar Meyer hatte recht. Wenn auch meine Arbeit von demselben Grundgedanken ausging wie diejenige van 't Hoff's, so war doch die Durchführung nicht mit derjenigen von van 't Hoff vergleichbar, und es ware vermessen von mir, wenn ich etwa die geringsten Prioritätsansprüche geltend machen würde."<sup>66</sup>

What could we learn from the Traube-case? It is sure that Van 't Hoff cannot have known that the young Traube was on the verge of proving the existence of the analogy. After all, the concerning article was never published, meaning that Van 't Hoff had independently arrived at his proof for the analogy. What the Traube-case nevertheless reveals is that not only the many suggestions, but also the derivation of the analogy had been practiced before Van 't Hoff embarked on the project. To speak with Walden, the case of Traube most clearly demonstrates that indeed at certain moments *bestimmte Ideen in der Luft liegen*. But let us take a look beyond Traube and ask whether Van 't Hoff was acquainted with the other analogy-suggestions that had been uttered throughout the nineteenth century? As already became clear, the discussion of the analogy, and the similarities between solutions and gases, seems to have been transferred into the field of thermodynamics. Particularly interesting is however, that Van 't Hoff must have



Figure 5: Julius Thomsen

been familiar with the several analogy-suggestions that arose in this particular field. From the eighties onwards, he had been intensively studying thermodynamics, which among others had resulted in the *Études*.<sup>67</sup> It is therefore no surprise that also the names of Horstmann and Thomsen appear in his work. Thomsen's *Untersuchungen* are for instance mentioned several times by Van 't Hoff, and the fact that Thomsen's suggestion appears in the conclusion makes it hard to believe that Van 't Hoff had overlooked this passage.<sup>68</sup> Also Horstmann's name appears several times in the *Études*.<sup>69</sup> Only a minor difficulty is formed by the lack of an explicit reference to the latter's article of 1873, but it has nevertheless been argued that Van 't Hoff was well aware of the article's

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<sup>65</sup> Edsall 1985, 391.

<sup>66</sup> Traube 1933, 119.

<sup>67</sup> Servos 1990, 24.

<sup>68</sup> For references to Thomsen, see: Van 't Hoff 1884, 6, 129, 171, 172, 205.

<sup>69</sup> For references to Horstmann, see: Van 't Hoff 1884, 6, 10, 11, 124, 126, 130, 172.

content.<sup>70</sup> As a consequence, it could convincingly be defended that Van 't Hoff had learned of the analogy through the suggestions done in the thermodynamical field. It is therefore not far-fetched to conclude that these suggestions could have inspired him to derive his own analogy, which thereby ended the nineteenth-century quest for similarities between solutions and gases.

Of course, as was said at the beginning of this paragraph, one must be aware of the fact that the eventual analogy as proposed by Van 't Hoff, did not resemble any of the earlier analogy-suggestions. Nevertheless, when Van 't Hoff in 1885 proved that the behaviour between solutions and gases was analogous, or even identical, this most probably had not been as much a surprise as one might infer from Cohen's biography. From the rather brief historical survey above, we learn that Van 't Hoff had not been the first to encounter this idea, and that he most plausibly knew of these earlier suggestions. In either case, Van 't Hoff stands in a tradition while his holidays in Hilversum had nothing to do with Eureka's. Was it the nightingale that sang, or were it Horstmann and Thomsen?

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<sup>70</sup> With regard to a certain passage in the *Études*, W. Hornix writes: "Presumably he [Van 't Hoff] refers to the publications of 1870 and 1873 of Horstmann on dissociation". See, Hornix, Mannearts 2001, 19 (note). John W. Servos writes: "Among the papers to which van 't Hoff had access, a memoir written in 1873 by August Horstmann of Heidelberg was the most significant." See: Servos 1990, 27.

## § 5. Conclusion

It is time to conclude our survey into the history of the analogy. There are two lessons to be learned from Arrhenius and Walden. First and foremost, the quotations of the several chemists indicate that the idea of an analogy was quite common in the nineteenth century. Van 't Hoff thus stands in a tradition with other analogy-proposers. Moreover, the case of Traube illustrates that even the derivation of the analogy had been practiced at least once before Van 't Hoff. This conclusion stands in contrast with the story as told by Cohen, who as we have seen, turns Van 't Hoff's discovery into a solitary event and embeds it into a romantic narrative. Secondly, with regard to the question how the analogy arose of Van 't Hoff's earlier problem of chemical affinity, we could assume that Van 't Hoff had been inspired by the several analogy-suggestions that already existed in the nineteenth century, most likely those of Horstmann and Thomsen. It might be hard to digest, but Van 't Hoff does not become a lesser chemist at the moment we stop ascribing to him the 'discovery' of the analogy. Contrary to what Cohen wants to express, Van 't Hoff did not develop the analogy from scratch. His geniality must be sought elsewhere: namely in his ability to construct the *underlying foundations* of the analogy. After all, from Gay-Lussac onwards, it endured half a century before the essence of the analogies had been finally understood.

### *Historiographical note*

Part of this paper had been the reintroduction of Walden and Arrhenius to the Van 't Hoff research. I am convinced of the valuable contribution they made to the history of nineteenth-century chemistry, especially with regard to the history of solutions. The fact that both were chemists might indeed have resulted in what could be called internal history. But regardless of one's opinion on style, they proved Kuhn wrong when the latter states that before the appearance of his article in 1962, historians of science, but especially the scientists themselves, depicted scientific discoveries mainly as events without a history. One thing becomes strikingly clear from Walden and Arrhenius, and that is exactly that Van 't Hoff's discovery has a history.

Nevertheless, Arrhenius and Walden are not the only ones who recognised the history behind Van 't Hoff. More recently, also J.R. Partington and W. Brock have argued that there is more to tell than the happenings in Hilversum, albeit that both are less descriptive than Arrhenius. Brock only mentions Horstmann, while Partington does not explicitly mention the history of the analogy itself, only the history of the kinetic similarities between solutions and gases is concisely described.<sup>71</sup> Unfortunately, I was not able to retrace this historical account of the analogy in the work of Snelders and Cordfunke. Both authors have made Van 't Hoff's work and biography accessible to the Dutch audience.

Hendrik-Ido-Ambacht, 22 October 2013

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<sup>71</sup> See: Brock 1992, 369; Partington 1964, chap. XX.

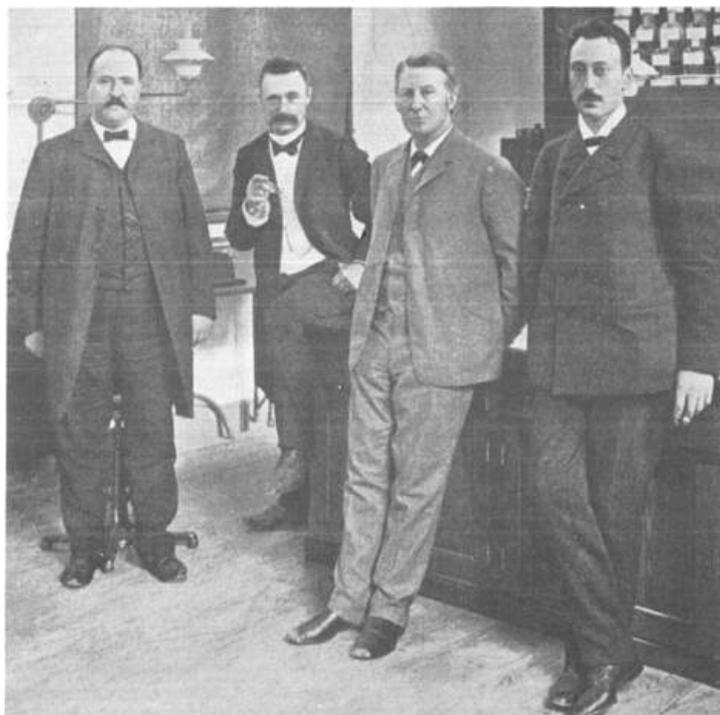


Figure 6: Arrhenius, Romburgh, Van 't Hoff and Cohen

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<http://kids.britannica.com/comptons/art-59236/Joseph-Louis-Gay-Lussac>

Figure 5 retrieved from:

[http://commons.wikimedia.org/wiki/File:Julius\\_Thomsen\\_PAST\\_2.png](http://commons.wikimedia.org/wiki/File:Julius_Thomsen_PAST_2.png)

Figure 6 retrieved from:

[http://www.dbnl.org/tekst/snel016gesc01\\_01/snel016gesc01\\_01\\_0009.php](http://www.dbnl.org/tekst/snel016gesc01_01/snel016gesc01_01_0009.php)