

UTRECHT UNIVERSITY

MASTER'S THESIS

The Polysemic Gibbs Paradox as a
Reflection of Foundational
Developments in Physics (1876–1911)

Author:

Lara VAN ZUILEN

Student ID:

3645851

Supervisors:

prof. dr. J.A.E.F. VAN DONGEN,

UU, UvA

prof. dr. J.B.M. UFFINK,

UMN

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Abstract

Graduation Colloquium September 18th, 2015: “Gibbs’ Paradox” OR What various perceptions of a persistent problem in physics can tell us about foundational developments from 1876 to the 1920s.

Since 1876, generations of physicists have concerned themselves with the so-called Gibbs paradox on the basis of two excerpts – published in 1876 and 1902 – written by Gibbs himself. A closer look at the offered solutions and other contemplations reveals that there is no such thing as a single, unambiguous Gibbs paradox. Instead, an arrangement of solutions can be found for distinct, yet related interpretations of the paradox. Despite the fact that over 150 works have been dedicated to the paradox, none contain a clear historical analysis of how the perception of the paradox itself has changed. The exception to the rule is Russian history of physics. As a matter of fact, one Russian historian has written an entire book on the solutions to the Gibbs paradox. However, seeing as most scholars don’t actually read the Russian language, these sources have remained largely unexplored. Using these Russian sources in addition to the more common sources then not only broadens the scope, but also introduces those sources into the English academic world.

To be more precise, my thesis attempts to answer the question of how the perception of the Gibbs paradox has changed from its inception in 1876 until its early inclusion in discussions surrounding quantum theory. Furthermore, partly under the assumption that physicists tend to focus on problems considered relevant in their time, I try to see whether the perspectives on the paradox reflect on developments within foundational concepts in physics. If so, the historical analysis of the paradox offers another means of describing the history of ideas in physics around the turn of the 20th century. Subsequently, the thesis might then be used to both clarify the notion of the Gibbs paradox and to offer a supporting role in the history of the development from thermodynamics to quantum mechanics.

Contents

| | |
|--|-----------|
| Abstract of the Graduation Colloquium | i |
| Contents | ii |
| Symbols | iv |
| 1 Introduction | 1 |
| 1.1 Background | 2 |
| 1.2 Research Question and Framework | 4 |
| 1.3 Note on Paradoxes | 5 |
| 1.4 Thesis Contents | 6 |
| 2 1876: The Thermodynamic Considerations | 8 |
| 2.1 A Short History of Thermodynamics prior to 1876 | 9 |
| 2.1.1 The Ideal Gas Laws | 9 |
| 2.1.2 Heat Theory and the Thermodynamic Laws | 10 |
| 2.1.3 Thermodynamic Concepts | 12 |
| 2.2 Gibbs' First Writings on the Thought Experiment | 15 |
| 2.3 J. Willard Gibbs | 27 |
| 2.3.1 Scientific Style | 28 |
| 2.3.2 Writings on Thermodynamics | 29 |
| 2.3.3 Position in the Scientific Community | 30 |
| 2.4 Conclusion | 32 |
| 3 1876-1902: The Initial Interpretations | 33 |
| 3.1 Maxwell's Inclusion of the Concept of Reversibility | 34 |
| 3.2 Neumann's Indication of a Discrepancy | 36 |
| 3.3 Duhem's and Poincaré's Entropy Principles Revisions | 37 |
| 3.4 Nernst's Experimental Limit | 40 |
| 3.5 Wiedeburg's Introduction of a Paradoxical Continuity | 43 |
| 3.6 Planck's Continuous Physical Properties | 44 |
| 3.7 Larmor's Impracticably Large Diffusion Time | 45 |
| 3.8 Van der Waals' Identical Molecules | 46 |

| | | |
|----------|---|------------|
| 3.9 | Van Laar's Diffusion Tendency | 50 |
| 3.10 | Ostwald's and Le Châtelier's Influence on Gibbs' Reach | 51 |
| 3.11 | Analysis of the Paradox Interpretations | 53 |
| 3.11.1 | Conclusion | 55 |
| 4 | 1902: The Statistical Considerations | 56 |
| 4.1 | A Short History of Statistical Mechanics prior to 1902 | 57 |
| 4.1.1 | Entropy and Probability | 58 |
| 4.1.2 | Ensembles and Analogies | 60 |
| 4.2 | Gibbs' Second Writings on the Thought Experiment | 61 |
| 4.2.1 | Comparison of Gibbs' Writings on the Thought Experiment | 65 |
| 4.3 | J. Willard Gibbs | 66 |
| 4.3.1 | Scientific Style | 67 |
| 4.3.2 | Writings on Statistical Mechanics | 68 |
| 4.3.3 | Position in the Scientific Community | 69 |
| 4.4 | Conclusion | 70 |
| 5 | 1902 - 1911: The Subsequent Interpretations | 71 |
| 5.1 | Larmor's Defense of the Molecular Principle | 73 |
| 5.2 | Byk's Symmetry in Optically Active Substances | 75 |
| 5.3 | Boltzmann's Relatedness of Entropy and Probability | 77 |
| 5.4 | Lorentz's Gravity and the Thermodynamic Potentials | 78 |
| 5.5 | Van Laar's and Van der Waals' Continued Discussions | 81 |
| 5.6 | Postma's 'Proof' of the Failure of Analogy | 83 |
| 5.7 | Beyond 1911 | 85 |
| 5.8 | Analysis of the Paradox Interpretations | 87 |
| 5.8.1 | Conclusion | 89 |
| 6 | Conclusion | 90 |
| 6.1 | Suggestions for further research | 92 |
| A | Correspondence and Reprints | 93 |
| B | Main Responses to the Paradox | 100 |
| C | Synopsis of Haitun's <i>History of the Gibbs Paradox</i> | 103 |
| | Bibliography | 106 |
| 1. | Primary Sources | 106 |
| 2. | Secondary Sources | 110 |

Symbols

| | |
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| AA | a gas ‘mixture’ of alike or identical gases A and A |
| AA' | a gas mixture of increasingly similar gases A and A' |
| AB | a gas mixture of unlike gases A and B |
| a | constant — pressure at $t=1$ and $v=1$ or volume at $t=1$ and $p=1$ |
| a_{if} | interactive forces in the Van Der Waals equation |
| b_{ms} | molecular size in the Van Der Waals equation |
| c | constant — specific heat at constant volume |
| f_t | time-dependent energy distribution function of particles |
| H | entropy of a unit of gas for $t = 1$ in equation (2.1), otherwise the H-theorem |
| k, k_B | Boltzmann’s constant |
| m, M | quantity of a substance |
| n | amount in moles or the number of molecules |
| N | number of particles |
| p | pressure of the system |
| p_i | probability |
| Q | quantity of heat |
| R | gas constant |
| r | number of molecules |
| S | entropy |
| t, T, Θ | temperature of the system |
| v, V | volume of the system |
| w | work |
| W | number of microscopic configurations corresponding to a macroscopic state |
| x | ratio of the gases in a mixture |
| ϵ | energy of the system |
| η | Gibbs’ notation for entropy of the system |
| Θ | modulus of a canonical ensemble |
| μ_i | chemical potential |
| ν | number of different kinds of particles |
| ϕ | free energy |

1

Introduction

Few topics lend themselves more readily to scientific and philosophical discussion than those related to foundational paradoxes. After all, the effort it takes to validate writing on a subject where the premises clash with the conclusions is less than writing on one that is considered to be internally consistent. This is also the case for physics related paradoxes of the late nineteenth and the early twentieth centuries, of which there are quite a few. One of the popular paradoxes in thermodynamics is the *Gibbs paradox*.

The exact paradoxical element of the Gibbs paradox is not easily indicated and the physicists' perception of it has changed over time. In other words, the term 'Gibbs paradox' has become *polysemic* since its inception. In addition to this, several alternative terms have been used to describe the paradox. Examples of this are the *mixing paradox*, the *entropic paradox*, and the *discontinuity paradox*. The Gibbs paradox is, however, always related to a thought experiment in which the entropy is calculated after two gases of equal volume are interdiffused into one single volume. The gases in the resulting mixture may either be different (AB), infinitely similar (AA'), or thought to be identical (AA). The value of the entropy of mixing may or may not, depending on the interpretation, rely on the degree of similarity between the gases. Renditions of the paradox almost always deal with comparing the various types of gas mixtures and their entropies.

Since its inception in 1876, over 150 articles and book chapters have been written on the subject,¹ most of which offer a solution to the paradox. Many well-known physicists considered the paradox at one point in their career. For instance, Boltzmann, Lorentz and Einstein all proposed solutions to the problematic thought experiment. Despite all these contributions, many feel that there still is no suitable solution. The abundance of publications, and the connection the paradox has to various branches in physics, makes it a suitable concept for a historical analysis of foundational issues around 1900.

¹Many sources up to and including 2009 on the Gibbs paradox may be found on the webpage <http://www.mdpi.org/lin/entropy/gibbs-paradox.htm>.

1.1 Background

One of the reasons so many works are dedicated to the Gibbs paradox is that it is not entirely clear what exact aspect of the paradox is supposed to be paradoxical. A quick survey of the articles on this subject reveals that the term ‘Gibbs paradox’ has been used to denote different conceptual difficulties, all related to similar sections in two of J. Willard Gibbs’ publications.² To avoid confusion, the first section discussing the paradox will be referred to as GP1876 while the second one will be referred to as GP1902. In addition to the paradox having multiple renditions or interpretations, the thought experiment has been extended to account for more and more physical phenomena and chemical substances. For example, Lorentz used gravity in his account of the interdiffusion. Having this background information on the paradox is vital when trying to provide a solution to one or more of these renditions.

Some authors show awareness of the multitude of Gibbs paradoxes. Hjalmar Peters,³ for example, noted that “there are two distinct paradoxes, which are both known as the ‘Gibbs paradox’”, and, that his own article “is concerned with only one of them”. A relatively successful attempt to clear up the confusion surrounding the Gibbs paradox has been the introduction of the term ‘mixing paradox’ for one variant of the Gibbs paradox. Most authors, however, do not acknowledge the paradox being polysemic and claim to solve THE singular Gibbs paradox. As a result, there still remains some uncertainty as to what exactly the term ‘Gibbs paradox’ denotes.

Historically tracing how the Gibbs paradox has been perceived and what concepts have been linked to it would serve to disentangle the many versions of, and solutions to, the paradox that roam the scientific publications. After which it should be easier for physicists to determine which versions of the paradox have a fitting solution and which ones do not. This thesis traces interpretations of the paradox from the first 35 years after its initial publication. In doing so, the focus will be on distinct statements of the paradox itself and not on the various solutions to each of those statements. The result of this tracing is a better understanding of how the interpretation of the paradox changed in accordance with developments in some branches of physics and chemistry.

Because the Gibbs paradox is related to several physical concepts, it can also be used as a tool to construct a history of foundational developments in various branches of physics.

²The sections on the paradox can be found in *On the Equilibrium of Heterogeneous Substances* (1875-1876), pp. 227–229, in [Gibbs] and [Gibbs, 1960, p. 206]. *On the Equilibrium of Heterogeneous Substances* will be referred to as *Equilibrium* and *Elementary Principles in Statistical Mechanics developed with especial reference to the rational foundation of thermodynamics* will be referred to as *Statistical Mechanics* in this thesis.

³[Peters, 2014, p. 1].

Disciplines the Gibbs paradox has been associated with include thermodynamics, statistical physics and quantum mechanics. Within thermodynamics, and in relation to the paradox, substantial attention has been given to the different natures of energy and entropy, the irreversibility of certain diffusion processes, and to degrees of (dis)similarity. Later, with the emergence of statistical mechanics, concepts such as the probability of ensembles and the equality of phases with exchangeable similar particles came to the forefront. Finally, the Gibbs paradox within a quantum-mechanical context deals with the quantum identity of particles and the notion of an indeterministic nature. All these concepts should be considered as relevant to a historical analysis that combines the Gibbs paradox with broader changes in the field of physics.

Some historical research on the Gibbs paradox has been done, but it usually is of secondary importance in books and papers. For instance, Martin J. Klein linked the paradox to Gibbs' belief in molecules in an article on Gibbs' physics.⁴ Enric Pérez Canals' *From Identity to Indistinguishability*, unlike Klein's work, addressed the paradox in its attempt to clarify the shift from identity to indistinguishability of particles before and during the quantum revolution.⁵ His paper dealt with the development of the interpretation of the paradox after the period described in this thesis.

A rather important work on the paradox is Sergei Haitun's *History of the Gibbs Paradox*⁶, which focused on the many solutions to the paradox. Haitun had three goals in mind: First, he wanted to explain why physicists are still working on the paradox; secondly, he deliberated on why there have not been any conventional solutions; finally, he attempted to determine why different scientists have declared the paradox solved on different grounds. In other words, Haitun wanted to describe the Gibbs paradox through what he called "its paradoxical history". Haitun's book is particularly useful for this thesis. For one because it summarized other Russian sources up to 1986, but mainly because it analyzed the evolution of the solutions to the paradox in relation to the evolution of some basic physical concepts.⁷ Appendix C contains an English synopsis of the book by the present author, which may be used in conjunction with this thesis. Other invaluable, secondary sources used in this thesis include Lynde P. Wheeler's biography of Gibbs⁸ and Stephen G. Brush's books on kinetic theory⁹ and statistical physics¹⁰.

⁴[Klein, 1989].

⁵[Pérez Canals, 2012].

⁶Title is a translation of [С.Д. Хаїтун, 1986]. This work is only available in the Russian language and tends to be cited by Russian authors only.

⁷Haitun divided each solution into phases such as thermodynamics, classical statistics and quantum statistics. He further separated the solutions into several variants. In comparing gas mixtures AA and AB there may or may not be a jump in the entropy of mixing when making AA and AB increasingly similar. The variants described by Haitun include a discrete jump, a continuous jump, no jump with the entropy of mixing being zero, and no jump with the entropy of mixing not being zero.

⁸[Wheeler, 1962].

⁹[Brush, 1976a] and [Brush, 1976b].

¹⁰[Brush, 1983].

1.2 Research Question and Framework

As explained, there is no historical narrative on the Gibbs paradox available in English despite its relation to many foundational concepts. Following the considerations in the previous section, this thesis was lead in the direction of the following research question:

How has the interpretation of the Gibbs paradox changed from its inception in 1876 until its early inclusion in discussions surrounding quantum theory, and how does this shifting perspective reflect on developments within foundational, physical concepts?

This thesis attempts to answer this question by looking at the historical actors involved with the Gibbs paradox, and the conceptual developments in thermodynamics, statistical physics, and quantum theory. The most obvious historical actor is Gibbs himself, but other actors include well-known physicists such as Boltzmann, Maxwell, Planck and Van der Waals. Two of Gibbs' publications have been considered as founding works in physics; *On the Equilibrium of Heterogeneous Substances* was vital for the interdisciplinary development of chemistry and thermodynamics and *Elementary Principles in Statistical Mechanics* played a similar role for statistical physics. As such, it is important to consider the roles of GP1876 and GP1902 on the Gibbs paradox – which are present in these works – in the whole of Gibbs' ideas. After all, knowing whether the paradoxical sections were considered to be accumulations of Gibbs' arguments or whether they were mere abnormalities helps to establish their initial interpretations. This should also render Gibbs' intentions with GP1876 and GP1902 and the concepts within them a little bit clearer. Furthermore, comprehending how the roles of the paradox have shifted has the potential to make Gibbs and his work in physics more understandable.

In between the chapters focusing on Gibbs' paradoxical sections, the reactions of the physical community will be elucidated. This includes both restatements of and solutions to the paradox, as well as those cases in which the actors tied the thought experiment to other physical phenomena and chemical substances. These discussions will shed light on some of the developments in physics at the turn of the century. The polysemy of the Gibbs paradox therefore has a positive aspect as well: it makes it adaptable to foundational developments. This renders the Gibbs paradox, as opposed to other entropy-related paradoxes, suitable as the key concept in a history of modern physics.¹¹

In addition to treating Gibbs' scientific work and the reactions to it, examining his scientific style and position in the scientific community also has proven to be valuable.

¹¹The term 'concept' is used loosely in this thesis. It represents theoretical or experimental ideas in both chemistry and physics. As a result, both *symmetry* and *semi-permeable membranes* can be considered a concept.

If it weren't for Gibbs non-committed style of reasoning, the paradox might never have been discussed to the same extent. It most certainly would not have been as adaptable. Both his scientific style and his position in the community explain why the other actors responded to the paradox when they did. Therefore, including these considerations in the thesis allows for a more comprehensive aggregation of conclusions.

While some quantum-mechanical foundations will be treated, the main body of this essay will deal with the period from 1876 to 1911. The end of this period was when the Ehrenfests' compendium¹² on the foundations of statistical mechanics was published. The recapitulative nature of the article makes it a natural endpoint of the period of the historical analysis. This thesis will also limit itself to the internalist perspective; cultural, economical or political elements will not be sought after in the analysis. Naturally, the scope of the thesis will be limited by the availability of the sources. Quite some of Gibbs' correspondence can be found in the Yale Archives, but hardly any documents prior to 1880 have been preserved. A table of the preserved correspondence can be found in Appendix A. Because Gibbs had a habit of sending his publications to his peers, this appendix also contains a list of recipients of *Equilibrium* and *Statistical Mechanics*.

1.3 Note on Paradoxes

As it turns out, the term 'paradox' by itself can indicate a number of oddities. It is mostly used to describe a contradiction within a set of statements or a deductive argument. An organism or thing, such as a concept, may also be called a paradox if it contains contradictory features or properties. Ideas typically associated with paradoxes include self-reference, infinite regress, and confusion between different levels of abstraction. A typical classification of paradoxes was introduced by Willard V.O. Quine in 1962.¹³ He determined that paradoxes could either be veridical, falsidical or an antinomy. A veridical paradox is one which, at first glance, appears to be nonsensical but which actually has a valid conclusion and therefore is true. A falsidical paradox, on the other hand, appears to be false and eventually does turn out to be false. Finally, an antinomy, or intractable paradox, is neither true nor false and reaches a self-contradictory result when accepted ways of reasoning are applied as they should be. The latter category, according to Quine, often leads to a revision of certain ideas. A fourth category, the *dialetheia*, has been suggested for paradoxes which are both true and false.

¹²[Ehrenfest and Ehrenfest, 2015]. Translation from P. Ehrenfest and T. Ehrenfest's *Begriffliche Grundlagen der statistischen Auffassung in der Mechanik*. Leipzig, Teubner, pp. 3–90, 1911.

¹³[Quine, 1962].

Because of the impossibility of experimental verification and the existence of multiple statements of the Gibbs paradox, each having various possible solutions, Quine’s classification is difficult to uphold. Moreover, Quine’s view has been criticized by William G. Lycan for its dependence on a person’s knowledge and reasoning skills.¹⁴ That is, there is the possibility of assuming that one’s own conclusion of the paradox is the correct one. As a result, two perfectly capable individuals or groups might reach a different conclusion on the same paradox. Lycan instead advocated for an interpretation in which a paradox is “an inconsistent set of propositions, each of which is very plausible.”¹⁵ One would then be able to resolve the paradox by “deciding on some principled grounds which of the propositions to abandon.”¹⁶ Naturally, even with Lycan’s definition, the term paradox remains somewhat dependent on the set of knowledge available to an individual or a group. However, Lycan’s definition is much easier to adapt to the multitude of Gibbs paradox interpretations. For this reason, each chapter in this thesis will conclude with a short analysis of how the Gibbs paradox, as described in those chapters, fits with Lycan’s definition.

1.4 Thesis Contents

The thesis will be chronologically divided into four chapters. The first chapter will start with a short description of the relevant foundational developments in thermodynamics and kinetic theory prior to 1876. Then, an exposition of GP1876 on what would be known as the paradox will be interwoven with an analysis of Gibbs’ thoughts on GP1876 itself. In this section, the concepts related to the paradox will be highlighted as keywords. Thereafter, there will be a section that links GP1876 to other relevant writings by Gibbs, especially to the work in which it was published. This final section also includes the subsections on Gibbs’ scientific style and his position in the scientific community.

The second chapter focuses on the reception of the paradox between 1876 and 1902. The selection of included writings is partly based on Haitun’s exposition of the solutions to the paradox. The interpretations of the historical actors will be treated primarily chronologically and in conjunction with the foundational background in which they worked. This includes Boltzmann and his visions on entropy, Maxwell and his demon, the discussions between Duhem and Poincaré, and the introduction of the term ‘paradox’ by Duhem and Wiedeberg.

The third chapter concentrates on GP1902 in Gibbs’ *Statistical Mechanics*, which was published in March 1902. Naturally, it will first acknowledge the foundational changes

¹⁴[Lycan, 2010].

¹⁵[Lycan, 2010, p. 5].

¹⁶Ibid.

that took place between 1876 and 1902. As in the first chapter, there will also be an exposition of GP1902 itself followed by another analysis of J. Willard Gibbs' conceptual developments. Finally, there will be an examination of how the description and perception of the Gibbs paradox, as understood by Gibbs himself, have shifted in the quarter of a century between the two publications.

The fourth chapter examines the reactions to the paradox from 1902 to 1911 and the related foundational developments in statistical mechanics and the early quantum theory. As in the second chapter, this chapter is a chronological narrative based, to some extent, on Haitun's work. However, due to not all contributions being original, some reactions have been grouped thematically. The interpretations of Larmor and Garrison are an example of this. Additionally, the fourth chapter will include a section on two main interpretations introduced after 1911, which is derived from Pérez Canals' work.

Finally, an overall conclusion ties the conclusions of the individual chapters together to show how the interpretation of what has been called the Gibbs paradox has changed over a period of 35 years and how these changes relate to broader foundational developments. Naturally, this also includes directions for future research.

2

1876: The Thermodynamic Considerations

A method involving the notion of entropy, the very existence of which depends upon the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension. This inconvenience is perhaps more than counterbalanced by the advantages of a method which makes the second law of thermodynamics so prominent, and gives it so clear and elementary an expression.

– J. Willard Gibbs, *Graphical Methods*

Josiah Willard Gibbs (1839–1903), the main actor of this thesis, was one of the first American mathematical physicists to be a major influence to scientists in Europe. Within his 30-year active period, Gibbs was responsible for three major works on chemical thermodynamics, vector analysis, and statistical mechanics. Two of those three works are foundational to the Gibbs paradox. For this reason, two chapters are devoted to those works. This chapter addresses the first of the major publications, *On the equilibrium of heterogeneous substances*, published between 1876 and 1878. It was not Gibbs' first encounter with thermodynamics. Earlier, in 1873, he had already lobbied for Clausius' concept of entropy, a concept that would be vital to the paradox as well.

The first section of this chapter describes developments in thermodynamics up to 1876, especially its laws and concepts. Doing so provides a proper background for Gibbs' contribution. It also allows for an understanding of how *Equilibrium* influenced thermodynamics. The second section provides and clarifies the section on the thought experiment, GP1876. Finally, the third section deals with the role of GP1876 in *Equilibrium*, Gibbs' scientific style, and his position in the scientific community. As mentioned in the introduction, the inclusion of these discussions clears up both Gibbs' interpretation of GP1876 and the interpretations of the other actors. Following these arguments, it should be clear that Gibbs' invocation of the thought experiment was not meant to be paradoxical in any way.

2.1 A Short History of Thermodynamics prior to 1876

Thermodynamics, with its various subdisciplines, is a scientific discipline that is said to have commenced with the practical invention of heat and work engines. Physicists such as Clausius, Kelvin, and Planck developed a phenomenological approach to describe thermal processes using empirical principles such as the impossibility of a perpetual mobile. From this, they managed to derive theoretical relations between macroscopic quantities. Boltzmann and Maxwell, in particular, tried to explain the thermal phenomena through statistics and an atomistic approach. In contrast to the phenomenological approach, Gibbs' *Equilibrium* used variations from equilibria and the abstract phase space representation. Later, in 1902, Gibbs would combine mechanistic and statistical elements by evolving the probability distributions on a phase space in order to provide thermodynamics with a rational foundation.

Many of the key works in thermodynamics focused on a few concepts. The developments of those concepts that turn out to be relevant to the Gibbs paradox are described in this first section. These include the formulations of the laws of Boyle, Charles, Gay-Lussac, and Avogadro; the theories of heat and matter; the conservation of energy and the introduction of the concept of entropy; and the concepts of reversibility and probability. Important historical actors predating Gibbs in thermodynamics are Clausius, Maxwell, and Boltzmann.

2.1.1 The Ideal Gas Laws

Our modern ideas about thermodynamics are based upon a few qualitative relations described roughly in a period of three centuries. Naturally, these relations were neither determined nor accepted in one single epiphany. Therefore, it remains difficult to link them to certain dates. However, it is possible to trace the relations by looking at the associated publication dates. In doing so, the first important relation is the inverse one between the pressure and volume of an ideal gas at constant temperature. Robert Boyle has been credited with noticing this relation in 1662 as a result of experimenting with his air pump.¹ A few decades later, Guillaume Amontons determined a direct proportionality between pressure and temperature at constant volume and used this to construct an air thermometer.² After another few decades, in the 1780s, Jacques Charles described a direct proportional relation between volume and temperature at constant pressure. This result was published and demonstrated to be generally valid

¹This and the following historical account is based on the first chapter of [Brush, 1976a] unless cited otherwise.

²[Barnett, 1941, p. 358].

by Joseph Gay-Lussac in 1802. Subsequently, in 1811, Amedeo Avogadro speculated that two different ideal gases, with the same volume and at the same temperature and pressure, would contain the same number of molecules.

Combining some of the laws, Émile Clapeyron wrote down a version of the ideal gas law, $pv = R(267+t)$, in 1834.³ Here, p , v , and t denote the pressure, volume and temperature of the ideal gas and R denotes a specific gas constant. From that point onwards the law developed via contributions of Henri V. Regnault and August Horstmann towards the form that is currently used: $pv = nRt$.⁴ In this form, n denotes the amount of substance of gas and R denotes an ideal, universal gas constant instead of a specific constant.

An attempt to make the law more appropriate for real fluids, which also turned out to be an improvement of the ideal gas law, had been made by Johannes van der Waals in his dissertation of 1873. Van der Waals would later be one of the first supporters of Gibbs' thermodynamics.⁵ In his dissertation, Van der Waals took the molecular size, b_{ms} , and interaction forces, a_{if} , into account to create a more accurate equation of state $(p + \frac{a_{if}}{v^2})(v - b_{ms}) = R(1 - at)$. Gibbs did not use this equation, nor did he ever refer to Clapeyron, Regnault, Horstmann or Van der Waals in his *Equilibrium*. However, one of the equations Gibbs considered in his *Equilibrium*, $pv = at$ with a denoting a different constant, is meant to indicate the ideal gas law. It has, in fact, been used in the derivation in GP1876.

2.1.2 Heat Theory and the Thermodynamic Laws

Even though the formulation of the ideal gas relations need not depend on the nature of heat, investigations into this phenomenon have been, and still are, a large subject in thermodynamics itself. In the early nineteenth century, two theories of heat were frequently cited: caloric theory and kinetic theory. Caloric theory viewed heat as an indestructible substance, while kinetic theory viewed heat as a type of movement. Stephen G. Brush's account of the history of kinetic theory also discussed another theory called the wave theory of heat as having played an important role. According to Brush, the caloric theory of heat was starting to be rejected by the 1840s because wave theory was so successful in explaining light phenomena. These phenomena were thought to be related in some way to heat phenomena. In Brush's opinion, with the establishment of the convertibility of heat and work in the 1850s, wave theory of heat was abandoned for the idea that heat is the motion of some kind of matter. Following this, molecular

³[Clapeyron, 1834, p. 164].

⁴[Jensen, 2003, p. 371].

⁵[Wheeler, 1962, p. 98].

motion, and thus kinetic theory, became tied to the concept of heat.⁶ Kinetic theory was therefore not only pushed to the forefront due to the need for understanding the structure of matter, but also due to the investigations into the nature of heat. By the time Gibbs started writing his papers on thermodynamics, most physicists were thought to have adhered to the kinetic theory of heat. Even so, kinetic theory was not directly confirmed until Jean Perrin's experiments in the early 20th century.

Around the same time the convertibility of heat and work was established, the Law of the Conservation of Energy became entrenched in physics as well. The *First Law* of thermodynamics, which is a version of the conservation law, was one of the developments that led to the introduction of the concept of energy. This was then used alongside the more mechanical concepts such as pressure, temperature and volume. In a similar manner, the attempts at deriving the *Second Law* of thermodynamics had led to the introduction of the concept of entropy. In this case, the Second Law is taken to state that during thermodynamic processes the total entropy of the system must either remain the same or increase.⁷

Although both Laws are based on an empirical background, the Second Law, unlike the First Law, was quickly questioned on its universal validity.⁸ Processes that were thought to be entirely irreversible might just have a very low probability of being reversed. Additionally, physicists, including Gibbs, were thinking of thought experiments in which the process might be reversible even if the total entropy had increased, thus rendering the Second Law probable instead of absolute.

William Thomson, or Lord Kelvin, is thought to be the first to speculate, in the 1850s, that there is an unavoidable loss of useful heat in most thermodynamic processes. In 1854, Rudolf Clausius introduced the "equivalence-value", or $\frac{Q}{T}$, in his statement of the "second fundamental theorem" as being the dissipated energy of a system.⁹ After redefining it several times, Clausius finally christened it *entropy*. $S = \int \frac{\delta Q}{T} \geq 0$ subsequently became both one of the versions of the Second Law and one of the many definitions of entropy. Clausius believed energy and entropy to be closely related and therefore named entropy appropriately. Gibbs was one of the first to advocate for Clausius' concept in his early papers, in which he also introduced the entropy-temperature

⁶That is not to say that kinetic theory and thermodynamics became equivalent. Kinetic theory approaches thermal phenomena upon molecular assumptions while pure thermodynamics tends to avoid atomistic concepts.

⁷Nowadays four thermodynamic laws have been defined. The First Law is typically stated as energy being conserved while its form can be converted. The Second Law, or one of the versions of it, is typically stated as entropy approaching a maximum value at equilibrium.

⁸According to [Myrvold, 2014, p. 6] such qualms already appear in Maxwell's correspondence starting around 1867.

⁹ Q is the quantity of heat and T is the temperature of the system. This physical quality therefore has the unit Joule per Kelvin.

diagram.¹⁰ The concept would also feature as the main physical quantity in GP1876. In fact, Gibbs was one of those physicists who worked out an experiment in which the total entropy might decrease.

2.1.3 Thermodynamic Concepts

Several concepts invoked in GP1876 have their origins in developments prior to 1876. The concepts invoked by Gibbs himself in 1876 are molecules, undistinguishable states, reversibility, and probability. Concepts not invoked specifically by Gibbs but associated with the paradox by later physicists include identity and continuity. This section will shortly describe the position of these concepts in thermodynamics prior to and around 1876.

As mentioned in the previous subsection, kinetic theory, which makes use of particles, gained some popularity from the 1850s onwards. It was, to some extent, fruitful in calculations surrounding thermodynamics. The partial success of kinetic theory in explaining thermodynamic phenomena also led to further speculation as to the ultimate constitution of matter. By 1876, several molecule models and structures had been proposed even though no one had actually observed or experienced a molecule or atom. In 1873, James Clerk Maxwell published a would-be famous article called 'Molecules' in which he clearly stated that "an atom is a body which cannot be cut in two while a molecule is the smallest possible portion of a particular substance."¹¹ Not all physicists were eager to employ these particles; Gibbs himself was rather reluctant to say anything about the constitution of matter. Nonetheless, he did use the concept of molecules in GP1876 despite them being imperceptible – through both human and experimental means – and unverified in his time.

Because of its roots in steam engines, 19th century thermodynamics largely focused on macroscopic quasi-static processes. That is, the processes made up of a sequence of equilibrium states describing sensible properties. That was also the subject with which Gibbs concerned himself. Molecules, and by extension atoms, on the other hand, belong to those physical branches which deal with things invisible to and imperceptible by our senses. They cannot be subjected to direct observational experiments. Using thermodynamics, one would not be able to distinguish between two substances or processes on the basis of molecular, dynamical movements. Only the thermodynamic state with its specific state variables can be used to describe a substance or a process. Thermodynamic equilibrium, then, is a condition that is satisfied when the macroscopic properties have reached a balance even if changes are still happening on a microscopic level. This

¹⁰[Gibbs, 1961a] and [Gibbs, 1961b].

¹¹[Maxwell, 1873, p. 437].

kind of equilibrium revolves around its stationarity. Another kind of equilibrium was introduced in 1872 by Boltzmann.¹² Instead of stationarity, Boltzmann defined his equilibrium by the macrostate that takes up the largest volume in phase space. Gibbs' later work *Statistical Mechanics* worked with these statistical equilibria, but *Equilibrium* only used thermodynamic concepts of equilibrium.

Gibbs, who introduced the chemical potential to the thermal potential equation $d\epsilon = td\eta - pdv + \sum_1^n \mu_i dm_i$, identified three types of equilibrium from the general condition of equilibrium.¹³ In *thermal equilibrium*, the temperature must be constant throughout the whole mass. In *mechanical* and *chemical equilibrium*, this must be the case for the pressure and the chemical potential respectively.¹⁴ Although Gibbs' *Equilibrium* revolves around equilibria, the paradoxical GP1876 is strangely devoid of it. Only chemical equilibrium plays a role in the thought experiment, as will be explained in the next section.

Another concept which plays a role in the paradox despite not being mentioned by its term is *reversibility*. As explained, in addition to being important for quasi-static processes, reversibility played a role in the doubting of the validity of the Second Law. Especially Maxwell concerned himself with this prior to Gibbs' publication. Even though thermodynamics only describes macroscopic properties, the Second Law can be and is continually violated on a microscopic scale. In 1871, Maxwell first published his ideas on this topic in a thought experiment that would later be known as Maxwell's demon.¹⁵ He imagined a container divided into two equal volumes containing the same gas at equal temperatures. The partition between the two volumes is then controlled by an imaginary demon which only allows fast molecules to pass into one chamber and slow molecules into the other. The volume with the faster molecules will then heat up while the other volume cools down. The entropy thus decreases and the Second Law is violated. Gibbs' thought experiment is somewhat similar to Maxwell's and might have been based on his book *Theory of Heat*.¹⁶

In Gibbs' *Equilibrium*, the concept of *probability* is closely related to reversibility and Maxwell's demon. Although it has been argued that these qualms about the Second Law led physicists to believe that probabilities and kinetic theory are necessary to understand

¹²Boltzmann (1872). *Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen*. Referenced in [Uffink, 2006b, p. 58–59].

¹³A thermodynamic potential is a scalar quantity used to represent the thermodynamic state of a system. Although the concept was introduced by Duhem in 1886, Gibbs used it in his paper under the term 'fundamental function'.

¹⁴[Gibbs, p. 64–65]. Gibbs defined the equilibria as follows: $t' = t'' = t''' = \text{etc.}$, $p' = p'' = p''' = \text{etc.}$ and $\mu'_i = \mu''_i = \mu'''_i = \text{etc.}$, with the accents indicating different parts of the whole mass.

¹⁵[Myrvold, 2014]. This first mention was in Maxwell's *Theory of Heat* (1871), in a section called "Limitation of the Second Law of Thermodynamics".

¹⁶Maxwell is not mentioned in *Equilibrium*, but earlier papers by Gibbs do cite *Theory of Heat*. Therefore it may be assumed that Gibbs knew of Maxwell's thought experiment.

the processes, statistical considerations such as the mean velocity and mean free path can already be found in publications as early as 1857.^{17,18} These statistical tools are non-existent in Gibbs' early publications. Prior to 1875, statistics concerned itself mostly with particles. This explains why Gibbs did not refer to it since he was not concerned with the microscopic structure of matter in his *Equilibrium*.

In addition to how the probabilities are used, their interpretations are important as well. In the 1950s, when the Laws of thermodynamics were being formulated, two main interpretations of probability were frequently cited. The classical interpretation states that probability is related to the human knowledge of the situation while the frequentist interpretation holds that probability is an objective reflection of reality. Moreover, probabilities can be and have been ascribed to various physical objects.

The main proponents of thermodynamics did not subscribe to a single unambiguous interpretation of probability. Maxwell adopted the frequentist interpretation in his statistical papers, but he also related probabilities to a state of knowledge. Boltzmann mainly adhered to the frequentist interpretation yet assigned probabilities to various objects. Both Boltzmann and Maxwell were crucial in the evolution of the interpretation of probabilities. At first they assigned the probabilities to particles and the macrostate of a gas, but later they assigned them to ensembles of systems.¹⁹ As with particles, Gibbs did not commit himself to a particular interpretation of probability. He furthermore refrained from referring to Boltzmann or his methods in *Equilibrium*. The concepts of statistical equilibrium and probability do become important in his later work on statistical mechanics.

Identity is a concept that became especially linked to the Gibbs paradox during the quantum revolution.²⁰ In the tradition of classical physics, objects and particles were considered to have a certain identity and individuality even if they were indistinguishable to the physicists and their devices. From 1897 onwards, indistinguishable individuals were used in statistical mechanics. A permutation of particles or points in phase space was considered the same as its original even if the particles were still identifiable.²¹ Finally, the invention of quantum mechanics largely introduced the notion that quantum

¹⁷[Myrvold, 2014, p. 1–2].

¹⁸Clausius (1857). *Über die Art der Bewegung, welche wir Wärme nennen*.

¹⁹The first inklings of this can be found in Boltzmann (1871b), *Einige allgemeine Sätze über Wärmegleichgewicht*; Boltzmann (1872), *Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen*; and Maxwell (1879), *On Boltzmann's theorem on the average distribution of energy in a system of material points*. Referenced in [Uffink, 2006b, p. 30–33, 58–59, 74].

²⁰*Identity* is taken as a condition of being something specific. *Individuality* and *Indistinguishability* are similar concepts which should not be used as synonyms. An individual is a single object with all its varying features of identification while two objects are indistinguishable if they are not recognized as distinct. Identity and indistinguishability in this sense are ontological concepts while indistinguishability is an epistemological concept.

²¹Boltzmann first toyed with this idea in his 1897 *Lectures on Mechanics*.

particles are without any individuality or identity. It was Gibbs' 1902 work that unintentionally allowed quantum physicists to tie the concept of particle non-identity to the paradox. His earlier work only focused on the epistemic indistinguishability between two gases and on identical processes, as will be explained in section 2.2.

The final concept to be discussed in this section is *continuity*. Continuity was proclaimed a universal principle by Leibniz in the early 18th century. The idea of this principle is that when causes are gradually increased or decreased, their effects will also change gradually. Additionally, infinitely small changes should never produce finite effects, which makes a discontinuous jump impossible in Leibniz's classical physics. Still, since the 1920s, physicists have become used to discreteness, which turned out to be a fundamental aspect of quantum mechanics. Gibbs' *Equilibrium* does appear to contain such a jump in GP1876 and thus already violated the continuity principle. In fact, attempts to render the thought experiment continuous have been counted as a solution to one interpretation of the paradox.

Most of the concepts described in this section were invoked in physics after the turn of the 18th century and, as a result, were made to be somewhat compatible with thermodynamics. Even those concepts that were around before 1800, i.e. *identity* and *probability*, were adapted to fit with the rapidly changing branch of physics. Later foundational developments within the branches of thermodynamics and statistical mechanics typically involved a foundational shift in those concepts as well.

2.2 Gibbs' First Writings on the Thought Experiment

The previously described conceptual developments formed the foundation upon which J. Willard Gibbs would build his greatest paper in thermodynamics. The dense 'On the Equilibrium of Heterogeneous Substances' ended up published in two parts, with the first part printed in the *Transactions of the Connecticut Academy* in 1876. With *Equilibrium* now considered one of the founding papers of chemical thermodynamics, it is not particularly surprising that some sections still attract the attention of physicists and non-physicists alike. Within a section on the fundamental equations of ideal gases and gas mixtures is a subsection called 'Considerations relating to the Increase of Entropy due to the Mixture of Gases by Diffusion' on which this section will primarily focus.²² This is the paradoxical GP1876 section which has been cited as containing the first brand of the Gibbs paradox.²³

²²[Gibbs, pp. 165–168].

²³By, among others, [Wiedeburg, 1894], [Klein, 1958], and [Peters, 2014].

As is evident from the title of the 1876 section, Gibbs considered several issues related to the increase of entropy due to diffusion. This entropy is called by some the *entropy of mixing*, in order to distinguish it from other definitions of entropy. In GP1876, Gibbs calculated the entropy increase due to the diffusion of two gases. From this, Gibbs managed to indicate several consequences for thermodynamics. These consequences can be separated into several considerations related to several concepts. The term “Gibbs paradox” has been used in relation to several of these considerations. There is thus not a single Gibbs paradox indicated by Gibbs himself in the 1876 section. By dissecting the assumptions, conclusions and intermediate reasoning, this author hopes to extract as many paradoxical elements relevant to the physical foundations in the late nineteenth century as possible. This may then be used to support later interpretations of GP1876 by other physicists.

Entropy in Gibbs’ fundamental equation

One of the things Gibbs introduced is a new fundamental equation for the combined, partial entropies of several *ideal gases* or gas mixtures:²⁴

$$\eta = \sum_1 (m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{v}{m_1}),^{25} \quad (2.1)$$

where η , t , and v respectively are the entropy, temperature, and volume of the system. In Gibbs’ notation, m_1 is the quantity of the gas and a , c , and H are constants.²⁶ This formula expresses the notion that the entropy of a gas mixture is equal to the sum of the entropies of the individual component gases with the same temperature and at the same volume.²⁷ It is one of the more important formulas in this thesis, for it has been doubted in later interpretations of the Gibbs paradox.

The form of this formula is quite different from Clausius’ $\int \frac{dQ}{T}$, despite the dimension, $kg\ m^2\ s^{-2}\ K^{-1}$, being the same. Gibbs obtained his formula by combining the First and Second law, integrating the whole thing, and adding an *additive integration constant*. From formula (2.1), it is obvious that Gibbs took entropy to be both *additive* and *non-intensive* since the sum of all subsystems equals the total entropy and the entropy value of every subsystem depends on the volume. Even though Gibbs adhered to the

²⁴This thesis, for the most part, uses the same symbols that Gibbs and the other actors employed themselves.

²⁵The operations log and ln were used interchangeably in this time.

²⁶The constants may be further specified: c is the specific heat at constant volume; H the entropy of a unit of gas for $t = 1$; and a is either, depending on the context, the pressure at $t = 1$ and $v = 1$ or the volume at $t = 1$ and $p = 1$. All of these quantities will, eventually, drop out of the final result.

²⁷In similar fashion to Dalton’s law of partial pressures, or $p = \sum_1 p_i$. This law was actually used by Gibbs in the derivation of formula (2.1).

extensivity of entropy for homogeneous gases earlier in *Equilibrium*,²⁸ the formula is not extensive in all thermodynamic processes. It will be shown in the next subsection that, in a special case of diffusion, one obtains the inequality $\eta_{A+B} \neq \eta_A + \eta_B$, which means that the entropy does not vary with the same proportion as the size of the system. Nevertheless, the assumptions used in *Equilibrium* and formula (2.1) include additivity of entropy, extensivity of entropy for homogeneous gases, ideal gas considerations, and Dalton's law.

Calculation of the entropy difference

Using formula (2.1), Gibbs calculated the increase of entropy due to the mixing of two different types of gases, keeping the pressure and temperature constant. He did so by assuming a system that allows two equal volumes of gas to diffuse into a total volume V . GP1876 is, as with most sections in *Equilibrium*, without images. For clarification, however, a typical representation of the system has been drawn in figure 2.1.

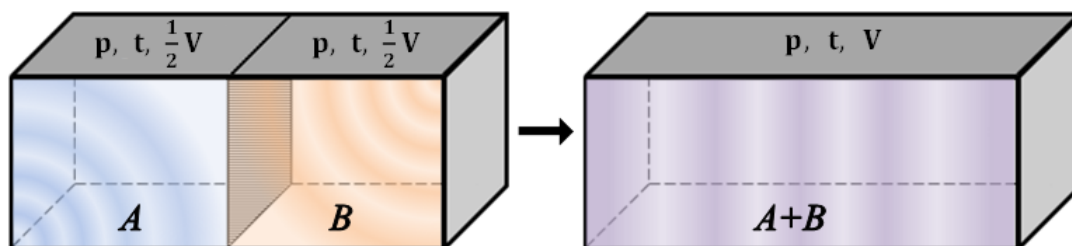


FIGURE 2.1: Diffusion of two equal volumes of gas.

We can see from the figure that by removing the partition, gases A and B diffuse, allowing the mixture $A + B$ to span the total volume V . Two processes are actually happening during this *expansion-diffusion*.²⁹ On the one hand, the gases are mixing as they do in a regular diffusion. On the other hand, both gases gain a larger available volume; there is expansion. This is important information to keep in mind for later considerations. The entropies of the individual gas components for the situation sketched in figure 2.1 are

$$\eta_A = m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{V}{2m_1}, \quad \text{and} \quad \eta_B = m_2 H_2 + m_2 c_2 \log t + m_2 a_2 \log \frac{V}{2m_2}.$$

Given that there are only two component gases, formula (2.1) for the diffused state becomes

$$\eta_{A+B} = m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{V}{m_1} + m_2 H_2 + m_2 c_2 \log t + m_2 a_2 \log \frac{V}{m_2}.$$

²⁸[Gibbs, pp. 85–86]: “We know, however, *a priori*, that if the quantity of any homogeneous mass containing n independently variable components varies and not its nature or state, the quantities ϵ , η , v , m_1 , m_2 , \dots , m_n will all vary in the same proportion.”

²⁹This is not a common term in thermodynamics. The present author uses it to denote a process in which gases are simultaneously interdiffused and expanded.

Gibbs calculated the entropy difference between the system in the unmixed and the mixed state. At this point, most of the terms cancel each other out, because the only difference between the two states lies in the volume. Therefore:

$$\begin{aligned}
 \Delta S_{AB} &= \eta_{A+B} - \eta_A - \eta_B \\
 &= m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{V}{m_1} + m_2 H_2 + m_2 c_2 \log t + m_2 a_2 \log \frac{V}{m_2} \\
 &\quad - (m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{V}{2m_1}) - (m_2 H_2 + m_2 c_2 \log t + m_2 a_2 \log \frac{V}{2m_2}) \\
 &= m_1 a_1 \log \frac{V}{m_1} + m_2 a_2 \log \frac{V}{m_2} - m_1 a_1 \log \frac{V}{2m_1} - m_2 a_2 \log \frac{V}{2m_2} \\
 &= m_1 a_1 \log V + m_2 a_2 \log V - m_1 a_1 \log \frac{V}{2} - m_2 a_2 \log \frac{V}{2} \\
 &= (m_1 a_1 + m_2 a_2) \log 2.
 \end{aligned}$$

Clearly, the entropy of the total system increases in the diffusion of two different kinds of gases into one volume. The entropy of the mixture is more than double the entropy of the system prior to the expansion-diffusion. This is actually due to the fact that the quantities of gas are constant in the diffusion. If one were to consider doubling the total system – that is, both the quantities of gas and the volume – the formula would spit out a zero value. The increase of entropy by itself thus is not necessarily paradoxical since formula (2.1) is proportional to the volume of the system. It follows from the additivity and non-intensivity assumptions. Next, using the thermodynamic relations for ideal gases illustrated in section 2.1.1,³⁰ Gibbs obtained

$$m_1 a_1 = \frac{pV}{2t}, \quad \text{and} \quad m_2 a_2 = \frac{pV}{2t},$$

after which he rewrote the entropy difference as

$$\Delta S_{AB} = \frac{pV}{t} \log 2. \tag{2.2}$$

The entropy of mixing therefore only depends on the macroscopic properties of pressure, temperature and volume.

Mathematical derivation of ΔS for a gas mixture with gases of the same kind

So far, there have been no inconsistencies or paradoxical conclusions between the assumptions and Gibbs' reasoning. It is the following paragraph in the GP1876 section that contains the first remarkable conclusion. Using Gibbs' words:

³⁰For ideal gases, the ideal gas law represents these relations. This ideal gas law is constructed from the following gas laws: Boyle's $p \propto \frac{1}{V}$ at constant t (1660s); Charles' $V \propto t$ at constant p (1780s); Amontons' $p \propto t$ with constant V (1800s); and Avogadro's $V \propto r$ at constant p and t (1810s).

It is noticeable that the value of this expression does not depend upon the kinds of gas which are concerned, if the quantities are such as has been supposed, except that the gases which are mixed must be of different kinds. If one should bring into contact two masses of the same kind of gas, they would also mix, but there would be no increase of entropy.³¹

Despite this declaration, a calculation of the entropy difference for the expansion-diffusion of the alike gases A and A does not provide a different value than the one displayed in formula (2.2). To be unambiguous,

$$\begin{aligned}\Delta S_{AA} &= \eta_{A+A} - \eta_A - \eta_A = \eta_{2A} - 2\eta_A \\ &= 2(m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{V}{m_1}) \\ &\quad - 2(m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{V}{2m_1}) \\ &= 2m_1 a_1 \log \frac{V}{m_1} - 2m_1 a_1 \log \frac{V}{2m_1} \\ &= 2m_1 a_1 \log 2 = \frac{pV}{t} \log 2,\end{aligned}$$

which is, evidently, a non-zero value. From a mathematical angle there is no difference between ΔS_{AB} and ΔS_{AA} , and thus no difference between a diffused gas mixture of unlike or alike gases. Note that if $\Delta S_{AA} = \eta_{2A} - 2\eta_A$ is assumed to be zero, as Gibbs stated, the entropy for homogeneous gases would be extensive without the thermodynamic system actually having doubled in size. This discrepancy between Gibbs' claim and what the calculation shows could potentially be seen as paradoxical.

Sensible properties and the thermodynamic state

However, when Gibbs stated that there will be no increase of entropy in the mixing of two gases of the same kind, he did not consider a calculation like the one executed in the previous paragraph. Rather than considering the mathematical angle, he approached the issue from a *thermodynamic point of view*. It is essential to understand what implications Gibbs associated with an increase of entropy:

When we say that when two different gases mix by diffusion, as we have supposed, the energy of the whole remains constant, and the entropy receives a certain increase, we mean that the gases could be separated and brought to the same volume and temperature which they had at first by means of certain changes in external bodies... But when we say that when two gas-masses of the same kind are mixed under similar circumstances there is no change of energy or entropy, we do not mean that the gases which have been mixed can be separated without change to external bodies. On the contrary, the separation of the gases is entirely impossible. We call the energy

³¹[Gibbs, p. 166].

and entropy of the gas-masses when mixed the same as when they were unmixed, because we do not recognize any difference in the substance of the two masses.³²

Two mutually pertinent aspects of this statement ought to be clarified. First, it needs to be understood what Gibbs implied with the words “we do not recognize . . .”. They are not meant to indicate a personal, subjective perception. Instead, the gas mixture appears the same because its thermodynamic state after the diffusion is equal to the thermodynamic state prior to the diffusion. There never was a deviation from the thermodynamic equilibrium unlike in the case of the different gases.³³ That is, the *sensible* thermodynamic properties of the total system have not changed during the diffusion. Similarly, our measuring apparatuses were, in Gibbs’ days, only capable of measuring a few state variables such as pressure, temperature, and volume. So no differences could be detected using those devices.

The second, not unrelated, aspect deals with the *impossibility of separating a gas mixture of alike gases*. This again refers to the perception of the system via the thermodynamic state. Non-identical gases can be set apart through processes such as distillation, membrane separation, or sorption, precisely because the thermodynamic state has changed. Reinserting the partition without separating the different gases results in a different thermodynamic state than the one in which *A* and *B* are kept apart.³⁴ On the other hand, reinserting the partition in the alike gas mixture does result in the same thermodynamic state as the one prior to the diffusion. For that reason Gibbs maintained that the increase of the entropy due to the diffusion of alike gases equals zero. Naturally, this impossibility of separating gases applies to both *epistemologically alike* and *ontologically identical* gases as neither can be separated.³⁵

The macro- and microscopic scales

Because Gibbs considered the diffusion from a *thermodynamic* angle, the microscopic details did not need to be included. It also allowed Gibbs to remain mostly indecisive about the ultimate constitution of matter. This is an attitude he actually preferred because it is one less assumption to consider. Most of *Equilibrium* thus is invariant to changes in the scientific theory of the nature of matter. Gibbs’ position on the *microscopic dynamics* of the system is confirmed in the following remark:

³²Ibid.

³³In neither cases is there a deviation from the thermal and mechanical equilibrium. Only the chemical equilibrium changes in the diffusion of two non-identical gases since the gases are not equally divided over the whole mass. That is, $\mu'_A \neq \mu''_A$ and $\mu'_B \neq \mu''_B$.

³⁴In a highly unlikely scenario the gas quantities *A* and *B* might find themselves separated without external influences.

³⁵In this thesis, alike gases are thought to be identical at some point in time but may later turn out to be different. Unlike gases are always non-identical, so those terms can be used interchangeably.

When gases of different kinds are mixed, if we ask what changes in external bodies are necessary to bring the system to its original state, we do not mean a state in which each particle shall occupy more or less exactly the same position as at some previous epoch, but only a state which shall be undistinguishable from the previous one in its sensible properties.³⁶

In theory, it is possible, but extremely unlikely, that the particles may, at some time, occupy the exact same position as they did initially. This is important for some thermodynamic functions, such as energy, which are properties of both the statistical macrostate and the microstate. Those properties are explained from both scales.³⁷ Entropy is, however, merely a property of the macrostate. Therefore, a consideration of the increase of entropy only requires the particles to be in the volume they originated from. This can solely be done via external influences when there is a distinction between particles of the first $\frac{1}{2}V$ and the second $\frac{1}{2}V$. Thus, for non-identical gases, the original thermodynamic state, which is defined by macroscopic quantities such as the total energy, volume, and quantity of gas, can be recovered by manipulation of macroscopic variables.

As mentioned earlier, for alike gases, the total thermodynamic state never changed beyond the larger available volume. No physicist or apparatus can determine which particle originated from which original volume. The only exception to this would be to track the particle, but then one is no longer working on the macroscopic scale. With entropy solely being a thermodynamic property, and no sensible macroscopic characteristics having changed, there cannot be an increase of entropy in the mixing of gases of the same kind since we cannot separate them macroscopically. These considerations show that it is essential to be rigorous in thermodynamic essays as “[i]t is to states of systems thus incompletely defined that the problems of thermodynamics relate.”³⁸ The divergence of the entropy difference between the macroscopic and microscopic scale could be interpreted as a paradox.

On the (ir)reversibility of diffusion

Gibbs himself made no mention of the (ir)reversibility of his considerations. However, it has been associated with the Gibbs paradox, therefore this thesis will also describe its relation to GP1876. Despite the acknowledged possibility, there is no guarantee that the particles will return to the same side of the partition as they were before the diffusion. It is not achievable, using thermodynamic means, to trace the particles and manually obtain the exact same particle positions as at the time of the partition removal.

³⁶Ibid.

³⁷In thermodynamics, phenomena are explained from a macroscopic thermodynamic perspective. In statistical physics, phenomena may be described from both a macroscopic and a microscopic perspective. Macroscopic descriptions from thermodynamics and statistical physics may differ; entropy is an example of this as will be elucidated later in this thesis.

³⁸Ibid.

However, for both the alike and the unlike gases the behavior of the particles are of no concern seeing as these thermodynamic considerations should be described from a macroscopic point of view. And this does not entail a detailed microscopic description of the movement and position of the individual particle.

One of the things to keep in mind is that there are multiple interpretations of the reversibility of a process $k \rightarrow l$. E.T. Jaynes identified three variations related to thermodynamics in a paper on the evolution of Carnot's principle.³⁹

Mechanical Reversibility: When each individual molecule can be returned to its original position by reversing all molecular velocities.

Carnot Reversibility: When the original macrostate can be restored by performing the opposite process $l \rightarrow k$.

Thermodynamic Reversibility: When the original macrostate can be recovered without external change by any means such as $l \rightarrow m \rightarrow k$.

Jaynes claimed that the distinction between mechanical and thermodynamic reversibility was stressed by Gibbs in GP1876. The mechanical reversibility of the diffusion was of no importance to Gibbs because he only considered the thermodynamic angle in GP1876. The diffusion of alike gases never led to a different macrostate. The diffusion of non-identical gases is therefore neither mechanically reversible nor Carnot reversible. It is, on the other hand, possible to separate the unlike gas mixture without any external change. Figure 2.2 provides an example of how a heterogeneous gas mixture may be separated.

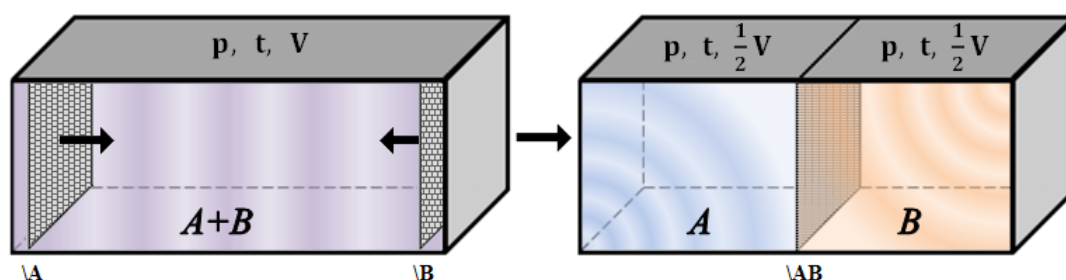


FIGURE 2.2: Two sensibly different gases may be separated when replacing the partition with two semipermeable membranes. One of the membranes, $\setminus A$, should be permeable to gas A and impermeable to gas B , the second membrane, $\setminus B$, should work the other way around. The gases will diffuse when the membranes are moved to opposite sides and will be separated when both membranes are moved to the middle.

The expansion-diffusion process is therefore *thermodynamically reversible*. To conclude the discussion on the separability of alike and unlike gas mixtures, it may be said that

³⁹[Jaynes, 1988, p. 280].

they differ from each other in that the former is indistinguishable from its unmixed state and the latter is not.

But if such considerations explain why the mixture of gas-masses of the same kind stands on a different footing from the mixture of gas-masses of different kinds, the fact is not less significant that the increase of entropy due to the mixture of gases of different kinds, in such a case as we have supposed, is independent of the nature of the gases.⁴⁰

As long as the process is an expansion-diffusion, where the diffusion is associated with the gas itself and the expansion is associated with the available volume, one might assume that the increase of entropy depends on the nature of the gases. Arieh Ben-Naim has argued that it is not surprising that it does not depend on the nature of the gases because the expansion is the only cause of the increase of entropy.⁴¹ The present author agrees with Ben-Naim that the increase of entropy stems from the increase of available volume but would also like to stress that that does not necessarily refute Gibbs' statement that alike and unlike gas mixtures are different from a thermodynamic point of view.

Degree of similarity and discontinuity

Gibbs delved further into the independence of the nature of gases in the entropy of mixing by imagining increasingly similar gases.

Now we may without violence to the general laws of gases which are embodied in our equations suppose other gases to exist than such as actually do exist, and there does not appear to be any limit to the resemblance which there might be between two such kinds of gas. But the increase of entropy due to the mixing of given volumes of the gases at a given temperature and pressure would be independent of the degree of similarity or dissimilarity between them.⁴²

Not only is the increase in entropy unrelated to the nature of the gases, it also is independent of the *degree of (dis)similarity* between the gases. Epistemologically speaking, the entropy difference disappears the exact moment two gases are *indistinguishable* in the sensible – either human or experimental – or molecular sense. From the ontological point of view, the entropy difference becomes zero when the gases are identical.

Seeing as there is no limit to the resemblance between unlike gases, one might imagine a situation where two unlike gases are made more and more similar in a continuous manner. However, the resultant function would not be continuous when the entropy difference is made to depend on the degree of similarity between the two gases. There

⁴⁰[Gibbs, pp. 166–167].

⁴¹[Ben-Naim, 2008, pp. 265–268].

⁴²[Gibbs, p. 167].

thus is a ‘jump’ in the entropy of mixing. This, proclaimed by some, paradoxical result is perhaps most easily understood via a graphical representation as the one in figure 2.3. From this figure, one can see a *discontinuity* when assuming that the entropy increase

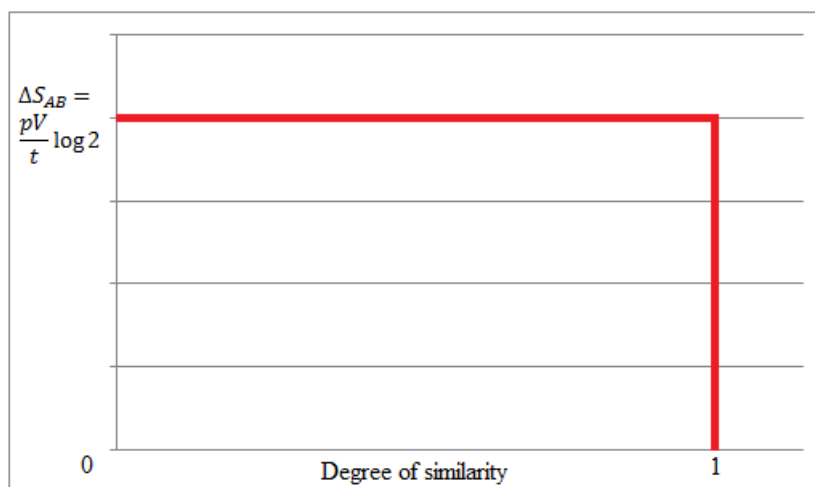


FIGURE 2.3: (In)Dependency of entropy increase on the degree of similarity between two gases in diffusion.

depends on a function of the (dis)similarity between the gases being mixed. The gases could be made infinitively similar to each other but there still would be an increase of entropy even though one might expect the value to continuously approach zero.⁴³ Note that Gibbs himself did not mention the discontinuity, but it has been mentioned in later renderings of the Gibbs paradox.

On atoms and the status of energy and entropy

It is in the next statement that Gibbs alluded to the existence of *atoms* and identical molecular properties:

We might also imagine the case of two gases which should be absolutely identical in all the properties (*sensible and molecular*) which come into play while they exist as gases either pure or mixed with each other, but which should differ in respect to the attractions between their atoms and the atoms of some other substances, and therefore in their tendency to combine with such substances. In the mixture of such gases by diffusion an increase of entropy would take place, although the process of mixture, dynamically considered, might be absolutely identical in its minutest details (even with respect to the precise path of each atom) with processes which might take place without any increase of entropy. In such respects, entropy stands strongly contrasted with energy.⁴⁴

⁴³It has been argued that a gradual decrease would be expected for those that adhere to Leibniz’s general postulate of continuity of cause and effect. [Landé, 1965] is an example of this. He also tried to get rid of this discontinuity by imposing a continuity in what is to be understood as alike and unlike.

⁴⁴[Gibbs, p. 167].

Regardless of whether Gibbs adhered to the existence of atoms, he was willing to include them as a possibility in the consideration that gases might be distinguishable despite them being identical in the dynamical sense.⁴⁵ The increase of entropy naturally takes place because it is possible to differentiate between two such gases, say A and A' , when we use the substance to which only one of the gases is attracted. From a thermodynamic point of view, there is no sensible difference but there still is a way to separate the two gases A and A' . Because A and A' are distinguishable in some way there must be an increase of entropy. From the dynamical, or microscopic, point of view, however, the mixing process might be identical to one where there is no increase of entropy. With A and A' being indistinguishable from the dynamical perspective yet separable via their different tendencies to combine with other substances, entropy cannot be associated with microscopic dynamics. Therefore, according to Gibbs, entropy is different from energy, which can, in fact, be associated with microscopic dynamics. The idea that entropy cannot be associated with microdynamics has been a reason for physicists to propose to get rid of the entire concept and replace it with something else.⁴⁶

On the Second Law

The inability of entropy to be associated with particle dynamics allowed Gibbs to make a statement on its relation to and consequences for the Second Law.

Again, when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motions in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have once been mixed. In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.⁴⁷

This statement seems a bit unclear at first sight, therefore some clarification seems quite appropriate.⁴⁸ Because this statement is part of the same paragraph as the former statement, it can be assumed that Gibbs referred to the AA' gas mixture. The AA' mixing process is, as explained, identical to the AA mixing process because the sensible and molecular properties are equal for both gas mixtures. Because the gases in the gas mixtures are indistinguishable, reinserting the partition would return the original thermodynamic state. However, due to the diffusion there has been an increase of entropy for the AA' gas mixture only. Now, for both gas mixtures, it is possible, but *highly improbable*, that all particles happen to have returned to their original side of

⁴⁵Note that the term indistinguishable is only used for gases while the term identity is used for gases and the mixing process. The atoms are not related by Gibbs to those concepts.

⁴⁶[Ben-Naim, 2008].

⁴⁷[Gibbs, p. 167].

⁴⁸A similar argument to this paragraph is given in [Jaynes, 2013, pp. 1–21].

the system, without any external influences, at the exact moment that the partition is reinserted.⁴⁹ This chance of this happening is equal for the two gas mixtures AA' and AA . But if this were to happen for the AA' mixture, the entropy would be decreased to its pre-diffusion value. Therefore, a decrease of entropy is not impossible, but merely highly improbable. This, in turn, means that the Second Law of thermodynamics, if taken to state that the entropy of the system will always increase, is probabilistic as well. So, although the diffusion of similar gases can be described as experimentally irreversible in a thermodynamic sense, a return to its original state is not impossible.

On Avogadro's Law

Near the end of the GP1876, Gibbs made a connection to Avogadro's law⁵⁰, when Gibbs stated that “[t]here is perhaps no fact in the molecular theory of gases so well established as that the number of molecules in a given volume at a given temperature and pressure is the same for every kind of gas when in a state to which the laws of ideal gases apply.” Hence the calculated value in formula (2.2) would have to be exclusively determined by the number of molecules in the mixture. As such, “the increase of entropy is therefore determined by the number of these molecules and is independent of their dynamical condition and of the degree of difference between them.”

This comment, once again, exhibits that Gibbs, at the very least, adhered to the molecular theory in regard to the constitution of matter. The increase of entropy at constant temperature and pressure is determined by the volume and thus, following Avogadro's law, by the number of molecules. This does not mean that the increase of entropy is in any way determined by the dynamics of the molecules or the differences between types of molecules. So even though molecular theory is not a necessary assumption for most of the considerations in GP1876, it does clarify them.⁵¹

Generalization of entropy increase due to diffusion

Finally, Gibbs generalized his considerations to the case in which the volumes are of different sizes or when more than two gases are mixed. By denoting the initial volumes of the different kinds of gas by v_1, v_2 , etc., and the total volume by V , the increase of entropy can be written as follows

$$\Delta S_{\Sigma} = \sum_1 (m_1 a_1) \log V - \sum_1 (m_2 a_2 \log v_2).$$

⁴⁹One might even imagine a Maxwellian demon governing the reverse process.

⁵⁰In which equal volumes of all gases, at the same temperature and pressure, have the same number of molecules or $V \propto n$ in Gibbs' notation.

⁵¹That is, the present author disagrees with R.J. Seeger's remark that “Gibbs himself had already indicated in 1876, in connection with his famous paradox, the need for supplementation of thermodynamics with atomistic ideas; [...]” [Seeger, 1974]. Nowhere in GP1876 does Gibbs denote the necessity of atoms, they are merely part of the later considerations.

Then, by denoting the numbers of the molecules of the different kinds of gases with r_1 , r_2 , etc., and by using the ideal gas law, Gibbs obtained

$$r_1 = Cm_1a_1 \qquad r_2 = Cm_2a_2, \qquad \text{etc.},$$

after which the increase of entropy can be rewritten as

$$\frac{\sum_1 r_1 \log \sum_1 r_1 - \sum_1 (r_1 \log r_1)}{C}. \qquad (2.3)$$

In this case C denotes a constant which is not further specified by Gibbs.⁵² We see that the general formula is of the same nature as formula (2.1) in that it still is entirely dependent on the number of molecules. It is this generalization that concludes the section ‘Considerations relating to the Increase of Entropy due to the Mixture of Gases by Diffusion’. Following this section in *Equilibrium* are more sections focused on gas mixtures which in turn conclude the first published part of Gibbs’ paper.

From these considerations, the relevant keywords that should be kept in mind are:

Ideal gas laws — entropy — additivity — extensivity — expansion-diffusion — separability and sensible properties — (dis)similarity — thermodynamic state — macroscopic and microscopic descriptions — atomic theory — molecular theory — reversibility — discontinuity — Second Law — probability.

These keywords will be used in later chapters to indicate the paradoxical elements that the historical actors have read into Gibbs’ GP1876.

2.3 J. Willard Gibbs

Although Gibbs was involved with ground-breaking developments in both physics and mathematics, he has never become a symbol of a great scientist to the public like Einstein and Maxwell have. In fact, the impression he left as a person is very much unlike that of an authoritative figure but more that of a silent scholar. He furthermore exerted the typical Yale calmness and unpretentiousness. Gibbs lived in New Haven his entire life and was appointed professor of mathematical physics at Yale in 1871. His devotion to Yale allowed him to remain a professor there until his death in 1903. He is mostly recognized for his ‘On the Equilibrium of Heterogeneous Substances’, *Elementary Principles of Statistical Mechanics* and work on vector analysis. Not much else needs to be known about Gibbs’ personal life for the argument in this thesis.

⁵²Since $r = \frac{CpV}{t}$, we know that C has to equal the inverse of Boltzmann’s constant or Avogadro’s number over the gas constant. That, however, was not introduced by Boltzmann until 1877.

2.3.1 Scientific Style

Gibbs' scientific style has remained the same from his earlier papers on thermodynamics to his later work on statistical mechanics. Those who have read Gibbs might classify his work as *abstract*, *comprehensive*, very *general*, but also very *difficult*. In fact, Gibbs seemed to have a reputation for writing difficult works.⁵³ Ostwald, in his 1892 translation of *Equilibrium*, even provided his readers with a warning:

Unzweideutigkeit des Ausdrucks geleitet, hat der Verfasser eine Form der Darstellung gewählt, welche durch ihre abstrakte Gestalt und ihre oft schwer übersehbare Darstellungsweise vom Leser eine nicht gewöhnliche Aufmerksamkeit und Hingabe fordert.⁵⁴

The abstract and general character of the paper thus would demand a lot of attentiveness and devotion from the reader. However, doing so might be very rewarding in the end.

According to Crowther, Gibbs might be best classified as a *synthetic thinker* because his main works in physics span entire regions of phenomena.⁵⁵ Both in *Equilibrium* and *Statistical Mechanics*, Gibbs managed to deduce many conclusions from a few fundamental assumptions.⁵⁶ As a synthetic thinker, he did not seek to establish the physical laws but instead tried to interpret them as part of the whole body of knowledge. Despite his focus on deduction, Gibbs also valued experimentation because he felt it necessarily precedes abstract deduction. However, as seen in the paradoxical GP1876, he did not shy away from imagining unrealizable hypothetical situations. In addition to the importance of the practical side, Gibbs appreciated the mathematical side as well even if he mostly regarded it as a tool. As stated by Gibbs' protégé Edwin B. Wilson, Gibbs "had a very even balance between the intuition of the geometer and the instinct of the algebraist."⁵⁷

Another important trait in Gibbs' writing is his carefulness. Not only did Gibbs try to avoid any speculation, he also strove to formulate his writings in an exceedingly precise manner. He seemed content with exploiting the known in order to avoid any contradictory conclusions and excessive complexities. His neutral position on the structure of matter is a prime example of his "innate tendency to avoid an expression of opinion on anything where he had not thoroughly explored all the implications or where for

⁵³[Klein, 1983].

⁵⁴[Gibbs, 1892, p. v]. ("Led by the unambiguity of the expressions, the author has chosen a form of representation, which calls for a non-ordinary attention and dedication from readers due to their abstract form and heavily loaded representation.") All translations, indicated by parentheses, are by the present author unless otherwise indicated.

⁵⁵[Crowther, 1937, p. 249].

⁵⁶Einstein is another physicist known for his synthesizing of phenomena. The Annus Mirabilis papers, such as the one on light quanta, are an example of this.

⁵⁷[Donnan and Haas, 1936b, p. 160].

any other reason he was not entirely sure of his ground.”⁵⁸ As a result of his carefulness and thoroughness, most of Gibbs’ writings remained valid throughout the quantum revolution.

2.3.2 Writings on Thermodynamics

According to his biographer L.P. Wheeler, Gibbs only became heavily interested in thermodynamics after 1871. Within two years, he published his first two papers in which he focused on the graphical representation and interpretation of Clausius’ concept of entropy. The legacy left behind by these papers is the entropy-temperature diagram still used as a preferred representation for thermodynamic cycles. His third paper, ‘On the Equilibrium of Heterogeneous Substances’, would, besides being his main work, also be the last work he published on the subject for years. Published over the period 1875–1878, this paper would become especially important to the intersection of chemistry and thermodynamics and was notably well-received in the Netherlands.^{59,60} It also has had a lot of influence in industrial techniques such as metallurgy, the manufacture of refractory materials, and the equilibria between liquid slags and molten metals.⁶¹

Gibbs recognized that his *Equilibrium* was built on Clausius’ principles and commenced his article with Clausius’ assertions that “Die Energie der Welt ist konstant” and “Die Entropie der Welt strebt einem Maximum zu”. In addition to his support for Clausius’ entropy, Gibbs aimed most of his attention at the concept of equilibrium, including entropy and mass as elements in his fundamental equilibrium equation.⁶² The larger part of the paper describes how the equation must be modified to accommodate for various situations such as the presence of gravity. Smaller sections within the paper, such as the section on the diffusion of gases, show Gibbs’ prowess at looking beyond the current physical assumptions. The limitation of the Second Law is one of the findings that Gibbs already foreshadowed in the paradoxical GP1876.

The considerations within GP1876 are not speculations but are derived from what Gibbs believed to be well-established assumptions on ideal gases. He only declared some of the conclusions to be remarkable and did not state that they clash with the assumptions. As

⁵⁸[Wheeler, 1962, p. 141].

⁵⁹Gibbs frequently corresponded with W.D Bancroft and J.E. Trevor, the editors of the *Journal of Physical Chemistry*, and even considered writing a supplement to *Equilibrium* due to his correspondence with Bancroft.

⁶⁰Dutch scientists who were influenced by Gibbs include J.D. van der Waals, J.H. van ’t Hoff, H.W. Bakhuis Roozeboom, and J.J. van Laar.

⁶¹According to [Crowther, 1937, p. 279], G. Tammann did some experiments based on Gibbs theoretical work. Furthermore, as stated in [Wheeler, 1962, p. 103–4], Gibbs’ four pages on the phase rule resulted in over 42 books by 27 authors covering its applications.

⁶² $d\epsilon = td\eta - pdv + \sum_1^n \mu_i dm_i$. As shown in section 2.1.3, this equation succeeds in describing the entire system since all thermodynamic properties can be altered in infinitively small ways.

such, in Gibbs' writings, none of the considerations were meant to become paradoxes. That also explains why Gibbs considered his *Equilibrium* a finished product and stopped his research on thermodynamics for fifteen years. However, in February 1903, Gibbs had signed a contract for a reprint of *Equilibrium* including a supplement. This supplement was meant to be largely explanatory, it should therefore not be considered an erratum. A list of additional subjects has remained from the unfinished manuscript. Two of these subjects seem of pertinence to GP1876: *On entropy as mixed-up-ness* and *On similarity in thermodynamics*. Unfortunately, no notes on those subjects have been found in the Gibbs Archives.

Even though Gibbs was appointed professor of mathematical physics in 1871 there are no records of him teaching his own discoveries in thermodynamics prior to 1893.⁶³ Instead of using his main paper as a source, Gibbs addressed those works that most interested him at that time. For instance, in 1895–1896, he lectured on Maxwell's *A Treatise on Electricity and Magnetism* which was originally published in 1873. Records from the Yale College Catalogue indicate that in his first years as a professor, the thermodynamics courses were provided by W.P. Trowbridge. In the 1880s, both Gibbs and A.J. DuBois, who was Trowbridge's replacement as the mechanical engineering professor, taught courses on thermodynamics. Earlier in his teaching career Gibbs seemed to have leaned towards dynamics in his teachings on thermodynamics; later, the focus shifted to the properties of matter as well. There is no indication that Gibbs discussed the thought experiment within GP1876 in his lectures.⁶⁴ After the 1870s, Gibbs went on to work on new subjects such as vector analysis and statistical mechanics.

2.3.3 Position in the Scientific Community

As expected, Gibbs was largely unknown until the publication of his papers on thermodynamics. Early biographies also suggested that Gibbs was not sufficiently recognized after the publication of *Equilibrium*.⁶⁵ However, writers such as M.J. Klein and Wheeler instead have claimed that Gibbs was in fact well-known by those he wanted to be known to: the chemists and physicists. One of the first physicists to become interested in Gibbs' work was Maxwell. There is no record of any correspondence between Gibbs and Maxwell, but it is likely that they wrote each other, directly or indirectly, at least

⁶³More precisely, Wilson is cited as stating that Gibbs did not lecture on chemical dynamics the first fifteen years after 1876 in [Crowther, 1937, p. 252]. [Wheeler, 1962, p. 169], on the other hand, noted that Gibbs taught on Clausius' writing in 1872–1873.

⁶⁴Likewise, there are also no notes in Yale's Collection on Gibbs that hint at the thought experiment. The lack of notes on GP1876 might be explained by the fact that Gibbs did not write that many notes at all. Wilson as quoted in [Crowther, 1937, pp. 294–5]: "It appeared that he composed his works in his head and then wrote them down".

⁶⁵[Crowther, 1937] is an example of such a biography.

once.⁶⁶ It appears, according to Wheeler, that Maxwell also familiarized those around him to Gibbs' papers since most of the letters in Gibbs' Scientific Correspondence were from Maxwell's students or co-workers.⁶⁷ Maxwell's correspondence is not the only one missing, Hermann von Helmholtz is another well-known physicist thought to have been in contact with Gibbs despite the complete lack of letters.

Even though there was an archive dedicated to Gibbs Scientific Correspondence⁶⁸, very few letters in the Scientific Correspondence actually discuss thermodynamics or statistical mechanics. Only S.H. Burbury and William Thomson wrote Gibbs about statistical mechanics. The thermodynamic questions were mainly posed by lesser-known physicists such as G.F. Becker, E.H. Griffiths, and J.E. Trevor. Not many replies of Gibbs to these inquiries have been preserved in the collection.⁶⁹

It has been claimed, by the translator himself among others, that *Equilibrium* was not really read until the German translation by Ostwald.⁷⁰ Contradictory to this claim is the 'emergence' of the Dutch interest in physical chemistry in the 1880s. The chemists J.M. van Bemmelen and H.W. Bakhuis Roozeboom had already worked on applications of Gibbs' phase rule when Ostwald and Van 't Hoff set up the journal *Zeitschrift für physikalische Chemie* in 1887.⁷¹ To further weaken the claim, it appears that the journal in which Gibbs published, *Transactions of the Connecticut Academy of Arts and Sciences*, was exchanged with 170 societies, of which 140 were outside of the United States. Additionally, Gibbs had personally send copies of his papers to dozens of chemists and physicists.⁷²

In any case, the distribution of *Equilibrium* and Gibbs' later work was large enough that most scientists would have been able to obtain a copy. Thus, the publication of his works brought Gibbs exactly the attention he needed: the recognition of his ability to carefully yet thoroughly explain thermodynamic equilibria whilst retaining his typical Yale modesty.

⁶⁶Maxwell built a thermodynamic surface model based on Gibbs' 1873 papers which he later actually sent to Gibbs.

⁶⁷[Wheeler, 1962, p. 85].

⁶⁸The New Haven Beinecke Library rearranged the Gibbs Collections in the winter of 2014. As of 2015, there is one single collection *Josiah Willard Gibbs Papers* with call number GEN MSS 1175.

⁶⁹[Wheeler, 1962, pp. 136–7]. Consult Appendix A for a list of the correspondence found at Yale.

⁷⁰[Gibbs, 1892]. Apparently Ostwald's translation would make *Equilibrium* more readily available to those in Europe. Additionally, in 1899, Le Châtelier published a French version of *Equilibrium*. [Gibbs, 1899].

⁷¹[Wheeler, 1962, pp. 102–3]. Even though they already knew about *Equilibrium*, Van Bemmelen still received a copy of the French translation by Le Châtelier. The Leiden Library copy of [Gibbs, 1899] has a hand-written note from the author to Van Bemmelen himself.

⁷²More on Gibbs' recognition may be found in [Wheeler, 1962, pp. 84–105]. A list of recipients of the *Equilibrium* reprints may also be found in Appendix A.

2.4 Conclusion

As described in the previous sections, Gibbs did not associate any contradictions with the considerations he derived from the thought experiment. Nor did he consider the situation to be inconsistent. For that reason, Gibbs' own interpretation of GP1876 does not fit with Lycan's definition of a paradox. Gibbs merely obtained an insight as to what entropy might or might not be as a concept. That is, from a few assumptions – additivity, extensivity, and ideal gases – he was able to conclude that entropy is a property explained on the macroscopic scale in contrast to energy and that the Second Law is not absolute. Furthermore, by using terms such as separation, degree of similarity, and atom, Gibbs implicitly paved the way for other concepts to be tied to the thought experiment. Examples of this given in section 2.2 include Jaynes' classification of reversibility and Ben-Naim's attempt to attribute the Gibbs paradox fully to the expansion of the volume.

The one thing Gibbs did attempt to answer in GP1876 is the question of why alike gases behave differently from unlike gases in an expansion-diffusion. The answer provided by Gibbs, as shown earlier in this thesis, is that the thermodynamic state of a mixture of alike gases is not distinguishable from the thermodynamic state the system had prior to the removal of the partition. Wheeler called this an “empirical solution” to the Gibbs paradox.⁷³ Haitun, too, considered Gibbs' narrative a solution to the paradox. He classified the solution as belonging to the thermodynamic phase and falling into the discrete entropy of mixing jump variant.⁷⁴ To the present author, classifying a solution to a non-problem, as described by Gibbs, seems quite odd. In this case the terms *consideration* and *explanation* seem to fit Gibbs' interpretation of GP1876 much better. Hence, Gibbs' contribution will be classified in this thesis as a *series of considerations in thermodynamics based on an expansion-diffusion thought experiment with a focus on the concept of entropy*.

⁷³[Wheeler, 1962, pp. 158–9].

⁷⁴[С.Д. Хайтун, 1986, p. 151].

3

1876-1902: The Initial Interpretations

*It is obvious, that, in the established situation, the solution of the physical Gibbs paradox is closely related to the resolution of the historical-scientific paradox of the Gibbs paradox.*¹

– Sergei D. Haitun, *History of the Gibbs Paradox*

In the 25 years after the publication of *Equilibrium*, Gibbs focused on vector analysis and statistical mechanics, leaving chemical physics to others. Slowly but surely, physicists began to read and understand Gibbs' compendium. Even though it has been said that, for a long time, Maxwell was the only one to understand the work, specific concepts such as the phase rule were used fairly quickly. The first specific references to the paradoxical GP1876 did not appear in scientific publications until 1891. However, that may be explained by the fact that some physicists, such as Gibbs himself, refrained from citing other authors too often. For instance, both Maxwell and Nernst never referenced GP1876, yet discussed an incredibly similar thought experiment.

Although this chapter describes those physicists who, according to Haitun, tried to offer a solution to one of the considerations in the 1876 section, it will not be limited to that. After all, having a collection of the reactions to the paradox helps in resolving the confusion, or what Haitun called the *historical-scientific paradox*, surrounding the Gibbs paradox. The main historical actors of this period indicated by Haitun include C. Neumann, P. Duhem, H. Poincaré, O. Wiedeburg and M. Planck.² In addition to

¹Translated by the present author from [С.Д. Хайтун, 1986, р. 5]: “Очевидно, что в сложившейся ситуации решение физического парадокса Гиббса оказывается тесно связанным с решением историко-научного парадокса парадокса Гиббса”.

²[С.Д. Хайтун, 1986], or Haitun, states that in the period before 1902, six scientists offered a solution to the paradox, including Gibbs himself. These scientists, Gibbs, Neumann, Duhem, Poincaré, Wiedeburg and Planck, all worked on the paradox using thermodynamics and all assumed a discrete jump between an AA mixture and the infinitely similar AA' mixture.

Haitun's actors, the Dutch scientists J.D. van der Waals and J.J. van Laar and the English mathematical physicist J. Larmor also worked on the paradox before 1902.³

Another important actor, who did not in any way directly respond to the 1876 section within this period, is L. Boltzmann.⁴ It was he who introduced the statistical interpretation of entropy just one year after the publication of the first part of Gibbs' *Equilibrium* paper. In a response to criticism by J. Loschmidt, Boltzmann gave a new interpretation of the concepts of equilibrium and probability. Equilibrium had become defined as the most probable macrostate instead of it being a stationary state, which meant that in thermodynamic processes, there is a tendency towards the more probable states.⁵ The entropy of the macrostate could then be interpreted as $S = k \log W$, with k denoting a constant and W being the number of microstates.

Despite the reinterpretation of entropy, the responses to GP1876 within this period were mainly of a thermodynamic nature. That is, they responded to Gibbs' considerations on the thought experiment in which entropy was defined as the unavailable work. The 1876 section thus was interpreted by the actors within one branch of physics, and, subsequently, only the status of the section changed in these twenty-five or so years. To recap Gibbs' position: he focused on several considerations surrounding the concepts of the limitation of the Second Law, the macroscopic limit, the molecular constitution and the classical definition of entropy. None of the thermodynamic considerations were considered to be paradoxical by Gibbs himself.

3.1 Maxwell's Inclusion of the Concept of Reversibility

The first, non-referenced, 'response' to the paradox is one by Maxwell. Maxwell, who is now remembered mostly for his unification of electromagnetism, gained his fame with the publication of *A Treatise on Electricity and Magnetism*. It was in this publication that he introduced his differential equations. During his research on electromagnetism, Maxwell also worked out the velocity distributions of gas particles, thus being one of the first to develop the kinetic theory of gases. Maxwell is furthermore known for his thermodynamic relations, which link various thermodynamic properties to each other via second derivatives.

³Haitun credits Van der Waals with having come up with a solution in 1908, however, these earlier reactions may also be seen as presenting a particular solution to Van der Waals interpretation of the paradox.

⁴However, he did use one sentence of Gibbs' *Equilibrium* as the opening sentence of the foreword to his *Lectures on Gas Theory, Part II* (1898). This sentence was, perhaps unsurprisingly due to his definition of entropy, the one that stated that "[t]he impossibility of an uncompensated decrease of entropy seems to be reduced to improbability." According to [Klein, 1972, p. 134], Boltzmann prided himself on having cited *Equilibrium* as early as 1883, nine years prior to the publication of the German translation by Ostwald.

⁵[Uffink, 2005, p. 541].

In his 1877 paper ‘Diffusion’, Maxwell referred to a situation in which it is supposed “that we have in a vessel two separate portions of gas of equal volume, and at the same pressure and temperature, with a movable partition between them.”⁶ The set-up of this situation is identical to the one in Gibbs’ *Equilibrium*. However, that need not mean that Maxwell did not think of this idea independently. On the other hand, the fact that Maxwell cited the *Equilibrium* paper in the first paragraph of the ‘Diffusion’ paper shows that Gibbs’ work was relevant to the subject.⁷ Therefore, it may be assumed that Maxwell knew of the considerations made by Gibbs in GP1876.

Like Gibbs, Maxwell did not find the situation problematic. Instead he had some further considerations. Maxwell immediately focused on the role of molecules in a gas by stating that the molecular motion need not differ for alike and unlike gases. He then turned his attention to the idea that the gases which were thought to be alike, A and A' in the previous chapter, might be separable in the future:

It appears, therefore, that the process of diffusion does not involve *dissipation of energy* if the two gases are the same, but that it does if they can be separated from each other by a *reversible* process. Now, when we say that two gases are the same, we mean that we cannot *distinguish* the one from the other by any *known* reaction. It is not probable, but it is possible, that two gases derived from different sources, but hitherto supposed to be the same, may hereafter be found to be different, and that a method may be discovered of separating them by a reversible process. If this should happen, the process of interdiffusion which we had formerly supposed not to be an instance of dissipation of energy would not be *recognized* as such an instance.⁸

One thing to note is that Maxwell referred to entropy as ‘dissipation of energy’. A few years prior to this, Gibbs had pointed out, in one of his earlier publications, that P.G. Tait, and by proxy Maxwell, misunderstood Clausius’ definition of entropy. A letter from Maxwell to Tait from the 1st of December 1873 confirms that Maxwell acknowledged that he had used the wrong definition.⁹

The paragraph written by Maxwell once again indicates that distinguishability depends on our knowledge of the properties of a substance and the processes that are involved. As a matter of fact, the later discovery of the existence of ions would prove Maxwell right. More so than Gibbs, Maxwell paid attention to the separation for reversible processes.

⁶[Maxwell, 1890, pp. 644–646].

⁷Maxwell furthermore greatly appreciated Gibbs’ work. A letter to L. Campbell mentions him making the thermodynamic surface model referred to in chapter 2. L. Campbell and W. Garnett (1884). *The life of James Clerk Maxwell : with selections from his correspondence and occasional writings*, London: Macmillan.

⁸[Maxwell, 1890, pp. 645–646].

⁹The letter has been reproduced in the second volume of *The Scientific Letters and Papers of James Clerk Maxwell* on page 944.

Whereas Gibbs did not mention anything about reversibility, Maxwell made it a key element in his consideration on the dissipation of energy. Neither the branch of physics in which it is described nor the status of GP1876 has changed with Maxwell's contribution. The only addition by Maxwell is the association of the concept of reversibility with the supposedly paradoxical section written in 1876.

3.2 Neumann's Indication of a Discrepancy

Carl Gottfried Neumann is one of the lesser known physicists in this chapter. He is, perhaps, better known as a mathematician. In his lifetime, Neumann concerned himself with geometric series, economic thermodynamics, electrodynamics, Bessel functions and hydrodynamics. He is recognized as a creator of the theory of integral equations and the co-founder of the journal *Mathematische Annalen*.¹⁰ An early publication on thermodynamics are his lectures *Vorlesungen über mechanische Theorie der Wärme* in 1875. In this book, Neumann summarized and built upon the work of, among others, Carnot, Clapeyron, Mayer, Clausius and Thomson.

Years later, in 1891, Neumann published his *Bemerkungen zur mechanischen Theorie der Wärme* in which he combined his distrust of the concept of entropy with Gibbs' GP1876. He regarded entropy as both unnecessary and ambiguously defined. Like Gibbs and Maxwell, he imagined a situation in which gases in two equal volumes are diffused into each other. Also like Gibbs, he defined the entropy of mixing difference as being dependent only on the quantity of the gases, or $S_{AB} = (MR + MP)\theta \log 2$.¹¹

Neumann was the first to indicate that one of Gibbs' considerations could be problematic. He mostly was bothered by Gibbs' claim that the entropy difference should be zero when the gases are alike:

Trotz alledem aber heftet sich an den Satz (23.) ein gewisses Misstrauen, in Folge des Umstandes, dass derselbe ungültig wird, sobald M und M zwei Quantitäten desselben Gases z.B. zwei Quantitäten Sauerstoff sind. Alsdann nämlich sind, falls man überdies unter einander *identisch*, so dass also in diesem Falle die in Betracht kommende Arbeit $S_{AB} = 0$ ist, während sie doch, zufolge des Satzes (23.), den Werth

¹⁰[Disalle, 1993].

¹¹Both R and P are constants while M is the quantity of gas and θ is the temperature.

$2MR\theta \log 2$ haben sollte. Man vgl. übrigens gewisse hier einschlagende Betrachtungen von Gibbs [...], durch welche aber in meinen Augen die hier *vorhandene Dunkelheit* nicht ganz beseitigt wird.¹²

Thus, in Neumann's eyes, the calculated value should be equal to the one Gibbs reached by reasoning. The discrepancy between the two values shows, according to Neumann, that the concept of entropy is too ambiguous. Neumann thus introduced the idea that GP1876, with its discrepancy between the calculated and reasoned values, is obscure to some extent.

3.3 Duhem's and Poincaré's Entropy Principles Revisions

The acclaimed Pierre Duhem was not only a physicist and mathematician; he is also regarded as a historian and philosopher of science. For that reason, Duhem not only worked on hydrodynamics and thermodynamics, he also wrote about the indeterminacy of the criteria in experimental physics. His first scientific publication, in 1886, already concerned itself with the entropy of gas mixtures.¹³ In this work, in which he mainly treated thermodynamic potentials, Duhem discussed the legacy of F. Massieu, Gibbs and Helmholtz in connection to these potentials. Within the two chapters devoted to Gibbs, Duhem noted that the formulas are catered towards ideal gases. Despite this, Duhem thought that the ideal gas laws describe the processes sufficiently in most cases. He concluded that Gibbs' theory, taken as a whole, seems satisfactory in describing chemical perturbations of gases.¹⁴

In 1886, Duhem had concluded that the entropy of a gas mixture need not be the sum of the gas components. Subsequently, in 1892, he had worked out some ideas of his earlier work regarding the concepts related to the paradoxical GP1876.¹⁵ Within those six years, Duhem had collected evidence for his idea that the mixing of identical gases should not be considered a mixing at all. Assuming that AA is a mixture will lead to a logical fallacy as a mixture necessarily implies the presence of at least two different substances. Even if it were not, the mixing of ideal gases should not be considered anything but an

¹²[Neumann, 1891, p. 129]. ("Despite all this, a certain mistrust attaches itself to equation (23), this is due to the fact that the same is valid as soon as M and M are two quantities of the same gas, for example, when two quantities are oxygen. Then they are identical to each other; so that in this case the work under consideration $S_{AB} = 0$, while, according to equation (23), they should have the value of $2MR\theta \log 2$. We compare, incidentally, certain striking considerations of Gibbs [...], by which, however, in my view, the existing darkness is not entirely eliminated.")

¹³[Duhem, 1886].

¹⁴[Duhem, 1886, p. 48]: "La théorie de M. Gibbs, fondée uniquement sur les lois relatives aux gaz parfaits, paraît rendre compte d'une manière très satisfaisante de l'allure générale des phénomènes chimiques présentés par les substances gazeuses."

¹⁵[Duhem, 1892].

abstraction because real gases are not fully described by it. His discussion of GP1876 was focused on discrediting Gibbs' definition of the mixing of gases in which the mixing of any two gases leads to a mixture.

At an early point in this analysis of Gibbs' definition, Duhem pointed to Neumann's discussion of GP1876: "Dans un récent et très important écrit, dont une bonne partie est consacrée à l'étude de cette définition, M. Carl Neumann signale une conséquence *paradoxe* de cette définition."¹⁶ Duhem here introduced the term *paradox* in connection to GP1876. In Duhem's opinion, by accepting Gibbs' definition, in which the diffusion of alike gases also leads to a mixture, one ends up with faulty derivations. In the case of the thermodynamic potentials, Duhem showed that Gibbs' definition leads to both external and internal inconsistencies.

Si l'on applique les formules relatives au mélange de deux gaz au cas où les deux gaz sont *identiques*, on peut être conduit à des *résultat absurdes*. [...] Donc la définition de M. Gibbs est *inacceptable*. [...] La majeure de ce *syllogisme* doit être niée. La notion de mélange de deux gaz différents quelconques ne peut, en aucun cas, être regardée comme impliquant la notion de mélange de deux gaz de même nature. [...] Donc toute définition acceptable d'un mélange de deux gaz quelconques doit, a priori, conduire à des résultats absurdes si l'on veut rappliquer au mélange de deux masses du même gaz. Nous ne devons pas nous étonner que la définition de M. Gibbs soit soumise à cette *loi*.¹⁷

So, according to Duhem, defining a 'mixture' of alike gases as a mixture is a logical fallacy. It simply makes no sense to talk about the diffusion of a gas into itself. Therefore, any definition which allows this will lead to inconsistencies. Although both Neumann and Duhem noted something problematic about GP1876, they indicated two different paradoxical elements. Unlike Neumann, who focused on entropy and the discrepancy between the calculated and the reasoned value, Duhem disagreed with the idea that identical gases can be mixed. To him, the discrepancy between the values was still paradoxical, but the cause of this is in the mixing of identical gases not in the definition of entropy. In any case, both Neumann's and Duhem's interpretations showed familiarity with GP1876 and other parts of Gibbs' *Equilibrium*.

¹⁶[Duhem, 1892, pp. 52–3]. ("In a recent and very important paper, much of which is devoted to the study of this definition, Mr. Carl Neumann noted a paradoxical consequence of that definition.")

¹⁷[Duhem, 1892, pp. 53–5]. ("When one applies the formulas relating to the mixture of two gases to two identical gases, absurd results are obtained. [...] Thus, the definition of Gibbs is unacceptable. [...] Most of this syllogism should be denied. The notion of a mixture of two different gasses cannot, under any circumstances, be regarded as involving the notion of mixing two gases with the same nature. [...] So any acceptable definition of a mixture of any two gases must, in principle, lead to absurd results when one wants to reapply it to a mixture of two masses of the same gas. We should not be surprised that the definition of Gibbs is subject to this law.")

In 1898, Duhem again discussed GP1876, however, the discussion largely remained the same. In fact, the above citations can also be found in this work.¹⁸ Duhem demarcated his discussion of Gibbs' definition of gas mixtures by adding a subtitle: "Objection à la définition précédente – Paradoxe de J.W. Gibbs". With this subtitle, Duhem, more so than in 1892, clearly stated that he considered the idea of an alike gas mixture paradoxical. Naturally, the argument that Gibbs' definition – which contains the assumption that alike gas mixtures exist – leads to internal and external inconsistencies in concepts such as the thermodynamic potentials is repeated in this account. In comparison to 1886, Duhem also put a stronger focus on the uniqueness of a gas. Duhem would be one of the few physicists to return to the paradoxical GP1876 around the turn of the century. A reason for this might be the mutual responses of Duhem and Poincaré to each other's works.

Henri Poincaré, like Duhem, was not only involved in mathematics and physics. He too engaged himself in philosophy of science. Poincaré is known for the many concepts and theorems named after him. Examples of this are the Poincaré conjecture, the Poincaré recurrence theorem, and the Poincaré space. Poincaré usually only concentrated on a specific subject for a short period of time, allowing him to work in many fields; thermodynamics was no exception to this. He based his main work, *Thermodynamique*,¹⁹ on lectures given in the late 1880s. Poincaré's book contained a considerable amount of mathematics and not so much mechanics, something most physicists were not used to. In fact, this prompted another physicist, by the name of Peter Guthrie Tait, to write a somewhat scathing review in which he stated that the book did not live up to its expectations.²⁰

Poincaré is included in this chapter, despite not discussing the paradoxical GP1876, because of his calculations on the diffusion into mixtures and his later influence on the paradox. Poincaré largely agreed with Duhem's work, only discussing a few of Duhem's assertions. Poincaré wrote the following about Duhem at the end of his preface:

J'ai eu deux fois l'occasion d'être en désaccord avec M. Duhem; il pourrait s'étonner que je ne le cite que pour le combattre, et je serais désolé qu'il crût à quelque intention malveillante. Il ne supposera pas, je l'espère, que je méconnais les services qu'il a rendus à la science. J'ai seulement cru plus utile d'insister sur les points

¹⁸[Duhem, 1898a, pp. 267–269].

¹⁹[Poincaré, 1892].

²⁰Tait, *Nature* (45, 1892, p.246) for the review. Poincaré's response to Tait may be found in the same volume, *Nature* (45, 1892, pp.414–415).

où ses résultats me paraissaient mériter d'être complétés, plutôt que sur ceux où je n'aurais pu que le répéter.²¹

One point on which Poincaré did disagree with Duhem was his derivation of the expression for the entropy of a gas mixture. In his *Thermodynamique*, Poincaré calculated the entropy of mixing for several quantities in a section of twenty pages and subsequently attempted to refute Duhem's principle of entropy addition.

Mais, bien que les conséquences de la formule précédente ne soient contredites par aucune expérience et soient même confirmées par quelques-unes, la théorie de M. Gibbs ne peut être acceptée sans *restriction*, la seconde des propositions qui lui servent de base reposant sur une hypothèse *absolument arbitraire*, l'hypothèse de M. Duhem. Il est facile de se rendre compte de l'arbitraire de cette hypothèse.²²

That is, Poincaré believed that there is some arbitrariness to the entropy of mixing and that it is related to the idealization of gases. Furthermore, he wanted to restrict Gibbs' theory to more genuine experiences. Poincaré calculated the difference between the entropy change in terms of temperature and volume, $S(v, T)$, and the entropy change in terms of pressure and volume, $S'(v, p)$. The value turned out to be non-zero, thus, in Poincaré's view, displaying the mentioned arbitrariness. His work on diffusions paved the way for interest in the experimental verification of the 1876 thought experiment. The combined force of Duhem and Poincaré thus steered the discussion of GP1876 towards experimental verification.

3.4 Nernst's Experimental Limit

Walther Nernst, a German physicist known for his accomplishments in chemical thermodynamics, is quite an interesting case. He is said to have possessed a keen and imaginative intuition for which thermodynamic processes were both experimentally feasible and credible.²³ This was, for one, used to theorize about the implications of the calculation of chemical affinity as embodied in the Third Law of thermodynamics. It also is visible in his discussion on interdiffusion.

²¹[Poincaré, 1892, p. xix]. ("I have had two opportunities to disagree with Duhem; it may come as a surprise that I wrote this to contend his view, and I would be sorry if he believed it to be out of some malicious intent. I hope that he does not assume that I have forgotten about the services he has rendered to science. I only believe that it would be more helpful to emphasize the points where its results, to me, seem to deserve to be complemented, rather than those where I could not repeat that.")

²²[Poincaré, 1892, p. 325]. ("However, although the consequences of the above formula are not contradicted by any experience and a few of them have even been confirmed, Mr. Gibbs's theory cannot be accepted without restriction, the second of the propositions that serve as its base rests on a totally arbitrary assumption, the hypothesis of Duhem. It is easy to realize the arbitrariness of this assumption.")

²³[Hiebert, 1983].

According to Haitun, Nernst did not directly address the paradox, but he did steer the discussion in another direction because he had shown that it would be impossible to verify the thought experiment. Haitun based this off a Russian translation of Nernst's work which had been published in 1904, and therefore believed Nernst to have offered this insight in 1904. However, the earlier German and English versions contain the same arguments, images and formulas. The first edition of *Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik*, published in 1893, could therefore also be indicated as Nernst's first contribution to the broader understanding of the context surrounding the paradox.

One of Nernst's first moves in the section on diffusion was to state his point of view on molecules and their relation to physics and chemistry: "In terms of the molecular hypothesis, physical mixtures differ from chemically simple substances, in that the latter consist of the same kind of molecules, while the former consist of different kinds of molecules."²⁴ However, like Maxwell, Nernst did not specifically refer to Gibbs in his analysis. In fact, he only referred to Rayleigh and Boltzmann, and that in connection to their formula for the work performed in an expansion-diffusion:

$$w = w_1 + w_2 = RT(n_1 \ln \frac{v_1 + v_2}{v_1} + n_2 \ln \frac{v_1 + v_2}{v_2}).^{25} \quad (3.1)$$

In Gibbs' thought experiment, where the subvolumes are of equal size, this equation is reduced to

$$w = nRT \ln 2.$$

Because the internal energy of the system does not change due to its constant temperature, the fundamental thermodynamic relation is reduced to

$$dS = \frac{\delta w}{T} = \frac{pV}{T} \ln 2.$$

The result obtained from equation (3.1) thus is in accordance with Gibbs' entropy of mixing.

One element of *Equilibrium* Nernst did use was Gibbs' phase rule. A reason for him to not include other elements may have been his dislike for abstract mathematics. Although he considered Gibbs' work to be very thorough, "the calculations of this author have a character which is entirely too generalized to be capable of a simple and direct application to special cases of investigation."²⁶

²⁴[Nernst, 1904b, p. 100].

²⁵[Nernst, 1904b, pp. 100–105], n denotes the number of molecules and v denotes the subvolumes. Important to know for this thesis is that R may either denote a specific or universal gas constant. The difference between the two lies in a division by the molar mass. Nernst originally used a capital A to denote the quantity work, this was changed by the present author to avoid confusion.

²⁶[Nernst, 1904b, p. 608].

In the fourth chapter of his book, Nernst focused on the properties of what he called the physical mixture. Immediately, he noted that a mixture has to consist of different substances, meaning that it has to be made up of different kinds of molecules. He then discussed what he considered the easiest case of mixing: mutual interpenetration, or interdiffusion. Because of the lack of chemical action associated with diffusion, the properties of the individual components remain unchanged. That is, according to Nernst, the gases behave as though the other gas is not present. He immediately imagined a situation in which two gases diffuse into each other at a constant temperature and with a constant total volume. The gases can, subsequently, be separated with semi-permeable membranes, a tool which Nernst noted to have been proved valuable shortly before 1893. He even drew two images of the situation, which have been replicated in figure 3.1.

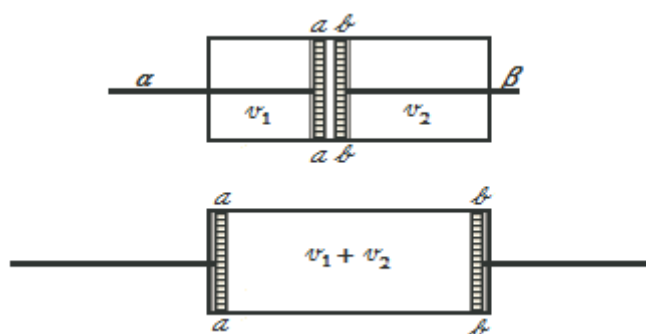


FIGURE 3.1: Diffusion and separation via semi-permeable pistons as drawn by Nernst.

As in figure 2.2, one of the piston membranes is permeable for gas *A*, while the other is only permeable for gas *B*. When the pistons are pushed up close to each other, both pistons will experience a pressure from the gas to which they are not permeable. As a result, assuming that there is no friction between the pistons and the container, both will move to the edges of the container resulting in a diffusion. Pushing the pistons back in to their original positions results in a separation and brings the gases back to their original volumes. This process is thus reversible and the work gained by the diffusion is given by equation (3.1).

After this calculation, Nernst started questioning the validity of this result and semi-permeable pistons in real experiments, but eventually reached the conclusion that “it is permissible to work with semipermeable partitions in all cases concerning the mingling or the separation of two gases which are chemically different.”²⁷ However, this meant that it is not possible to test the paradox in the case of the two gases *A* and *A*. The paradox can therefore not be resolved experimentally on the basis of the knowledge available from thermodynamics.

²⁷[Nernst, 1904a, p. 105].

Even if the gases were slightly different, it would still be difficult to get reasonable results. When gas A' approaches gas A in similarity, it will be more and more challenging to find membranes that are only permeable to one of the gases. Conclusively, in Nernst's account of the thought experiment, the continuous transition from the AA' mixture to the AA mixture cannot be subjected to experimental analysis. Therefore, the paradoxical leap in the entropy of mixing is immeasurable.

3.5 Wiedeburg's Introduction of a Paradoxical Continuity

Otto Wiedeburg, another lesser-known physicist, would be the one to fully bring the term 'Gibbs Paradox' to the light in his 1894 paper 'Das Gibbs'sche Paradoxon'. His publication spree was ended in 1901 by his early death. Wiedeburg's papers cover the subjects of heat theory, metals, and polarization, though the majority of his papers addressed issues in thermodynamics.

'Das Gibbs'sche Paradoxon' was one of the first papers published by Wiedeburg. Similar to Neumann, Wiedeburg considered it paradoxical that the entropy of mixing value one could calculate is not equal to the thermodynamically reasoned value in the case of alike gases.²⁸ Citing Neumann, Nernst, Duhem and Poincaré, he too imagined the thought experiment with a semipermeable partition. But even then, he discovered that the paradox remained:

Bei unserer Art der Herleitung liegt aber klar auf der Hand, wodurch dieses *paradoxe* Ergebniss zu Stande kommt. Die Annahme selbst, auf Grund deren wir den Werth von N berechneten, wird in diesem besonderen Falle zu einem Paradoxon: wir können uns doch keine Wand denken, die von einer durchaus gleichartigen Gasmasse einen nach Belieben ausgewählten Theil durchlässt, den anderen nicht. Der Begriff „halbdurchlässige Wand“ setzt an sich schon eine gewisse *endliche Verschiedenheit* der zu mischenden Gasmassen voraus, [...]. Die paradoxen Folgerungen entstehen eben erst dann, wenn man mit Gibbs Gase sich denkt, die ihrer ganzen Natur nach nur *unendlich wenig von einander verschieden* sind, und so den Fall gleichartiger Gase als stetig zu erreichenden *Grenzfall* des allgemeinen verschiedenartiger Gase auffasst.²⁹

²⁸Again, the calculated value is non-zero because the formula is independent of the nature of the gases while, on the other hand, thermodynamics tells us that the value should be zero.

²⁹[Wiedeburg, 1894, pp. 693,697]. The symbol N is equal to equation (3.1) divided by T , or δw . ("In our type of derivation it is obvious, what brings out this paradoxical result. The assumption itself, on which we calculated the value of N , becomes in this particular case a paradox: we cannot think of a wall which allows the passage of one part of an alike gas, but not the other. The term 'semipermeable wall' constitutes in itself a certain finite difference in the gas masses being mixed, [...]. The paradoxical consequences arise only when one thinks of Gibbs' gases, which by its very nature only differ infinitesimally from one another, and so conceives the case of alike gases to continually reach the limiting case of different types of gases.")

That is, it is impossible to let two different gases approach similarity in a continuous manner. There are no two gases that only differ in an infinitively small amount. Therefore, a certain discreteness in the other properties of matter should not be surprising either. In addition to this argument, Wiedeburg, like Gibbs, noted that the Second Law does not appear to be correct: “Mit anderen Worten: der zweite Hauptsatz scheine nicht absolut richtig zu sein.”³⁰ Wiedeburg thus not only further distributed the term ‘Gibbs Paradox’ by naming his article for it, he also more prominently linked the concepts of continuity and the limitation of the Second Law to GP1876.

Only a year after Wiedeburg’s publication, his work was summarized in *Journal de Physique Théorique et Appliquée* by the French physicist E. Bouty.³¹ This introduced the actual term ‘paradoxe de Gibbs’ to the French scientific community. Another year later, in a work on the applications of thermodynamics, L. Graetz referenced several works in connection to “das sogenannte ‘Gibbs’sche Paradoxon’”. This marked the first time these sources were mentioned together, allowing physicists and chemists to revisit those works thought to be relevant to the paradox.³²

3.6 Planck’s Continuous Physical Properties

The final physicist named by Haitun with an original contribution to the paradox before 1902 is Max Planck, who published the German version of his first major work, *Treatise of Thermodynamics*, in 1897. Planck now is often cited as having originated quantum theory in his work on black-body radiation. He was not immediately aware of Gibbs’ *Equilibrium* and eventually rediscovered many of his results. Nevertheless, the works may be seen as complementary because Planck focused on irreversible processes while Gibbs discussed equilibria. As Planck’s discussion of GP1876 is short, but rather recapitulatory, it will be fully recited here.

Zugleich ersehen wir, dass die durch Diffusion bedingte Vermehrung der Entropie nur von den Molekülzahlen n_1 und n_2 der diffundirenden Gase, nicht aber von ihrer Natur, z.B. ihrem Molekulargewicht, abhängt. Es macht also in Bezug auf die Entropievermehrung durch Diffusion gar keinen Unterschied, ob die Gase sich chemisch mehr oder weniger “ähnlich” sind. Nimmt man nun beide Gase identisch, so wird offenbar die Entropievermehrung Null, weil man dann überhaupt keine Zustandsänderung erhält. Daraus folgt, dass der *chemische Unterschied* zweier Gase, und überhaupt zweier Substanzen, nicht durch eine stetig veränderliche Grösse

³⁰[Wiedeburg, 1894, p. 696].

³¹[Bouty, 1895].

³²[Graetz, 1896, p. 506]. Gibbs, Neumann, Duhem, and Wiedeburg were declared to be authors discussing the paradox prior to 1895.

dargestellt werden kann, sondern dass man hier nur von sprungweisen Beziehungen: entweder von Gleichheit oder von Ungleichheit, reden kann. In diesem Umstand liegt ein *principieller Gegensatz zwischen chemischen und physikalischen Eigenschaften* begründet, da die letzteren immer als stetig veränderlich anzusehen sind.³³

Planck was not the first to note that the increase of entropy does not depend on the nature of the gases or that this may be seen as a fundamental distinction between chemical and physical properties. However, while Nernst saw the distinction in the molecular hypothesis, Planck specifically used the word ‘continuity’ to denote the distinction. In his account, where gases are *chemically* alike or unlike, only physical properties need always be continuous. As a result, the discontinuity in the entropy of mixing is not paradoxical to Planck. It should furthermore be noted that Planck considered the concepts of entropy and irreversibility to be entangled. Irreversibility can be reduced to the concept of entropy because, in most cases, an increase of the total entropy occurs when the process is irreversible. Hence, Planck’s discussion of GP1876 revolved around the concepts of continuity and reversibility.

3.7 Larmor’s Impracticably Large Diffusion Time

Joseph Larmor, a British physicist and mathematician who worked on rendering electricity, matter theory, and thermodynamics more understandable, published a paper on dynamics in 1897. Within this paper, in which he acknowledged the work of Gibbs, Maxwell(1877), and Planck(1897), he imagined the interdiffusion of two gases. In a similar fashion to Nernst, Larmor’s contribution fully focused on the concept of work instead of the concept of entropy.

If we imagined two gases in which the molecular mass differed only infinitesimally, just the same amount of work could still be gained by mixing given volumes of them in a reversible manner as if they were gases wholly unlike ; but the transpiration pressure would then be infinitesimally small and the time of transpiration infinitely great. It is thus impracticable to proceed to a limit, and no paradox is here involved such as the assertion that a finite amount of work could be gained by mixing two gases which are practically identical in properties.³⁴

³³[Planck, 1897, pp. 203–4]. The English translation of this paragraph appeared in [Planck, 1903, pp. 214–5]: (“It also appears that the increase of the entropy depends solely on the number of the molecules n_1 , n_2 , and not on the nature, *e.g.* the molecular weight, or the diffusing gases. The increase of the entropy does not depend on whether the gases are chemically alike or not. By making the two gases the same, there is evidently no increase of the entropy, since no change of state ensues. It follows that the chemical difference of two gases, or, in general, of two substances, cannot be represented by a continuous variable; but that here we can speak only of a discontinuous relation, either of equality or inequality. This fact involves a fundamental distinction between chemical and physical properties, since the latter may always be regarded as continuous.”)

³⁴[Larmor, 1897, pp. 274–75].

Larmor's discussion of the thought experiment seems very reminiscent of a process called thermal transpiration, which is a type of non-equilibrium thermodynamics. However, his contribution is not meant to indicate a thermal force on the gases due to a temperature difference. Instead, the diffusion of two different gases through semi-permeable walls is thought to establish a difference in pressure. It is the difference in pressure which ensures that there is available a certain amount of energy, which is depleted in the diffusion itself. However, as Larmor argued, it would be impossible to consider a gain in work in the mixing of alike gases A and A . Two gases which might differ only infinitesimally would lead to an immensely small transpiration pressure and so would take an immensely long time to mix, making the process practically infeasible. This is, usually, not a problem in the case of mixing A and B . However, as Larmor noted, it includes the assumption that "the gases are really different and that means exist for separating them." In addition to two gases which differ in the molecular mass, Larmor noted that the argument would also hold for the osmotic pressure of a dissolved substance and its nearly identical solvent.

Because Larmor did not link Gibbs to this excerpt, one might argue that it does not actually involve the Gibbs paradox. However, in 1902, Larmor would make the same argument and actually name it the Gibbs paradox.³⁵ For this reason, his contribution is considered a valid one to the present discussion. In conclusion, besides extending the thought experiment with solvents, Larmor tied the paradox to the notion of a diffusion rate, and therefore, to time.

3.8 Van der Waals' Identical Molecules

Johannes Diderik van der Waals was one of the first Dutch physicists to react to the Gibbs paradox. At this time, he was already known for his work on the equation of state and the Law of Corresponding States. In a meeting of the Koninklijke Akademie van Wetenschappen, a society dedicated to the advancement of science in the Netherlands, on the 30th of January 1897, Van der Waals used the paradox to answer a question on the basis of his own molecular theory of mixtures. The question, based on a remark from H.A. Lorentz on behalf of the experimental chemist A. Smits, was one on whether the molecular state of a solvent has any influence on the pressure reduction that is triggered by dissolved salts. Despite Van der Waals' focus on solvents, his address of the issue was classified by the editor as belonging to physics rather than chemistry. Van der Waals started his argument by stating the dependence of his theory on Gibbs' *Equilibrium*:

Die theorie gaat uit van de onderstelling van de juistheid van de regels omtrent het evenwicht door Gibbs opgesteld; en wel in het bijzonder van de stelling, dat een

³⁵[Larmor, 1902].

gegeven hoeveelheid stof zich bij gegeven temperatuur in een gegeven ruimte aldus schikt, dat de gezamenlijke waarde van de vrije energie een minimum is – en aan de juistheid van dat beginsel kan wel niet getwijfeld worden. Verder wordt in die theorie om de waarde der vrije energie voor mengsels te vinden evenzeer de juistheid aangenomen van wat wel eens het Gibbs'sche paradox genoemd wordt – en dat hierop neerkomt, dat voor een mengsel van stoffen in verdunnen gastoestand de entropie gevonden kan worden door de som der entropieën, die men verkrijgen zou door elk dier gassen alleen in die ruimte te denken. Ook aan de juistheid van dezen regel kan niet getwijfeld worden. De overeenstemming van de theorie met wat de ervaring tot hiertoe heeft geleerd is zoo groot, dat afgezien nog van alle redeneeringen die voor de juistheid pleiten, twijfel ongeoorloofd schijnt. [...] Zooals ik hiervoor reeds aangeduid heb, wordt de wijziging die verschillende molekuulgroepeeringen aan de waarde van ϕ geven met behulp van het Gibbs'sche paradox bepaald.³⁶

Van der Waals interpretation of what he called the ‘Gibbs’sche paradox’ is quite interesting as it does not fit any of the other interpretations mentioned in this chapter. Instead of referring to the comparison between the *AB* and the *AA* mixtures, he referred to the concept of molecules and the additivity of entropy, equation (2.1), using it to give a value to his free energy function, $\phi(x)$.³⁷ Naturally, as this report was not written by Van der Waals himself, one might surmise that this address was shortened and does not contain his full argument. In any case, Van der Waals considered the additivity and extensivity of entropy to be beyond any doubt. In this meeting of January 1897, several prominent researchers working in the field of thermodynamics were present and thus familiarized with the term Gibbs paradox.³⁸

A synopsis of Van der Waals argument made available in French by the Dutch mathematician P.H. Schoute in two different journals, *Revue générale des sciences pures et appliquées paraissant* and *Bulletin des sciences mathématiques et astronomiques*, held

³⁶[Waals, 1897, pp. 342–4]. (“That theory is based on the assumption of the correctness of the rules regarding the equilibrium by Gibbs; in particular the argument that a given amount of substance for a given temperature in a given space adapts in such a way, that the combined value of the free energy is a minimum – and the validity of this principle cannot be doubted. Additionally, in finding the value of the free energy for mixtures, the correctness of what is sometimes called the Gibbs’sche paradox is assumed – which comes down to that, for a mixture of substances in a diluted gaseous state, the entropy can be found by the sum of the entropies, which one could obtain by imagining each of the gases as being alone in that space. Also the validity of this rule cannot be doubted. The agreement between theory and what the experience has taught is so great, that apart from all the reasoning in favor of the correctness, doubt seems impermissible. [...] As I have already indicated, the change that the various molecule groups assign to the value of ϕ is determined by the paradox of Gibbs.”)

³⁷Van der Waals’ function: $\phi(x) = MRT[(1-x)\log(1-x) + x\log x]$, where x denotes the ratio of the gases in the mixture. If both gases take up half of the total volume, then $\phi(x) = 0$.

³⁸The attendees include Van Bemmelen, Engelmann, J.A.C. Oudemans, Kamerlingh Onnes, Lorentz and Van de Sande Bakhuijzen.

the same interpretation of the Gibbs paradox.³⁹ In 1900, Van der Waals himself would publish a French article on the subject, delving further into the relation of his theory with the Gibbs paradox.

Cette valeur de $\phi(x)$ montre qu'elle est aussi indépendante de la nature des composants; observation important, parce que cette propriété de $\phi(x)$ expliquera les lois connues des solutions diluées. Quand on pose $\phi(x)$ indépendante de la nature des molécules mélangées, il faut faire exception pour le cas où les deux composants seraient identiques. On pourrait regarder une substance simple comme un mélange de $(1-x)$ et x molécules identiques. Mais, dans ce cas, il faut poser $\phi(x) = 0$; c'est pour cette raison qu'une parle quelquefois de paradoxe de Gibbs. M. Wiedeburg a essayé d'expliquer le paradoxe par l'emploi de parois semi-perméables don't on pourrait faire usage dans le cas de molécules entre lesquelles il y a une différence, mais qui ne peuvent servir dans le cas de molécules identiques, la fonction $-\phi(x)$ représentant l'accroissement de l'entropie dans la diffusion. A la rigueur, c'est une question qu'on pourrait passer sous silence dans notre théorie, parce que toutes les conséquences auxquelles nous parviendrons seront aussi applicables dans *le cas de molécules identiques*.⁴⁰

The paradox is, in this account, associated with the independence of the nature of the gases and the case of the *identical molecules*. With the inclusion of identical molecules, Wiedeburg's semi-permeable walls would not be able to make a distinction. Therefore, assuming that $-\phi(x)$ represents the increase of entropy in the diffusion, there will not be an increase of entropy for identical molecules and gases. In this paragraph, Van der Waals thus explained, on the assumption of identical gases being made up of identical molecules, why there is a difference in the entropy of mixing for alike gases AA and infinitely similar gases AA' . Another paper in the same publication also made a short reference to the paradox in connection with semi-permeable walls. J. Perrin, later known for his work on proving the existence of atoms, wrote that Carnot's principle may be

³⁹[Schoute, 1897, pp. 219–20] and [Schoute, 1898, pp. 106–7]: “Puis, pour trouver l'énergie libre des mélanges, elle accepte le paradoxe de Gibbs en admettant qu'on trouve l'entropie d'un mélange de matières gazeuses rares contenues dans un espace en prenant la somme des entropies qui correspondent aux divers cas de ce même espace contenant chacune de ces matières l'une après l'autre.”

⁴⁰[Waals, 1900, p. 592]. (“This value of $\phi(x)$ shows that it is also independent of the nature of the components; an important observation, because the $\phi(x)$ property explains the known laws of dilute solutions. When we set $\phi(x)$ to be independent of the nature of mixed molecules, we must make an exception for cases in which the two components are identical. One could look at a simple substance as a mixture of $(1-x)$ and x identical molecules. But in this case, one has to put $\phi(x) = 0$; it is for this reason that one sometimes speaks of Gibbs paradox. Mr. Wiedeburg tried to explain the paradox by using semi-permeable walls which one could use in the case of molecules between which there is a difference, but which cannot be used in the case of identical molecules, the function $-\phi(x)$ then represents the increase in entropy in the diffusion. Strictly speaking, this is a question that could be ignored in our theory, because all the consequences achieved will also be applicable in the case of identical molecules.”)

applied to a reversible mixing process with semi-permeable walls without being bothered by the Gibbs paradox.⁴¹

Another year later, Van der Waals, again, published an article containing a reference to the Gibbs paradox.⁴² The argument in this is much more similar to the 1987 rendition of his argument than to the 1900 rendition.

Dans ma théorie je pars de cette hypothèse, que les règles d'équilibre établies par M. W. Gibbs sont absolument exactes ; je me base en particulier sur ce théorème que, dans un espace donné et à température déterminée, une quantité donnée de matière se distribue de telle façon que la valeur totale de l'énergie libre est un minimum ; et l'exactitude de ce principe doit être regardée comme hors de doute. Dans cette théorie j'admets en outre, pour trouver la valeur de l'énergie libre d'un mélange, l'exactitude de ce que l'on appelle parfois le paradoxe de Gibbs, et qui consiste en ceci, que pour un mélange de substances gazeuses très diluées l'entropie est égale à la somme des entropies que l'on trouverait si chaque gaz remplissait séparément l'espace. C'est là encore un principe dont l'exactitude est indubitable.⁴³

The similarity between this and his earliest rendition may perhaps suggest, assuming that the 1900 and 1901 renditions are compatible, that Van der Waals already implicitly invoked the concepts of identical molecules and semi-permeable walls in the 1897 rendition. His confidence in Gibbs' derivations, had, in any case, not wavered.

Despite the fact that Van der Waals wrote on the subject multiple times, Haitun did not classify his early responses to the paradox as a solution, unlike his response in 1908.⁴⁴ This may simply be because Haitun may not have been familiar with this work by Van der Waals. There are, anyhow, no references to Van der Waals' publications in Haitun's *History of the Gibbs Paradox* from prior to 1908. Nonetheless, from the excerpts denoted in this section, it ought to be clear that Van der Waals' interpretation of the Gibbs paradox was quite a twist from the usual interpretations in this period.

⁴¹[Perrin, 1900, pp. 544–5]: “Réciproquement, on peut la faire pénétrer dans le mélange par voie réversible. On conçoit ainsi comment, au moyen de parois semi-perméables, on peut effectuer réversiblement des séparations et des mélanges. D'autre part, il est aisé de calculer le travail extérieur correspondant. Il pourra donc être particulièrement facile d'appliquer le principe de Carnot. Au moyen de raisonnements de ce genre qu'il n'y a pas lieu de détailler ici, on calcule aisément, sans être gêné par le paradoxe de Gibbs, le potentiel thermodynamique et l'entropie des mélanges de gaz ou de matières dissoutes.”

⁴²[Waals, 1901].

⁴³[Waals, 1901, p. 332]. (“In my theory I start from this assumption that the equilibrium rules established by M.W. Gibbs are absolutely correct; I rely particularly on this theorem that in a given space and given temperature, a given amount of material is distributed so that the total value of the free energy is a minimum; and the accuracy of this principle must be regarded as beyond doubt. In this theory I admit also to find the estimate of the free energy of a mixture, the accuracy of what is sometimes called the Gibbs paradox, which consists in this, that for a mixture of very dilute gaseous substances the entropy is equal to the sum of the entropies would be found if each gas separately filled space. This again is a principle whose accuracy is unmistakable.”)

⁴⁴[Waals, 1908].

3.9 Van Laar's Diffusion Tendency

Van der Waals would not be the only Dutch scientist to refer to the paradox in the period 1876–1902. One of his students, the chemist Johannes Jacobus van Laar who is known for his equation of chemical activity, wrote on the subject at least four times, in 1898, 1901, 1905, and 1908. In addition to Van der Waals, Van Laar also worked with Van 't Hoff and Bakhuis Roozeboom. In both the 1898 paper and the 1901 book, Van Laar's goal was to study equilibria in dissolutions with Gibbs' methods as adapted by Planck. The title of the second chapter of both works translates to 'Planck's entropy separation and the Gibbs Paradox', indicating that the paradox did play a significant role in Van Laar's work.

Unlike Van der Waals, Van Laar did not focus on the addition of entropy and the inclusion of semi-permeable walls. Instead, in Van Laar's account, the increase in entropy, $R \sum (n_i \log c_i)$,⁴⁵ is caused by the fact that, before the mixing the two gases can only spread through the partial volumes, while after mixing they may spread throughout the combined volume. And so, the removal of the partition, which starts the expansion-diffusion process, results in the increase of the total entropy. Therefore, Van Laar reasoned that the non-increase of the entropy of mixing for identical gases is obvious because the molecular volume remains the same.⁴⁶ Still, Van Laar did consider GP1876 to be paradoxical:

Néanmoins il se trouve dans cela quelque chose de paradoxale. Car si les deux gaz ne diffèrent chimiquement que très peu, il y aura toujours la même augmentation de l'Entropie [...]; tandis que cette grandeur s'évanouit aussitôt que les gaz deviennent tout à fait identiques. Pourtant de tels exemples de fonctions discontinues ne sont pas exceptionnels. En dernière instance l'accroissement de l'Entropie résulte de *la tendance de diffusion* des deux gaz: quand les gaz sont identiques, cette tendance cesse d'exister; tandis qu'elle se maintient dans toute son intensité, lorsque les gaz diffèrent chimiquement, quelque faible que soit apparemment la différence. Souvent cette contradiction apparente est nommée *le Paradoxe Entropique de Gibbs*.⁴⁷

⁴⁵Where R is the non-specific gas constant, n is the number of molecules, and c is the molecular concentration.

⁴⁶That is, for x moles of gas A in the partial volumes $\frac{1}{2}V$, we have $\frac{1}{2x}V + \frac{1}{2x}V = \frac{1}{x}V$. Thus, the sum of the molecular volumes of the partial volumes equals the molecular volume of the total volume for the 'mixture' AA .

⁴⁷[Laar, 1898, pp. 11-12]. ("Nevertheless there is in this something paradoxical. For if the two gas chemically differ very little, there will always be the same increase of Entropy [dots]; whereas this quantity vanishes as soon as the gases become quite identical. Yet such examples of discontinuous functions are not exceptional. Ultimately, the increase of entropy results from the distribution tendency of the two gases: When the gases are identical, this tendency ceases to exist; while it remains in all its intensity, when the gases chemically differ, however weak apparently the difference. Often this apparent contradiction is called the Entropic Gibbs Paradox.")

According to Van Laar, the entropy of mixing not being zero no matter how small the chemical difference between the gases A and A' is what is called the “Entropic Gibbs Paradox”. The discontinuity pointed out by Planck is not exceptional, the disappearance of the diffusion tendency in the case of chemically identical gases, on the other hand, is. Van Laar reiterated this point three years later in his *Lehrbuch der mathematischen Chemie*, stating that the difference only disappears when the gases are identical.

Es liegt darin in gewissem Sinne etwas Paradoxales. Denn sind die Gase Chemisch auch noch so wenig verschieden, so bleibt nach der Mischung immer eine *endliche* Entropieänderung - $R \sum n_1 \log c_1$ bestehen, welche Grösse sofort verschwindet, wenn im Grenzfall die Gase identisch werden. In letzter Instanz steht die Entropievermehrung mit dem *Diffusionstrieb* der Gase in Beziehung. Nun hört bei vollständiger Identität der Gase dieser Trieb zu bestehen auf, während dieser bei, sei es noch so geringer Verschiedenheit der Gase in seiner ganzen Intensität bestehen bleibt.⁴⁸

Naturally, the gases are meant to be identical in the thermodynamic sense, not in the dynamical sense. Both of Van Laar’s statements of the entropic Gibbs paradox are thus similar to the interpretations of Wiedeburg in 1894 and Van der Waals in 1900, with the focus being on the difference between the diffusion tendencies and entropies of the mixtures AA and AA' . Between Van der Waals, who was cited by Schoute, and Van Laar, who worked with Bakhuis Roozeboom and Van ’t Hoff, it appears that quite a large amount of the prominent Dutch scientists were aware of the Gibbs paradox by the turn of the century. This is perhaps not surprising, as the Netherlands in particular was favorable of Gibbs’ work, especially of his phase rule.

3.10 Ostwald’s and Le Châtelier’s Influence on Gibbs’ Reach

Lastly, two figures responsible for the further distribution of Gibbs’ *Equilibrium* by translating it into German and French are Ostwald and Le Châtelier. Ostwald, who called Gibbs the founder of chemical energetics, was one of the chemists responsible for the establishment of physical chemistry as a scientific discipline. He is recognized for his theoretical and experimental work on chemical equilibria and his opposition to atom theory. Ostwald learned of Gibbs’ *Equilibrium* in the mid-1880s. From that point onwards, he began to use elements such as the phase rule within his works on

⁴⁸[Laar, 1901, p. 7]. (“There is, in a sense, something paradoxical about this. Because the gases differ chemically ever so slightly, so remains after mixing always a finite entropy - $R \sum n_1 \log c_1$, which vanishes immediately in the limit where the gases become identical. In the last instance, the entropy increase is related to the diffusion tendency of gases. Now when the gases are completely identical, this tendency ceases to exist, while it remains in all its intensity, when the gases chemically differ, however weak apparently the difference.”)

physical chemistry. In 1892, he published the German translation of *Equilibrium* after deliberating with Gibbs on the subject for some 5 years.⁴⁹ Ostwald, in this period, was the main advocate of Gibbs' ideas in Germany.

The French translation was published in 1899 by Le Châtelier. Le Châtelier, known for his principle of chemical equilibrium, made use of Gibbs' *Equilibrium* as early as 1888 in the approach of equilibrium conditions in industrial reactions.⁵⁰ The decision to translate Gibbs' work had come after Le Châtelier had worked with Gibbs' mathematical formalization of systems in equilibrium for nearly a year. He would then, together with Duhem, promote Gibbs' ideas in France in a similar fashion to Ostwald in Germany.

The German translation by Ostwald is more true to Gibbs' *Equilibrium* than Le Châtelier's French translation, perhaps due to the communication between Ostwald and Gibbs. For example, Gibbs' famous phrase "[t]he impossibility of an uncompensated decrease of entropy seems to be reduced to improbability" is translated by Ostwald to "[m]it anderen Worten, die Unmöglichkeit einer nicht compensirten Abnahme der Entropie scheint auf eine Unwahrscheinlichkeit reducirt zu sein" while Le Châtelier's "[e]n d'autres termes, une diminution d'entropie semble être bien improbable" is much shorter and more trivial. Both translations contain small errors within the formulas used in GP1876. Ostwald miswrote a factor 2 as a subscript indice in the derivation of equation 2.2 and Le Châtelier accidentally replaced an addition operator with a subtraction operator. Both mistakes would, if used in further calculations, lead to a different ΔS_{AB} .⁵¹ However, these mistakes were not copied by other actors responding to the paradox between 1876 and 1911.

As mentioned in section 2.3.3, a common overstatement is that Gibbs' work was largely unknown or ignored until the translations by Ostwald and Le Châtelier.⁵² Although the translation definitely made *Equilibrium* more accessible in Europe, the *Transactions of the Connecticut Academy* was not nearly as obscure as has been stated in those overstatements. Furthermore, the reprints sent by Gibbs had already established him his desired reputation among chemists and physicists. If anything, his work remained largely unappreciated because it was not understood.⁵³ Nonetheless, the reach of Gibbs' *Equilibrium* was, to some extent, enlarged by both translations.

⁴⁹The first letter from Ostwald to Gibbs, sent in April 1887, pleads for a German translation in order to make *Equilibrium* more accessible. Gibbs, who corresponded with both Ostwald and Veit & Co about the translation in 1888 and 1889, eventually allowed Ostwald to translate it.

⁵⁰[Servos, 1996, p. 333].

⁵¹In the case of Ostwald, if $m_1 a_1 = \frac{pV}{1t}$ and $m_2 a_2 = \frac{pV}{2t}$, then $\Delta S_{AB} = (\frac{pV}{1t} + \frac{pV}{2t}) \log 2 = \frac{3pV}{2t} \log 2$. For Le Châtelier, if $\Delta S_{AB} = (m_1 a_1) - m_2 a_2) \log 2$, then $\Delta S_{AB} = (\frac{pV}{2t} - c = 0$.

⁵²Examples of this overstatement include [Crowther, 1937], [Servos, 1996], and, unsurprisingly, the English Wikipedia page on *Equilibrium*.

⁵³For example, chemist M.M. Pattison Muir wrote to Gibbs in 1880 that he only understood *Equilibrium*'s merit after he had Maxwell translate it to understandable jargon.[Wheeler, 1962, p. 86-87].

3.11 Analysis of the Paradox Interpretations

In section 2.4, the conclusion was reached that Gibbs' interpretation of GP1876 was nothing more than a series of considerations on the concept of entropy. In the period discussed in this chapter, the interpretation of GP1876 shifts from being a series of considerations to becoming a paradox. Although the reactions of the historical actors all refer to the difference in behavior of alike and unlike gases, they do not all indicate the same concept as being paradoxical.

At this point, additional useful input on paradoxes to include is D.A. Cubic's work on scientific paradoxes, although it must be noted that he has a specific interpretation of the Gibbs paradox himself.⁵⁴ He classified the Gibbs paradox as a paradox with both false assumptions and a false conclusion due to some mathematical predictions contradicting real events. Even though he does not acknowledge multiple interpretations of the paradox, Cubic's description does fit with some of the interpretations given in this chapter. His ideas will therefore be alluded to when needed.

Maxwell, the first historical actor in this chapter, paraphrased the diffusion-expansion thought experiment and tied it explicitly to the concept of reversibility. Instead of focusing on entropy, he described the diffusion process, more resolutely than Gibbs, through the notions of separability and distinguishability. Maxwell did not indicate any inconsistencies and instead addressed the ability of the thought experiment to accommodate for yet undiscovered differences in gases thought to be alike. For this reason, Maxwell's discussion will be categorized by the present author as a *consideration focusing on the concept of reversibility, and the associated notions of separability and distinguishability*.

Neumann, on the other hand, did point out a contradiction within GP1876. He considered the discrepancy between the calculated and reasoned value of the entropy of mixing of similar gases problematic. From a mathematical point of view, ΔS_{AA} should be $\frac{pV}{t} \log 2$, while, according to thermodynamics, this value should be 0. Neumann's attention to the calculations puts his interpretation within Cubic's classification of the Gibbs paradox. That is, there is conflict between two different levels of abstraction: the mathematical prediction of ΔS_{AA} and the unchanged state in thermodynamics. As a result, his contribution categorizes as a *discrepancy due to a mathematical calculation contradicting the thermodynamic state*.

Duhem, fueled by Poincaré's reactions to his work, vied for the thought experiment to account for real gases instead of ideal gases and implicitly drew attention to the experimental verification of the thought experiment. In actuality, a mixture of two

⁵⁴[Cubic, 2008] and [Cubic, 2009]. Cubic ascribes the paradox to the removal of the partition not being a macroscopic process.

gases A and A should not be called a mixture at all because it leads to faulty derivations and inconsistencies within the theory. Using Gibbs' definition of a AA mixture results in the problem which Neumann had pointed out, called a paradox by Duhem. The joint reaction of Duhem and Poincaré took issue with Gibbs' mixture definition and his real gases restriction, two assumptions which, according to Duhem, lead to the paradoxical difference in the behavior of AA and AA' gases. Their debate thus categorizes as a *paradox due to Gibbs' definition not matching real gases*.

Nernst did not directly address the Gibbs paradox. He did, however, both in his text and his figures, combine an expansion-diffusion thought experiment with semi-permeable pistons. In addition to this, Nernst deduced that both this situation and another thought experiment would only be experimentally verifiable if the two gases to be diffused are chemically different. That is, the two gases should react differently to a particular solvent or semi-permeable wall. Nernst's musings may be categorized as an *association of the thought experiment with semi-permeable membranes and solvents*.

Wiedeburg agreed with Neumann on the discrepancy between the mathematical calculation and the thermodynamical reasoning of ΔS_{AA} . He extended Gibbs' thought experiment by including Nernst's semi-permeable walls but concluded that doing so would not resolve the issue. He ascribed the discrepancy to the impossibility of continuity in our understanding of likeness and unlikeness, believing a certain discreteness to be necessary. This again falls in the category of paradoxes due to an abstraction between two levels of reasoning. Important also is that Wiedeburg was responsible for introducing the compound term 'Gibbs Paradox'. It therefore categorizes as a *paradox due to the false assumption of continuity in degrees of similarity*.

Planck, like Maxwell, did not consider GP1876 a paradox. He explained the discontinuity in going from similar to alike gases to be due to the fact that the thought experiment relies on chemistry as well as physics. Only in physics should properties always be continuous. Thus, his narrative categorizes as a *verification of a fundamental difference between chemical and physical properties*.

Larmor, unlike Planck and Maxwell, did regard the idea that work could be gained from mixing nearly identical gases paradoxical. He argued that, although work could still be gained from mixing A and A' , it would take an incredibly long time for the two gases to diffuse. Thus making the process impracticable. Larmor's contribution to the understanding of the paradox categorizes as a *paradox due to the impracticability of mixing infinitely similar gases*.

Van der Waals had quite an original contribution to the discussion on the paradox. He considered the additivity and extensivity of entropy to be indisputable and used his own

molecular theory to explain the difference between ΔS_{AA} and ΔS_{AB} . On the assumption that identical gases consist of identical molecules, his $-\phi(x)$, identical to ΔS_{AA} , reduces to 0. This explanation is, however, not on the level of thermodynamics, in which two gases need only be indistinguishable not identical. Therefore, this interpretation of the paradox is also due to the abstraction between two levels. This argument categorizes as a *paradox due to the macroscopic limit of thermodynamics*.

Although Van Laar, a student of Van der Waals in the early 1880s, considered the non-increase of the entropy for the mixing of AA to be evident, he too saw a paradox in the non-continuous transition from the nearly identical mixture AA' to the identical mixture AA . While Van Laar used the term identical gases, this was only meant from a thermodynamic point of view. Van Laar's contribution thus fully falls within the branch of thermodynamics, making it categorizable as a *paradox due to the discontinuity in the degrees of similarity*.

3.11.1 Conclusion

Even though the named physicists disagreed on what concept led to the discrepancy paradox, they mostly worked on the same problem and in the same branch: solving the discrepancies derived from the 1876 section using thermodynamic means. Only Van der Waals used identical molecules to explain the paradox. The different interpretations of Gibbs' original writings show that many concepts in it can be and have been challenged. These challenged concepts – entropy, reversibility, identity and distinguishability, continuity, molecules, and thermodynamics itself – were, at this time, all disputed by physicists and chemists to some degree. Thus, perhaps unsurprisingly, the development of the concepts associated with this paradox mirrored the development of those concepts in physics itself.

In any case, all these interpretations and the translations by Ostwald and Le Chatelier served to further distribute the knowledge of GP1876 in Europe. Up until this point, the distribution of the paradox, and scientific publications for that matter, was mostly constrained to those who read and published in either English, French, German or Dutch. However, as will be seen in chapter 5, in the early twentieth century, publications were also written in and translated to Russian and other languages. When Gibbs reintroduced the thought experiment with a statistical coating, the term 'Gibbs Paradox' came to be used for several problems in several branches, making the use of the term even more problematic.

4

1902: The Statistical Considerations

But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics.

– J. Willard Gibbs, *Statistical Mechanics*

It is no particular surprise that Gibbs, being the synthetic thinker that he was, managed to construct his *Statistical Mechanics* in such a way that it not only further established statistical mechanics as a proper field of its own, but also made it valid as a more rational foundation to both thermodynamics and molecular mechanics. Correspondingly, Gibbs was one of the first to formalize the branch of physics as a general approach to mechanical systems. The, to some extent analogical, relation between his statistical mechanics and thermodynamics is maintained throughout the entire book. This includes his reiteration of the thought experiment associated with the so-called Gibbs paradox. Consequently, the paradox became entrenched with statistical mechanics, making it more polysemic than it already was.

This third chapter, on Gibbs' statistical interpretation of the thought experiment, is structured in a manner similar to chapter 2. It first presents a short history of statistical mechanics prior to Gibbs' publication. Then, subsections 4.1.1 and 4.1.2 delve into the development of the relevant concepts – entropy and probability as well as ensembles and analogies – in the period between 1876 and 1902. It is a necessary discussion because the dynamically changing use and interpretation of these concepts is pertinent to the interpretation of the Gibbs paradox. Subsequently, the second section will be an elucidation of Gibbs' writings on GP1902, which is the 1902 section on the paradoxical thought experiment. Naturally, this will be succeeded by a comparison of GP1902 with GP1876, the section on the thought experiment written in 1876. Thereafter, as in chapter 2, in order to understand both the role of GP1902 in *Statistical Mechanics* and

the reception of Gibbs' work by his fellow physicists and chemists, there will be a section on Gibbs himself, which consists of subsections on his scientific style, his book, and his position in the scientific community. Finally, the chapter will conclude with an analysis of the historical actors' interpretations of the paradox.

4.1 A Short History of Statistical Mechanics prior to 1902

When Daniel Bernoulli laid, what many believe to be, the basis for the kinetic theory of gases in his *Hydrodynamica*, gases were represented as consisting of a great number of molecules moving in all directions. A connection between thermodynamics and statistical mechanics thus already seemed to have been present in the early stages of their existence. Therefore, the development of statistical mechanics as the rational foundation for thermodynamics was to be somewhat expected. It is not unusual to assume that the history of thermodynamics has continued to become entangled with the history of statistical mechanics since the publication of *Statistical Mechanics*.

Many concepts invoked by thermodynamics went through some conceptual developments with the increasing use of statistics in physics. However, not all those concepts are relevant to this thesis. For this reason, the history described in this section only consists of those changes that seem pertinent to the development of the Gibbs paradox.

Statistical mechanics, unlike thermodynamics, mainly commenced via theoretical ideas and concepts. Although the basis for kinetic theory had already been constructed by Bernoulli in the 18th century, the first works on statistical mechanics were not published until the second half of the 19th century. It was Maxwell who would do the honors. Between 1859 and 1866, he adapted the law of error into a distribution of molecular velocities and obtained further results by assuming that molecular motion is random. Boltzmann picked up the subject after reading Maxwell's work and soon improved on concepts such as his own *H*-theorem, thermal equilibria, and the statistical ensemble. The combined product of their work, the Maxwell-Boltzmann statistical approach, is known for providing probabilities to molecular states. These Probabilities do not reflect an ontological uncertainty in nature, but the human lack of knowledge of the molecular behavior.¹ Statistical mechanics in the 1870s thus combined elements from kinetic theory and probability theory with the concept of equilibrium.

In 1884, the new branch of physics was christened "statistical mechanics" by Gibbs.² Gibbs formalized this new branch, as he had done with chemical thermodynamics, in

¹It is actually very difficult to pinpoint Maxwell's and Boltzmann's interpretations of probabilities, especially because their interpretation of them had changed over time. More on their views on probability can be found in [Uffink, 2006b, pp. 26–39].

²[Gibbs, 1961a]. The term may have been coined by Maxwell in 1871. In any case, Gibbs credited Maxwell with the term in the preface of his 1902 book.

one major publication: *Elementary Principles in Statistical Mechanics developed with especial reference to the Rational Foundation of Thermodynamics*. However, this time, instead of concentrating on the thermodynamic concept of equilibrium, Gibbs built his compendium on the statistical concept of ensembles, which are probability distributions for the state of the system. The ensemble, along with the concept of entropy, was one of the concepts thoroughly developed in the period between 1876 and 1902.

In the upcoming subsection, the developments in the combined concepts of entropy and probability will be elucidated. After that, the emergence of the combined concepts of ensembles and analogies between mechanical statistics and thermodynamics will be explained. Those discussions should be sufficient for understanding Gibbs' contribution to statistical mechanics and the paradox.

4.1.1 Entropy and Probability

The new statistical branch of physics had some consequences for the concepts of entropy, which implicitly includes the notion of reversibility, and probability. The above-mentioned H -theorem is a prime example of a development in probability interpretation in the final quarter of the century. The H -theorem, where $H|f_t| = \int f_t(v) \ln f_t(v) d^3v$,³ basically states that the quantity H decreases in time until the particles reach a Maxwell-Boltzmann probability distribution. In 1877, Boltzmann, who believed the mechanical theory of heat to be rooted in probability calculus,⁴ intended H to correspond to the Second Law and to be proportional to the entropy for ideal gases in equilibrium. However, the H -theorem was heavily criticized by both physicists and mathematicians. Some of these critiques were formulated as paradoxes themselves. Two well-known examples of paradoxes related to the H -theorem are Loschmidt's 1876 reversibility paradox and Zermelo's 1896 recurrence paradox.

Loschmidt imagined a gas container in a homogeneous gravitational field in which a single particle sets in motion the remaining stationary particles until a stationary state is reached. One may then assume the case in which the velocities of all particles are reversed. As a result, the particles will no longer have a Maxwell-Boltzmann distribution, resulting in an increase of H . This allowed Loschmidt to claim that the H -theorem is incompatible with microscopic reversibility.

In his response, Boltzmann stated that the probability of Loschmidt's thought experiment, an example in which a non-uniform microstate is evolved in time and reversed in velocity, is unlikely to the extent of it being practically impossible. Boltzmann therefore

³ f_t is the time-dependent energy distribution function of particles.

⁴[Uffink, 2006b, p. 43]. The following paragraphs are largely based on Uffink's 2006 Compendium.

linked H , and entropy, to the notion of probability by making entropy a measure of the probability of a macrostate, or the number of possible microstates.⁵ Boltzmann concluded that thermodynamic processes, usually irreversible, have to proceed from a less probable state to a more probable state. As a result, entropy, and reversibility, became a part of the statistical branch of physics.

Zermelo, who disliked mechanical elements in thermodynamics, introduced the other paradox centered on the H-theorem in 1896. It states that, according to Poincaré's recurrence theorem,⁶ a gas must return to its initial non-equilibrium state after a sufficiently long amount of time. Processes subject to the theorem, therefore, cannot be strictly irreversible. This means that H has to decrease after a sufficiently long amount of time as well, and that it cannot explain the Second Law in a satisfactory manner.

Boltzmann, once again, replied that it would be highly likely for the state to approach the Maxwell-Boltzmann distribution and, thus, for H to decrease. He conceded that the original state will recur eventually, as Poincaré theorem states. However, according to Boltzmann, this need not lead to any revisions of the mechanical viewpoint because no one would live long enough to observe the recurrence, the duration of it being very long. Furthermore, there would be no problems with his account and the Second Law, because, as a consequence of statistical mechanics, Boltzmann considered it to be of a probabilistic nature.⁷ Boltzmann's response to Zermelo's paradox also fits with Gibbs' famous statement on the Second Law being reduced to an improbability.⁸ In any case, Boltzmann's responses to the non-Gibbsian paradoxes led to another definition and interpretation of the concept of entropy, and the related concepts of probability and reversibility.

⁵In more technical terms, Boltzmann showed the proportionality of entropy to a $6N$ -dimensional phase space volume occupied by the corresponding macrostate of an N -particle system, or $S = k \text{Log} W$. Here, W is the number of microscopic configurations corresponding to a given macroscopic state. Phase space is a mathematical space in which all the possible states of a system are represented. It often consists of the position and momentum variables. In any case, the dissipation of energy leads to a less ordered state, ensuring that transitions usually happen from ordered states to less ordered states.

⁶[Uffink, 2006b, p. 66]. For a Hamiltonian mechanical system of which the phase space is bounded with exception of a set of singular states.

⁷This may easily be explained through Maxwell's Demon. As discussed previously, Maxwell's Demon showed that the irreversible can be reversed. Statistical mechanics tells us that the flow of heat to a colder container is a transition to a less ordered state. It is therefore possible, but highly unlikely, that the system becomes more ordered and that the entropy decreases, rendering the second law probabilistic instead of absolute in Boltzmann's and Maxwell's statistics as well.

⁸He quoted a sentence from Gibbs' GP19876 on the Second Law in the foreword of his *Lectures on Gas Theory Part II*: "The impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability".

4.1.2 Ensembles and Analogies

Both ensembles and thermodynamic-statistical analogies were introduced in the second half of the 19th century. Ensembles, which are large numbers of copies of a system representing one of its possible states, are a solid approach to statistical physics because of the statistical averaging of independent variables.⁹ They can be applied to many physical concepts, such as ideal gases, phase equilibria, and chemical reactions. The concept furthermore provides a microscopic understanding of macroscopic concepts and processes.

Ensembles were introduced in 1871 by Boltzmann as a set of systems, when he tried to generalize the Maxwell-Boltzmann distribution. In this early approach, one ensemble represented one single system. Other systems in the proximity of said ensemble would be similar enough that they could be said to have the same state. Maxwell, in 1879, seemingly independently, introduced ensembles to gases as well as liquids and solids. He did so without mentioning the term ‘ensemble’. Instead of assigning one system to an ensemble, Maxwell considered a large number of similar systems. He subsequently defined probability as the ratio of systems with the same state to the total number of systems in an ensemble. Ensemble theory is said to have been introduced by Boltzmann and Maxwell as an alternative to kinetic theory with the ability to be applicable to any kind of matter in equilibrium.¹⁰ This might explain why Gibbs used the mathematically elegant ensembles instead of the intractable kinetic theory in his *Statistical Mechanics*.

Analogies between mechanics and thermodynamics are another example of a concept that would be important in Gibbs’ *Statistical Mechanics*. According to H. Inaba, within thermodynamic analogies, there is typically a link in terms of equations and operations. An example of this is Helmholtz, who showed a correspondence between mechanics and thermodynamics in his monocyclic systems in 1884. After Clausius criticized Helmholtz’s work for not incorporating heat into its mechanical description, Helmholtz stated his intentions with the paper more clearly:

In this sense I have at any rate everywhere emphasized the analogies that appear between the behavior of the thermal motion and the monocyclic motion examined by me, but expressed also from the beginning (p. 159) that the thermal motion is not monocyclic in the strict sense. Consequently I have never laid claim to have given “an explanation” of the second law of the mechanical theory.¹¹

⁹[Brush, 1983, p. 74].

¹⁰[Inaba, 2015, p. 3]. Inaba’s dissertation is the main source for this subsection. His focus lies on describing the development of ensembles in conjunction with the development of analogies between thermodynamics and mechanics.

¹¹Quote from Helmholtz’s *Studien zur Statik monocyclischer Systeme* in [Inaba, 2015, p. 49].

Analogies, in this sense, should thus not be considered as explanatory tools. However, as Inaba stated, they may lead to new insights on the correspondence between thermodynamics and mechanics. Gibbs' use of analogies would be along the same lines as Helmholtz's. Boltzmann is another example of a physicist writing on analogies, though he only did so from 1884 to 1887. He extended Helmholtz's work to ensembles while focusing on making the equations analogical. This makes Boltzmann one of the very few physicists who worked on most relevant concepts in the period described in this thesis.

The concepts of ensembles and analogies are grouped together in this section because of Inaba's interpretation of *Statistical Mechanics*. He believed Gibbs' book to be an integration of the genealogies of those concepts.¹² In *Statistical Mechanics*, Gibbs introduced three types of ensembles and used analogies to provide thermodynamics with a rational foundation. The ensembles, *microcanonical*, *canonical*, and *grand canonical* say something about what is fixed and what may vary. In microcanonical ensembles, both the energy of the system and the number of particles in the system are fixed at particular values; in canonical ensembles, only the number of particles is fixed; finally, in grand canonical ensembles, neither energy nor the number of particles are fixed. The use of these concepts by Gibbs will be explained in the following sections. Both concepts are, anyhow, used in relation to the paradoxical thought experiment as well.

4.2 Gibbs' Second Writings on the Thought Experiment

Statistical Mechanics is a book composed of fifteen chapters, of which the first thirteen deal with the concepts of statistical equilibrium and probability of phase. The fourteenth chapter handles the thermodynamic analogies mentioned in section 4.1.2. Finally, the fifteenth and last chapter, which deals with systems composed of many similar particles, contains Gibbs' thoughts on the diffusion thought experiment. Although Gibbs' musings are restricted to one paragraph, this paragraph covers quite some concepts. Some of these concepts were introduced by Gibbs himself, making it necessary to elucidate further on the subject. Therefore, this section is divided into several parts, each describing Gibbs' use of a relevant concept.

Generic and Specific Phases

In order to fully understand Gibbs' second encounter with the thought experiment, some introductory definitions are needed. In his final chapter, Gibbs defined two types of phases, generic and specific, which lead to different entropy values in the canonical ensemble.¹³ The reason for the existence of these two types of phases is the consideration

¹²That is, a merging of the histories of ensembles and analogies into one combined result.

¹³The canonical ensemble is an ensemble of many systems each containing the same number of particles but with different possible values of the total energy.

as to whether a permutation of the phase points in phase space, or a permutation of similar particles, leads to a new state or not. In Gibbs' words:

If two phases differ only in that certain entirely similar particles have changed places with one another, are they to be regarded as identical or different phases? If the particles are regarded as *indistinguishable*, it seems in accordance with the spirit of the statistical method to regard the phases as *identical*.¹⁴

A phase is generic when the phases are identical, and thus when the particles are indistinguishable. Conversely, a phase is specific when the particles are distinguishable. Figure 4.1 contains a visualization of the situation sketched by Gibbs.

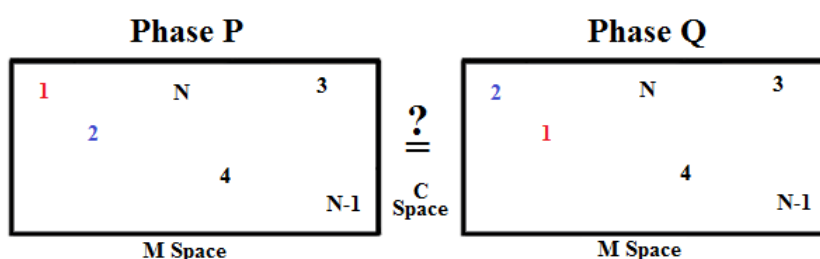


FIGURE 4.1: A 2-dimensional representation of phase space with the configuration space (C Space), or the 3-dimensional spatial coordinates, and momentum space (M Space) on the axis.

The drawn phases are identical with the exception that the indistinguishable particles 1 and 2 have switched places. If, despite the switch, phase P is believed to be fully identical to phase Q, the phases are called generic. If the switch does matter – that is, when P and Q are not taken to be identical – the phases are called specific. The choice for a certain type of phase does not have any experimental consequences, but, as will be explained shortly, may lead to a different entropy of mixing than the one calculated in section 2.2.

Identity and Indistinguishability

It is important to note that Gibbs did not hint at the identity of individual particles in his fifteenth chapter. Rather, he regarded the particles as similar and indistinguishable in particular systems, which was a reason for him to denote the phases as identical.¹⁵ Gibbs' stated preference for the generic phase does not influence the status of the particles. A phase space permutation might or might not count as a different phase, but the particles themselves maintain some semblance of individuality anyway.

¹⁴[Gibbs, 1960, p. 187].

¹⁵The following metaphysical definitions of these 'I-concepts' are often maintained: *Identity* is the condition of being oneself or itself, and not another; *Indistinguishability* is the circumstance of not being recognized as distinct or different; *Individuality* is the state or quality of existing as an individual.

Any inability to identify particles is only mentioned between two different systems, not within systems. Gibbs further remarked that “the perfect similarity of several particles of a system will not in the least interfere with the identification of a particular particle in one case with a particular particle in another.” A Maxwellian type of demon might still be able to label the individual particles, thus allowing them to have an identity. So unlike Van der Waals’ interpretation, the particles are not identical, and unlike the branch of quantum physics, particles can be identified in Gibbs’ statistical mechanics.¹⁶ Nevertheless, it is not particularly surprising that the identity of particles has been related to the paradox by some authors.¹⁷

Sensible Restrictions and the thermodynamic-statistical analogy

The previous parts of this section illustrated the relevant concepts that were explained in Gibbs’ fifteenth chapter. The actual paradoxical section in *Statistical Mechanics*, GP1902, is confined to the very last paragraph of the book. It is cited here wholly:

To fix our ideas, let us suppose that we have two identical fluid masses in contiguous chambers. The entropy of the whole is equal to the sum of the entropies of the parts, and double that of one part. Suppose a valve is now opened, making a communication between the chambers. We do not regard this as making any change in the entropy, although the masses of gas or liquid diffuse into one another, and although the same process of diffusion would increase the entropy, if the masses of fluid were different. It is evident, therefore, that it is equilibrium with respect to *generic* phases, and not with respect to specific, with which we have to do in the evaluation of entropy, and therefore, that we must use the average of H or of η_{gen} , and not that of η , as the equivalent of entropy, except in the thermodynamics of bodies in which the number of molecules of the various kinds is constant.¹⁸

From this paragraph, it becomes clear that Gibbs incited the same thought experiment as sketched in figure 2.1. He even restressed the same assumptions for entropy: additivity, extensivity, and the thermodynamic limit in distinguishing between two alike masses. In fact, Gibbs explicitly stated that this section would focus on “properties sensible to human faculties”, proving that thermodynamics remained of importance in the thought experiment. The mentioned connection to thermodynamics might further explain why Gibbs used the term indistinguishable to describe particles. Indistinguishability, unlike identity, is regarded as an epistemological concept, meaning that it depends on one’s

¹⁶It is assumed that most physicists take quantum physics to imply that quantum particles cannot be taken as individual objects in the same way as classical particles. There are, of course, exceptions to this.

¹⁷For instance, Van der Waals, with his assumption that identical gases contain identical molecules. Schrödinger is an example of an author who linked the quantum interpretation of identical particles to the Gibbs paradox. A more direct example is the following quote by Mandl in [S. French, 2006, p. 146]: “Historically, failure to appreciate the significance of the identity of the particles in a system led to certain inconsistencies, known as the Gibbs paradox”

¹⁸[Gibbs, 1960, pp. 206–7].

knowledge of the situation. In the case of this thought experiment, that knowledge would be mostly limited to the thermodynamic state of the system.

This version of the thought experiment has an analogical relation to the 1876 version. Not only do the sections have the same assumptions, there also exists a connection between the entropy concepts and the obtained results: Both Clausius' thermodynamic entropy and Gibbs' statistical entropy lead to an entropy difference that is fully dependent on the number of particles. The final paragraph of *Statistical Mechanics* is thus also part of the analogy between thermodynamics and statistical mechanics.

The only original addition to the existing discussion of the 'paradox', besides the renewed interpretation of entropy, were the phases. This time, the experiment actually appeared to revolve around phases. As a matter of fact, Gibbs seems to have invoked it to lobby for the use of generic phases. Interestingly enough, the discrepancy between the calculated and the reasoned entropy of mixing values as calculated in section 2.2 disappears when using specific phases.¹⁹ Using generic phases, however, would lead to the same values as in 1876. Therefore, it appears that Gibbs – who preferred generic phases – considered the results obtained in 1876 desirable instead of paradoxical.

Entropy and Ensembles

Nowadays, Gibbs' definition of entropy is typically portrayed as the generalization of the Boltzmann entropy, valid for all systems, or $S = -k_B \sum_i p_i \ln p_i$.²⁰ However, in *Statistical Mechanics*, Gibbs began by introducing η as the index of probability for the phase. Only in the fourteenth chapter did Gibbs precisely describe the analogical relation between η and entropy.²¹

Although the term 'ensemble' is not mentioned in the paragraph, it is part of the initial set-up of the phase-specific entropy. The difference in generic and specific phases in this thought experiment is said to only be relevant in the case in which the number of particles is not constant. When there is a constant number of particles, this difference only affects an integration constant in the entropy of mixing. The three symbols in the section, H , η_{gen} , and η , represent the entropies of the generic grand ensemble, the generic petit ensemble, and the specific petit ensemble respectively. According to Gibbs, because the grand ensemble appears to be microcanonical – or petit as Gibbs calls it – from a thermodynamic point of view, the ensemble-type specific differences in the calculations may be neglected. This then leads to the following equations for entropy,

¹⁹As a reminder, Gibbs reasoned from a thermodynamic point of view that ΔS_{AA} should be zero while a quick calculation showed that this value would be equal to $\Delta S_{AB} = \Delta S_{AA'} = \frac{pV}{t} \log 2$.

²⁰ k_B is the Boltzmann constant and p_i are the probabilities.

²¹ $\eta = \log P = \frac{\psi - \epsilon}{\Theta}$, where ψ and Θ are constants and ϵ is the energy of the system. Θ is the modulus of a canonical ensemble, which is the analogue to temperature. Taking the proper analogies and the thermodynamic limit in account will then lead to a thermodynamic interpretation of entropy, $S = \int \frac{\delta Q}{T}$.

or the probability of a phase, in an ensemble:

$$H = \frac{\Omega + \mu_1\nu_1 + \cdots + \mu_h\nu_h - \epsilon}{\Theta}, \quad (4.1)$$

$$\eta_{gen} = \eta + \log \nu_1 \dots \nu_h, \quad (4.2)$$

$$\eta = \frac{\psi - \epsilon}{\Theta}, \quad (4.3)$$

where ν_i are the numbers of the different kinds of particles, ϵ is the energy of the system, and Ω , μ_i , Θ , and ψ are constants. In this case, η_{gen} expresses the notion that one generic phase will contain $\nu_1! \dots \nu_h!$ specific phases.

Using Gibbs' notation in a mathematical proof would not serve to clarify the results in this thesis. Instead, generic and specific phases are more often denoted by, respectively, $S_{gen} = S_{spec} - \log N! = \frac{3}{2}k_B \log \frac{V}{N}$ and $S_{spec} = \frac{3}{2}k_B N \log V$. From this, the following results can easily be obtained for the thought experiment:

$$\begin{array}{ll} AA \text{ and } AB & : \quad \Delta S_{spec} = 3kN \log 2, \\ AB & : \quad \Delta S_{gen} = 3kN \log 2, \\ AA & : \quad \Delta S_{gen} = 0. \end{array}$$

Generic phases thus return the same results Gibbs obtained in 1876. Ironically, the specific interpretation of phases would solve, what many before 1902 called, the Gibbs paradox. The fact that Gibbs choose generic phases over specific phases shows that he did not regard the discrepancy as problematic. Therefore, instead of providing his reader with further considerations, Gibbs used the thought experiment to lobby for the use of generic phases.

To recap this section, the relevant concepts from this paragraph, GP1902, are:

Identity — distinguishability — generic phases — specific phases — ensembles —
macroscopic and microscopic descriptions — probability.

These keywords will be used in chapter 5 to indicate the paradoxical elements that the historical actors have read into Gibbs' GP1902.

4.2.1 Comparison of Gibbs' Writings on the Thought Experiment

Even though both GP1987 and GP1902 revolve around a diffusion-expansion thought experiment, the associated concepts and the role of the sections differ from each other. In GP1987, Gibbs mostly concerned himself with molecules, the thermodynamic limit, and the second law, while in GP1902, the focus lay on the distinguishability of particles and the identity of phases. GP1987 is written as a series of considerations, enticing

his readers to investigate for themselves. Contrarily, GP1902 has Gibbs reasoning for his preference of generic phases which are, besides the entropy calculations in some ensembles, no different from specific phases. Minor differences in Gibbs' discussions of the thought experiment thus exist.

In 1876, Gibbs gave an empirical solution as to why there is no entropy increase in the diffusion of alike gases while there is one for the diffusion of unlike gases. In 1902, Gibbs evidently managed to explain this difference from a logical point of view. The fact that GP1902 was placed in the back of the last chapter of the book shows that Gibbs was quite confident in his assertions. After all, Gibbs carefulness would have demanded him to place a mitigating paragraph after GP1902 if he were not quite sure of his case. Part of the decision to put the chapter, 'Systems Composed of Molecules', as the last chapter was because "it seemed desirable to separate sharply the purely thermodynamic laws from those special modifications which belong rather to the theory of the properties of matter."²² Even though Gibbs also appeared quite confident in GP1987, he seemed to have formulated it as slightly weaker claims than in GP1902. Nevertheless, both GP1987 and GP1902 attracted the attention of other chemists and physicists. After the 1902 publication, additional branches besides thermodynamics began to apply themselves to both GP1987 and GP1902.

Because GP1902 is not a standalone publication, its position in *Statistical Mechanics* needs to be explained for a proper understanding of how other actors viewed the paradox. Naturally, Gibbs' scientific style and position in the scientific community in 1902 are, too, decisive for the analysis of an interpretation of Gibbs paradox.

4.3 J. Willard Gibbs

After the 1870s, Gibbs moved on from thermodynamics to work on new subjects such as vector analysis and statistical mechanics. Even though his book *Statistical Mechanics* was published only a year before his death in 1903, he had already been working on the subject since 1884.²³ Very little was published on the subject prior to 1902. To those who did not know that Gibbs had already worked on statistical mechanics, it seemed like he had built the foundation to a new approach to thermodynamics overnight. However, the carefully constructed structure of the book, typical of his rhetoric style, suggests that Gibbs had had his arguments sorted for a while.

²²[Gibbs, 1960, p. xii]. This is the final sentence of the preface.

²³Gibbs presented a paper to the American Association for the Advancement of Science called 'On the Fundamental Formula of Statistical Mechanics with Applications to Astronomy and Thermodynamics'. [Bumstead and Gibbs Van Name, 1961b, p. 16]. Additionally, he presented "On a certain Theorem in Theoretical Mechanics" in 1894, which would become part of *Statistical Mechanics* in 1902.

4.3.1 Scientific Style

As mentioned previously on Gibbs' scientific style, in section 2.3.1, not much had changed in terms of his approach and methods. Once again, the generality with which Gibbs wrote his book allowed it to easily be adapted to quantum mechanics. This final publication renewed Gibbs' status as a synthetic thinker with the ability to write main compendia which would remain of importance for a long time. His carefulness had not changed either. Gibbs still strove to clearly state whenever he was certain of something and whenever he saw limitations in a certain approach. He even went so far as to mention the limit of his aims in the preface to his book: "Moreover, we avoid the gravest difficulties when, giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics."²⁴ Unfortunately, also in *Statistical Mechanics*, there was a perceived difficulty in understanding the material due to the abstractness of the book.

The above-stated quote shows that Gibbs did not consider the molecular theory to be proven beyond doubt, which, nonetheless, does not mean that Gibbs did not believe in it. It does mean that Gibbs was also careful in denoting whether something was a 'mere' consideration or whether it was actually proven.²⁵ He had been careful with the constitution of matter since his earliest works, but never stated his thoughts on this manner as clearly as he had in 1902.

Difficulties of this kind have deterred the author from attempting to explain the mysteries of nature, and have forced him to be contented with the more modest aim of deducing some of the more obvious propositions relating to the statistical branch of mechanics. Here there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall, is the want of agreement between the premises and the conclusions, and this, with care, one may hope, in the main, to avoid.²⁶

The difficulty referred to is the discrepancy between the six expected degrees of freedom per molecule in a gas and the five experimentally found degrees of freedom. This statement has been taken by some as proof that Gibbs opposed molecular theory. However, as indicated by Brush in 1983, this is a gross overstatement since Gibbs merely abstained from using calculations based on specific molecular models. Furthermore, Gibbs did actually write about systems composed of molecules in the final chapter, in which GP1902 is contained. If anything, this attitude towards non-proven hypotheses in his

²⁴[Gibbs, 1960, p. ix].

²⁵[Klein, 1972, p. 132]. Klein, above all, believed that "Gibbs knew when he had proved something rigorously and when he had not."

²⁶[Gibbs, 1960, p. x].

publications allowed Gibbs' work to survive the emergence of quantum mechanics with few changes to the main structure.

4.3.2 Writings on Statistical Mechanics

Statistical Mechanics was the culmination of Gibbs' work on the use of statistics in thermodynamics on which he had already been working for some 15 years. To some of his associates, the publication of a cohesive book on statistical mechanics incorporating earlier work by Boltzmann and Maxwell might have come as a surprise since he had scarcely published on the subject prior to 1902. Yet, a paper presented in 1884 and the lecture notes taken by G.P. Starkweather in 1894–95 on Gibbs' course on Dynamics and Thermodynamics show that he had already worked out most of the material – on the relation of thermodynamic behavior to the probable behavior of ensembles, and thus to many systems containing large numbers of particles – by the end of the 19th century.²⁷

As in *Equilibrium*, Gibbs centered his ideas on the concept of equilibrium. Because the book was written with reference to thermodynamics, his statistical mechanics had to supply some mechanism for understanding equilibria and the fundamental equation in this new discipline. It did so by introducing ensembles with a density function that depends on coordinates, momenta, and time. When a system evolves in time – that is, when a system is not in equilibrium – the phase point representing that system will move along a trajectory and the density function will change. An ensemble which does not evolve in time, a stationary ensemble, then represents thermodynamic equilibrium.²⁸

As stated earlier in this chapter, Gibbs introduced three types of ensembles to deal with the various limits in the fixedness of the energy of a system and the number of particles in said system. Gibbs himself believed the canonical ensemble to be “the most simple case conceivable, since it has the property that when the system consists of parts with separate energies, the laws of the distribution in phase of the separate parts are of the same nature – a property which enormously simplifies the discussion, and is the foundation of extremely important relations to thermodynamics.”²⁹ Ultimately, by comparing the properties of this canonical ensemble with the thermodynamic fundamental equation, Gibbs showed that the equations (4.1)–(4.3) correspond to entropy.

In addition to formalizing statistical mechanics with reference to thermodynamics, Gibbs used analogies to provide thermodynamics with a rational foundation. For instance, the statistical equilibrium equation, $e^{-\frac{\psi}{\Theta}} = \int (e^{-\frac{\epsilon}{\Theta}}) d\Omega$, combines the mechanical structure of

²⁷Lectures notes on Gibbs' courses are kept in the Yale Archives. [Inaba, 2015] has an appendix with the lecture notes by Starkweather.

²⁸This is represented by the equation $e^{-\frac{\psi}{\Theta}} = \int (e^{-\frac{\epsilon}{\Theta}}) d\Omega$.

²⁹[Gibbs, 1960, p. 33].

the system with its thermodynamic properties. Apart from the fundamental equation, Gibbs also deliberated on mechanical processes which could be seen as analogical to isothermal and adiabatic processes such as the Carnot cycle. In fact, the entire fourteenth chapter is dedicated to thermodynamic analogies, with Gibbs mainly focusing on the fundamental principles:

We may therefore confidently believe that nothing will more conduce to the clear apprehension of the relation of thermodynamics to rational mechanics, and to the interpretation of observed phenomena with reference to their evidence respecting the molecular constitution of bodies, than the study of the fundamental notions and principles of that department of mechanics to which thermodynamics is especially related.³⁰

Gibbs thus clearly considered his work, centered around ensembles, to be related to thermodynamics. This is the exact reason why Inaba regarded *Statistical Mechanics* as an integration of the developments in ensembles and analogies.

4.3.3 Position in the Scientific Community

In order to appreciate the impact of *Statistical Mechanics*, an analysis provided by Brush is useful. It states that, in explaining and predicting physical properties of macroscopic matter from microscopic properties, three things are needed. The first two things, a theory of the interactive structure of individual particles and fundamental laws determining the state of particles in terms of their structure and interactions, had already been developed to some extent before 1902. It was Gibbs who, based on the work of Boltzmann and Maxwell, managed to generalize the third: a statistical technique for estimating properties of systems of large numbers of particles.³¹ Gibbs not only made a coherent account of statistical mechanics in a mathematically aesthetic manner, he also rendered it useful to other branches, such as quantum mechanics. Even Zermelo, who opposed Boltzmann and the mechanical viewpoint in the 19th century, ended up supporting Gibbs' *Statistical Mechanics*, as can be inferred from his role in the translation of the book to German in 1905.

By this time, Gibbs was already well-known for his work on thermodynamics and his role in the debate between the supporters of quaternions and the supporters of vector analysis. Contrary to the case of *Equilibrium* in the 1870s, his 1902 publication was read widely from the beginning, although it was not always fully understood. Many of the

³⁰[Gibbs, 1960, p. ix].

³¹[Brush, 1983, p. 72]. Brush' analysis actually focused on atoms, but the present author considers the terms microscopic structure and particles more accurate for Gibbs' contribution.

physicists who had received a copy of *Statistical Mechanics* wrote Gibbs to thank him, but few actually discussed elements of the book. Nevertheless, Gibbs would be known as one of the earliest American mathematical physicists to earn a reputation outside of the United States, receiving the Copley Medal of the Royal Society of London in 1901.

4.4 Conclusion

Although Gibbs' position as a member in the scientific community had improved, very few colleagues actually understood the contents of *Statistical Mechanics* and its value. This is also true for his 1902 discussion of the thought experiment. Indeed, the position of GP1902 in the book makes it more likely that it would have gone unnoticed by those struggling with the subject. That does not change the fact that GP1902 fits very neatly in *Statistical Mechanics* as a whole. It uses Gibbs' improved definition of Boltzmann's entropy, connects to all three types of ensembles, and makes use of the thermodynamic-statistical analogy. Moreover, Gibbs managed to do all this without making too many assumptions and whilst retaining his carefulness.

Having said that, even in the statistical setting, Gibbs did not associate any contradictions with the thought experiment. Because he considered his set of propositions in the thought experiment to be consistent, GP1902 does not fit with Lycan's definition of a paradox. Instead, Gibbs used it as an illustration for the choice of generic phases over specific phases even though both alternatives are equally plausible in non-grand ensembles. The role of the thought experiment, and the increasingly more polysemic paradox associated with it, thus has changed from being a series of considerations to being a tool for verification.

As in 1876, Gibbs maintained that there should be a difference in the mixing of AA and AA' due to a human observer being limited to sensible properties. In the chapter preceding GP1902, he had related the relevant statistical functions to thermodynamic quantities, thus establishing an analogical relation between the two disciplines. In this sense, GP1902 is a statistical reinterpretation of the 1876 thought experiment with a foundation in thermodynamics. Hence, Gibbs' statistical contribution will be classified as a *analogical tool to demonstrate the choice for generic phases*.

5

1902 - 1911: The Subsequent Interpretations

An important scientific innovation rarely makes its way by gradually winning over and converting its opponents: [...] What does happen is that its opponents gradually die out and that the growing generation is familiarised with the idea from the beginning.

– Max Planck, *The philosophy of physics*

The first decade of the twentieth century was an eventful one. It marked the start of a series of revolutions in quite some physical disciplines. For instance, after Planck had formulated his quantum hypothesis, in which energy is quantized, in 1900, Einstein reasoned that light itself consists of particles in order to explain the photoelectric effect. This was not Einstein's only contribution to physics. In the same year, 1905, Einstein also published papers on what would later be known as special relativity and on Brownian motion. In the latter, Einstein explained the phenomenon by assuming that the random motion of the suspended particle is caused by the collision with smaller particles. In reaction to this work, Jean Perrin performed experiments to test Einstein's predictions, a moment that has often been indicated as the eradication of the anti-atomic view.¹

This period furthermore marked the start of Frederick Soddy's attempts to prove the existence of isotopes for radioactive elements. By 1911, it had become clear that certain processes associated with radioactivity could transform one element into another.² Another relevant development in thermodynamics before the publication of the Ehrenfests' review of Boltzmann's statistical mechanics was Nernst's statement of the Third Law in 1906. Unfortunately for Gibbs, he never had the opportunity to oppose or support these

¹[Perrin, 1910, p. 90]. Perrin calculated Avogadro's number in several independent experiments focusing on, among others, Brownian movement, alpha decay, x-ray diffraction, and blackbody radiation. The values of the calculated constant varied from $(45 - 200) \times 10^{22}$ and Perrin considered 70.5×10^{22} to be the most probable value. That Avogadro's number, now thought to be 6.02×10^{23} , was constrained to such a small interval really pushed the validity of atomic theory.

²This meant that there was another way for gases to be distinguished. As has been explained in Maxwell's considerations of the thought experiment, this has no consequences for the Gibbs paradox.

developments, though his statistical conception of physical phenomena was so broad and rigid that it supported them.³

Gibbs passed away a year after publishing *Statistical Mechanics*, while working on a supplement to *Equilibrium*. His 1876 work had, by then, finally been partially understood and recognized for its merit. Gibbs' latest publication would follow in the footsteps of his earlier publication. That is, the abstract and general exposition of statistical mechanics also was not picked up immediately. Selections of the book would prove to be useful early on, but other elements, such as GP1902, Gibbs' second paradoxical section, did not attract a significant amount of attention in the decade following the publication. Such elements were, at times, 'reinvented' by other scientists, only for them to discover that the idea already had been discussed in *Statistical Mechanics*. For example, Obe Postma – according to Haitun the first after Gibbs to put a statistical twist to the paradox – stated that he only noticed a remark by Gibbs after he had already written something similar himself.⁴

The number of references to the paradox has relatively increased in the first decade of the twentieth century. However, it is not nearly as unmanageable as in the 1950s. This was when the continuous flux of contributions to the paradox really took off.⁵ While it was both adequate and necessary to analyze all of the responses to the paradox in the period 1876–1902, doing so for the period 1902–1911 would be non-sensical. The reason for this is that many of the works referring to the paradox in the second period are mere mentions or duplications of existing arguments. Discussions actually relevant to the interpretation or the distribution of the term 'Gibbs paradox' are treated in separate sections. Minor reviews of the paradox are only described as part of the sections discussing major interpretations.

Once again, a portion of the selection of the scientists in this chapter is based on Haitun's *History of the Gibbs Paradox*. Comparable to Haitun's account, this chapter of the thesis encompasses sections on Alfred Byk, Johannes Diderik van der Waals, Lorentz, and Postma. As it turns out, some of the dates and references given by Haitun are incorrect or were preceded by earlier writings. These instances have been corrected by the present author. In addition to the actors supplied by Haitun, interpretations by Boltzmann and Nabl, and Van Laar have also been included. The availability of scientific publications and search tools on the internet prevented the present author from missing those publications. Naturally, even with the enlarged accessibility of historical works, there is no guarantee that all significant contributions have been included. Non-original

³[Seeger, 1974, p.283].

⁴[Postma, 1908, p .342]: “toen ik het bovenstaande geschreven had, bemerkte ik, dat het laatste niet nieuw is. Ook Gibbs zelf heeft reeds in den laatsten zin van zijn boek de opmerking gemaakt.”

⁵Appendix B contains a list of reactions and solutions to the paradox up to 1986.

references to the paradox, which became more and more frequently incorporated, have likewise been omitted. Original references enclosed in this chapter are the ones by Larmor, Lucien Poincaré, E.B. Wilson, Rudolf Ruer, and Kohnstamm and Scheffer.

5.1 Larmor's Defense of the Molecular Principle

An interesting reference to the paradox was made in 1902, the same year as *Statistical Mechanics* was published. In the 10th edition of *The New Volumes of the Encyclopædia Britannica*, Larmor returned to the argument presented in 1897.⁶ Within the section on energetics, it was noted that there had been a recent trend among chemists to try to replace the atomic principle with the principle of available energy.⁷ However, according to Larmor, neither principle is more certain and definite than the other. Both principles have their own problematic consequences, something he thought to be demonstrated by the Gibbs' paradox.

[T]he energy that is available for mechanical effect in the inter-diffusion of given volumes of two gases depends only on these volumes and their pressures, and is independent of what the gases are; if the gases differed only infinitesimally in constitution it would still be the same, and the question arises where we are to stop, for *we cannot suppose the inter-diffusion of two identical gases to be a source of power*. This then looks like a real failure, or rather limitation, of the [principle of available energy]; and there are other such, that can only be satisfactorily explained by aid of the complementary doctrine of molecular theory. That theory, in fact, shows that the more nearly identical the gases are, the slower will be the process of inter-diffusion, so that the mechanical energy will indeed be available, but only after *a time that becomes indefinitely prolonged*. It is a case in which the simple doctrine of energetics becomes inadequate before the limit is reached.⁸

As in 1897, Larmor tied the increasing similarity between the gases A and A' to the diffusion rate. Of course, when a process becomes progressively slow, the amount of work one may obtain from the diffusion becomes more and more inefficient. This time though, he did not mention this to be due to the thermal transpiration pressure being infinitesimally small.

In questioning the principle of entropy, something he had not done in 1897, Larmor also questioned the validity of the doctrine of energetics and defended the molecular hypothesis. Important also is that he included this knowledge in a widely read encyclopedia,

⁶[Larmor, 1897], [Larmor, 1902]. The 27th volume was published in the second half of 1902, after the publication of *Statistical Mechanics*.

⁷The term 'entropy' still had not been adopted by all physicists and chemists.

⁸[Larmor, 1902, p. 171]. Larmor's entry had not changed its position on the Gibbs paradox in the 11th edition, published in 1910.

which by then had gained the status of being a landmark encyclopaedia for scholarship and literary style focusing on both established and recent events and developments. Information on the paradox thus was made available to those with no regular access to scientific publications, augmenting the overall scope of the term ‘Gibbs paradox’.

In 1909, Fielding Hudson Garrison, neither a physicist nor or chemist, wrote an article on Gibbs’ influence on modern science.⁹ The article would, perhaps, be the first historical review which also discussed the Gibbs paradox. Whilst describing the diffusion of infinitesimally similar gases, Garrison cited Maxwell’s and Larmor’s contributions to the paradox.

Maxwell explained this paradox by saying that our ideas of dissipation of energy depend upon the extent of our knowledge of the subject. Could we invoke Maxwell’s demon and borrow his gift of molecular vision, we should perceive that when two identical gases mix there is in reality a complete dissipation of energy, which the demon’s intelligence might turn into available energy if he liked ; [...] In the reasoning of energetics, the paradox is explained by saying that the more nearly alike the gases are, the slower will be the process of diffusion, so that work or available energy might indeed be gained, but only after the lapse of indefinite or infinite time, if we have such time at our disposal.¹⁰

Garrison thus explicitly tied the term ‘Maxwell’s demon’ to the paradox. Noteworthy of this review of Maxwell’s and Larmor’s work is that Larmor’s argument was misunderstood. According to Larmor, molecular theory, not energetics which sought to abolish molecular theory, explains the slowing down of the diffusion of infinitely similar gases. Garrison and Larmor were not the only ones to combine the paradox with a reaction rate. A German chemist by the name of Rudolf Ruer discussed a similar argument in his paper on phase diagrams of ternary systems and the law of combining weights. In this paper, Ruer named the law of mass action – which states that the rate of a chemical reaction is proportional to the product of the masses of the reactants – to be a consequence of the paradox.¹¹ For diffusion, this result, as well as Larmor’s, would be equal to Fick’s second law of diffusion, which predicts how the concentration of a gas changes with time. These actors, thus, adapted Larmor’s earlier interpretation, and combined it with the school of energetics, the molecular principle, Maxwell’s demon, and the law of mass action. Overall, however, these discussions still come down to the impracticability of mixing infinitely similar gases.

⁹Garrison was actually a historian, bibliographer, and librarian who focused on medicine.

¹⁰[Garrison, 1909, p. 46].

¹¹[Ruer, 1910, p. 31]: “[...] des sog. Gibbsschen Paradoxons und seiner Folgerung, des Massenwirkungsgesetzes [...]”.

5.2 Byk's Symmetry in Optically Active Substances

Alfred Byk, a rather unknown German-born Jewish professor of physical chemistry whose career was cut short in the Second World War, was mainly known for his *Einführung in Die Kinetische Theorie Der Gase* and for being an early proponent of symmetry principles. He published a paper in 1903 called 'Ausnahmen von der Phasenregel, besonders bei optisch-aktiven Körpern' in reaction to a lecture by Van 't Hoff on the behavior of optically active bodies in terms of the phase rule.

Although most of Byk's paper focused on these optically active compounds in conjunction with the Phase rule as treated by Planck, there is a short discussion of the thought experiment. This, again, is linked to the writings of Planck, who is stated by Byk as the one to have come up with a thermodynamic criterion of identity of distinguishability of two substances.¹² Byk combined the semi-permeable membranes with racemization, the conversion of an enantiomerically pure mixture into a mixture where more than one of the enantiomers are present. An enantiomer is one of two isomeric molecules that are mirror images of each other which are not identical. Byk's version of the thought experiment therefore is associated with chiral symmetry. Starting with the claim that the usual assumption of the left-hand substance and right-hand substance being indistinguishable does not apply in all generality, Byk commenced his recapitulation of the diffusion:

Bringt man zwei Körper im Gaszustande oder in verdünnter Lösung nebeneinander, so wird eine Entropievermehrung durch Diffusion stattfinden, wenn sie verschieden sind; die Entropie bleibt konstant, wenn sie identisch sind. Sofern sich verdünnte Lösungen von d- und l-Weinsäure vollständig miteinander mischen, und dieser Prozess nicht umkehrbar ist, findet erfahrungsgemäss eine Entropievermehrung statt, und man kann sich durch einen Prozess mit semipermeablen Wänden⁵) überzeugen, dass sie den normalen, für je zwei verschiedene Substanzen stets gleichen Betrag hat. Die semipermeablen Wände müssen in diesem Falle natürlich innerlich *unsymmetrisch* sein; man kann sich solche sehr wohl vorstellen.¹³

Byk thus considered the diffusion of enantiomer mixtures, which might then be separated via unsymmetrical semi-permeable walls. He further imagined the walls to contain many

¹²[Byk, 1903, p. 466]: "Planck gibt ein thermodynamisches Kriterium, welches speziell über Identität oder Verschiedenheit zweier Körper entscheidet."

¹³[Byk, 1903, p. 466–7]. ("When two bodies in a gaseous state or in dilute solution are side by side in a diffusion, an increase in entropy will take place when they are different; the entropy remains constant when they are identical. Insofar as dilute solutions of D- and L-tartaric acids completely mix with each other, and this process is irreversible, an increase in entropy takes place, and one may be convinced through a process with semi-permeable walls that it is normal for two different substances to always have the same value. The semipermeable walls must be internally asymmetrical in this case, of course; as one might imagine.") The footnote in the excerpt refers to Planck's discussion of the thought experiment.

small doors with locks which could only be opened by the enantiomer with the right symmetry, which would act as a key. For example, semi-permeable wall α permeable to specific *d*-enantiomers would only contain locks that can be opened by *d*-enantiomers, *l*-enantiomers would not be able to open the ‘locks’ and may therefore not pass the semi-permeable wall. The opposite would be true for wall β , which is only permeable to *l*-enantiomers. Naturally, since the enantiomers are not considered identical, this does not solve Gibbs paradox, but merely adds another way to distinguish between two similar gases. As stated by the Austrian chemist Rudolf Wegscheider in a reaction to Byk “the ‘thermodynamically same’ phases are counted as separate phases when they are actually different in any respect.”¹⁴ Even when the difference in the chemical substances lies only in chiral symmetry, the thermodynamic phases of the individual gas components are still distinct.

Byk’s assembly of the thought experiment and the chemical notion of optically active substances were picked up by the German chemist Hans Goldschmidt. Goldschmidt, who had previously patented thermic welding, believed that the constant c in $A = cT$ ¹⁵ may be determined in a consideration similar to Byk’s version of the thought experiment, which Goldschmidt noted to be relevant to Wiedeburg’s paper on the paradox. He too imagined a diffusion of enantiomers

Bringen wir nun mittels zweier, jeweils nur für einen der optischen Antipoden durchlässigen Stempel die beiden Lösungen isotherm und reversibel zur Vermischung, [die maximale] Arbeit die der Prozess leisten kann, wird $A = 2RT \ln 2$. [...] Vorausgesetzt ist hierbei die Existenz von Membranen, welche verschiedene Durchlässigkeit für zwei optische Antipoden besitzen, Solche Membranen – mit deren experimenteller Realisierung ich augenblicklich beschäftigt bin – müssten natürlich, wie schon Byk³⁾ betont hat, selbst optisch-aktiv sein und somit ein Analogon zu den optisch-aktiven Lösungsmitteln bilden, die ja ebenfalls eine Trennung racemischer Gemische ermöglichen.¹⁶

In addition to supporting Byk’s view and seeking to experiment with membranes permeable to optically active substances, Goldschmidt also noted that such membranes

¹⁴[Wegscheider, 1903, p. 697]: “Die von mir auf Seite 98 gewählte Form der Phasenregel steht damit nicht im Widerspruch; sie bezieht sich, wie Seite 93 und 97 hervorgehoben ist, auf eine andere Betrachtungsweise, die sich der üblichen Auffassung des Phasenbegriffes anschliesst, und bei der ”thermodynamisch gleiche” Phasen als gesonderte Phasen gezählt werden, wenn sie tatsächlich in irgend einer Beziehung verschieden sind.”

¹⁵This relation was also derived by Nernst in 1893. It states that the maximum work (A) of a process is directly related to the absolute temperature (T) of a system.

¹⁶[Goldschmidt, 1906, p. 417]. (“Let us now bring together two membranes, respectively permeable to only one of the optical antipodes solutions, to intermingle isothermally and reversibly, [the maximum] work of the process becomes $A = 2RT \ln 2$. [...] Assumed here is the existence of membranes which possess different permeability for two optical antipodes, such membranes – with which the experimental realization I am currently busy – would, of course, as has already been emphasized by Byk, be optically-active and thus form an analogue to the optically active solution emitters, which allows for a separation of racemic mixtures.”) The footnote in the excerpt refers to Byk’s discussion of the thought experiment.

might be of use in inactive mixtures by fungal cultures.¹⁷ Byk and Goldschmidt were thus responsible for extending GP1876 to symmetry and enantiomers, the latter being a typical subject in chemistry but not in physics.

5.3 Boltzmann's Relatedness of Entropy and Probability

In 1905, Boltzmann and his assistant, the Austrian physicist Josef Nabl, finished writing an overview of kinetic theory for Arnold Sommerfeld's *Encyklopädie der mathematischen Wissenschaften*.¹⁸ In a section on entropy they narrated that when one calculates Boltzmann's H for a gas in thermal equilibrium, an expression would be obtained that is nearly identical to the entropy of that gas. This is, of course, a restatement of what Boltzmann had already established in 1877. Boltzmann and Nabl then discussed Boltzmann's work on the relation between entropy and probability, once again stating that natural processes are more likely to pass from improbable to more probable states. It is in this relation that Boltzmann and Nabl found use for the Gibbs paradox:

Die Beziehung zwischen Entropie und Wahrscheinlichkeit zeigt sich im Gibbs'schen Paradoxon⁵³), dass die Entropie eines Gemisches zweier sehr ähnlicher Gase plötzlich viel grosser ist, wenn beide Gase vollständig gleich sind.¹⁹

Boltzmann and Nabl did not elaborate any further on the subject. However, a quick calculation of Boltzmann's entropy of mixing clarifies this view on the relation between entropy and probability. In a statistical consideration, the thought experiment consists of two subvolumes, each containing N particles, and Boltzmann's entropy for a single gas is given by

$$S = k \log W = k \log \frac{V^N}{N!}.^{20} \quad (5.1)$$

The total entropy for two unmixed gases then equals $2k \log \frac{V^N}{N!}$, twice the value of equation (5.1). When the partition is removed, gas A and gas B expand into double the original volume. This means that the number of available microstates per particle

¹⁷[Goldschmidt, 1906, pp. 417–18]: “Vielleicht spielen solche halbdurchlässige Zellwände auch bei der Spaltung von inaktiven Gemischen durch Pilzkulturen eine gewisse Rolle.”

¹⁸[Boltzmann and Nabl, 1905].

¹⁹[Boltzmann and Nabl, 1905, p. 519]. (“The relation between entropy and probability is reflected in the Gibbs paradox, in that the entropy of a mixture of two very similar gases is suddenly much larger, than when both gases are completely equal.”) The footnote in the excerpt refers to Ostwald's translation of GP1876.

²⁰The factor $\frac{1}{N!}$ is included to avoid overcounting. In Gibbs' terms, including the factor results in generic phases, while excluding it results in specific phases.

is also doubled, or $S = k \log \frac{(2V)^{2N}}{(2N)!}$. The entropy difference then becomes

$$\Delta S_{AB} = S_{AB} - S_A - S_B = 2Nk \log 2 - k \log \frac{(2V)^{2N}}{(N!)^2}.^{21} \quad (5.2)$$

In the case of mixing A and A , one also needs to account for all permutations in the exchange of particles from the one subvolume with the other subvolume, thus excluding another $N!$ factor. This mixing of A and A does not give rise to a new physical state. As a result, there can neither be any mixing nor an increase in the entropy of mixing.²² Thus, in Boltzmann and Nabl's view, the Gibbs paradox did indeed display the relation between Boltzmann's entropy and probability in the case of generic phases. Although the authors cited GP1876, the combination of the paradox with Boltzmann's statistical equation makes this interpretation somewhat in between the disciplines of thermodynamics and statistical mechanics.

5.4 Lorentz's Gravity and the Thermodynamic Potentials

By 1907, one of the bigger names in this thesis, Hendrik Antoon Lorentz, had already made contributions to electrodynamics and written a paper that laid the foundation of Einstein's special relativity. The Dutch Nobel prize winner devoted the 11th chapter of his *Abhandlungen über theoretische Physik* to the Second Law of thermodynamics, a subject he is not known for.²³ The paradox is also discussed in this chapter. Lorentz apparently deemed the paradox famous enough to have it included in his register.²⁴

In connection with the Second Law, Lorentz considered the relation between the thermodynamic potential free energy and entropy:

$$\psi = \epsilon - T\eta. \quad (5.3)$$

He reasoned that Gibbs' law – in which the total entropy is the sum of the entropies of the components – is also applicable to free energy when the temperature and volume of a system remain constant. After noting the possibilities of including semi-permeable walls and multiple gases to prove Gibbs' law, Lorentz calculated the decrease in free energy to be $2RT \log 2$, which is equivalent to Nernst's equation of the maximum work.

²¹[Cheng, 2009].

²²[Dieks, 2010, p. 4].

²³[Lorentz, 1907a].

²⁴That is, assuming Lorentz put the register together.

According to Lorentz, comparing values of entropy or the free energy only makes sense when the gases can be diffused as well as separated. Thereafter, he offered an interesting manner of separating two non-identical gases.

Ein solches finden wir nun in äußeren Kräften, die wir auf die Gase wirken lassen; schon die Schwerkraft reicht hin, wenn, wie wir annehmen dürfen, zwei miteinander vermischte Gase sich im Gleichgewichtszustande gerade so über den ihnen gebotenen Raum verteilen, als ob jedes allein vorhanden wäre.²⁵

Thus, in Lorentz's contemplation, when the gases are not identical, they most likely have different molecular weights and would behave differently in a gravitational field. It would therefore be possible to separate two gases using gravity if the container were to be considered infinitely high.

Like Nernst and others before him, Lorentz was more concerned with work, or free energy, than with entropy. This is reflected in his discussion of the mixing of identical gases:

Man würde indes einen Fehler begehen, wenn man nun das Resultat auch auf zwei Portionen ein und desselben Gases anwenden wollte. Sind nämlich solche vollkommen gleiche Gasmengen zunächst durch eine Scheidewand voneinander getrennt, und wird diese dann entfernt, so findet gar keine Änderung der freien Energie statt; bei der jetzt behandelten Frage dürfen wir daher den Fall zwei gleicher Gase nicht als einen Grenzfall betrachten, dem wir ein aus verschiedenen Gasen bestehendes System sich in unserer Vorstellung nähern lassen können. Daß dies etwas paradoxal klingt, kann man nicht leugnen und leider läßt sich das Befremdliche unseres Ergebnisses schwerlich beseitigen. Wir können nur sagen, daß der für den Gibbs'schen Satz gegebene Beweis gültig bleibt, solange die beiden Gase, sei es noch so wenig; verschieden sind, nicht aber, wenn sie ganz gleich sind, und daß der Satz in seinen Anwendungen nie zu Widersprüchen geführt hat.²⁶

Lorentz concluded in this excerpt that Gibbs' law is valid as long as the gases are not identical. As a result, according to Haitun, Lorentz seemed to have offered a solution

²⁵[Lorentz, 1907a, p. 237]. ("As such we find in external forces the ability to act on the gases; even gravity is sufficient when, as must we assume, two mutually mixed gases in equilibrium spread in such a way over the space offered to them, that it is as if each were the only one present.")

²⁶[Lorentz, 1907a, p. 240]. ("One would, however, make a mistake, when one wants to apply the result on two portions of one and the same gas. For if such completely equal gases are initially separated by a septum, which is then removed, no change in free energy takes place; in the now treated question we must therefore not consider the case of two identical gases as a borderline case, where we can leave a system composed of different gases in our imagination. That this sounds a bit paradoxical, one cannot deny and unfortunately the strangeness of our results is difficult to eliminate. We can only say that the evidence provided by Gibbs' law remains valid as long as the two gases, be it ever so little; are different, but not, when the gases are the same, and that the law was never carried out in its applications to contradictions.")

to the paradox by considering the application of Gibbs' law to an *AA* mixture a logical error. In the same year, Lorentz made a similar argument for Boltzmann's *H*-theorem, stating it to be of great importance. The *H*-theorem, in Lorentz's view, shows how the entropy increases when the density of a gas becomes higher in the bottom of the container than in the top of the container due to a gravitational field. This then, again, results in the Gibbs paradox.²⁷

Another physicist who had used the paradox in connection to the second law and potentials was the French inspector general of physical science, Lucien Poincaré, a cousin of the more famous Henri Poincaré. In 1906, one year before the publication of Lorentz's work, Poincaré noted that the concept of potentials had not been fully adopted before Gibbs' *Equilibrium*. Even then, Gibbs', and later Duhem's, work on potentials had not convinced every scientist of their worth. According to Poincaré, many felt that the value of the thermodynamic potential would not always be certain. The paradox is an example of that:

Mais, dans l'esprit de beaucoup de personnes, un doute grave subsistait, la dissolution paraissait un phénomène essentiellement irréversible, l'on ne pouvait par suite, en toute rigueur, calculer l'entropie d'une solution, et par suite non plus être certain de la valeur du potentiel thermodynamique. L'objection, aujourd'hui encore, serait sérieuse, dans les calculs, on serait gêné par ce que l'on appelle le paradoxe de Gibbs.²⁸

Poincaré thus argued that the essential irreversible nature of dissolutions would lead to an uncertainty in the potential. However, this need not be problematic for the thought experiment imagined by Gibbs. As has been explained in previous interpretations of the paradox, gases, at the very least, may be separated as long as they are not identical. This can be done in various ways, such as using solvents, semi-permeable membranes, or even gravity.

²⁷[Lorentz, 1907b, p. 230]: "Übrigens ist das H-Theorem von großer Tragweite; es läßt sich auf alle Körper ausdehnen, die aus getrennten Molekülen bestehen. Es zeigt genau, wie die Entropie zunimmt, wenn unter dem Einfluß der Schwerkraft ein Gas, das ursprünglich einen Raum gleichmäßig füllt, unten eine größere Dichte annimmt als oben. Ebenso läßt es uns erkennen, um wieviel die Entropie eines Gasmisches, wie Boltzmann es oft behandelt hat, von der Entropie der ungemischten Bestandteile verschieden ist. Es ergibt sich dabei der bekannte, oft als Gibbssches Paradoxon bezeichnete Satz."

²⁸[Poincaré, 1906]. ("But in the minds of many, a serious doubt remained, dissolution seemed an essentially irreversible phenomenon, one could therefore, strictly speaking, calculate the entropy of a solution, and as a result not be sure of the value of the thermodynamic potential. The objection, even today, would be serious, in the calculations, it would be bothered by what is called the Gibbs paradox.")

5.5 Van Laar's and Van der Waals' Continued Discussions

Both Van Laar and Van der Waals had already discussed the Gibbs paradox several times before 1902. They continued to invoke it after 1902 as well. Johannes van Laar revisited the paradox several times, though his invocations were usually mere mentions of the paradox. The second volume of the Dutch journal *Chemisch Weekblad*, published in 1905, contained three separate papers by Van Laar with a mention of the paradox. In January 1905, Van Laar indicated the paradox in connection to diluted solutions. He claimed that the paradox plays an explanatory role in the fact that the osmotic pressure of diluted solutions behaves according to the gas laws.²⁹ Van Laar's second mention had him claiming that the osmotic pressure of diluted gases does not actually follow gas laws, it merely give that impression. Instead, he proposed a boundary law, similar, but not identical to the gas laws:

Het z.g. volgen van de wetten der verdunde gassen door den osmotischen druk is dus slechts schijn, en louter toevallig, wat de eerste termen der beide uitdrukkingen voor den druk betreft. Er komt een grenswet, die - tengevolge van het Gibbs'sche paradox, theoretisch gesproken; en tengevolgde der diffusie, praktisch gesproken - wel wat heeft van de wetten der verdunde gassen, maar daarmee toch in geen geval identiek is.³⁰

Thus, according to Van Laar, the desire for the boundary law was stimulated, in a theoretical sense, by the Gibbs paradox. The third article had Van Laar even further continuing his musings on the paradox, osmotic pressure, and thermodynamic potentials. This time, he considered the increase of entropy to be nothing more than the reduction of the value of total potential, a point that was repeated in 1909.^{31,32}

Johannes Diderik van der Waals also revisited the paradox. In 1908, he published the first edition of his *Lehrbuch der Thermodynamik*, the work which Haitun believed to

²⁹[Laar, 1905a, p. 4]: "Hoe het nu eigenlijk komt, dat bij verdunde oplossingen de "osmotische" druk (bij aanwezigheid van een tweede oplossing of zuiver water altijd) die gaswetten schijnt te volgen - dit kan ik u hier niet uitleggen. Dat is een thermodynamische kwestie, die verre van gemakkelijk is. Alleen wil ik vermelden, dat hierbij het z.g. Gibbs'sche paradox een rol speelt, en dat daarbij een zekere term optreedt, nl. - $RT \log(1 - c)$, die alleen bij uiterst verdunde oplossingen overgaat in RTc ."

³⁰[Laar, 1905b, p. 146]. ("The so-called following of the laws of diluted gases by the osmotic pressure is only apparent, and purely by chance, as regards the first terms of both expressions for the pressure. There will be a border case which - as a result of the Gibbs paradox, theoretically speaking; and as a result of the diffusion, practically speaking - has something of the laws of dilute gases, but is not identical to it.")

³¹[Laar, 1905c, pp. 428-429]: "Hieruit blijkt ten duidelijkste, dat na de menging de entropie van den beschouwen component met de (positieve) grootheid - $R \log c_1$ is vermeerderd. Mengt men b.v. 1 Gr. mol. O₂ met 1 Gr. mol. N₂, dan is na de menging de entropie van elk der componenten verhoogd met het bedrag - $R \log 1/2 = R \log 2$. Dit is het z.g. paradox van Gibbs."

³²[Laar, 1909]: "Der Wert [...] $RT \log 2$ ist nichts anderes als die Erniedrigung des Wertes des totalen Potentials für gleiche Mengen der zwei Komponenten nach der Mischung, zufolge des sogenannten 'Gibbsschen Paradoxon'."

contain a solution to the paradox. In reality, the first volume does not discuss the paradox, although it does focus Gibbs' thermodynamic functions. It is the second volume, published in 1912, which devoted a section to the paradox. Because the actual publication of Van der Waals' *Lehrbuch der Thermodynamik* vision of the paradox happened after the period discussed in this thesis, the analysis will be limited to the following statement:

Dies Paradoxon läßt sich in der Tat auf dem Boden der Thermodynamik nicht heben. Nur wenn man tiefer auf die Probleme eingeht und nach der physikalischen Bedeutung der Entropie fragt, d. h. also auf dem schon oft genannten statistischen Wege, ließe es sich klar machen, weshalb man bei der Entropie in Widerspruch gerät, wenn man auf dieselbe einen Satz anwenden will, der sonst überall ohne Schwierigkeit anwendbar ist.³³

Van der Waals evolved interpretation of the paradox thus comes down to it being unexplainable in the thermodynamic view of entropy.

He also communicated a paper by his successor, the physicist Philip A. Kohnstamm, and chemist Frans E.C. Scheffer on December 24, 1910, which made a short mention of the paradox. Kohnstamm and Scheffer explained that the mutual entropy of a system's catalytic agent and reacting mixture in the ideal gas state would have different values than the one they believed to be given by the Gibbs paradox. The value that they associated with the paradox is the $RT \log \mu$ factor of the thermodynamic potential.³⁴ The paper does not describe any version of the thought experiment associated with the paradox, which might mean that they simply used the paradox as a synonym for the entropy of mixing.

None of the interpretations analyzed in this section contain major rethinkings of what the Gibbs paradox is supposed to represent. Van der Waals merely extended his argument that the thought experiment should be considered with identical molecules to an opinion that the paradox is unexplainable in thermodynamics. Van Laar and Kohnstamm and Scheffer, on the other hand, respectively associated the thought experiment with osmotic pressure and catalytic agents.

³³[Waals, 1908, p. 67]. ("This paradox can, on the ground of thermodynamics, not be cancelled. Only when one enters deeper into the problems and asks for the physical meaning of entropy, i.e. in the often-mentioned statistical way, it would be made clear, why one gets entropy in opposition, when one wants to use the same phrase that is applicable everywhere without difficulty otherwise.") The entire discussion of the paradox within the pages 64–68 is both extensive and interesting, however, the essence of it is captured by this quote.

³⁴[Kohnstamm and Scheffer, 1911, p. 791, 802].

5.6 Postma's 'Proof' of the Failure of Analogy

Obe P. Postma, a Frisian Dutch mathematician and poet, had been appointed by Haitun the first scientist after Gibbs to offer a solution from the statistical angle to the paradox. He was, however, not the second to involve statistics in the thought experiment, Boltzmann and Nabl had already done so in 1905. In 1908, Postma wrote a paper on the kinetic derivation of the Second Law which was communicated by Lorentz in *Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeling*. Within this paper, he mentioned an objection to Gibbs' entropy, which Postma denoted as $\eta = - \int P \log P dr$. He argued that this definition no longer allows the addition of an arbitrary constant as was the case in thermodynamics. The constant in statistical mechanics is chosen in such a way that the free energy (ψ) of a system equals the sum of its parts. The constriction of the constant was then related to the paradox by Postma:

In verband hiermee heeft men de eigenschap dat als twee hoeveelheden van verschillende gassen, zich bevindende in gelijke volumes bij dezelfde T , vermengd worden in hetzelfde volume bij dezelfde T , de vrije energie dezelfde blijft, terwijl deze afneemt als men het doet met twee hoeveelheden van hetzelfde gas. Een dergelijke eigenschap bestaat voor de entropie (paradoxe van Gibbs).³⁵

After describing the paradox, Postma posed the question on what would happen to the paradox when considering the kinetically defined entropy of free energy. In answering this question, Postma used another form of Gibbs' entropy:

$$-\eta = \frac{3}{2}N + \frac{3}{2}N \log(2\pi mT) + N \log v. \quad (5.4)$$

According to Postma, in a homogeneous gas, the total entropy does *not* equal the sum of its parts:

$$-\eta_{tot} = 3N + 3N \log(2\pi mT) + 2N \log 2v \neq 3N + 3N \log(2\pi mT) + 2N \log v = -2\eta. \quad (5.5)$$

However, the *increase in entropy* would be equal to the sum of the increases in entropy of the parts. A similar result is obtained when considering the increase in entropy of a mixture of two gasses. The total entropy then becomes

$$-\eta = \frac{3}{2}N + \frac{3}{2}N \log(2\pi T) + \frac{3}{2}N_1 \log(m_1) + \frac{3}{2}N_2 \log(m_2) + N \log v, \quad (5.6)$$

³⁵[Postma, 1908, p. 339]. ("In relation to this, one has the feature that when two amounts of different gases, with equal volumes at the same T , are mixed in that same volume with the same T , the free energy remains the same, while it diminishes when one does the same for two quantities of the same gas. Such a feature exists for the entropy (paradox of Gibbs).")

while the entropies of the parts are

$$- \eta_i = \frac{3}{2} N_i + \frac{3}{2} N_i \log(2\pi T) + \frac{3}{2} N_i \log(m_i) + N_i \log v. \quad (5.7)$$

Subtracting these from each other leads to the entropy of mixing being 0. As a result of this calculation, Postma made the following claim:

Hieruit blijkt $-\eta = -\eta_1 + -\eta_2$, of de entropie van het mengsel is gelijk aan de som der entropieën van de gassen, die het mengsel vormen, wat nu ook geldt als de samenstellende deelen uit hetzelfde gas bestaan. Er is dus geen volkomen analogie met de thermodynamica : voor deze entropie bestaat niet meer het paradoxe van Gibbs.³⁶

Postma thus believed his calculations to prove that, for statistical entropy, $\Delta S_{AB} = \eta_{A+B} - \eta_A + \eta_B = 0$. This would be the case for both different gases and identical gases. As a result, the analogy between thermodynamics and statistical mechanics would fail for the Gibbs paradox. However, as noted by Haitun, Postma's result is erroneous. The volume in Postma's derivations of equation 5.7 is taken to be the total volume, while it should be the partial volume $\frac{V}{2}$. A correction for this factor once again leads to a positive entropy of mixing, $\Delta S = N \log 2$, for all types of mixtures.

Postma explained the non-additivity of absolute entropy to be due to there being more possibilities in the phase space of the mixture than in the phase spaces of the individual gases. That is, $(v_1 + v_2)^{N_1+N_2}$ does not equal $v_1^{N_1} \times v_2^{N_2}$. However, Gibbs' entropy can be made to match thermodynamics by excluding a factor $N!$, which means using generic phases, not specific phases.³⁷ Despite the mistake in Postma's derivation, his is still one of the first attempts to explain the paradox from a statistical point of view.

The mistake was not immediately pointed out. A mention of Postma's work in the bibliography of *Handelingen van het XIIIde Nederlandsch Natuur- en Geneeskundig Congres*, which recapitulated Postma's point perfectly, still contained it:

Terwijl de thermodynamische entropie een integratie-constante bevat, mist men deze bij een kinetische afleiding als bij Gibbs. Deze additieve contante, die bij elke afzonderlijk beschouwde gasmassa een speciale waarde heeft, geeft aanleiding tot de Gibbs'sche paradox. Voor de kinetisch door Gibbs gedefinieerde entropie geldt deze paradox niet : [...] ook al zijn [de gasmassa's] identiek. Wil echter de

³⁶[Postma, 1908, p. 342]. The English version, [Postma, 1909], excludes parts of the discussion on the paradox and uses slightly different terms: "So there is no perfect harmony with thermodynamics: for this entropy Gibbs's paradox no longer holds."

³⁷After Postma had written this, he discovered that Gibbs had already remarked the same. [Postma, 1908, p. 342]: "Toen ik het bovenstaande geschreven had, bemerkte ik, dat het laatste niet nieuw is. Ook Gibbs zelf heeft reeds in den laatsten zin van zijn boek de opmerking gemaakt [...]."

stelling doorgaan, dat de entropie eener homogene gasmassa gelijk is aan de som van de entropieën harer deelen, dan moet bij de berekening der entropie niet op de "specifieke" phasen, doch op de "generieke" phasen worden gelet.³⁸

Another physicist to continue on the subject of analogies was Edwin B. Wilson, not to be confused with the zoologist Edmund B. Wilson. Wilson, Gibbs' student who compiled the textbook on vector analysis, set out to present analogies between the statistical properties of gases and their thermodynamic considerations. Although Wilson perceived the analogous relation between the canonical ensemble and thermodynamics to be quite strong, he noted that the mixing of gases might be an exception.

As a matter of fact the mixing of gases depends on a principle in addition to those here given for a simple gas and contains a somewhat troublesome paradox known as Gibbs's paradox. The matter of mixing gases and the analogous combinations of dynamical systems will therefore be omitted from the present discussion.³⁹

Nevertheless, as explained by Gibbs in 1902 and by Postma in 1908, the analogy might be valid when one restricts himself to generic phases. The discussion of Gibbs' statistical entropy and the thermodynamic-statistical analogy marks the end of the interpretations on the paradox in the period 1902–1911.

5.7 Beyond 1911

In 1911, the same year as the famous first Solvay conference on radiation and quanta, the Ehrenfests' had their overview of statistical mechanics published in Arnold Sommerfeld's *Encyklopädie*. Prior to this, in 1906, Paul and Tatjana Ehrenfest had already co-written a paper on Gibbs' statistical mechanics. In both works, they considered Gibbs' attempt inadequate. According to Klein, this may simply have been because Paul Ehrenfest considered the problem of irreversibility – not the focus in Gibbs' work – the key concept in statistical mechanics.⁴⁰ Gibbs and Ehrenfest were thus involved in different aspects of the discipline. Instead, Boltzmann's approach, which supposedly gave a larger insight into what was happening, was considered to be far superior. The Ehrenfests did not discuss the paradox and even limited their thoughts about the famed canonical ensemble

³⁸[Dalfsen, 1909]. ("While the thermodynamic entropy contains an integration constant, this is missing in a kinetic derivation such as the one by Gibbs. This additive constant, which has a special value for each independent body of gas, leads to the Gibbs paradox. For Gibbs' kinetically defined entropy this paradox is not valid: [...] even when the gas masses are identical. However, when one wants to continue the argument that the entropy of a homogeneous mass of gas is equal to the sum of the entropies of its parts, then the entropy in the calculations is not given by the "specific" phases, but by the "generic" phases.")

³⁹[Wilson, 1909, p. 158].

⁴⁰[Klein, 1972, p. 129].

to it being “ein analytischer Kunstgriff”.⁴¹ Only in 1920 would Paul Ehrenfest co-publish a paper with Viktor Trkal which discussed the paradox. Nevertheless, 1911, the year in which the overview was published, remains the end of the period to be fully considered in this thesis.

The progression of the paradox after 1911 may be described shortly using Pérez Canals’ account. In the first decade after 1911, the debate seemed to diverge into a debate on the justification of the inclusion of various N -factors in the thermodynamic probability W . Historical actors involved in this debate include Otto Sackur, Hugo Tetrode, Postma, Otto Stern, Lorentz, Einstein, Ehrenfest and Trkal, and Planck.⁴²

The 1910s were marked by discussions between Sackur, Tetrode, Planck and Lorentz on whether one should account for the extensivity of entropy in the probability W . Sackur introduced the factor N^{-N} in 1912 while Tetrode offered, like others before him, the factor $(N!)^{-1}$ in his *interchangeability argument*. This argument states that in order to obtain an extensive entropy, the total number of microstates must be divided by $N!$. In a revision stimulated by Lorentz’s comments, Tetrode noted that the justification for including the $N!$ factor remained vague. Nevertheless, Planck, for one, supported both Tetrode’s factor and justification. Not every scientist reacted the same to this factor. In 1906, Postma argued that this factor was nothing more than an element stemming from the extensivity condition, while Einstein expressed his doubts on the classical kinetic models that were used in these arguments. Ehrenfest and Trkal’s account, perhaps, best formulated the situation as it was in the 1920s:

It is not an accident that it is always the same point that remains obscure in these theories, viz., how an expression of the form N^{-N} (Sackur) or $(N!)^{-1}$ (Tetrode) can be forced into the – thermodynamic probability W in order to obtain an admissible value for the entropy. [...] The law of dependence on N can only be satisfactorily settled by utilizing a process in which N changes reversibility and then comparing the ratios of the probability with the corresponding differences of entropy.⁴³

Ehrenfest thus once again paid special attention to the concept of reversibility. This publication and one by Planck in 1921 signified the end of the main focus of the paradox being on the N factor.

After the establishment of quantum mechanics, the discussion turned to the notions of identical quantum particles and non-extensive entropy. Especially in the 1950s, this

⁴¹[Ehrenfest and Ehrenfest, 1911, p. 59].

⁴²[Sackur, 1911], [Sackur, 1912], [Sackur, 1913], [Tetrode, 1912], [Tetrode, 1915], [Stern, 1913], [Stern, 1914], [Lorentz, 1914], [Postma, 1916], [Einstein, 1916], [Ehrenfest and Trkal, 1920], [Planck, 1916], and [Planck, 1921].

⁴³[Ehrenfest and Trkal, 1920, pp. 162–63].

lead to the claim that the paradox in a certain sense predicted the need for quantum mechanics. This discussion was, according to Pérez Canals, fueled by Erwin Schrödinger, John C. Slater, and Kerson Huang.⁴⁴ In 1939, Slater reasoned that there is no diffusion of identical gases because the particles are quantum identical. Schrödinger, who is often cited as the instigator, repeated this argument in his Seminar Lectures delivered in 1944. Finally, in 1963, Huang justified the introduction of the N factor with the inherent indistinguishability of quantum particles. This common point of view can be found in Alfred Landé's discussion of the paradox:

Yet classical statistical mechanics suffers from a discontinuity pointed out first by W. Gibbs in the 1870's. This is the *discontinuity paradox of Gibbs*, which classical theory cannot solve, although various answers have been proposed. The results that one must subtract from the classical entropy expression the term $Nk \ln N$, which for large N is the same as $k \ln N!$, means that the classical probability of a configuration of N identical parts must be divided by the permutation factor $N!$. That is, count the $N!$ permutations of N identical particles as only one single case. Quantum theorists have come to this conclusion only in connection with rather late developments about the symmetry character of ψ -functions.⁴⁵

All these developments led to the polysemic Gibbs paradox obtaining even more interpretations and being associated with quantum statistics as well.

5.8 Analysis of the Paradox Interpretations

Although Gibbs had acquired quite some fame by 1902, his *Statistical Mechanics* was not read to that extent that his peers immediately picked up on the statistical version of the thought experiment. With the exception of Boltzmann and Nabl, and Postma, the reactions in the period between 1902 and 1911 still addressed the thermodynamic version of the paradox. Even so, in comparison with the earlier reactions, a more extensive diversion of the interpretations had started to set in. Many of the interpretations did not focus on the paradoxical problem itself, but on extending the associated thought experiment. Remarkable is the amount of suggestions for separating two gases.

Several of the references to the paradox discussed in this period are continuations of earlier interpretations of the paradox. Van der Waals and Van Laar are examples of this. Van Laar did not reinterpretate his thoughts on the paradox. He did, however, connect osmotic pressure and thermodynamic potentials to the thought experiment. The increase of entropy was then thought to be due to the reduction of the value of the total potential.

⁴⁴[Schrödinger, 1946], [Slater, 1939], [Huang, 1963].

⁴⁵[Landé, 1965, pp. 65–66].

Lucien Poincaré, on the other hand, believed the paradox to show discrepancies in the concept of thermodynamic potentials. Van der Waals also reformulated his assertion that the paradox cannot be explained from within thermodynamics; the statistical definition of entropy is the one that should be used in connection to the thought experiment.

Other examinations of the paradox solely consisted of variations of earlier interpretations. Goldschmidt, like Byk, discussed symmetrical substances and Ruer, similarly to Larmor, considered a diffusion rate of the gases. Kohnstamm and Scheffer introduced new chemical substances that might be adaptable to the thought experiment: a catalytic agent and its reacting mixture. Those examinations did not consider the actual paradox itself, leaving a categorization unnecessary. Mere citations, such as the account of Garrison, will not be categorized as well.

The first dialogue on the paradox seems to have been Larmor's *Encyclopædia Britannica* article. Larmor's association of the paradox with the diffusion rate had not substantially changed since 1897. His contribution is therefore still categorized as a *paradox due to the impracticability of mixing infinitely similar gases*. However, the inclusion of the paradox in a widely-read encyclopedia was vital to the distribution of the knowledge of the existence of the paradox to those who may not have read actual scientific publications. This makes Larmor's second contribution valuable to this thesis.

Byk imagined the thought experiment for optically active substance. As a result, the semi-permeable walls, introduced to the paradox by Nernst in 1893, would only be permeable to either *l*-, or *d*-enantiomers. The notion of molecule symmetry was hence connected to the paradox. His contribution was more of a suggestion than an interpretation of the paradox. It may therefore be categorized as a *consideration of symmetry in the thought experiment*.

Boltzmann and Nabl were the first besides Gibbs to connect the idea of many particles to the paradox, thus making their contribution partly statistical. In their view, the paradox merely shows that there is a strong connection between entropy and probability. Their interpretation is categorized as a *verification of the relation between entropy and probability*.

Lorentz also introduced a new way to separate non-identical gases in the thought experiment. When constructing the container holding the gases to be infinitely long, gravity may be used to separate two gases with different molecular weights. This method only works for different gases as identical gases cannot be mixed. Lorentz's interpretation of the paradox is similar to the ideas echoed by Nernst and Duhem. That is, despite his *consideration of gravity in the experiment*, the paradox persists. It is caused by the *logical error of allowing identical gases to mix*.

Postma calculated the entropy of mixing to be zero in statistical mechanics. This result, which turned out to be a miscalculation, contrasts with the thermodynamic result due to a difference in the integration constant. Postma believed the paradox to be a failure of the analogy between thermodynamics and statistical mechanics. Similarly, Wilson also believed the analogy for the paradox to be invalid. Their reactions may therefore be categorized as a *failure of the thermodynamic-statistical analogy due to the exclusion of the thermodynamic integration constant*.

Further major trends in the interpretations of the paradox can roughly be divided into two phases, not including Haitun's informational and operational phases:

- *Statistical: The inclusion of any N -factor in statistical entropy and its justification.*
- *Quantum mechanical: Solving the paradox by using quantum identical particles.*

Pérez Canals' account of the association switch in particles from identity to indistinguishability dealt with these trends to some extent. However, in order to fully understand the evolution of the polysemic Gibbs paradox, the responses to the paradox would have to be constructed without the identity of particles bias.

5.8.1 Conclusion

Although most of these reactions were not actual interpretations of the paradox, they did collectively offer many ways to extend the thought experiment. While the period 1876-1902 resulted in the inclusion of the semi-permeable walls, this period had contributions on gravity, fungi, enantiomers, catalytic agents, and osmotic pressure. Only Postma and Wilson made an attempt to consider the concept of analogy in a way that Gibbs used it, though they both rejected the idea. Postma and Wilson, in addition to Boltzmann and Nabl, were the only ones to treat the paradox from a statistical angle. Even so, already this early, the diversion of the interpretations of the paradox is noticeable.

In comparison to the reactions from 1876–1902, the number of references to the paradox has relatively increased in 1902–1911. In addition to original contributions, arguments were now repeated as well. The term 'Gibbs paradox' had become famous enough that many did not feel the need to fully state the thought experiment that usually accompanied it. Unfortunately, this means that the overall interpretation of the paradox, with its many associated physical phenomena and chemical substances, was even more difficult to pinpoint. Hence the confusion that reigned and still reigns over most publications on the Gibbs paradox.

6

Conclusion

This chapter is an overall conclusion to the four main chapters of the current exposition. It briefly recaps how the term ‘Gibbs paradox’ became polysemic. As noted, the polysemy has both positive and negative consequences. While the many interpretations of the thought experiment have led to a significant confusion in the current literature on the paradox, these interpretations might be used for a specific history of the development of the related concepts. In the introduction of this thesis, the following research question was posed to encapsulate this duality:

How has the interpretation of the Gibbs paradox changed from its inception in 1876 until its early inclusion in discussions surrounding quantum theory, and how does this shifting perspective reflect on developments within foundational, physical concepts?

The answer to this lies in recognizing that at least two types of adjustments to the paradox have been made. On the one hand, new physical phenomena and concepts were associated with the interpretation of the paradox itself. On the other, different chemical substances would be made subject to the thought experiment connected to the paradox.

In 1876, Gibbs discussed a thought experiment with a similar set-up to the container of Maxwell’s demon in order to obtain an insight as to what entropy might or might not be as a concept. In this discussion, Gibbs considered the question of why alike gases behave differently from unlike gases in an expansion-diffusion. Eventually he reached the conclusion that a diffusion of identical gases would not lead to a new thermodynamic state, while a diffusion of two different gases would. This response was very much in agreement with the physics at that time. That is, thermodynamics was the prevailing discipline for considerations of this sort. Gibbs did not associate any contradictions with the considerations he derived from the thought experiment. Nor did he believe the situation to be inconsistent when he published the paper. The Gibbs paradox therefore did not exist as a paradox in 1876.

In the period 1876–1902, a handful of physicists reacted to either the paradox as a whole or to the thought experiment by itself. Maxwell and Nernst extended the thought experiment only, by, respectively, introducing reversibility and semi-permeable membranes to it. While Neumann was the first to notice something odd about the mathematical calculation of the entropy of mixing contradicting the thermodynamic state, Duhem first used the term ‘paradox’ to denote this oddity. He stated it to be due to Gibbs’ illogical definition of mixing identical gases. Wiedeburg finally declared Gibbs’ considerations the ‘Gibbs paradox’ in 1893. Unlike Duhem and Neumann, he focused on the false assumption of continuity in degrees of similarity, an interpretation Van Laar also adhered to. Planck, like Gibbs and Maxwell, did not consider it to be a paradox, but a mere verification of a fundamental difference between chemical and physical properties. Larmor and Van der Waals, on the other hand, did regard it as a paradox, though both, again, tied it to distinct physical concepts. Larmor believed the paradox to be due to the impracticability of mixing infinitely similar gases while Van der Waals considered it to be a result of the macroscopic limit of thermodynamics.

Even though they disagreed on what concept led to the discrepancy paradox, these historical actors mostly worked on the same problem and in the same discipline. The different interpretations of Gibbs’ thought experiment show that many concepts in it can be and have been challenged. These challenged concepts – entropy, reversibility, identity and distinguishability, continuity, molecules, and thermodynamics itself – were, at this time, all disputed by physicists and chemists to some degree. For example, entropy was given a new statistical definition and the collaboration between thermodynamics and kinetic theory led to different insights on continuity and distinguishability. Therefore, the development of the concepts associated with the paradox reflected the development of those concepts in physics itself.

Gibbs returned to the thought experiment in 1902, when he combined a statistical definition of entropy with ensembles in a book constructed as a thermodynamic-statistical analogy. This time, Gibbs had a logical explanation for the discrepancy between different gases and identical gases, instead of an empirical one. While it was invoked in 1876 to explain some properties of entropy, this rendition was more of an analogical tool to demonstrate the choice for generic phases over specific phases. In any case, Gibbs still did not describe his findings as paradoxical.

The responses in the period 1902–1911 marked a more pervasive diversion of the interpretations of the paradox. With the exception of Boltzmann and Nabl, and Postma, the reactions still addressed the thermodynamic version of the paradox. Many focused on extending the associated thought experiment. It resulted in the inclusion of gravity, fungi, enantiomers, catalytic agents, and osmotic pressure. The actual original

interpretations of the paradox were given by Byk, Boltzmann and Nabl, Lorentz, and Postma. Byk imagined the thought experiment for optically active substance and, as a result, connected symmetry to the paradox. Boltzmann and Nabl viewed the paradox as a verification of Boltzmann's relation between entropy and probability. Lorentz considered the mixing of identical gases a logical error. And, finally, Postma blamed the exclusion of the arbitrary thermodynamic integration constant for the failure of the thermodynamic-statistical analogy.

The interpretations by these actors are split in two physical disciplines – thermodynamics and statistical mechanics – and are related to foundational developments of the involved concepts. For instance, Boltzmann used the paradox to support his own findings and Postma considered the statistical version of the paradox while the use of analogies was still in practice. The overall interpretation of the paradox, with its many associated physical phenomena and chemical substances, was becoming more difficult to pinpoint in this period. The thermodynamic version, nowadays often denoted by the term 'mixing paradox', tended to focus on the idea that the value of the entropy of mixing would only be zero for identical gases but not for two infinitely similar gases. The statistical version revolved around the idea that entropy is not extensive and that this should be corrected for by a factor proportional to N . New solutions to the "Gibbs paradox" should keep these, and further, distinctions in mind.

6.1 Suggestions for further research

Although the first 35 years of the Gibbs paradox, described in this thesis, are quite informative, a full understanding of the polysemic Gibbs paradox can only be established when the recent developments are accounted for as well. This thesis mentioned two further major trends in the interpretations of the paradox: The inclusion of any N -factor in statistical entropy and the solving of the paradox with quantum identical particles. Although Pérez Canals' account deals with these trends to some extent, his focus lay mainly on the identity of particles. Other concepts may be assumed to have been involved as well. An extension of the research in this thesis would therefore have to sift through the many papers and books on the paradox in order to pinpoint key works in the development of the paradox itself. A good starting point, besides Pérez Canals, would be Haitun's *History of the Gibbs Paradox*. In any case, a historical account of the paradox and the thought experiment would serve to disentangle the confusion surrounding it. Only then might it be possible to construct solid solutions to the valid versions of the Gibbs paradox.

Appendix A

Correspondence and Reprints

Gibbs kept track of whom he sent copies of his papers and book. A list of the recipients and the scientific correspondence between Gibbs and the scientific community can be found in the Appendices of Wheeler’s Biography.¹ This appendix contains an alphabetically ordered list of correspondents.

As counted by [Wheeler, 1962, pp. 93–4], the list “comprises 160 names from [the United States] and Canada, 119 from Great Britain, 104 names from Germany, 57 from France, 11 from Italy, 10 from Holland and Belgium, 10 from Austria, 8 from Russia, 8 from Switzerland, 6 from Norway and Sweden, 5 from Poland, 3 from Denmark, 2 from India, and one each from Spain, Brazil, China, and Japan – a total of 507 names.” This shows that it is highly unlikely that Gibbs’ work was unknown until the translations by Ostwald and Le Châtelier.

Distribution of Gibbs’s main works sent by Gibbs himself:²

| Work | To Individuals | To Institutions |
|--------------|----------------|-----------------|
| EHS Part I | 89 | 10 |
| EHS Part II | 92 | 10 |
| EHS Abstract | 116 | 11 |
| EPSM | ≥ 21 | ≥ 9 |

List of correspondents and recipients of *Equilibrium* and *Statistical Mechanics*:

| Person | Correspondence | Eq. | S.M. |
|-------------|------------------|-----|------|
| Abbe, C. | 1885, 1893, 1902 | ✗ | ✗ |
| Abraham, M. | 1899 | ✗ | ✗ |
| Adams, J.C. | ✗ | ✓ | ✗ |
| Adams, W.G. | ✗ | ✓ | ✗ |

¹[Wheeler, 1962, p. 219–248].

²The Connecticut Academy distributed even more copies of *Equilibrium* Part I and II, making the total distribution about 270 copies. Scribners send *Statistical Mechanics* to an additional 20 institutes. [Wheeler, 1962, p. 247].

| | | | |
|-----------------------|------------------|---|----|
| Airy, G.B. | ✗ | ✓ | ✗ |
| Aitken, J. | 1876, 1877 | ✓ | ✗ |
| Andrews, T. | ✗ | ✓ | ✗ |
| Appell, P.E. | ✗ | ✗ | ✓ |
| Bakhuis Roozeboom, B. | 1902 | ✗ | ✓ |
| Ball, R.S. | 1902 | ✓ | ✓ |
| Bancroft, W.D. | 1898, 1899 | ✗ | ✗ |
| Barker, G.F. | ✗ | ✓ | ✗ |
| Barrett, W.F. | ✗ | ✓ | ✗ |
| Barth, J.A. | 1902 | ✗ | ✗ |
| Baynes, R.E. | 1879 | ✓ | ✗ |
| Becker, G.F. | 1886 | ✗ | ✗ |
| Berthelot, M.P.E. | ✗ | ✓ | ✗ |
| Bertrand, J. | ✗ | ✓ | ✗ |
| Besant, W.H. | 1885 | ✗ | ✗ |
| Birely, W.E. | 1881 | ✗ | ✗ |
| du Bois-Reymond, P. | ✗ | ✓ | ✗ |
| Boltzmann, L. | 1892 | ✓ | ✓* |
| Bossche, J. | 1902 | ✗ | ✗ |
| Boussinesq, V.J. | ✗ | ✗ | ✓ |
| Bowditch, H.P. | 1891 | ✗ | ✗ |
| Braun, K.F. | ✗ | ✓ | ✗ |
| Briot, Ch. | ✗ | ✓ | ✗ |
| Bucherer, A.H. | 1902 | ✗ | ✗ |
| Buchholz, H. | 1898 | ✗ | ✗ |
| Brunhes, B. | 1902 | ✗ | ✗ |
| Bunsen, R.W. | ✗ | ✓ | ✗ |
| Burbury, S.H. | 1902, 1903 | ✗ | ✓ |
| Cahours, A. | ✗ | ✓ | ✗ |
| Cayley, A. | ✗ | ✓ | ✗ |
| Cazin, A. | ✗ | ✓ | ✗ |
| Challis, J. | ✗ | ✓ | ✗ |
| Chambers, C. | 1880 | ✓ | ✗ |
| Claus, A. | ✗ | ✓ | ✗ |
| Clausius, R. | ✗ | ✓ | ✗ |
| Clifton, R.B. | ✗ | ✓ | ✗ |
| Cooke, J.P. | 1889 | ✓ | ✗ |
| Cornelius, C. | ✗ | ✓ | ✗ |
| Couterat, L. | 1899 | ✗ | ✗ |
| Craig, T. | 1882, 1883, 1888 | ✗ | ✗ |
| Cremona, L. | ✗ | ✗ | ✓* |
| Dana, J.D. | ✗ | ✓ | ✗ |
| Darwin, G.H. | 1902 | ✗ | ✓ |

| | | | |
|-------------------------|------------------------------------|---|----|
| Dewar, J. | 1883 | ✓ | ✓* |
| Duclaux, E. | ✗ | ✓ | ✗ |
| Duhem, P. | 1887, 1900, 1902 | ✓ | ✓ |
| Dühring, E. | ✗ | ✓ | ✗ |
| Dumas, J.B. | ✗ | ✓ | ✗ |
| Dupré, A. | ✗ | ✓ | ✗ |
| Earnshaw, S. | ✗ | ✓ | ✗ |
| Eddy, H.T. | ✗ | ✓ | ✗ |
| Engel, F. | 1893 | ✗ | ✓* |
| Engelmann, W. | 1892, 1895 | ✗ | ✗ |
| Everett, J.D. | ✗ | ✓ | ✗ |
| Favre, P.A. | ✗ | ✓ | ✗ |
| von Feilizsch, F.K.O. | ✗ | ✓ | ✗ |
| Föppl, A. | 1902 | ✗ | ✗ |
| Forster, A. | ✗ | ✓ | ✗ |
| Foster, G.C. | ✗ | ✓ | ✗ |
| Frankland, Ed. | ✗ | ✓ | ✗ |
| Freeman, A. | 1875, 1878, 1880, 1881, 1884, 1890 | ✓ | ✗ |
| Fresenius, R. | ✗ | ✓ | ✗ |
| Gibbs, W. | 1881, 1897, 1902 | ✓ | ✓ |
| Glazebrook, R.T. | 1893 | ✗ | ✗ |
| Gould, A.B. | 1897 | ✗ | ✗ |
| Gould, B.A. | 1889 | ✗ | ✗ |
| Grant, R. | ✗ | ✓ | ✗ |
| Grassmann, H. | 1888, 1889, 1891, 1892, 1893 | ✗ | ✗ |
| Griffiths, E.H. | 1895 | ✗ | ✗ |
| Grove, W.R. | ✗ | ✓ | ✗ |
| Grunert, J.A. | ✗ | ✓ | ✗ |
| Guthrie, F. | ✗ | ✓ | ✗ |
| Hadamard, J. | ✗ | ✗ | ✓ |
| Hagen, J.G. | 1893 | ✗ | ✗ |
| Hagenbach-Bischoff, Eh. | ✗ | ✓ | ✗ |
| Hall, A. | 1886 | ✗ | ✗ |
| Handl, A. | ✗ | ✓ | ✗ |
| Hart, D.S. | ✗ | ✓ | ✗ |
| Hastings, Ch.S. | ✗ | ✓ | ✗ |
| Heaviside, O. | 1888, 1894 | ✗ | ✗ |
| von Helmholtz, H. | ✗ | ✓ | ✗ |
| Hertz, H. | 1889 | ✗ | ✗ |
| Herwig, H. | ✗ | ✓ | ✗ |
| Hill, T. | 1890 | ✗ | ✗ |
| Hirn, G.A. | ✗ | ✓ | ✗ |
| Hirst, T.A. | ✗ | ✓ | ✗ |

| | | | |
|-------------------|------------------|---|----|
| van 't Hoff, J.H. | X | X | ✓* |
| Horstmann, A. | X | ✓ | ✓* |
| Jamin, J. | X | ✓ | X |
| Jenkin, H.C.F. | X | ✓ | X |
| von Jolly, J.P.G. | X | ✓ | X |
| Joule, J.P. | X | ✓ | X |
| Kekulé, A. | X | ✓ | X |
| Kelland, P. | X | ✓ | X |
| Kimura, S. | X | X | ✓ |
| Kirchhoff, G. | X | ✓ | X |
| Klein, F. | 1892, 1893, 1895 | X | ✓* |
| Klein, H. | X | ✓ | X |
| Klein, J.F. | X | ✓ | X |
| Knott, C.G. | 1893 | X | X |
| Kohlrausch, F. | X | ✓ | ✓* |
| Kolbe, H. | X | ✓ | X |
| Kopp, H. | X | ✓ | X |
| Krebs, G. | X | ✓ | X |
| Kronecker, L. | 1891 | ✓ | X |
| Kundt, A. | X | ✓ | X |
| Lamarle, E. | X | ✓ | X |
| von Land, V. | X | ✓ | X |
| Langley, S.P. | 1886, 1894, 1895 | X | X |
| Larmor, J. | X | X | ✓* |
| Le Châtelier, H. | 1902 | X | ✓ |
| Levy, M. | X | ✓ | X |
| Liouville, J. | X | ✓ | X |
| Lippich, F. | X | ✓ | X |
| Lippmann, G. | X | ✓ | X |
| Lodge, O. | 1887 | ✓ | X |
| Loomis, F.E. | X | X | ✓ |
| Lorentz, H.A. | 1884, 1902 | X | ✓ |
| Loschmidt, J. | X | ✓ | X |
| Lovering, J. | 1880 | X | X |
| Macfarlane, A. | 1899, 1901 | X | X |
| Magie, W.F. | X | X | ✓ |
| Massieu, F. | 1878 | ✓ | X |
| Mathieu, E. | X | ✓ | X |
| Maxwell, J.C. | X | ✓ | X |
| McAulay, A. | 1894 | X | X |
| McCulloch, R.S. | X | ✓ | X |
| Meldola, R. | 1897 | X | X |
| Mellor, J.W. | 1902 | X | X |

| | | | |
|------------------------|------------------------------|---|----|
| van der Mensbrugge, G. | X | ✓ | X |
| Merriman, M. | X | ✓ | X |
| Meyer, E.S.C. | X | ✓ | X |
| Meyer, L. | X | ✓ | X |
| Meyer, O.E. | X | ✓ | X |
| Meyerhoffer, W. | 1893 | X | X |
| Michelson, A.A. | 1884, 1885, 1886, 1890 | X | X |
| Mittag-Leffler, G. | X | X | ✓ |
| Mohr, F. | X | ✓ | X |
| Moore, E.H. | 1890, 1902 | X | X |
| Mousson, A. | X | ✓ | X |
| von der Mühle, C. | X | ✓ | X |
| Müller, W. | X | ✓ | X |
| Naumann, A. | X | ✓ | X |
| Neumann, C. | X | ✓ | X |
| Neumann, F. | X | ✓ | X |
| Newcomb, S. | 1901, 1902 | ✓ | ✓ |
| Newton, H.A. | 1884 | ✓ | X |
| Ohrtmann, C. | X | ✓ | X |
| Omnes, H.K. | 1900 | X | ✓* |
| Ostwald, W. | 1887, 1888, 1889, 1891, 1895 | X | ✓* |
| von Oettingen, A. | X | ✓ | X |
| Pattison Muir, M.M. | 1880 | X | X |
| Peirce, Bn. | X | ✓ | X |
| Peirce, B.O. | X | ✓ | X |
| Peirce, C.S. | 1881 | X | X |
| Peirce, J.M. | 1884 | X | X |
| Person, C.C. | X | ✓ | X |
| Pfanneller, L. | X | ✓ | X |
| Phillips, E. | X | ✓ | X |
| Pirie, G. | 1878 | ✓ | X |
| Planck, M. | 1902 | X | ✓ |
| Plateau, J.A.F. | X | ✓ | X |
| Playfair, L. | X | ✓ | X |
| Poincaré, H. | 1901 | X | ✓* |
| Price, B. | X | ✓ | X |
| Pritchard, Ch. | X | ✓ | X |
| Quincke, G.H. | X | ✓ | X |
| Ramsey, Wm. | 1884, 1885, 1897 | ✓ | X |
| Regnault, V. | X | ✓ | X |
| Reinold, A.W. | X | ✓ | X |
| Remsen, I. | X | ✓ | X |
| Resal, H. | X | ✓ | X |

| | | | |
|------------------------------|------------------------|---|----|
| Richards, C.B. | X | ✓ | X |
| Ritter, A. | X | ✓ | X |
| Rood, O.N. | 1893 | X | X |
| Roscoe, H.E. | X | ✓ | X |
| Rowland, H.A. | 1879, 1884 | ✓ | X |
| Rüdorf, Fr. | X | ✓ | X |
| Rühlmann, R. | X | ✓ | X |
| de Saint-Robert, P. | X | ✓ | X |
| Saint-Claire Deville, H. | X | ✓ | X |
| Sampson, W.T. | X | ✓ | X |
| Schlegel, V. | 1888, 1891 | X | X |
| Schlömilch, O. | X | ✓ | X |
| Schneider, Th. | X | ✓ | X |
| Schwalbe, B. | X | ✓ | X |
| Smith, T.A. | X | ✓ | X |
| Smyth, C.P. | X | ✓ | X |
| Städel, W. | X | ✓ | X |
| Stallo, J.B. | 1884 | X | X |
| Stefan, J. | X | ✓ | X |
| Stevens, A.J. | X | ✓ | X |
| Stewart, B. | X | ✓ | X |
| Stokes, G.G. | X | ✓ | X |
| Strutt (Lord Rayleigh), J.W. | 1892, 1901, 1902 | ✓ | ✓ |
| Study, E. | 1889 | X | X |
| Subic, S. | X | ✓ | X |
| Sylvester, J.J. | 1883, 1886 | ✓ | X |
| Szily, C. | X | ✓ | X |
| Tait, P.G. | X | ✓ | X |
| Thomson, Dr. J. | X | ✓ | X |
| Thomson, J. | X | ✓ | X |
| Thomson, J.J. | 1884, 1899, 1901, 1902 | ✓ | ✓ |
| Thomson (Lord Kelvin), W. | 1901, 1902 | ✓ | ✓ |
| Thurston, R.H. | X | ✓ | X |
| Todhunter, I. | 1879 | X | X |
| Trevor, J.E. | 1895, 1896, 1897, 1899 | X | X |
| Troost, L. | X | ✓ | X |
| Trowbridge, J. | 1881 | ✓ | X |
| Trowbridge, Wm.P. | X | ✓ | X |
| Tyndall, J. | X | ✓ | X |
| Van Name, J.B. | X | X | ✓ |
| Vicain, W. | X | ✓ | X |
| Vieweg, F. | 1902 | X | X |
| van der Waals, J.D. | 1900 | ✓ | ✓* |

| | | | |
|----------------------|------------|---|----|
| Wald, F. | 1895, 1896 | ✗ | ✗ |
| Waldo, L. | ✗ | ✓ | ✗ |
| Watson, H.Wm. | ✗ | ✓ | ✓* |
| Watts, H. | ✗ | ✓ | ✗ |
| Weber, H.F. | ✗ | ✓ | ✗ |
| Weber, W. | ✗ | ✓ | ✗ |
| Weirstrass, K. | ✗ | ✓ | ✗ |
| Wichelhaus, H. | ✗ | ✓ | ✗ |
| Wiedemann, G. | ✗ | ✓ | ✗ |
| Williamson, A.W. | ✗ | ✓ | ✗ |
| Winkelman, A. | ✗ | ✓ | ✗ |
| von Wróblewski, Z.F. | ✗ | ✓ | ✗ |
| Wüllner, A. | ✗ | ✓ | ✗ |
| Wurtz, C.A. | ✗ | ✓ | ✗ |
| Young, C.A. | 1884 | ✗ | ✗ |
| Zeuner, G. | ✗ | ✓ | ✗ |

* On list of personal distribution of *Statistical Mechanics* but not checkmarked.

Appendix B

Main Responses to the Paradox

Many physical concepts and chemical substances have been associated with the Gibbs paradox. This is also true for the period 1876–1911. The categorizations of the individual interpretations of the paradox are reproduced in this appendix along with the branch in which it was considered. Additionally, a list of works relevant to the paradox, up to 1986, is included as well.

Categorization of the responses to the Gibbs paradox in the period 1876–1911:

| Year | Author | Branch | Categorization |
|------------------|--------------------|--------|--|
| 1876 | J.W. Gibbs* | TD | Series of considerations based on an expansion-diffusion thought experiment with a focus on the concept of entropy. |
| 1877 | J.C. Maxwell† | TD | Consideration focusing on the concept of reversibility, and the associated notions of separability and distinguishability. |
| 1891 | C. Neumann* | TD | Discrepancy due to a mathematical calculation contradicting the thermodynamic state. |
| 1892 | P. Duhem** | TD | Paradox due to Gibbs' definition not matching real gases. |
| 1892 | A. Poincaré* | TD | – (fueled Duhem's reaction). |
| 1893 | W. Nernst† | TD | Association of the thought experiment with semi-permeable membranes and solvents. |
| 1892 | W. Ostwald | TD | German translation of <i>Equilibrium</i> |
| 1894 | O. Wiedeburg** | TD | Paradox due to the false assumption of continuity in degrees of similarity. |
| 1897 | M. Plank* | TD | Verification of a fundamental difference between chemical and physical properties. |
| 1897, 1902 | J. Larmor | TD | Paradox due to the impracticability of mixing infinitely similar gases. |
| 1897– 1912(!) | J.D. van der Waals | TD | Paradox due to the macroscopic limit of thermodynamics. |
| 1898– 1909 | J.J. van Laar | TD | Paradox due to the discontinuity in the degrees of similarity. |

| | | | |
|---------|--------------------------|----|---|
| 1899 | H.L. Châtelier | TD | French translation of <i>Equilibrium</i> Analogical tool to demonstrate the choice for generic phases. Consideration of symmetry in the thought experiment. |
| 1902 | J.W. Gibbs* | CS | |
| 1903(!) | A. Byk* | TD | |
| 1905 | L. Boltzmann and J. Nabl | TD | Verification of the relation between entropy and probability. Consideration of gravity in the thought experiment; logical error of allowing identical gases to mix. Failure of the thermodynamic-statistical analogy due to the exclusion of the thermodynamic integration constant. – |
| 1907 | H.A. Lorentz* | TD | |
| 1908 | O.P. Postma* | CS | |
| 1911 | P. and T. Ehrenfest | CS | |

TD – Thermodynamics

CS – Classical statistics

(!) – Correction of the year provided by Haitun.

* – Gave a solution according to Haitun.

★ – Vital in the distribution of the term Gibbs paradox.

† – Not clear whether this was based on Gibbs' work.

List of works relevant to the Gibbs paradox in the period 1912–1986:¹

| Year | Author | Branch |
|------------|----------------------------|--------|
| 1911–1913 | O. Sackur† | CS |
| 1912 | Nernst† | CS |
| 1912–1915 | H. Tetrode† | CS |
| 1913–1914 | O. Stern† | CS |
| 1914 | H.A. Lorentz† | CS |
| 1914–1916 | O.P. Postma† | CS |
| 1916 | A. Einstein† | CS |
| 1916, 1921 | M. Planck† | CS |
| 1918 | Г. Вейхард* | QS |
| 1920 | P. Ehrenfest and V. Trkal† | CS |
| 1921 | E. Schrödinger* | QS |
| 1922 | E. Schottky* | TD |
| 1924 | E. Fermi* | QS |
| 1924 | A. Einstein* | QS |
| 1926 | И.Е. Тамм* | QS |

¹Based on С.Д. Хайтун [1986] and Pérez Canals [2012].

| | | |
|------------|---------------------------------|--------|
| 1927 | А.В. Раковский* | TD |
| 1929 | Б.М. Кедров* | TD, QS |
| 1932 | J. Von Neumann* | QS |
| 1938 | R. Tolman* | QS |
| 1939 | J.C. Slater† | QS |
| 1941 | P.W. Bridgman* | O |
| 1946–1948 | E. Schrödinger*† | TD, QS |
| 1952 | H. Grad* | CS |
| 1955 | A. Landé* | QS, I |
| 1956 | L. Brillouin* | I |
| 1958 | P. Shambadal* | TD |
| 1959 | M.J. Klein* | QS |
| 1961 | R.M. Noyes* | O |
| 1963 | Ю.С. Варшавский, А.Б. Шейнин* | O |
| 1963 | К. Huang† | QS |
| 1964 | J.V. Barnett* | I |
| 1966 | D. Ter Haar, G. Wergeland* | O |
| 1967 | Н.И. Кобозев* | I |
| 1970 | T. Boyer* | O |
| 1970 | В.Л. Любошиц, М.И. Подгорецкий* | TD, QS |
| 1970 | D. Hestenes* | O |
| 1971 | P. Shambadal* | CS |
| 1972, 1975 | И.П. Базаров* | TD, QS |
| 1973 | B. Casper, S. Freier* | CS |
| 1975 | В.Б. Губин* | CS |
| 1975 | P. Lellouche* | TD |
| 1976 | Р.Г. Геворкян, З.В. Геворкян* | TD |
| 1976 | З.А. Терентьева, Н.И. Кобозев* | I |
| 1978 | P.T. Landsberg, D. Tranah* | QS |
| 1978 | L.B. Levitin* | I |
| 1980 | A. Lesk* | O |
| 1981 | Р.П. Поплавский* | O |
| 1981 | D. Home, S. Sengupta* | QS |

TD – Thermodynamics

CS – Classical statistics

QS – Quantum-statistics

I – Informational

O – Operational

* – Named by Haitun.

† – Named by Pérez Canals.

Appendix C

Synopsis of Haitun's *History of the Gibbs Paradox*

Book details:

| | | |
|--------------|--------------------------|------------------------------|
| Title: | история Парадокса Гиббса | History of the Gibbs Paradox |
| Author: | С.Д. Хайтун | S.D. Haitun |
| Publication: | Наука Мокква - 1986 | Science Moscow - 1986 |
| Language: | Russian | No translation |

Haitun's *History of the Gibbs Paradox* seems to be the only historical compendium on the Gibbs Paradox. Although this makes it a valuable source, it has a limited distribution scope due to it only being available in Russian. For this reason, this appendix contains a synopsis of the work, including the table of Haitun's classification of the solutions to the paradox. Because the book focuses on the solutions, it is important to make apparent what Haitun conceived the Gibbs paradox to be:

The Gibbs paradox is simple in formulation. It arises when considering the mixing of ideal gases: [...] [The entropy of mixing] does not depend on the type of gas, and therefore, if we take more and more similar gases, the entropy of the system by the mixing of gases would increase by the amount $[kN \ln 2]$. In the limit of mixing identical gas, the entropy of the system is increased by the same amount. On the other hand, when the same gas is being mixed, absolutely nothing happens, in particular also the entropy of the system shouldn't increase. In this way, two true [methods of] reasoning lead to the opposite conclusion: On the one hand, the

entropy of mixing of identical gases is equal to the value of $[kN \ln 2]$, on the other - the entropy of mixing of such gases is zero. This situation is indeed paradoxical.¹

Within *History of the Gibbs Paradox*, Haitun then attempted to map the solutions given to the paradox in order to solve the historical-scientific paradox surrounding the Gibbs paradox.² He argued that, up to the publication of his book, no satisfactory conventional solutions have been given despite the fact that several famous scientists involved themselves with the paradox. Haitun felt that writing a historical account of the paradox, and the related concept of entropy, would allow physicists to work on the paradox from the most productive angle, as indicated by the *History of the Gibbs Paradox*. He believed there to be about 50 different original solutions to the paradox and classified them into five phases: thermodynamics, classical statistics, quantum statistics, informational, and operational. After analyzing the five phases, Haitun came to the conclusion that a conventional solution to the paradox should most likely be found in the operational phase.

The following table contains Haitun's classification of the solutions:

| Variant | Phase | | | | |
|----------|--|--------------------------------|---|---|--|
| | <i>Thermodynamics</i> | <i>Classical Statistics</i> | <i>Quantum Statistics</i> | <i>Informational</i> | <i>Operational</i> |
| Discrete | Gibbs, Neumann, Poincaré, Duhem, Wiedeburg, Planck, Nernst, Byk, Lorentz, Schrödinger, Schottky, Раковский, | Gibbs, Casper and Freier | Вейхард, Fermi, Einstein, Тамм, Кедров, Tolman, Schrödinger, Базаров | Brillouin, Терентьева and Кобозев | Bridgman, Hestenes, Boyer, Lesk |

¹[С.Д. Хайтун, 1986, pp. 3–4]: “Парадокса Гиббса прост по формулировке. Он возникает при рассмотрении смешения идеальных газов: [...] Эта величина, называемая энтропией смешения, не зависит от рода газов, и поэтому, если брать все более подобные газы, энтропия системы в результате смешения газов будет возрастать на величину $[kN \ln 2]$. В пределе при смешении одинаковых газов будет возрастать на величину $[kN \ln 2]$. Но, с другой стороны, при смешении одинаковых газов равным счетом ничего не происходит, в частности не должна возрастать и энтропия системы. Таким образом, два верных рассуждения приводят к противоположным выводам: с одной стороны, энтропия одинаковых газов равна величине $[kN \ln 2]$, с другой - энтропия смешения таких газов равна нулю. Эта ситуация действительно парадоксальна.”

²Haitun divided what he called the historical-scientific paradox into three questions:

1. *Why are physicists still working on the paradox?*
2. *Why have there not been any conventional solutions?*
3. *Why have different physicists declared the paradox solved on different grounds?*

Other secondary sources simply call it the *confusion* surrounding the Gibbs paradox.

| | | | | | |
|-----------------------|----------------------------------|----------------------|---|------------------------------|---|
| | Кедров, Базаров, Lellouche | | | | |
| $\Delta S = 0$ | Shambadal | Postma, Shambadal | - | - | - |
| $\Delta S = kN \ln 2$ | Van der Waals | Grad | - | Кобозев | - |
| Continuous | Геворкян and Геворкян | Губин | Lande | Lande, Barnet, Levitin | Noyes, Варшавский and Шейнин, Ter Haar and Wergeland, Поплавский |
| Combined | Любошиц and Подгорецкий | - | Von Neumann, Klein, Любошиц and Подгорецкий, Landsberg and Tranah, Home and Sengupta | - | - |

Even if one were to disagree with Haitun's conclusion, his classification of many of the responses to the Gibbs paradox is incredibly useful. As expected, not all responses are named in *History of the Gibbs Paradox* due to the focus on the solutions. An example of a historical actor whose early work on the paradox has been ignored is Van der Waals. Van der Waals' earliest known writing on the subject was of January 1897, yet Haitun did not include any of his work from before 1908. Naturally, there are not any sources from beyond 1986 included in this book. A useful source for works on the paradox up to 2009 is Shu-Kun Lin's website <http://www.mdpi.org/lin/entropy/gibbs-paradox.htm>.

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