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Review

Victor Henri: 111 years of his equation

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ABSTRACT

Victor Henri's great contribution to the understanding of enzyme kinetics and mechanism is not always given the credit that it deserves. In addition, his earlier work in experimental psychology is totally unknown to biochemists, and his later work in spectroscopy and photobiology almost equally so. Applying great rigour to his analysis he succeeded in obtaining a model of enzyme action that explained all of the observations available to him, and he showed why the considerable amount of work done in the preceding decade had not led to understanding. His view was that only physical chemistry could explain the behaviour of enzymes, and that models should be judged in accordance with their capacity not only to explain previously known facts but also to predict new observations against which they could be tested. The kinetic equation usually attributed to Michaelis and Menten was in reality due to him. His thesis of 1903 is now available in English.

1. Introduction

A recent paper [1] in the context of the centenary of Leonor Michaelis and Maud Leonora Menten's paper [2] discussed the work of their predecessor, Victor Henri [3,4]. They themselves were quite clear about their debt to him, but later authors have tended to be less so. In fact, the thesis that Henri wrote for his doctorate at the Sorbonne [4] contains ideas that still repay careful reading today, and to facilitate this we have prepared an annotated translation into English that forms the Supplementary material for this paper. Here we shall discuss why Henri's work continues to be important for biochemistry, after first drawing attention to his groundbreaking work in the field of experimental psychology [5–7], which is almost completely unknown to biochemists, and also giving a brief account of his later work in physical chemistry.

2. Henri's life and scientific career

As this is dealt with in detail in the Supplementary material and elsewhere [1,8,9] we give only a brief summary here. Henri (Fig. 1) was born in Marseilles in 1872, but despite his French name, nationality and place of birth he was wholly Russian in origin. His natural and adoptive mothers were sisters, and came from the very distinguished Lyapunov family: they were cousins of the mathematician Alexander Lyapunov, and Henri's niece married the physicist Peter Kapitsa. His early work was in experimental psychology, initially as assistant to Alfred Binet, the pioneer of intelligence testing. He spent a long period in Germany, and in one of his later visits he became acquainted with enzymes and physical chemistry in Wilhelm Ostwald's laboratory in Leipzig. Afterwards he moved from psychology to physiology, and from there to the mechanisms and kinetics of enzyme catalysis. In his later career he contributed to many fields, mostly with some relationship to physical chemistry, and at different times occupied major posts in France, Russia, Switzerland and Belgium. He died in La Rochelle in 1940. The principal steps in Henri's life and career are listed in Table 1.

3. Experimental psychology

Experimental psychology as a discipline came to prominence in the 1880s with the foundation of the first laboratories in Germany, the most famous being the one founded in Leipzig by Wilhelm Wundt in 1879. These laboratories were primarily intended to allow studies on the elementary forms (sensations, perceptions) of mental life. At the time, the French authorities wanted to develop experimental psychology, in order to follow the German research movement, and

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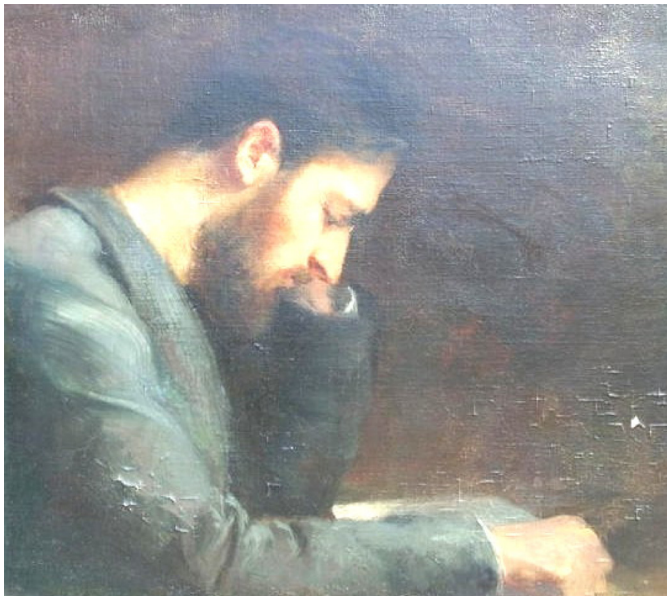


Fig. 1. Victor Henri. This is a detail from a painting by Mme. Laure Binet (wife of Alfred Binet), painted in about 1900. It is now in the possession of Mrs. Christine Henri, widow of Victor Henri's son Victor, and is published with her permission.

created a chair in the Collège de France in 1888 and a laboratory at the Sorbonne in 1889. As a young student of mathematics at the Sorbonne, Victor Henri was attracted by psychology as taught by Théodule Ribot at the Collège de France and by the new laboratory directed by the physiologist Henry Beaunis and his assistant Alfred Binet. When the first laboratory of experimental psychology was founded in Paris, work was first dedicated to the sensory domain. Henri was first interested by the study of the sensory domain working with hysterics at the Salpêtrière Hospital in the service of Jean-Martin Charcot under Binet's supervision. In 1892 Binet brought Henri into a research programme on memory, and he became a specialist in this new domain, writing papers in *L'Année Psychologique*, the journal of the laboratory, until 1901. The most famous one was a paper on infantile amnesia published in 1897 [10], now available in English [11], which inspired Sigmund Freud. It was impossible at that time to obtain a doctorate in psychology in France, and Henri decided to go to Germany. He studied with Wundt at Leipzig and Müller in Göttingen, obtaining a doctorate there in 1897 on tactile discrimination. During this period he kept French philosophical and psychological journals informed about the development of psychology in Germany [12,13]. He was an active researcher, and Binet enrolled him in his new programme of individual psychology.

Binet and Henri were dissatisfied with the studies made by their predecessors [14–17], which they considered incomplete, too much concerned with sensations that could easily be measured, and too little with higher intellectual processes. They undertook an extensive programme of research in which they set out to measure many aspects: memory; the nature of memory images; imagination; attention; the capacity to understand, observe, define and distinguish; suggestibility; aesthetic feeling; moral sentiments; muscular force and force of will; and motor ability. The ambitious nature of this programme is evident from the fact that even today some of these aspects, for example the nature of memory images, are not fully understood. Nonetheless, they devised a series of ingenious tests that could allow all of them to be assessed in about 90 min, and succeeded in making substantial progress. Their major paper from this work [5], now available in English [18], begins with a warning:

> We tackle here a new, hard and still very little investigated subject; you should not expect to find in our work final answers to the questions that will be raised. Our main purpose will be to indicate the problems with which individual psychology has to deal in order to highlight the practical importance it has for the teacher, the doctor, the anthropologist and even the judge…

Stimulated by this work with Binet, which also included studies of intellectual fatigue [6], Henri decided to study whether different degrees of intellectual effort had any physiological effect on the composition of the excretion products of subjects with a controlled diet and controlled muscular activity, which he called nutritional exchanges (*échanges nutritifs*) [7].

Binet continued with his psychological studies after Henri had moved on to physiology and physical chemistry, but we shall not discuss this here beyond mentioning his work on the measurement of mental capacity [19]. This has had enormous educational repercussions that continue to this day, though for many years it was applied in exactly the opposite way from what he intended: he believed that such tests could be used to identify children who needed specific kinds of remedial help, but in practice intelligence tests were long used for classifying children, and even adults, according to supposedly innate levels of ability [20].

4. Henri's research on enzymes

4.1. Introduction

After he left the psychology laboratory of the Sorbonne, Henri moved to the physiology laboratory, where he undertook very different research, becoming the pupil and close collaborator of Albert Dastre (Fig. 2), who supervised his work on enzymes. This is the main theme of this paper, and concerns the studies described by Henri in his thesis [4] (Fig. 3), principally of invertase, but also of elastase, emulsin and amylase. He approached all of these enzymes with a scientific rigour that can still stand as a model. In particular, he insisted that any explanation of a biochemical phenomenon must be consistent with the principles of physical chemistry, and that one should not use one explanation for some of the observed properties but a different one for others. This may seem to be too obvious to be worth saying, but papers continue to be published in which basic principles of thermodynamics and physical chemistry are violated, as well as models that are not internally consistent. In 1903 Eduard Buchner's overthrow of vitalism [21] was recent enough not to be universally accepted; it was still possible to believe that the laws of chemistry might not apply in full to biological systems, and thus Henri's attitude was advanced for its time. He was critical of his predecessors for failing to observe all of these principles, but he did not exempt himself, and was equally critical of a paper of his own [22] that he considered lacking in rigour: it proposed a model that was purely empirical but could not be applied over the whole range of substrate concentrations without invoking arbitrary changes in assumptions.

4.2. Invertase

Most of Henri's work dealt with invertase, which catalyses the hydrolysis of sucrose: sucrose + H_2O ⇄ fructose + glucose. The name *invert sugar* for the mixture of products, and the name *inversion* for the reaction, derived from the observation that the products rotate the plane of polarized light in a direction opposite from that of sucrose, and thus “invert” it. The name *invertase* refers, of course, to this. It was chosen for many of the early studies of enzyme action because, as an extracellular enzyme secreted into the medium by yeast, it is readily available for study, and because the reaction is easily followed polarimetrically.

Table 1
Principal steps in Victor Henri's life and career.

Year	Event	Place
1872	Birth	Marseilles, France
1880–1889	Education at the German school	St Petersburg, Russia
1889–1891	Undergraduate university studies in mathematics and science	Paris, France
1892–1904	Collaboration with Alfred Binet, Psychology Laboratory of the Sorbonne	Paris, France
1894–1896	Laboratory of Physiological Psychology (Wilhelm Wundt)	Leipzig, Germany
1897	Doctor of Philosophy in psychology (Georg Müller); thesis: *Über die Raumwahrnehmungen des Tastsinnes*	Göttingen, Germany
1897–1901	Publication secretary, *L'Année Psychologique*	France
1900–1901	Visit to Wilhelm Ostwald's laboratory	Leipzig, Germany
1903	Doctor of Physiology (physical chemistry); thesis: *Lois générales de l'action des diastases*	Paris, France
1900–1915	Lecturer at the Sorbonne	Paris, France
1913	Deputy Director, Physiology Laboratory of the Sorbonne	Paris, France
1915	French adviser to the Russian government on organization of the chemical industry	Moscow, Russia
1917–1918	Professor of Physical Chemistry, Cherniavsky Institute	Moscow, Russia
1920–1930	Professor of Physical Chemistry	Zürich, Switzerland
1923	Marriage to Vera Lyapunova (third wife)	
1930–1931	Planning of petrochemical complex	Berre-l'Étang, France
1931–1939	Professor of Physical Chemistry	Liège, Belgium
1938	Director, *Journal de Chimie Physique et Physico-Chimie Biologique*	France
1939	Volunteer, Centre National de la Recherche Scientifique Appliquée	France
1940	Death from pulmonary congestion	La Rochelle, France

4.3. O'Sullivan and Tompson (1890)

All of the earlier work was open to more or less serious objections, beginning with that of Cornelius O'Sullivan and Frederick Tompson [23], who reported that the invertase-catalysed reaction followed an exponential (first-order) process comparable with that observed with acid hydrolysis, and they also showed that the rate was proportional to the enzyme concentration. However, Henri pointed out that their explanation demanded a rate constant that ought to be strictly constant during the course of reaction: C. S. O'Sullivan and Tompson had failed to calculate this, and when Henri calculated it from their data he found that it increased smoothly from the beginning to the end of the reaction. Their model could not therefore be correct. In addition Henri considered that it was important to study the dependence of the kinetic behaviour on the concentration of sucrose, but C. S. O'Sullivan and Tompson had not done this. A little afterwards J. O'Sullivan [24] found that the rate constant was inversely proportional to the initial concentration of sucrose.

4.4. Tammann (1895)

Tammann [25] studied invertase and emulsin in experiments that also attracted severe criticism from Henri. Unlike C. S. O'Sullivan and Tompson he did not consider that the reactions followed first-order kinetics, and asserted that they did not go to completion, because the enzyme became “worn out”. This was an important point for understanding enzyme catalysis, and contradicted C. S. O'Sullivan and Tompson's finding that invertase remained active after catalysing the transformation of 100 000 times its weight of sucrose. The major objection to Tammann's work concerned his experimental approach: even though he himself reported that his solutions became turbid in an experiment that lasted 3046 min (more than two days!) he did not consider growth of microorganisms to be an important cause of the failure to go to completion. Later Henri showed that Tammann was wrong about the loss of activity.

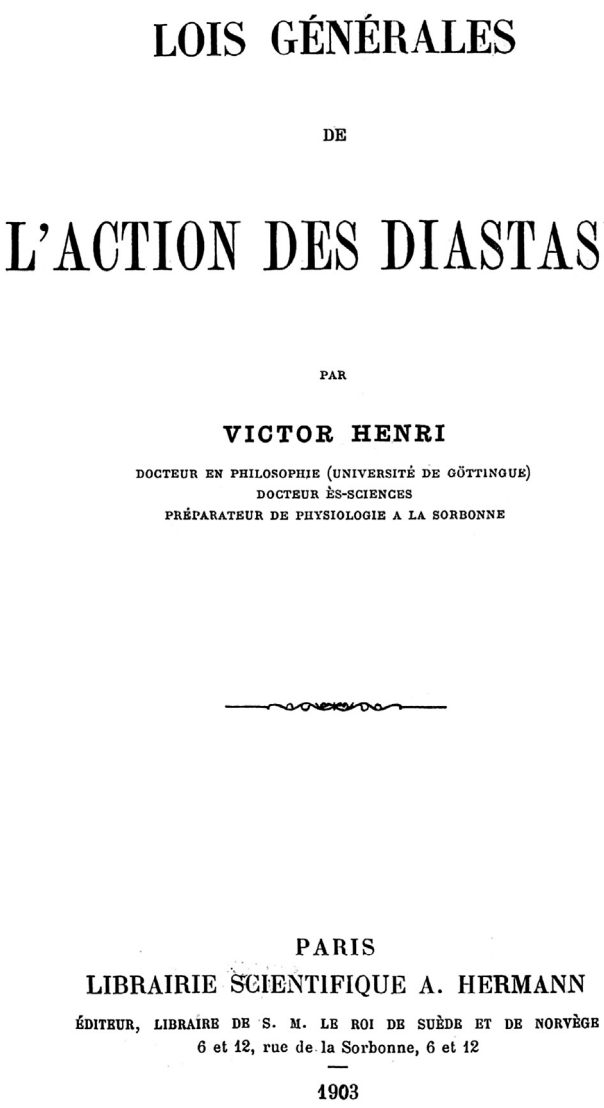
4.5. Duclaux (1899)

Émile Duclaux [26] showed that the report by C. S. O'Sullivan and Tompson of first-order kinetics could not be correct, because the time for inversion of a given quantity of sucrose in the enzyme-catalysed reaction was not proportional to the sucrose concentration, as would be expected if the reaction followed the same kinetic behaviour as acid hydrolysis. He tried to allow for the inhibitory effects of the reaction products on the reaction. However, he introduced a serious error of his own, because, as Henri described, he arbitrarily assumed two different laws for the reaction: one for the effect of the enzyme on the substrate, and a different one for the effects of the products. Henri considered this approach to violate the principles of physical chemistry.

4.6. Henri (1901)

In 1901 Henri [22] used trial and error to arrive at an empirical equation that would allow some of the earlier faults to be overcome. As this equation was incorrect (and rightly criticized by Henri himself [4] for its lack of theoretical basis) we do not need to consider it in detail. However, it is worth noting that it allowed

Fig. 2. The physiology laboratory of the Sorbonne. Albert Dastre is seated at the front; Victor Henri is standing directly behind him, in the middle of the back row. The picture was scanned by S.N. from a contemporary postcard in his private collection.


LOIS GÉNÉRALES

DE

L'ACTION DES DIASTASES

PAR

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6 et 12, rue de la Sorbonne, 6 et 12
1903

Fig. 3. The front cover of Henri's thesis on general laws for the action of enzymes.

Henri to show that the enzyme did not lose activity during the course of a reaction; in his words it "remained comparable with itself". C. S. O'Sullivan and Tompson [23] had shown this in a more qualitative way a decade earlier.

4.7. A. J. Brown (1892, 1902)

Adrian J. Brown [27] reported in 1892 that the action of yeast on sucrose did not follow the kinetics expected for acid hydrolysis. His important contribution came a decade later [28], when he revisited his work in the light of the overthrow of vitalism [21]: he then became the first to propose that saturation kinetics could be explained in terms of formation of an enzyme–substrate complex, as the rate could not increase further with increases in substrate concentration once the enzyme existed entirely in the form of this complex. Henri [4] accepted the general idea, but he strongly objected to the highly qualitative way in which it was presented: the idea that a complex would exist for a fixed time and then abruptly decompose to products and regenerate the free enzyme was contrary to principles of physical chemistry that were very well established by that time.

A. J. Brown's theory was also criticized by Horace T. Brown and T. A. Glendinning [29], who developed one more in accord with physical chemistry. However, as Henri [4] pointed out, it was also incomplete as it took no account of the effects of reaction products on the rate of reaction.

4.8. Bodenstein's formula

Max Bodenstein, then an assistant in Ostwald's laboratory in Leipzig, proposed a mechanism to explain Henri's data that he did not publish until much later [30], but which Henri used in his paper [3], which was republished in facsimile in 2006 [31], and his thesis [4]. Bodenstein suggested that in the presence of substrate and product the quantity of active enzyme would be decreased on account of complexation with substrate and with products. The equation that resulted from this mechanism was again not correct, though it was closer to being correct than the earlier ones. It gave a satisfactory account of the kinetic behaviour at sucrose concentrations above 0.1 M, but clearly unsatisfactory agreement at concentrations below 0.05 M. In modern terminology it applied well at substrate concentrations at K_m and above, when K_m started to be negligible in comparison with the concentration, but failed at lower concentrations, when it could not be neglected.

4.9. Henri's thesis

In addition to the papers that we have mentioned, and some others [32–35] that added little extra, the situation at the beginning of the 20th century was that there had been numerous attempts (including Henri's own [22]) to explain the kinetic behaviour of enzymes, in particular invertase, but no one had arrived at a correct kinetic equation. Nonetheless, several salient facts had been established: the rate was proportional to the enzyme concentration; the rate as a function of time was constant at the beginning of the reaction; and the kinetics could not be explained in terms of first-order chemical kinetics without "massaging" the data. Henri therefore set out to develop a theory that would explain all of these facts and would overcome the faults in the work of his precessors.

He undertook this task with great rigour: no deviations from the laws of physical chemistry such as the law of mass action; no vitalism; no setting inconvenient facts aside; no arbitrary evocation of different laws to explain behaviour in different concentration regimes; no qualitative arguments—what we call "hand-waving" today; insistence on the capacity of a good theory to predict new observations, as well as explaining existing ones; use of observations to exclude false hypotheses. This last idea is now mainly associated with Karl Popper's principle of *falsifiability* [36,37], but it was already well understood by Henri [4] (and by others, of course) when Popper was one year old. After listing several hypotheses about enzyme action Henri expressed it clearly:

> If one studies the law according to which a catalytic reaction occurs, discussion of the law will allow classification of the reaction studied into one of the preceding groups, and in consequence this study will give important indications about the detailed mechanism responsible for the catalysis. Sometimes the response will not be absolutely unambiguous, but one will be able, in contrast, to affirm with certainty that a whole series of hypotheses about the explanation for the catalytic activity can be ruled out. Thus, for example, we can state after studying the rates of diastatic reactions that Arthus's physical theory is unacceptable.

This is the only mention of Arthus in the thesis, and Henri gave no reference. Probably he was referring to Nicolas Maurice Arthus's book *Nature des Enzymes*, published in 1896. He continued:

> In consequence, the kinetic study of catalytic reactions will always teach us something new about the nature of these reactions. That is why it is necessary to resume the study of the rates of all the diastatic reactions, as it is only in that way that we can arrive at an understanding of their mechanisms.

Henri also understood another concept associated with Popper, that of a *demarcation criterion* that separates science from religion and other beliefs unsupported by evidence. He referred to vitalism as follows:

> Two groups of theories have been proposed for studying the general phenomena of the life of organisms: some consider that vital manifestations are due to physico-chemical actions; the others deny this reduction and admit the existence of new forces that are in themselves "vital", as they are called. As experimentation is based on the methods and data of chemistry and physics, vitalist theories renounce any possibility of experimenting on this vital force; they constitute a sort of brake on experimental research, that is to say on scientific research, and remove the discussion from the domain of experimentation to that of speculation. The action of such theories is thus harmful, as the usefulness of any theory is measured by the number and importance of new facts that it leads one to discover.

Henri carried out many experiments on invertase, elastase, emulsin and amylase to establish the facts and to rigorously apply the principles of mass action that he had enunciated. These led him to some fundamental equations. The first shows the rate in terms of a quantity Φ of enzyme, initial sucrose concentration a and concentration of accumulated products x, rate constant K, and equilibrium constants m and n: $\mathrm{d}x/\mathrm{d}t = [K{\cdot}m{\cdot}\Phi(a - x)]/[1 + m(a - x) + nx]$. He also sometimes combined $K{\cdot}m{\cdot}\Phi$ into a single constant K_3, writing the same equation as $\mathrm{d}x/\mathrm{d}t = [K_3(a - x)]/[1 + m(a - x) + nx]$. Apart from the unfamiliar symbols we can easily recognize either of these as the equation for the rate v at time t of a reaction subject to competitive inhibition by products: $v = [V(a_0 - p)]/[K_\mathrm{m}(1 + p/K_\mathrm{i}) + a_0 - p]$, with V the limiting rate, a_0 the initial substrate concentration, p the product concentration at time t, K_m the Michaelis constant, and K_i the inhibition constant for product.

Today we usually measure initial rates, whereas Henri, in common with everyone at his time, wished to explain the kinetics as a function of time, so he could not ignore the effects of accumulated product. By integration he obtained an expression for the progress of the reaction, noting that the logarithmic term implied a first-order reaction with respect to time, and the second term on the right-hand side a zero-order reaction: $K_3t = (1 + na)\ln[a/(a - x)] + (m - n)x$. It was not until half a century later that integrated rate equations were again taken up, most notably by Carl Niemann and his collaborators [38], and more recently by Elizabeth Boeker [39,40].

Although serious analysis in terms of initial rates had to wait for another decade [2], Henri did briefly note the simplification that results from considering the system at time zero: Initial rate $= K_3a/(1 + ma)$. This is, of course, easily recognizable as what is often called the *Michaelis–Menten equation*: $v = Va/(K_\mathrm{m} + a)$. However, as it was given and based on a valid theoretical analysis a decade before it was used by Michaelis and Menten [2], it would be more appropriate to call it the *Henri–Michaelis–Menten equation*. One of us [41] has been guilty of failing to do that in the past, even as recently as in 2013 [42], but has become fully convinced that the name should be modified.

In the context of the initial rate equation Henri noted that it implies that a plot of initial rate against substrate concentration should be a rectangular hyperbola through the origin with an asymptote at initial rate $= K_3/m$ and said that this was what he observed in practice. However, he did not illustrate it with a figure.

4.10. Michaelis and Menten's criticisms of Henri's work

Michaelis and Menten [2] recognized the validity of Henri's work, especially in relation to the relationship between the mechanism that he proposed and the equations that followed from it. They did have some criticisms of his experimental technique, however, and it is worth mentioning these briefly. First of all, buffers were unknown in Henri's time and he took no steps to control or measure the hydrogen ion concentration. Hans Friedenthal developed techniques for doing this a little afterwards [43] but these were not widely known or used until Søren Sørensen [44] introduced the pH scale and popularized the concept, as did Michaelis himself [45,46]. A second point, essential for an enzyme like invertase that was assayed polarimetrically, but of much less general importance, is that Henri's measurements ignored the mutarotation of the reaction products. Henri's failure in this regard is baffling, as he was aware of mutarotation and he did take account of it in his experiments with emulsin. However, the experiments on emulsin were done later than those on invertase, and one may surmise that by the time he was conscious of the problem of mutarotation it was too late to revise his earlier work.

Hudson [47] had earlier used Henri's failure to take account of mutarotation to claim that it invalidated his theoretical analysis. However, as pointed out by Sørensen [44], Hudson's criticisms were partly nullified by his own failure to take account of the hydrogen-ion concentration. Nonetheless, Boyde [48] has suggested that Hudson's criticisms partly explain the failure of biochemists to give Henri's achievements the credit they merited. By the time these papers were published Henri had moved on to other research, as outlined below, and he never revisited the topic of invertase, or commented on the criticisms that had been made.

5. Henri's later work in spectroscopy and photobiology

Not only is Henri's earliest work in experimental psychology almost unknown to biochemists, but also, less excusably, his later research in physical chemistry is little known. After 1903 he worked on various large-scale industrial projects, including the reorganization of the Russian chemical industry for defence, and the planning of the large petrochemical complex at Berre-l'Étang (near Marseilles), but also found time to work for 10 years as Professor of Physical Chemistry in Zürich. After 1930 and until his retirement he was Professor of Physical Chemistry in Liège, where he used absorption spectroscopy to study the structures of such organic molecules as naphthalene [49] and phosgene [50].

In Henri's work in photobiology we may note, for example, a study of the decomposition of glycine under the influence of ultraviolet light [51]. This was a collaboration with Chaim Weizmann, the great chemist who had discovered how to make acetone and other solvents by bacterial fermentation, later the first President of Israel. The last of Henri's publications listed in Web of Science was also a collaboration with Weizmann, and described the use of ultraviolet spectroscopy to detect aromatic compounds in mineral oil [52].

6. Discussion

111 years after it earned him a doctorate from the Sorbonne, Henri's thesis continues to be worth reading, as it illustrates how much can be achieved with an uncompromising attachment to intellectual rigour and rejection of fuzzy thinking. Although many

experiments on invertase and other enzymes had been done by other researchers in the decade after 1890, none of them had led to valid conclusions until Henri [3,4] studied the question in depth, insisting on adherence to the laws of physical chemistry and refusing to "massage" the data to fit in with the hypothesis that he wanted to adopt. His thesis remains a model of how a scientific investigation should be carried out. His other research, both before and after his study of invertase, is also worthy of our attention.

Conflict of interest

None.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biochi.2014.09.018.

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