Whatever Happened to the Nascent State?

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1. Introduction

In 1884 the British chemist, M. M. Pattison Muir (figure 1), published a textbook on theoretical chemistry entitled *A Treatise on the Principles of Chemistry* in which he attempted to summarize many of the recent results "on the subjects of dissociation, chemical change and equilibrium, and the relations between chemical action and the distribution of the energy of the changing system" – in short, most of the topics which would, within the next ten years, come to become identified with the new and rising field of physical chemistry and the work of Ostwald, Arrhenius and van't Hoff (1). Though Muir himself did not succeed in establishing a British school of physical chemistry and did not make any significant experimental contributions to the new field, he did play a role in disseminating its early results through his review of Ostwald's work on the measurement of affinity coefficients (2), the writing of a monograph on thermochemistry (3), the editing of an influential dictionary of chemistry (4) and, of course, through his textbook.

Muir, who was later to write an important history of chemistry (5), also had an unusual appreciation of

Figure 1. Matthew Moncrieff Pattison Muir (1848 -1931).

the history of his subject and in his textbook attempted to use the new views on chemical equilibrium and kinetics to unravel some long-standing paradoxes of chemical affinity that had been known since the end of the 18th century. Among these were the problems of predisposing affinity, contact actions, and the so-called *status nascens* or nascent state. The first of these topics has long since disappeared from the textbooks, whereas the second, under the rubric of heterogeneous catalysis, has survived. In many ways, however, it is the third topic that is the most fascinating, as not only the explanation of the nascent state, but the very question of whether it really exists, are still unresolved problems. A history of the various attempts to explain this phenomenon provides one with an interesting cross-section of 19th- and 20th-century chemical theory and, though an explicit treatment of this subject has been missing from the textbook literature since the 1940's, it is of interest to note that the term is still to be encountered, albeit in passing and without explanation, in more recent textbooks (6).

2. Origin and Use of the Nascent-State Concept

A knowledge that freshly prepared gases, when generated *in situ* within a reaction system, are frequently more reactive than when added already prepared from an external source seems to date from the late 18th century. This enhanced, but short-lived, reactivity appeared to be associated with the gases only at the moment of their "chemical birth," so to speak, and the resulting metaphor became enshrined within the chemist's lexicon in the phrase "nascent state," though the chemical poet who first coined the term is not known with certainty.

The first explicit use that I have been able to locate occurs in the 1790 edition of Joseph Priestley's work, *Experiments and Observations on Different of Kinds Airs* (7). Having incorrectly postulated that both fixed air (carbon dioxide) and nitrous acid (nitric acid) were compounds of inflammable air (hydrogen) and dephlogisticated air (oxygen), Priestley (figure 2) attempted to rationalize the different products as a function of differences in the reaction conditions, arguing that:

... when either inflammable or dephlogisticated air is extracted from any substance in contact with the other

kind of air, so that one of them is made to unite with the other in what may be called its nascent state, the result will be fixed air; but that if both of them be completely formed before the union, the result will be nitrous acid.

A year earlier, William Higgins, in his book, *A Comparative View of the Phlogistic and Antiphlogistic Theories*, also invoked the unusual reactivity of hydrogen "at the very instant of its liberation" to rationalize the necessity of water for the oxidation of iron (8). Though he did not describe the hydrogen as nascent, he did use the term when paraphrasing his original statement in 1814 (9).

In the examples cited by both Priestley and Higgins, the nascent gases were generated chemically. In 1807 Humphry Davy reported that a similar enhanced reactivity was also present in the case of electrochemically generated gases (10). Upon electrolyzing water, he observed that some nitric acid was invariably formed at the anode and a trace of ammonia at the cathode. These he attributed to the "combination of nascent oxygen and hydrogen respectively with the nitrogen of the common air dissolved in water," since he knew that these reactions did not occur at room temperature when the fully formed gases were allowed to interact. In modern terms, the observed secondary electrode reactions can be represented as:

$$\text{anode:} \quad 5O^* + N_2 + H_2O \rightarrow 2H(NO_3) \qquad [1]$$

$$\text{cathode:} \quad 6H^* + N_2 \rightarrow 2NH_3 \qquad [2]$$
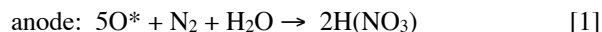
where we have used the starred symbol to represent the

Figure 2. Joseph Priestley (1733-1804).

nascent state of the element in question in order to avoid the explicit representation of any hypothesis concerning its molecularity or structure.

An examination of the 19th century chemical literature shows that the nascent state soon became the accepted rationale for a number of otherwise puzzling chemical reactions. Among these were the varying products observed when metals lying above hydrogen on the activity series reacted with either sulfuric (11, 77) or nitric acid (12). At low acid concentrations dihydrogen gas is the major product in both cases, whereas at higher acid concentrations sulfur dioxide, nitrogen oxides and, in some cases, even ammonia are obtained instead. To explain this concentration dependency it was assumed that nascent hydrogen was initially generated in both systems. At low acid concentrations this reverted to normal dihydrogen gas, whereas as at higher acid concentrations it was entirely consumed in reducing the respective acids and dihydrogen gas was no longer observed among the reaction products:

$$2H^* + H_2(SO_4) \rightarrow SO_2 + 2H_2O \qquad [3]$$

$$H^* + H(NO_3) \rightarrow NO_2 + H_2O \qquad [4]$$

$$3H^* + H(NO_3) \rightarrow NO + 2H_2O \qquad [5]$$

$$8H^* + H(NO_3) \rightarrow NH_3 + 3H_2O \qquad [6]$$

Figure 3. Marsh's apparatus for testing for the presence of arsenic. The unknown is placed in the short arm of the U-tube along with aqueous HCl and a piece of arsenic-free Zn metal. The nascent hydrogen reacts with any arsenic in the sample (usually in the form of the oxide) to generate arsine. The hydrogen/arsine mixture issuing from the end of the tube is lit. The arsine decomposes in the flame and deposits a mirror of elemental arsenic on a cool surface held in the flame.
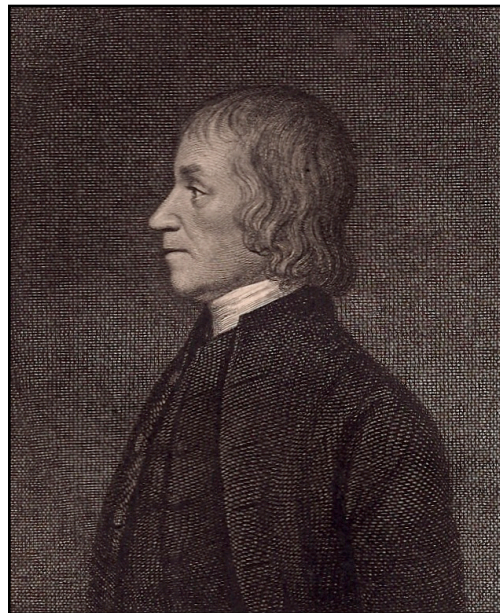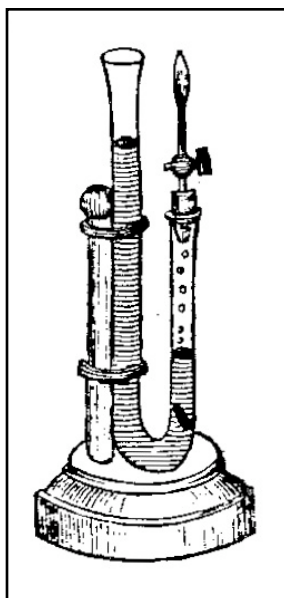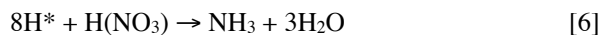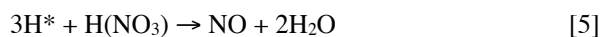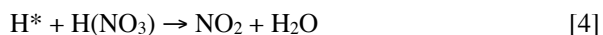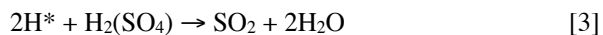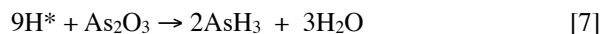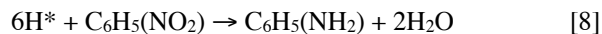
Other classic examples include the use of nascent hydrogen to generate arsine in the famous Marsh test (figure 3) for arsenic (13):

$$9H* + As_2O_3 \rightarrow 2AsH_3 + 3H_2O \qquad [7]$$

in the reduction of nitrobenzene to aniline:

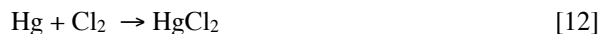$$6H* + C_6H_5(NO_2) \rightarrow C_6H_5(NH_2) + 2H_2O \qquad [8]$$

in the Clemmensen reduction of carbonyls, and in the Jones reduction column. In each case the hydrogen is generated *in situ* by means of zinc and hydrochloric acid and the reactions are not observed under the same conditions if externally generated dihydrogen gas is used instead.

In all of these examples the actual generation of dihydrogen can be observed as a competing reaction. However, the nascent state concept was soon extended to systems in which the gas corresponding to the nascent intermediate is never observed under the conditions of the experiment and which apparently involve a single overall net reaction rather than two competing reactions. For example, nascent oxygen was used to explain the production of dichlorine oxide in the reaction (14):

$$2Cl_2 + HgO \rightarrow Cl_2O + HgCl_2 \qquad [9]$$

via the mechanism:

$$HgO \rightarrow Hg + O* \qquad [10]$$

$$O* + Cl_2 \rightarrow Cl_2O \qquad [11]$$

$$Hg + Cl_2 \rightarrow HgCl_2 \qquad [12]$$

where again it was not possible to produce the highly endoenergetic dichlorine oxide by direct reaction between molecular dioxygen and dichlorine, though in step 11 it is presumed to occur with nascent oxygen.

Likewise, nascent oxygen was frequently invoked to explain the bleaching (or oxidizing) ability of *eau de Javelle* or hypochlorite solutions, via the initial step (15):

$$MClO \rightarrow MCl + O* \qquad [13]$$

a supposition apparently supported by the fact that their water solutions eventually decompose on standing to give the corresponding metal chloride and dioxygen gas.

Many of the oxidation reactions of nitric acid with the less active metals and with the nonmetals were also
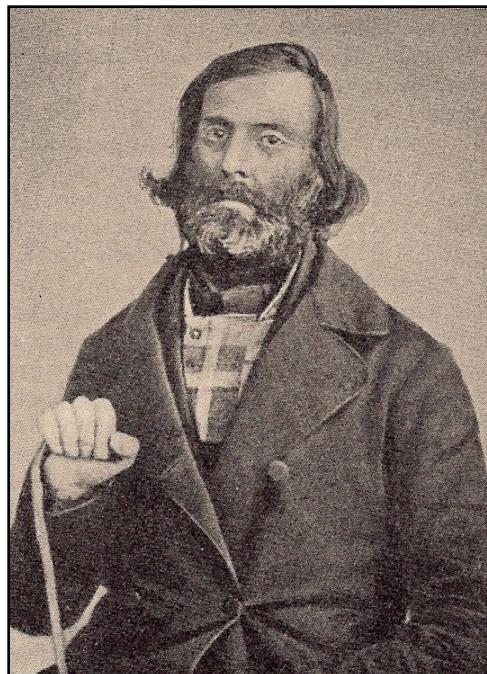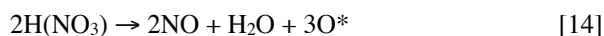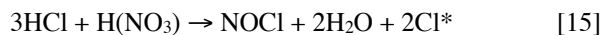

Figure 4. Auguste Laurent (1807-1853).

rationalized in the same fashion (16):

$$2H(NO_3) \rightarrow 2NO + H_2O + 3O* \qquad [14]$$

and the ability of *aqua regia*, in contrast to either dichlorine or hydrogen chloride gas, to chlorinate gold was likewise attributed to the initial production of nascent chlorine (16):

$$3HCl + H(NO_3) \rightarrow NOCl + 2H_2O + 2Cl* \qquad [15]$$

As will be seen, the use of the nascent state in these cases became the basis of much of the criticism later directed at the concept.

3. The Free-Atom Hypothesis

The first, and by far the most historically significant, attempt to rationalize the nascent state was made by the French chemist, Auguste Laurent (figure 4), in 1846. Laurent and his collaborator, Charles Gerhardt, were early proponents of the concept that the elements in their standard states were composed of polyatomic molecules rather than isolated atoms. Contrary to the usual accounts found in most histories of chemistry, the supporting evidence for this proposition was based not just on Gay-Lussac's law of combining volumes, but on considerations related to the energetics of chemical reactions as well.

Rephrasing the original arguments of Laurent and

Gerhardt in terms of modern bonding terminology, the implied assumption was that chemical bonds could be broken in the course of a spontaneous reaction only if they were replaced by stronger bonds. Given this premise, and the assumption that the elements were monoatomic, it was difficult to understand why some compounds spontaneously dissociated into their elements and, conversely, why it was not possible to synthesize certain compounds directly from the elements themselves, though they could be made indirectly by means of displacement reactions. However, once one accepted the existence of elemental polyatomic molecules, these paradoxes vanished, since in both cases the breaking or making of the bonds in the compounds was competing with the making or breaking of bonds within the elemental molecules or, as Gerhardt put it, with the synthesis or decomposition of a "hydride of hydrogen," a "chloride of chlorine," etc (17).

Applying this concept to the nascent state, Laurent wrote (18):

A binary association of atoms might allow us also to account to a certain extent for the affinity possessed by substances in the nascent state. If two free molecules of bromine and of hydrogen, BB' and HH', are brought together, the affinity of B for B' and of H for H' may suffice to prevent the combination of B and B' with H and H'. But if the substances present are H and B, these two, which have no affinity to overcome, will be able to combine readily. This is what will occur when hydrogen is in the nascent state. That is, whenever it is evolved from hydrochloric acid by the action of a metal, we shall have the equation:

$$HCl + M = ClM + H$$
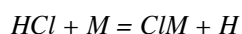
and there will be a tendency to a reconstruction of a binary molecule either by combination with bromine or with another atom of hydrogen.

Similar arguments were also put forward by the English chemist, Benjamin Brodie, in the early 1850's (19-21).

The value of this interpretation of the nascent state as a minor, but useful, piece of evidence in favor of elemental polyatomic molecules was fully appreciated by the 19th-century chemist, and it is in this context, rather than as a topic in chemical kinetics, that the subject found a place in most chemistry textbooks after 1860. Adolphe Wurtz devoted three pages to the subject in his classic historical study of the development of the atomic theory in 1875 (17) and Pattison Muir was quite explicit about its pedagogical value in his 1884 text (1):

A study of the reactions in which nascent substances play important parts appears to me to keep before the student that all important distinction between the atom and the molecule which is so vital in chemical considerations, and also to draw attention in a marked way to the complexity of all chemical changes.

Though several 19th century chemists (11, 22-23) felt that their experimental investigations of the nascent state were not inconsistent with the free-atom interpretation, there was in fact very little direct experimental evidence for the theory until the second and third decades of the 20th century. This came from studies by Irving Langmuir (24), Karl Bonhoeffer (25-26), Hugh Taylor (27) and others of the gas-phase chemical reactions of atomic hydrogen that had been generated either by thermal dissociation on a heated wire or by means of high voltage electrical discharges. But even here the proof was really indirect and was based on the similarity between the reactions observed in the gaseous phase for atomic hydrogen and those observed in the liquid phase for chemically or electrochemically generated nascent gases. Attempts to bubble gaseous atomic hydrogen into solutions gave negative results due to rapid recombination into dihydrogen gas, whereas attempts to detect the existence of a soluble, diffusible, nascent species in the liquid-phase chemical and electrochemical systems were inconclusive at best (28, 29). Indeed, the results seemed to indicate that in these systems the nascent activity was confined to the surface of either the chemically reacting metal or the active electrode.

4. The Thermal Excitation Hypothesis

Not all 19th-century chemists were enamored of the free-atom theory of the nascent state and in many ways the opposing experimental evidence was more convincing than the supporting evidence. Much of this was the result of the efforts of the Italian electrochemist, Donato Tommasi (30-33). He pointed out that, if nascent hydrogen was really atomic in nature, its properties should be independent of the metal/acid system used to generate it. But in actual fact, as shown by his own experiments, its reducing ability was highly dependent on the nature of the metal. Thus nascent hydrogen generated by means of zinc and hydrochloric acid was able to reduce chlorates to chlorides, whereas that generated either electrolytically or by means of sodium amalgam produced no reaction. Tommasi further noted that all of the reductions observed for nascent hydrogen at room temperature could also be observed for fully formed dihydrogen gas at higher temperatures. He therefore postulated that nascent hydro-

gen was nothing more than thermally hot dihydrogen that had not yet had time to thermally equilibrate with the surrounding solvent molecules and that its reducing abilities should directly parallel the enthalpy of the reaction used to generate it. Thus he wrote in 1879 (31):

And if this gas in the nascent state possesses greater affinity than in the natural state, it is solely due to the fact that the hydrogen, the moment it issues from a combination, is found to be accompanied by the whole quantity of the heat produced during the setting free of the hydrogen. Consequently, nascent hydrogen is nothing else than ordinary hydrogen in [different] thermic conditions or, speaking generally, in different physical conditions. To my mind, the expression nascent hydrogen is synonymous with hydrogen + calories. In fact, all the reactions produced by nascent hydrogen can be obtained quite as well with ordinary hydrogen and a high temperature; and the differences observed between the hydrogen resulting from different chemical reactions are simply due to the fact that these reactions do not develop the same quantity of calories.

Aside from a correction of some of his thermodynamic data by Julius Thomsen (34), Tommasi's theory was generally well received and was often quoted by the authors of advanced textbooks and chemical dictionaries after 1880 (1, 4, 35). Muir expressed a somewhat more sophisticated version of it in his 1884 text, writing (1):

In a reaction wherein [a] given compound is produced there must be a moment of time when this compound can only be said to exist potentially, when the atoms which constitute its molecules have not settled down into stable configurations; at this moment the compound may be said to exist in the nascent state. If the atomic vibrations and interactions are allowed to run what might be called their normal course, the compound molecules are certainly produced, but if these interactions are interfered with, a new set of molecules may be formed, which molecules bear a more or less simple genetic relation to those produced in the normal process of chemical change.

This view of the nascent state has recently been revived among chemists working in the field of molecular reaction dynamics (36), where it is applied to the vibrationally and/or electronically excited species which are the initial products observed in molecular cross-beam studies of gas-phase reactions. Indeed, in 1976, Simon Bauer of Cornell University wrote a short note in which he argued that (37):

It is now time to restore the term "nascent" to legitimacy. Much evidence has accumulated, both experimental and theoretical, which demonstrates that in many reactions the partition of nascent products among their characteristic rotational, vibrational, and electronic states differs substantially from that expected were these generated in statistical equilibrium. "Nascent" contrasts with "state relaxed," i.e. a system for which a single temperature and corresponding thermodynamic functions can be defined.

Though Bauer cited several examples of how the reactivity of these nascent products differed from that of the corresponding state-relaxed products, it is open to question, as in the earlier case of the gas-phase atomic hydrogen experiments, whether this explanation can be extended to the classical liquid-phase chemical and electrochemical systems which gave rise to the concept of the nascent state in the first place.

5. The Allotrope Hypothesis

Yet a third theory of the nascent state was proposed by the German chemist, Gottfried Wilhelm Osann, in a series of more than a dozen papers published between 1852 and 1864 (38). By electrolysis of a dilute solution of freshly distilled Nordhäusen sulfuric acid (figure 5), Osann obtained a form of activated hydrogen which was capable of reducing solutions of silver salts to metallic silver and mixtures of potassium hexacyanoferrate(III) and iron(III) chloride to Berlin blue. Platinum and porous carbon cathodes were capable of storing the active hydrogen and could be removed from the electrolysis apparatus and placed in other solutions, where they produced reactions not normally observed for dihydrogen gas under similar conditions.

Heavily influenced by Christian Schönbein's discovery of ozone, Osann decided he had discovered an analogous allotrope of hydrogen and since, like ozone, it was much more chemically reactive than the normal form of the element, he gave it the name of *Ozonwasserstoff* (39). In later work he reported that the atomic weight of his new gas was 0.66 or about two thirds that of normal hydrogen (40).

Similar ideas were expressed by T. L. Phipson in 1858 (41):

What is called the "nascent state" is, I think, nothing more or less than the allotropic state of bodies entering into combination ... it seems incontestable that every time oxygen enters into or leaves compounds, it is in the state of ozone. When we reflect further on the results already obtained with hydrogen, chlorine, bro-

mine, sulphur, and phosphorus, we are inclined to be-lieve that all simple bodies should behave in the same manner; that is to say, that all bodies may have an allotropic state analogous to ozone, and that they are in this state at the moment of entering into combina-tion, or when they are in the nascent state.

Osann's results were criticized by J. Löwenthal in 1858, who suggested that the enhanced reducing prop-erties of the gas were due to the presence of sulfur di-oxide from the Nordhäusen acid used in its preparation (42). This criticism was disproved by Osann (43), but more serious problems were uncovered by Gustav Magnus (44), who was unable to duplicate many of Osann's results. He concluded that Osann's materials were contaminated with iron and that this was actually responsible for the observed reductions. Though Her-mann Fehling summarized Osann's work in his 1864 *Handbuch* (45), he was critical and, by 1895, Albert Ladenburg felt that Osann's hypothesis had been "aus der Welt geschafft" (35).

Actually Ladenburg's funeral oration proved to be premature as, in a series of papers published between 1920 and 1922, Gerald Wendt and Robert Landauer of the University of Chicago revived a form of Osann's hypothesis (46-47). By means of α-radiation, electrical discharge under reduced pressures, and high potential coronas at atmospheric pressure, they generated an activated form of hydrogen which showed a reactivity different from both normal dihydrogen gas and atomic hydrogen. This they equated with the H_3 molecule originally postulated by Joseph J. Thomson in 1913 (now known to be the H_3^+ ion). Because of both its increased reactivity relative to dihydrogen and the analogy between its formula and that for O_3, they pro-posed that the new species be called *hyzone*.

Figure 5. Osann's appa-ratus for the preparation of *Ozone-Wasserstoff* via the electrolysis of freshly distilled Nordhäusen acid.
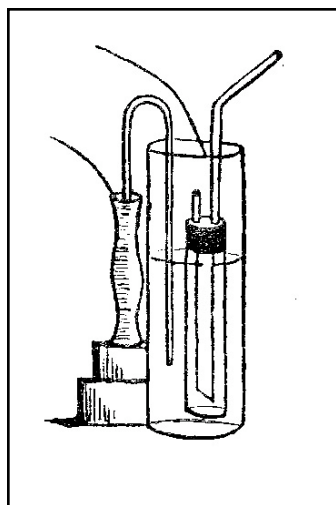
As with the work on atomic hydrogen, these re-sults could not be extended to the traditional liquid-phase chemical and electrochemical methods of gener-ating nascent hydrogen (47), though A. C. Grubb, in a short note published in 1923, claimed to have prepared traces of the species by dropping acid on pieces of sus-pended metal so as to avoid emersion of the metal in liquid (48).

6. The Polarity Hypothesis

The phenomenon of allotropism was a difficult prob-lem for the 19th century chemist. Rationales based on variations in either the degree of molecular complexity (i.e. polymerization) or variations in molecular struc-ture (i. e., isomerism) had to await the work of Brodie in the 1850's on the concept of elemental polyatomic molecules (49). Indeed, it was because of this very problem that Berzelius had introduced the distinctions between isomerism and polymerism, on the one hand, and allotropism, on the other (50), and he himself fa-vored the idea that allotropes corresponded to different electrical states of an element's atoms.

This concept was widely used to rationalize allo-tropism in the first half of the 19th century and was applied in great detail by Schönbein in his attempts to explain the behavior of ozone (thought to be negative) and its relationships to normal oxygen (thought to be neutral) and to the antozones (i.e., peroxides, thought to be positive) (51). Not surprisingly, it also made its appearance in discussions of the nascent state via the allotropic theory. Thus Phipson contended that the transient allotropic modification of an element which appeared at the moment of its formation was equiva-lent to having rendered the element "infinitely more electropositive or electronegative" than its normal state (52).

Like many of the other rationales of the nascent state, this so-called "polar" theory experienced a brief revival in the early 20th century, this time within the context of early electronic theories of the chemical bond. This modernized version was apparently sug-gested by Harry Shipley Fry (figure 6) of the Univer-sity of Cincinnati, who was an early proponent of a polar theory of organic chemistry based on the electron transfer model of chemical bonding first proposed by J. J. Thomson (53). Consistent with the fact that this the-ory viewed all bonding as ionic, diatomic molecules of the simple substances were written as H^+H^-, Cl^+Cl^-, etc. This formulation meant that in the generation of di-hydrogen gas by reduction of aqueous H^+ solutions, the reduction of the H^+ ion had to proceed all the way to H^-. This then combined with another H^+ ion from the solution to generate the dihydrogen gas. Likewise,

Figure 6. Harry Shipley Fry (1875-1948).

generation of dichlorine via oxidation of aqueous chloride solutions required the generation of Cl^+, which then combined with Cl^- to generate the final product. Thus Fry equated the nascent state with the generation of transient free ions having unusual and highly reactive oxidation states. This view was also supported by A. Pinkus (54), but fell out of favor with the eclipse of the polar bonding model by the electron-pair covalent model of G. N. Lewis.

7. The Occlusion Hypothesis

Even these permutations fail to exhaust the speculations of the 19th-century chemist relative to the nature of the nascent state. Yet a fifth model – the so-called "occlusion" model – was developed by the British chemists, John Gladstone (figure 7) and Alfred Tribe, in the late 1870's as a result of their work on the copper/zinc couple (55- 58). Made by placing a strip of zinc foil in a copper sulfate solution for a few minutes in order to plate out a small quantity of copper on the zinc, Gladstone and Tribe found that in water solutions the resulting couple was able to perform many of the reductions observed for nascent hydrogen, whether generated electrochemically or via metal-acid reactions. Among these were the reduction of chlorate to chloride, nitrate to nitrite and ammonia, hexacyanoferrate(III) to hexacyanoferrate(II), nitrobenzene to aniline, sulfurous acid to sulfur, and diarsenic trioxide to arsine (57).

As a result of their experiments, they became convinced that the zinc portion of the couple reduced the water, that the resulting hydrogen became occluded in the copper, and that this occluded hydrogen was responsible for the observed reductions (56). In support of this model they compared the reducing abilities of the couple with those of hydrogen occluded in platinum, palladium, copper, and porous carbon, concluding that (57):

... the increased power of the hydrogen is due to its condensed condition [upon occlusion in the metal], while the observed differences between the action of the different combinations result from variations in this respect, and perhaps also from the more or less firm hold which the metal has upon the gas.

The above chemical changes are effected more or less perfectly by nascent hydrogen. But this hydrogen in every case is set free in contact with, or in very close proximity to a metal, which in virtue of the power known to be possessed by such solids very probably condenses and fixes some of this gas. It may therefore be conceived that the activity of the hydrogen under these circumstances is but the consequence of its intimate association with the metals, or, in other words, of its being in the occluded condition.

This hypothesis is perhaps the most satisfactory when it comes to explaining the known facts about chemically and electrochemically generated nascent hydrogen in the liquid phase. It explains the dependency of the reducing power of the hydrogen on the
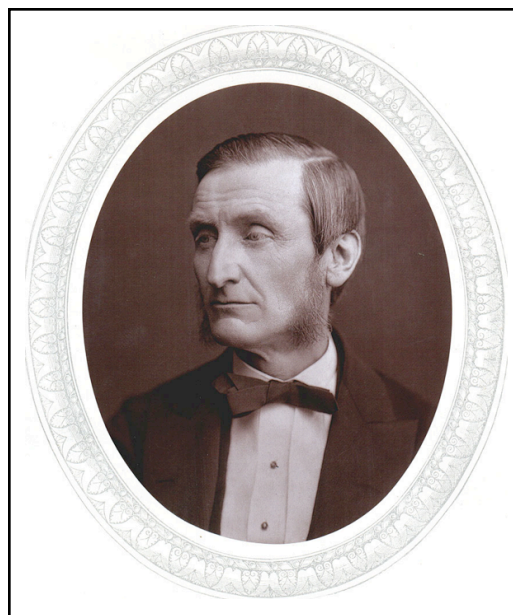

Figure 7. John Hall Gladstone (1827-1902).

method of its preparation (variations in the ability of the metals to adsorb or occlude hydrogen), the absence of a soluble, diffusible, active intermediate in the solutions (it is really a surface reaction at the metal or electrode), and the problems with reproducibility and sensitivity to contamination (both highly characteristic of surface reactions). Of course, Gladstone and Tribe were necessarily vague about the exact nature of the chemical species corresponding to the occluded hydrogen, though at one point they did draw an analogy with the reducing ability of copper hydride. Indeed, this question is still a subject of debate among chemists (59).

In 1927 Joseph Mellor drew attention to the close relationship between this subject and the problem of the hydrogen overpotential in electrochemistry (60). In general, metals with low overpotentials tend to strongly occlude hydrogen, and to act as effective catalysts for the recombination of hydrogen atoms into dihydrogen gas, the hydrogenation of alkenes, etc. (61).

8. The Active Intermediate Hypothesis

A close examination of these five theories – the free-atom, the thermal nonequilibrium, the allotropic, the polar, and the occlusion – shows that, despite of their apparent diversity, they actually have some fundamental points in common. In all five cases, one is postulating that the generation of a gas, X, either chemically, via the reaction of A and B, or electrochemically, proceeds through a short-lived intermediate, I, which, upon further reaction with more B, gives the final product:

$$A + B \rightarrow [I] \qquad [16]$$

$$B + [I] \rightarrow X \qquad [17]$$

If this intermediate is generated in the presence of another chemical species, D, capable of reacting with it to form an alternative product Z

$$D + [I] \rightarrow Z \qquad [18]$$

then one has an example of nascent reactivity. These common features might be characterized as belonging to a generalized "active intermediate" model of the nascent state. Since the intermediate, I, is presumably more endoenergetic than the product gas, X, this means that reaction 18 will be thermodynamically more favorable than the corresponding reaction between X and D:

$$D + X \rightarrow Z \qquad [19]$$

and will necessarily entail a change in its kinetics as well. The only disagreement among the five theories is over the precise nature of the intermediate.

This model further implies that nascent activity can be manipulated by controlling the relative rates of reactions 16-18. Increasing the rate of reaction 17 will increase the rate of evolution of gas X and decrease the amount of product Z, whereas decreasing its rate and/or increasing the rate of reaction 18 will increase amount of product Z. This fact was explicitly recognized by several investigators in the 19th century. Thus, Gladstone and Tribe tested this hypothesis in their study of the reduction of nitric acid during electrolysis, postulating that the failure to observe the production of dihydrogen at the cathode in the case of concentrated acid solutions was due to the fact that reaction 18 consumed all of the intermediate (occluded hydrogen in their theory) in the production of NO and NO_2, leaving none for the generation of dihydrogen gas via reaction 17 (58). By increasing the rate of reaction 16 for a given acid concentration, via an increase in the rate of electrolysis, they were able to provide sufficient intermediate for both reactions 17 and 18 to be observed simultaneously.

Likewise, Thomas E. Thorpe, in his 1882 study of the reduction of ferric salts with nascent hydrogen generated by various acid-metal systems, wrote (23, 62):

Any condition which increases the rapidity of the evolution of the hydrogen, without to an equal degree increasing the chance of contact of the hydrogen-atom [i.e., the nascent intermediate, Thorpe accepted the free-atom model] with the ferric sulphate, diminishes the proportion of hydrogen which does work as a reducing agent. By increasing the amount of free acid, we increase the rate at which the hydrogen is evolved, without to an equal degree increasing the molecular movement of the ferric sulphate, and hence an increased amount of hydrogen escapes ... by keeping the amount of acid constant and heating the liquid, we increase the chances of contact between the ferric sulphate and hydrogen-atom, and accordingly obtain an increased reduction ... By diluting the ferric sulfate solution the chances of contact between the hydrogen [atom) and ferric sulphate are of course diminished, and hence more of the hydrogen escapes in the free state.

9. Thermodynamics versus Kinetics

Given that the active intermediate model requires an

alteration in both the kinetics and thermodynamics of the reactions, the modern chemist cannot resist asking which of these factors is the most important in explaining the enhanced reactivity of the nascent state. There were in fact proponents of both the thermodynamic and kinetic points of view during the 19th century, though both necessarily rejected the active intermediate models, which imply the simultaneous alteration of both.

In a series of papers and books published in the late 1860's and 1870's, the French thermochemist, Pierre Eugene Marcelin Berthelot, argued that the nascent state did not exist and that the phenomena usually attributed to its operation could be explained in terms of thermochemistry alone (14. 63). All of his examples in involved the use of the nascent state to explain the indirect synthesis, by means of displacement reactions, of endoenergetic compounds that could not be directly synthesized from the elements themselves. A case in point is the synthesis of dichlorine oxide outlined earlier in equations 9-12. The difference between the direct synthesis and indirect synthesis, Berthelot argued, had nothing to do with nascent intermediates but was due to the fact that in the latter case the production of the unstable endothernic product (Cl_2O) was accompanied by the simultaneous production of a highly exothermic by-product ($HgCl_2$) and this made the overall process exothermic and hence thermodynamically favorable.

In 1918 Alexander Smith pushed Berthelot's observations on the imaginary role of the nascent state in indirect versus direct syntheses a step further, sarcastically remarking that (74):

... since hydrogen and chlorine do not unite in the cold, when sulfuric acid and common salt give hydrogen chloride, to be consistent we must suppose that nascent hydrogen and nascent chlorine were formed and combine. In other words, every union of two elements, other than direct union, must be explained by nascent action, although in double decomposition this logical necessity is uniformly overlooked.

Nevertheless, not everyone was satisfied by Berthelot's approach. Adolphe Wurtz, for example, characterized Berthelot's arguments as "useless," largely because they were not mechanistic in nature and therefore failed to provide a "natural" explanation (17). More telling were the comments of Tommasi in 1880 (64):

M. Berthelot ... not long ago pretended that he was the first to give a rational theory of the nascent state ... But if you open these two volumes, you will not be able to find a single sentence which makes one even suspect

why nascent hydrogen is more active than ordinary hydrogen.

In other words, though Berthelot had given a proper thermodynamic rationale of the indirect synthesis of endothermic compounds, these cases a represented questionable extensions of the nascent state concept in the first place, and he had completely ignored the competitive gas-generating reactions which had originally given rise to the concept.

Indeed, the inappropriateness of Berthelot's rationale in the case of these competitive systems becomes apparent if one evaluates the thermodynamics of most of the classic reduction reactions involving nascent hydrogen, for one quickly discovers that the corresponding reductions with normal dihydrogen gas are all thermodynamically feasible at room temperature. This is true, for example, of the reduction of chlorate to chloride, nitrate to ammonia, diarsenic trioxide to arsine, nitrobenzene to aniline, iron (III) to iron (II), permanganate to manganese(II), etc. Thus our failure to observe these reactions must be kinetic rather than thermodynamic in nature, and a favorable change in the reaction kinetics is both necessary and sufficient to produce an observed reaction at room temperature. Though a change in mechanism may also alter (via coupling) the reaction thermodynamics, this is not a requirement.

Figure 8. Wilhelm Ostwald (1953-1932).

The concept of a purely kinetic rationale of the nascent state brings us finally to our last model. This was proposed by Wilhelm Ostwald (figure 8) in 1902, almost as a passing thought, in his famous *Lehrbuch* (65). He pointed out that. when initially formed, small submicroscopic bubbles must be under enormous pressure due to the high surface tension of the surrounding water. At molecular dimensions, a newly formed bubble with a diameter of 10^{-1} cm would contain gas under a pressure of approximately 15,000 atmospheres, and this increased pressure, via the law of mass action, might well account for the enhanced reactivity of so-called nascent hydrogen. Today we would also emphasize the importance of the increased surface area between the smaller bubbles and the surrounding liquid.

This latter aspect was further pursued by the Greek chemist, Constantine Zenghelis, in a series of papers published between 1920 and 1921 (66-68). He created superfine gas bubbles by forcing gases through fine filter paper or through dialysis membranes. When this was done in solutions of various reactants, he obtained many of the reactions usually attributed to the nascent state. In the case of dihydrogen, these included the reduction of chlorate to chloride, nitrate to nitrite, and mercury(II) to mercury(I). In the case of mixtures of dihydrogen and dinitrogen, he obtained ammonia, and in the case of carbon dioxide, a variety of reduction products, including formaldehyde. Zenghelis concluded that (68):

We believe that on the basis of the preceding results we must reject the generally received hypothesis which attributes the considerable activity of certain gases in the nascent state to the excess energy of free atoms. On the contrary, we believe we have demonstrated that this activity is due to the extreme subdivision of the active masses in contact.

Using this theory to account for the dependency of the activity of the nascent hydrogen on the nature of the metal-acid system used to generate it, would require that different metals nucleate different size bubbles, a factor that should, in turn, depend as much on the physical roughness of the surface as on the chemical nature of the metal itself.

Some anticipation of the kinetic rationale was already present in the occlusion theory. The enormous decrease in volume accompanying the occlusion of hydrogen in palladium had been noted by Thomas Graham as early as 1868 (69-71). Indeed, he calculated that the density of the hydrogen went from a value of 0.0895 g/mL in the gas phase to a value of 0.733 g/mL in the metal. Chemists had long speculated that hydrogen was an analog of the alkali metals and, under this

extreme condensation, Graham felt that it had in fact become a metal, for which he proposed the name *hydrogenium*. He also felt that the proper view of occluded hydrogen in palladium was that it was a metallic alloy of palladium and hydrogenium.

The idea that the increased concentration of occluded hydrogen versus gaseous hydrogen was partly responsible for its increased activity was already hinted at in the statement from Gladstone and Tribe quoted earlier and a similar idea was suggested by Edward Willm in 1873 (72). This is, of course, a purely kinetic effect only if one assumes that the occluded hydrogen is still diatomic and does not chemically interact with the metal lattice – fine points on which the 19th century chemist was understandably vague.

10. Summary and Conclusions

Having come to the end of our historical survey, what can be said about the fate of the term "nascent state"? Despite its apparent renaissance among chemists in the field of chemical reaction dynamics, it is unlikely that the term will return to the introductory textbook. With the demise of the free-atom model, it no longer has value as a minor piece of evidence for the polyatomic nature of elemental molecules and, though one might argue that historically it represents one of the first sustained attempts to deal with reaction mechanisms, its status as a well-defined concept in chemical kinetics is even more tenuous.

Our survey points to the fact that nascent activity is primarily a kinetic phenomenon and that it basically subsumes any change in reaction conditions that will favorably alter the kinetics of an otherwise thermodynamically allowed reaction. The precise nature of this alteration may vary from one system to the next. Thus the occlusion or gas adsorption model seems best suited to describe nascent activity in the case of gases generated electrochemically or via heterogeneous reactions in the liquid phase; the nonequilibrium model seems best suited to the vibrationally excited products formed in molecular cross-beam studies, and the gas bubble model for activation of absorbed gases in porous carbon. In short, there is no single explanation of nascent activity and hence no well-defined nascent state. Even if one accepts the generalized active intermediate model, the fact remains that similar active gases can be stored in platinum and porous carbon or produced by means of superfine bubbles and that the literal meaning of the term nascent no longer applies under these conditions.

It is of interest to compare these conclusions with those of earlier writers. In a memoir written in 1870, Henri Sainte-Claire Deville objected to the use of the

term "state" in conjunction with a transient species which, by its very definition, could not be isolated and assigned definite properties (73). Muir, on the other hand, attempted to weigh both the pros and cons of the concept in his 1884 text (1):

The term "nascent action" has probably been at once helpful and harmful to the progress of chemistry. By classing under a common name many phenomena that might otherwise have been lost in the vast mass of fact with which the science has to deal, the expression has, I think, done good service; but in so far as its use has tended to prevent investigation - for it is always easier to say of any unusual reactions, "these are of nascent action" than to examine carefully into their course and conditions ... the use of the expression has, I think, been unfavorable to the best interests of chemical science.

Indeed, examples of its use as a chemical scapegoat are not hard to find (78-79).

But it was Alexander Smith (figure 9), in the 1918 edition of his popular *Introduction to Inorganic Chemistry*, who came closest to our own conclusion when he wrote (74):

The term nascent hydrogen is used in different senses, in a very confusing way. (1) It may mean nascent, literally, that is newly born or liberated. (2) It is also used to mean different-from-ordinary, or, in fact, an allotropic form of hydrogen. (3) It is often used to mean one particular allotrope, namely, atomic hydrogen. (4) It is used ... to mean hydrogen activated by contact with a metal. (5) Finally, its activity is explained as being due to the larger amount of free energy contained in zinc plus acid plus reducing agent, as compared with the free energy contained in free hydrogen plus reducing agent ... The word nascent is, of course, a misnomer, excepting in connection with [usage] 1.

Finally, in closing, we might briefly note a positive example of the use of the nascent state concept. In 1882 the German chemist, Moritz Traube, successfully used it to unravel the structure of hydrogen peroxide (75-76). Previous to his work chemists had viewed this compound as oxygenated water. In contrast, Traube insisted that it "was not an oxidation product of water ... but rather a compound of an undamaged molecule of oxygen with two added hydrogen atoms." This he proved by comparing the products obtained by passing dihydrogen gas over nascent oxygen generated at the anode, via the electrolysis of water, with those obtained by passing dioxygen gas over nascent hydrogen
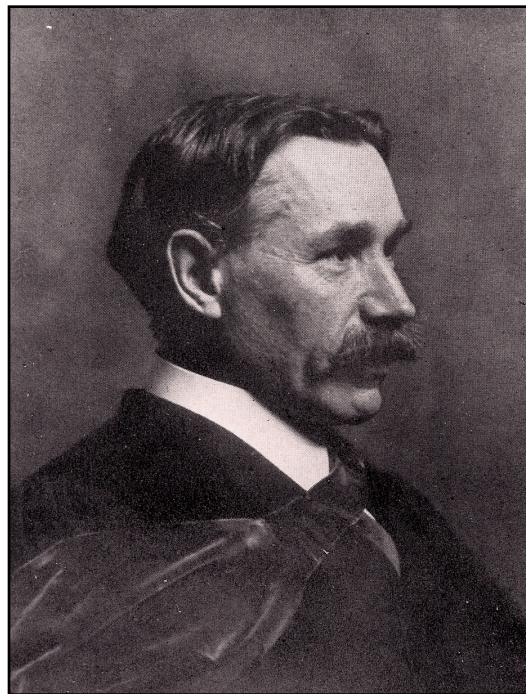

Figure 9. Alexander Smith (1865-1922).

generated at the cathode. Assuming the free-atom interpretation of the nascent state, Traube reasoned that, if the traditional view of hydrogen peroxide was correct, then it should be produced at the anode via the reaction:

$$H_2 + 2O \rightarrow H_2O_2 \qquad [20]$$

whereas if his interpretation was correct, it should be produced at the cathode via the reaction:

$$O_2 + 2H \rightarrow H_2O_2 \qquad [21]$$

In fact, only water was produced at the anode, whereas a small amount of hydrogen peroxide was formed at the cathode, thus both verifying Traube's hypothesis and providing a sobering reminder of how incorrect assumptions (i.e., the free-atom interpretation of the nascent state) can sometimes lead to correct results.

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Update

In preparing a new reprint of this paper, I have taken the liberty of adding section headers, as well as several new illustrations taken from the Oesper Collections at the University of Cincinnati. I have also since discovered evidence that most reductions attributed to nascent hydrogen generated in acid-metal systems are due to the metal and that the H_2 generation is merely a competing side-reaction.