

LEOPOLD PFAUNDLER AND THE ORIGINS OF THE KINETIC THEORY OF CHEMICAL REACTIONS

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1. Introduction. Both the historical development of the kinetic theory of matter and the mechanical theory of heat¹ have been extensively studied by the American historian, Stephen G. Brush, and are the subject of several detailed monographs.^{2,3} In addition, Brush has also provided collections and translations of most of the key foundational documents.^{4,7} However, as with the case of available collections and translations of papers related to the foundations of thermodynamics, these collections are missing the first examples of the application of these fundamental concepts to the phenomena of chemical reactions and equilibrium. In the case of thermodynamics, this missing document was August Horstmann's seminal paper of 1873, "Theorie der Dissociation" (The Theory of Dissociation),⁸ which has only recently been made available in English translation.⁹ In the case of the kinetic theory of matter and heat, this missing document is Leopold Pfaundler's 1867 paper "Beiträge zur chemische Statik" (A Contribution to Chemical Statics),¹⁰ an English translation of which appeared in the previous issue of the *Bulletin* and for which this paper serves as an introductory commentary.¹¹

2. The Kinetic Theory of Matter and Heat. Since, as just indicated, both the history of the kinetic theory of matter and of the mechanical theory of heat are the subjects of detailed monographs, all that is required here is to briefly summarize their early historical development in order to provide a proper chronological context for Pfaundler's seminal paper of 1867.

With the revival of the atomic theory in the 17th-century, several writers, such as Francis Bacon and René Descartes, dropped occasional hints that heat might correspond to some kind of "intestine" motion of either the molecules or the underlying ether – a view later supported by both the famous cannon-boring experiment of Count Rumford (1798)¹² and ice rubbing experiment of Humphry Davy (1799).¹³ However, the specific association of heat with the translational motions of molecules, rather than with just their vibrational and rotational motions, was due to the development of the kinetic theory of gases. Though its origins date back as far as the 18th century and the work of Daniel Bernoulli (1738),¹⁴ and failed attempts were made to revive it in the first half of the 19th century by both John Herapath (1821, 1847)¹⁵ and John Waterston (1846),¹⁶ this theory did not attract widespread acceptance until the 1850s, when it was revived once more and developed by, among others, August Krönig (1856)¹⁷ and

Rudolf Clausius (1857)¹⁸ in Germany, and by James Joule (1851)¹⁹ and James Clerk Maxwell (1860)²⁰ in England. Clausius referred to the new approach as the “mechanical theory of heat” and the British physicist, John Tyndall, captured its essence in the title which he gave to his popular lectures on the subject in 1862: *Heat Considered as a Mode of Motion*.²¹

The reason for the significant time delay separating the work of Bernoulli from that of Krönig and for the failure of Rumford, Davy, Herapath and Waterston to stimulate a widespread acceptance of the kinetic theory of heat and matter in the late 18th and early 19th centuries, was, of course, due to the overriding success of the caloric theory²² of heat championed by, among others, Joseph Black, Antoine Lavoisier, and Adair Crawford in the last half of the 18th century. This viewed heat as a conserved imponderable fluid, rather than as a form of molecular motion, and, in turn, fostered a static Newtonian model of the three states of matter in which solids, liquids and gases were viewed, not as differing in their degrees of intermolecular organization and freedom of motion, as they are today, but rather as fixed arrays which differed solely in terms of the distance between their statically equilibrated molecules (i.e., in terms of the sizes of their combined caloric envelopes). In the opinion of Brush, it was the gradual recognition of the principle of the conservation of energy during the 1840s and the accompanying realization that it was not just the heat alone that was conserved in most processes, but rather the sum of the heat and work together, which undermined one of the key assumptions of the caloric model and which is largely responsible for the more favorable reception accorded the kinetic theory in the 1850s, as this approach allowed one to reduce the interconversion of work and heat to a concomitant interconversion of macroscopic motion versus molecular motion.

The realization that the mathematical development of the kinetic model in the cases of gases and liquids required the use of statistical concepts gradually evolved as well, beginning with the work of Clausius and Maxwell and culminating in the formal development of statistical mechanics by the Austrian physicist, Ludwig Boltzmann,²³ and the American physicist, Josiah Willard Gibbs,²⁴ near the end of the century. In his paper of 1856 Krönig had assumed that each molecule possessed only translational motion. It was Clausius, in his elaboration of Krönig's work the following year, who first pointed out that polyatomic molecules could also possess internal rotational and vibrational motions as well and that, as a result, the various molecular collisions should result in a redistribution of the *vis viva* or kinetic energy among these various modes and thus lead to a spread or distribution of the various molecular velocities rather than to a fixed value. In other words, a given temperature would correspond, not to a fixed value of kinetic energy for the individual molecules, but rather to a fixed *average* value. This statistical view was further elaborated by Clausius in 1858 with his introduction of the concept of mean free path²⁵ and by Maxwell in 1860 with the introduction of his famous velocity distribution function.²⁰ As we will see, both the concept of the interconversion of translational energy with internal rota-

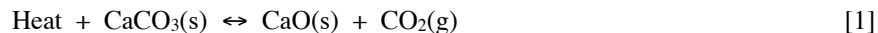
tional and vibrational energies and the concept that each temperature corresponded to a characteristic energy distribution or average, rather than to a fixed value, would prove central to Pfaundler's application of the kinetic model to chemical reactions.

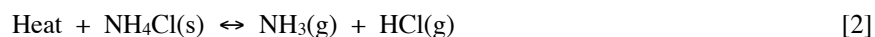
3. The Origins of Pfaundler's Paper. It was the work of the German physicist, Rudolf Clausius (figure 1), that served as the inspiration for both Horstmann's



Figure 1. Rudolf Julius Emanuel Clausius (1822-1888) in old age. (Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati).

paper of 1873 on the application of the second law of thermodynamics to chemical equilibrium and for Pfaundler's paper of 1867 on the application of the kinetic theory of heat and matter. In the case of Horstmann, it was Clausius' 1865 paper on the entropy function²⁶ which provided the necessary conceptual foundation, whereas in the case of Pfaundler it was Clausius' 1857 paper on the mechanical theory of heat.¹⁸ Thus in both cases roughly a decade separated the first enunciation of the underlying concepts in the physics literature and their first explicit application to chemical systems in the chemical literature. Likewise, both Horstmann and Pfaundler relied primarily on the work of the French chemist, Henri Sainte-Claire Deville (figure 2), and his associates for information on the experimental behavior of equilibrium systems involving either solid or gaseous dissociation, of which the following reactions were typical:





In his famous overview summary of his experimental work on dissociation,²⁷ Deville had emphasized the analogy between the behavior of equilibria resulting from the thermal dissociation of solids and those resulting from the evaporation of pure liquids. Just as each temperature for the latter process corresponded to a certain characteristic vapor pressure, so each temperature for the former process corresponded to a fixed degree of dissociation. Just as the vapor pressure increased with increasing temperature and decreased with decreasing temperature,



Figure 2. Henri Etienne Sainte-Claire Deville (1818-1881). (Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati).

so did the degree of dissociation. And, finally, just as removal of vapor led to further evaporation of the liquid at constant temperature, whereas addition of vapor led to further condensation, so addition of one or more of the gaseous dissociation products at constant temperature led to deposition of the undissociated solid, whereas removal of one or more of the products led to its further dissociation. Indeed, since we know that Pfaundler studied physical chemistry in Paris in the years 1864-1865 and that, while there, attended Deville's lectures, he may well have heard of these analogies directly from Deville himself.

The epiphany came, however, only after Pfaundler had read Clausius' 1857 paper on "The Kind of Motion Which We Call Heat," in which Clausius applied

his concepts of internal modes of molecular motion and of characteristic molecular velocity distributions at constant temperature to an explanation of evaporation. Pfaundler quickly put two and two together and was thus inspired:

*... to investigate whether, as a consequence of the similarity between these two phenomena [i.e., dissociation and evaporation], an hypothesis, like that used by Clausius to explain evaporation, might also be useful in explaining dissociation.*¹⁰

4. Kinetically Rationalizing Dissociation Reactions. Entitled “A Contribution to Chemical Statics,” Pfaundler’s paper was divided into three major parts, plus a conclusion and a lengthy addendum. In Part I he dealt with the application of the kinetic model to simple thermal dissociation reactions of the form:



beginning with the dissociation of solids and liquids, as originally studied by Deville and his associates, and then generalized the approach to include the dissociation of gases as well.

As already hinted in Section 2, both of these applications rested on two key assumptions:

1. Gaseous polyatomic molecules possess not only translational motion as a whole, but also internal rotational and vibrational motions, and the latter motions are also present in the liquid and solid states as well. Pfaundler referred to the former as “external motions” and to the latter as “internal motions,” and further noted that there is a characteristic upper limit to the internal motions, that varies from one chemical species to another, and which, if exceeded, leads to bond cleavage and dissociation.

2. Because of intermolecular collisions not all molecules at a given temperature possess the same magnitude for their external and internal motions or *vis viva* (mv^2 – a quantity closely related to kinetic energy). Rather there is a continuous redistribution of these motions, leading not only to a variation in the magnitudes of each type but to an interchange between the magnitudes of the external and internal motions. In other words, a fixed temperature corresponds to a fixed average for the *vis viva* of the molecules and not to a constant value common to all.

Though both of these assumptions seem commonplace and unexceptional to the modern chemist, they were, prior to Pfaundler’s paper, totally missing from the earlier chemical literature.

Pfaundler first applied these assumptions to the thermal dissociation of calcium carbonate or chalk, as shown above in equation 1. As the solid is gradually heated the internal motions of its molecules (in 1867 it was not known that Ca-

CO₃ was a nonmolecular solid) gradually increase until a few of them exceed the upper limit required for dissociation and release gaseous CO₂ molecules into the space above the solid. The greater the temperature, the greater the number of chalk molecules that exceed the upper limit for internal motion, and the greater the degree of dissociation. However, the released CO₂ molecules are not only simultaneously colliding with one another, leading to a redistribution of their external and internal motions, but also with the surface of the chalk itself and, at each temperature, a certain fraction will have lost sufficient *vis viva* to recombine with the solid. Eventually the rates of dissociation and readsorption will become equal, leading to an equilibrium and to a characteristic dissociation pressure for the temperature in question.

Not only may this equilibrium be disturbed by altering the temperature, it may also be disturbed by removing CO₂ from the space above the solid by flushing it with a stream of air or some other nonreactive gas. By thus lowering the concentration of the CO₂ gas, the rate of absorption is lowered but not the rate of dissociation, which will continue until it replaces the displaced CO₂ and reestablishes the previous equilibrium:

*Therefore the calcium carbonate evolves carbon dioxide in the air stream at the same temperature as it absorbs carbon dioxide in its absence. The calcium carbonate and carbon dioxide behave in the air stream in a manner similar to that of a hydrated substance that is being dried.*¹⁰

Extension of these concepts to the dissociation of a gaseous compound is straightforward.

5. Activated Complex Theory. In Part II of his paper Pfauder extended his theory beyond simple dissociation reactions to include gas-phase single-displacement reactions:



and, in so doing, also introduced the concept of a collision complex. Depending on how the energy of collision redistributed itself among the internal modes of motion of this complex, it could either decompose back into the original reactant molecules (thus giving rise to a nonreactive collision) or into an new set of product molecules (thus giving rise to a reactive collision). As pointed out by Lund many years ago,²⁸ this concept anticipated in all but name our modern concept of an activated complex or transition state:

Let us examine a molecule of the substance AB, which, because of the high temperature, has already acquired sufficient motion of its components that it is close to decomposition, and which now encounters a molecule C. The external

motion of both molecules is now completely or partially converted into internal motion by the impact. The result now depends on whether the affinity is or is not strong enough, given this enhanced internal motion, to keep all three bodies together. If not, then the components are repelled again, which means a part of the internal motion is once again converted to external motion. Apparently the mode of separation now depends on how the internal motion is distributed among the individual parts. If the internal motion of the original AB molecule was already very large prior to impact, and was further increased by the impact, then the cleavage of the transient ABC molecule to form A and BC is more likely than to form AB and C. Therefore, a certain definite portion of the AB molecules which collide with the C molecules will react according to the equation $AB + C = A + BC$. Here we have a dissociation process which is different from pure dissociation; but also equally different from a complete chemical decomposition in which all of the molecules are decomposed at once. The peculiarity of our process consist in the necessity of only partial decomposition.¹⁰

These comments were then followed by a detailed analysis of the effects of mass action on this equilibrium in terms of changes in relative collision frequencies and the question of whether it was possible to drive the reaction to completion at constant temperature by simultaneously increasing the concentration of AB and removing product A or whether the reaction could be completely reversed by simultaneously removing AB and adding A.

In Part III of his paper, Pfaundler, in addition to addressing the issues discussed below in section 6, further extended his concept of a collision complex to include the case of gas-phase double-displacement reactions as well:



and also provided a drawing of the assumed collision complex itself (figure 3):

The molecules collide under such conditions that the interplay of the internal motions of the components of the transient double-molecule induce its splitting in a different direction. AB and CD collide and momentarily form ABCD. If the impact was – as we wish to assume in the simplest case – linear and central, the whole system will continue to initially move in accordance with the redistribution of various quantities of motion, the lost external motion having been trans-

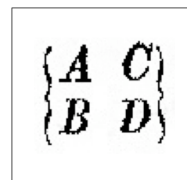


Figure 3. Pfaundler's structure of the collision complex formed in the double displacement reaction $AB + CD \leftrightarrow AC + BD$.

formed into internal motion. Now it depends on the magnitude of the affinity of A, B, C and D for one another and, at the same time, on the previously existing internal motions of the components of AB and CD, as to whether the split due to the increased internal motions occurs in the direction of AB/CD or in the direction of AC/BD. The larger the internal motions of the molecules prior to collision, the greater the preparation for the separation of A, B, C and D and the easier it is for a split in the direction AB/CD to occur.¹⁰

Pfaundler was not the first to suggest that displacement reactions involved the initial formation of some sort of transient complex. A particularly famous example (figure 4), often reproduced in histories of chemistry but not mentioned by Pfaundler himself, was given by the German chemist, August Kekulé (figure

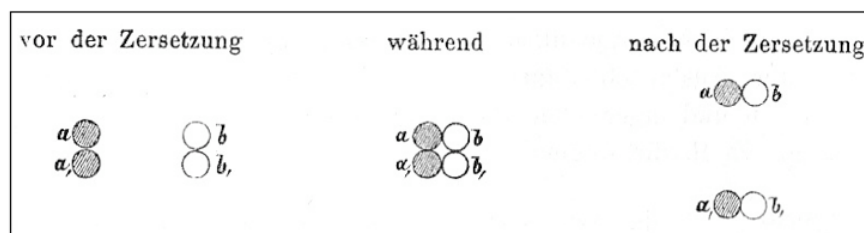


Figure 4. Kekulé's picture of a reaction complex leading to double displacement. (Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati).

5), in his famous paper²⁹ of 1858 on "The Constitution and Metamorphoses of Chemical Compounds and the Chemical Nature of Carbon" and later repeated in his equally famous textbook of 1861.³⁰ However, Kekulé envisioned both the formation and decomposition of this complex to be purely a function of competing forces of affinity in which molecular and atomic motions played no part whatsoever:

When two molecule react, they first attract each other by virtue of their chemical affinity, and align themselves next to each other. The affinities of the individual atoms then cause atoms which previously belonged to different molecules to come into intimate contact. For that reason, the group that was divided in one direction prior to reaction, now falls apart in another direction. On comparing the product and starting material, the decomposition can be conceived of as a mutual exchange.²⁹

Interestingly, in a footnote, Kekulé further envisioned that this mechanism could also explain mass action and the phenomenon of catalysis, again sans any

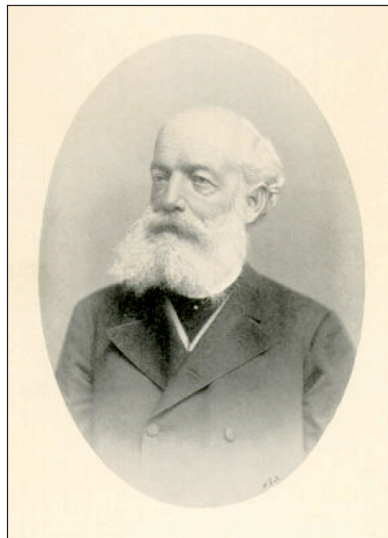


Figure 5. Friedrich August Kekulé (1829-1896).
(Image courtesy of the Oesper Collections
in the History of Chemistry, University of
Cincinnati).

reference to molecular collisions or various internal molecular motions:

One may consider that during the approach of the molecules to each other, the connection between the atoms is already loosened, because part of the force of affinity becomes bound by the atoms of the other molecule, until at last the previously united atoms lose their connection together, and the newly formed molecules separate. On this assumption, the conception supplies a certain representation of mass action and catalysis. For in the same manner as a molecule of one substance acts on a molecule of another substance, so also all other molecules in the vicinity will act: they loosen the connection among the atoms. The closest molecule acts most powerfully and suffers double decomposition with the molecule of the other substance. Those further away aid it; while they loosen the connection of the atoms in the other molecule, they suffer the same change. As soon, however, as the decomposition has taken place they regain their earlier state. Mass action and catalysis differ, according to this conception, only in that in the case of the former the catalyzing molecule is of the same kind as one of those decomposing, while in catalysis it is different in substance from both.²⁹

All of this is a far cry from Pfaundler's later kinetic-molecular rationale. Not only is there no mention of molecular motions and collision frequencies, there is also no mention of reversible reactions and equilibrium, all of which, as brilliantly elaborated by Pfaundler, would require an interplay between both affinity forces and molecular motions for their complete rationalization:

In this manner it becomes obvious that, in addition to the affinities, the mode of decomposition further depends on the state of motion, and that, consequently, even those reactions that are apparently opposed by affinity may occur (reciprocal reactions).¹⁰

6. Relationship to the Exchange Theory of Williamson. In addition to his explication of the collision complex for a double-displacement reaction, in Part III of his paper, Pfaundler also took great care to explain the relationship between his newer kinetic theory of mass action and an earlier kinetic theory of chemical reactions first proposed by the British chemist, Alexander Williamson (figure 6) in a series of papers and notes published in the years 1850-1851.³¹ In these publications Williamson had suggested that the analogous parts (whether atoms or radicals) of neighboring molecules were continuously exchanging



Figure 6. Alexander William Williamson (1824-1904). (Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati).

places with one another at a rate that varied inversely with their bond strengths. In a pure substance, AB, all of the neighbors were identical and the system looked exactly the same before and after the exchange of A and B among the neighbors. However, in a binary mixture of two different molecules, AB and CD, the fraction of the exchanges producing AD and CB rather than reproducing AB and CD would obviously increase as more and more of the molecules adjacent to a given AB molecule corresponded to CD rather than AB. In other words, the amount of AD and CB formed would increase as the concentration of CD

was increased and vice versa as the amount of AB was increased.

From this summary it should be apparent that, while Williamson's mechanism, unlike that later given by Kekulé, did indeed invoke a limited kind of molecular motion (atom or radical exchange between nearest neighbors) and was able to explain mass action without recourse to changes in stoichiometry, it was, in common with Kekulé's later attempt, also totally lacking the concepts of both collision frequency and threshold energies which formed the centerpieces of Pfaundler's approach and thus had little in common with either the mechanical theory of heat or the kinetic theory of gases then coming into vogue.

Pfaundler took great trouble to explain the differences between Williamson's exchange theory of chemical reactions and his own kinetic-molecular collision theory and clearly demonstrated that the former was inconsistent with the experimental facts in a number of instances. Indeed, Williamson had originally presented his theory of chemical reactions in connection with his work on the synthesis of ethers and, to drive home his point, Pfaundler presented a detailed reinterpretation of the acid catalyzed synthesis of ethers from alcohols in terms of his own collision theory of chemical reactions and equilibrium. However, in the end this effort was largely wasted on his fellow chemists. As we will see in Section 9, later writers would often misrepresent Pfaundler's work as a mere elaboration of Williamson's hypothesis, and most histories of chemistry would all but ignore Pfaundler, while continuing to incorrectly credit Williamson as the originator of our current kinetic-molecular theory of chemical reactions.

7. Conclusion and Addendum. In his brief conclusion (labelled Part IV in the translation), Pfaundler once more credited Clausius with having provided the key ingredients underlying his own kinetic theory of chemical reactions via both Clausius' initial application of the kinetic-molecular hypothesis to the process of evaporation and his elaboration of Krönig's earlier kinetic theory of gases via the added assumption that polyatomic molecules could possess internal as well as external modes of motion. This was followed by mention of an 1857 paper by Clausius³² in which he foreshadowed Arrhenius's later theory of ionic dissociation via the application of the kinetic-molecular hypothesis to composition of electrolyte solutions, leading to the conclusion that they contained a small equilibrium population of dissociated ions and thus explaining why they conducted electricity even at low values of the applied voltage. Pfaundler seems to have been under the false impression that Clausius had based his discussion of this subject on Williamson's exchange theory and promised to write a future paper in which he would instead reinterpret Clausius' conclusions in terms of the kinetic-molecular theory, as well as write several future papers applying the theory to various other aspects of solutions and mixtures in general. As it turned out, Clausius' mention of Williamson's theory was only incidental and, as he had already given a proper kinetic-molecular rationale of electrolyte solutions in the paper of 1857, Pfaundler's projected paper on this subject never appeared, al-

though, as also promised, he did later published a paper applying his theory to such miscellaneous, and apparently mysterious, subjects as supersaturated and supercooled solutions, explosions, and the crystallization of amorphous solids.³³ In addition, he also published several later accounts of his general theory, the most famous of which applied the Darwinian metaphor of “The Struggle for Existence” to the competition between the various molecular components of an equilibrium mixture.³⁴⁻³⁵

The addendum to Pfaundler paper was originally inserted between Parts I and II but in the translation has been transferred to the end of the paper and labelled Part V. It deals with a criticism of the some of the work of Henri Sainte-Claire Deville on dissociation by a physicist by the name of H. W. Schröder van der Kolk, much of which was rendered moot by Pfaundler’s kinetic-molecular interpretation of the dissociation process and is now of little or no interest to the modern reader.³⁶

8. Who was Pfaundler? Leopold Pfaundler (figures 7 and 8) was born on 14 February 1839 in Innsbruck, Austria, the son of a local advocate and Professor of Law at the University of Innsbruck.³⁷ After attending the local *Volkschule* and *Gymnasium*, Pfaundler entered the University of Innsbruck in 1857, where he studied organic chemistry under Professor Heinrich Hlasiwetz, while also attending lectures in physics and mathematics. In 1859 his university studies were interrupted by military service in the Austro-Sardinian War, also known as the Second War of Italian Independence, followed in 1861 by a semester in Liebig’s



Figure 7. Portrait of Leopold Pfaundler in middle age. (Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati).

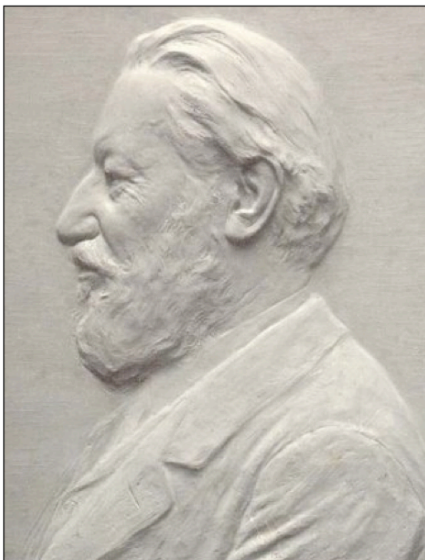


Figure 8. Memorial bas relief of Pfaundler at the University of Innsbruck.

laboratory at the University of Munich and receipt of a doctorate from the University of Innsbruck. Following three years as an assistant in Hlasiwetz's laboratory, Pfaundler, as already noted, spent the years 1864-1865 in Paris studying physical chemistry, where he worked in the laboratories of Wurtz and Regnault, and also attended lectures by Deville and Berthelot. In 1866 he became a Privatdozent in physical chemistry at Innsbruck, though once again his academic career was interrupted by military service, this time in the Third War of Italian Independence of 1866. The next year, at age 28, he published his seminal paper on the application of the kinetic theory of matter and heat to chemical reactions and was appointed as Professor of Physics at Innsbruck. Here he remained until 1891, when he succeeded Ludwig Boltzmann as Professor of Physics at the University of Graz. In 1910 he became Professor Emeritus at Graz and was also ennobled by the emperor, receiving the title of Pfaundler von Hadermur.

Like his contemporary – the German physical chemist, Wilhelm Ostwald – Pfaundler was highly eclectic in his scientific interests and often wrote on subjects having broader cultural and social implications. His earliest publications dealt not only with botanical and organic chemistry, as might be anticipated from his association with Hlasiwetz, but also with geodesic measurements – an interest which developed during his military service. His seminal paper of 1867 and several subsequent contributions dealing with the application of the kinetic theory to the phenomena of solutions and crystallization were the obvious result of his study of physical chemistry in Paris during the early 1860s. Because of the poor condition of the physical laboratories at both Innsbruck and Graz, Pfaundler began, starting

in the mid 1870s, to increasingly focus on teaching and the writing of popular scientific articles, rather than on laboratory research. Known for his excellent lecture demonstrations – many of which were of his own design (see figure 9) – and his clear delivery, he was also increasingly in demand as a popular lecturer.

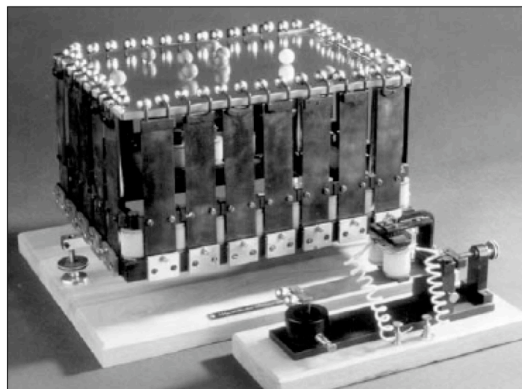


Figure 9. A vibrating bead plate used to illustrate the kinetic theory of the three states of matter designed by Pfaundler for use as a lecture demonstration while at the University of Gratz, circa 1903.

After his move into the field of physics, his work often focused on the development of new instrumentation, much of it connected with the teaching of physics, including the first demonstration of a direct current electrical generator (1870) and of a working telephone (1877). Kipnis estimates that Pfaundler published more than 110 articles and roughly 10 books and pamphlets during his career, including several editions (1877, 1886, 1906) of Müller-Poulett's textbook *Lehrbuch der Physik und Meteorologie*,³⁸ which he used as a text in his physics lectures, and his own popular, *Die Physik des täglichen Leben* (1904).³⁹

Pfaundler was active in several scientific societies and also served as Rector of the University of Innsbruck in 1880. He was an avid mountain climber and photographer of mountain landscapes, for which he received a silver medal at the 1901 International Photographic Exhibition, as well as an early enthusiast of the Japanese game of *Go* on which he published a book in 1908. Other interests included ecology and the carrying capacity of the earth and advocacy of an artificial international language for use in the scientific literature. Indeed, in 1914 he published a photographic lexicon in Ido, a simplified version of Esperanto. He died in Graz in May of 1920 at age 81.

9. The Fate of Pfaundler's Work Shortly after its publication, Pfaundler's paper came to the attention of the German thermochemist, Alexander Naumann, who quoted it extensively in a review on dissociation phenomena which he wrote for Liebig's *Annalen* later the same year.⁴⁰ In 1868 August Horstmann attempted to quantify Pfaundler's qualitative arguments by using a probability distribution to

calculate the change in the density (and hence the degree of dissociation) of various vapors as a function of temperature.⁴¹ By 1873, however, Horstmann had become disillusioned with the kinetic approach – in large part because he felt that it failed to explain why pure solids did not exert a mass action effect.⁸ This criticism was repeated by Pattison Muir⁴² in 1884 and again, in greater detail, by the French chemist, Pierre Duhem,⁴³ in 1898, who triumphantly concluded that failure to resolve this issue meant that a theory of “chemical statics based on the kinetic hypothesis is thus condemned.” Instead, both Horstmann and Duhem came to favor a purely thermodynamic approach based on either the maximization of the entropy function or the minimization of the Gibbs free-energy. However, it wasn’t until Horstmann repeated his criticism in 1876⁴⁴ that it finally came to Pfaundler’s attention and he published a rejoinder,⁴⁵ though the true reason for the apparent lack of a mass action effect for solids – namely that their kinetic influence depended on the number of collisions per unit area rather than per total area – seems to have eluded him.

In this regard, it is interesting to note that most accounts of the history of the kinetic theory of matter are written from the standpoint of the physicist^{2,3} and tend to emphasize the successes of the theory in rationalizing not only the ideal gas law and Graham’s law of diffusion, but also in making the nonintuitive prediction that the viscosity of gases should be independent of density and should increase, rather than decrease, with temperature. The fact that a significant segment of the chemical community rejected the theory because of its mistaken belief that it could not adequately rationalize the absence of a mass action effect for solids is never mentioned. Even more interesting is the fact that this same argument over the relative correctness of kinetic versus purely thermodynamic rationales continues to persist in the current chemical literature, particularly with respect to the rationalization of Raoult’s law, and involves the same error of failing to distinguish between collisions per unit area versus per total area.⁴⁶

The first references to Pfaundler’s work in the monograph literature do not appear until roughly 15 years after the publication of his paper. In 1882 Naumann repeated much of what he had said in his review of 1868 in his book, *Lehr- und Handbuch der Thermochemie*,⁴⁷ and also added a diagram of a probability distribution similar to that used by Horstmann. This book, in turn, served as the stimulus for the detailed, albeit somewhat confused, account of Pfaundler’s views which appeared in the textbook of theoretical chemistry published by the British chemist, M. M. Pattison Muir, in 1884,⁴² as well as for the briefer summary in his subsequent, *A Textbook of Thermal Chemistry*, which was published the following year.⁴⁸ Pfaundler was also mentioned by van’t Hoff in the introduction to the first edition of his *Études de dynamique chimique* of 1884,⁴⁹ where he is ironically credited with being the first to show that chemical equilibrium was a result of the equalization of the velocities of the forward and reverse reactions – ironic because most historians incorrectly attribute this concept to van’t Hoff instead. In fact, it had already been proposed, not only by Pfaundler, but by Williamson (1850),

Malaguti (1857) and by Guldberg and Waage (1867) many years earlier.

Interestingly there appears to be no mention of Pfaundler in the 1884 edition of Lothar Meyer's *Die modernen Theorien der Chemie*, though it contains a detailed discussion of thermal dissociation reactions and the mass action effect, nor is there any mention in Meyer's shorter *Grundzüge der theoretischen Chemie* of 1890.⁵⁰ Continuing into the 1890s, a single-sentence mention is found in Nernst's 1893 text, *Theoretische Chemie von Standpunkte der Avogadro'schen Regel und der Thermodynamik*,⁵¹ where it is implied that Pfaundler had simply amplified Williamson's original exchange theory. Likewise, though several aspects of Pfaundler's various publications are mentioned in Ostwald's massive, multi-volume, *Lehrbuch der allgemeinen Chemie*,⁵² those sections dealing with his applications of the kinetic theory to chemical reactions are generally highly critical and once again repeat the argument that the kinetic model is unable to account for the absence of a mass action effect for solids. The same is true of Ostwald's more popular textbook, *Grundriss der Allgemeinen Chemie*.⁵³ Though Pfaundler's theory is discussed in the 1890 edition, where it is once again criticized, all references to both Pfaundler and the kinetic molecular theory of equilibrium are missing from the 4th edition of 1908.

Following the trend set by Ostwald, all mention of Pfaundler's various contributions appears to have disappeared from the contemporary chemical literature by the second decade of the 20th century. Thus no mention of him is to be found in the papers by Trautz (1916)⁵⁴ and Lewis (1918),⁵⁵ which laid the foundations of our current collision model of chemical kinetics, nor in the first detailed book-length treatment of the collision model – C. N. Hinshelwood's 1926 monograph, *The Kinetics of Chemical Change in Gaseous Systems*.⁵⁶ Nor is he mentioned in the early literature dealing with absolute rate theory,⁵⁷ though his concept of a critical collision complex is a direct qualitative anticipation of the modern concept of an activated complex, as pointed out earlier by Lund.²⁸

A somewhat similar scenario played out in the history of chemistry literature. No mention of Pfaundler is to be found in early 20th-century British histories of chemistry, such as those by Thorpe (1909), Pattison Muir (1909), and Hilditch (1911), though he is briefly mentioned in several early German histories, such as those by Ernst Meyer (1889),⁵⁸ Albert Ladenburg (1900),⁵⁹ and Richard Meyer (1922).⁶⁰ However these brief mentions, with the exception of Ladenburg, uniformly failed to properly describe the nature and significance of his contribution. Thus, like Nernst, Ernst Meyer also implied that Pfaundler had simply amplified Williamson's original exchange theory, and, in the case of Richard Meyer, only Pfaundler's early work with Hlasiwetz on the organic chemistry of plant materials is mentioned. The same is largely true as we move into the 1930s, where the standard histories by Moore (1931, 1939) and Partington (1937) fail to mention him, though he is briefly mentioned in the short history of 19th-century chemistry by Findlay (1938),⁶¹ where, following van't Hoff's earlier error, he is again given credit for being the first to show that chemical equilibrium was dynamic rather

than static. This pattern of neglect and misrepresentation continued throughout the 1950s and 1960s, where again there is no mention in the standard histories by Farber (1952, 1964), Leicester (1956) and Ihde (1964), though he is discussed in Partington's massive four-volume reference work (1964).⁶² More recent histories, such as those by Brock (1992) and by Fruton (2002), have continued this pattern, the sole exception being the short history by Hudson (1992),⁶³ which devotes a single sentence to him.

Thus we see that by the early decades of the 20th century Pfaundler's work was all but forgotten. Most histories of chemistry continue to incorrectly attribute the first application of the kinetic theory to chemical reactions to Williamson rather than Pfaundler and most modern textbooks and monographs on chemical kinetics begin their somewhat perfunctory historical introductions with the Arrhenius equation of 1889 rather than with Pfaundler's paper of 1867 – despite the fact that Pfaundler was the first to rationalize the law of mass action in terms of collision frequencies and anticipated significant aspects of both the collision theory and transition-state theories of chemical kinetics via his concepts of critical threshold energies and collision complexes.

The reasons for this neglect are complex. Certainly the strong bias towards purely phenomenological models based on classical thermodynamics shown by such influential physical chemists as Ostwald and Duhem and by such physicists as Ernst Mach, with their concomitant undervaluation of the kinetic-molecular approach, played an important role in the gradual marginalization of Pfaundler's work as the 19th century drew to a close. Likewise, Pfaundler's progressive career move from chemistry into physics may have also contributed to his equally progressive disappearance, not only from the contemporary chemical community, but from the contemporary chemical literature as well. And, finally, the fact that Pfaundler's approach was essentially qualitative, rather than quantitative, meant that his paper was ultimately equally unsatisfying to both the chemical and physical communities. Its use of statistical arguments, even in a qualitative form, was foreign to most chemists raised to think almost exclusively in terms of static molecular structures and semi-anthropomorphic affinity concepts, whereas its purely qualitative treatment made it largely irrelevant to those physicists concerned with developing ever more sophisticated mathematical formulations of the kinetic theory of gases.

There is some indication that this pattern of neglect is slowly changing. Though the 1968 appreciation by Lund²⁸ remains, to the best of my knowledge, the only English-language tribute to Pfaundler's work, an analysis, in German, of his contributions has more recently appeared in Berger's⁶⁴ 1997 study of the impact of the mechanical theory of heat on the study of chemical reactions. Likewise, though the Canadian kineticist, K. J. Laidler, failed to mention Pfaundler in his 1967 collection of readings in the history of kinetics,⁶⁵ he did include a short summary in the historical appendix to the 3rd edition (1987) of his well-known textbook of chemical kinetics⁶⁶ and also repeated that summary, which

was based largely on Partington, in his 1993 history of physical chemistry.⁶⁷ Ironically, however, neither of these accounts mentions Pfaundler's anticipation of the activated complex concept, though this is a subject on which Laidler was an expert, having coauthored the first monographic treatment of absolute rate theory in 1943.^{57,68} On the other hand, there is apparently no mention of Pfaundler in the 1993 history of chemical kinetics by Kritsman *et al.*⁶⁹

10. References and Notes

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LUDWIG PFAUNDLER AND THE KINETIC THEORY OF CHEMICAL REACTIONS

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LUDWIG PFAUNDLER AND THE KINETIC THEORY OF CHEMICAL REACTIONS

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11. Update

I have only recently (2015) become aware of the 1977 article by H. A. M. Snelders ("Dissociation, Darwinism and Entropy," *Janus*, **1977**, *64*, 51-75) which also discusses Pfaundler's kinetic treatment of dissociation reactions.