Beyond Fossil-Fuel-Driven Nitrogen Transformations

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Abstract

Nitrogen is fundamental to all of life and to many industrial processes. Nitrogen in its various oxidation states comprises the global nitrogen cycle, with the change between forms being redox reactions involving electrons and protons. The interchange of nitrogen oxidation states constitutes some of the most important industrial processes, with the energy for these processes being provided largely by fossil fuel. A key goal of research in the field of nitrogen chemistry is to minimize the use of fossil fuels by developing more efficient heterogeneous, homogeneous, or biological catalysts, or by inventing new energy-efficient processes that rely on catalysts. These approaches, as well as the challenges involved, are discussed in this review.

One-Sentence Summary

This review article reports on the current state of the field of nitrogen activation chemistry and discusses future directions.

Reduced forms of nitrogen, particularly ammonia (NH_3), are vital to life. Prior to the early 1900's, all reduced N came from biological nitrogen fixation occurring in microbes. This landscape changed in the early 1900's with the invention of an industrial process to reduce N_2 to NH_3 ($N_2 + 3H_2 \rightleftharpoons 2NH_3$) by Haber and Bosch (H-B). The H-B process, in turn, has led to fundamental changes in the way food is produced, and its impact is underscored by the fact that about 50% of the N atoms in humans today originate from the H-B process (1). For these reasons and others, the H-B process has been called the most impactful invention of the 20th century (2). The H-B process is, however, energy intensive, consuming 1–2% of the world's annual energy output (3). The main energy requirements arise from the high reaction temperatures (~700 K) and pressures (~100 atm), and, most importantly, from the need for large quantities of H_2. Nevertheless, at scale H-B is surprisingly energy efficient. In addition to the high energy demand, however, there is a second problem with H-B that is potentially more serious. Specifically, the source of H_2 is usually natural gas, (4) and consequently H-B generates about 1.9 metric tons of CO_2 per metric ton of NH_3 produced (3 CO_2 per 8 NH_3) (5).

Nitrogen in its more oxidized forms is also industrially, biologically, and environmentally important. Oxidation of N_2 to nitric oxide (NO) and nitrogen dioxide (NO_2), which are collectively referred to as NO_x (the representation of neutral forms of oxidized nitrogen), occurs naturally in lightning and also during combustion of fuels in air (6). In fact, plasma-driven oxidation of N_2 to NO (the Birkeland-Eyde, or B-E, process) preceded H-B as the

first commercial nitrogen fixation process (7). However, B-E is not economically competitive with the H-B process, and as a result the demand for oxidized nitrogen, primarily in the form of nitric acid (HNO_3), is satisfied by catalytic oxidation of H-B-generated NH_3 at elevated temperatures via the Ostwald process (8).

Nitrogen oxides (NO_y, which represents both neutral and anionic forms of oxidized nitrogen) are also produced on a large scale by bacteria. These processes include oxidation of NH_3 to nitrate (NO_3^-) by nitrifying bacteria and reduction of NO_3^- to nitrite (NO_2^-), NO, nitrous oxide (N_2O), and ultimately to N_2 by denitrifying bacteria. The conversion of NH_3 and NO_3^- to N_2 by the action of these bacteria is used in waste-water treatment and is the primary pathway for loss of applied fertilizers in agriculture. Nitrogen oxides are common environmental pollutants, and thus catalysts to reduce these oxides to N_2 are also of considerable practical importance. For example, NO_x generated during combustion is a primary component of photochemical smog (9). The development of active catalysts for reducing NO_x to N_2 (the TWC, or three-way catalytic converter) led to remarkable improvements in air quality in the late 1970's (10), and there are now TWCs operating on hundreds of millions of vehicles worldwide. However, increasingly stringent emissions regulations coupled with the low exhaust temperatures from high efficiency engines present challenges for future combustion emissions control (11). The soluble forms of the nitrogen oxides, primarily NO_2^- and NO_3^- 2 3 , are similarly hazardous to human health and contribute to the eutrophication of waterways (12). Sustainable approaches for catalytically converting these pollutants to N_2 remain an unmet challenge (13).

In the present article, we report on the results of a U. S. Department of Energy workshop held in October, 2016 that focused on the challenges and opportunities associated with fundamental aspects of nitrogen chemistry. We begin by discussing the thermochemistry of nitrogen transformations, and then focus on the reduced forms of nitrogen, primarily NH_3, followed by the oxidized forms.

Thermochemistry of nitrogen fixation

The energy expenditures for various reductive and oxidative N_2 fixation pathways are compared in Figure 1 (14–16). Hydrocarbons, including biomass and fossil fuels (particularly methane), and water are the only two sources of hydrogen atoms that can sustain long-term, large-scale NH_3 production. The use of water as the hydrogen source for NH_3 production requires substantially more energy than methane (by 613.4 kJ/mol N_2), but it is also more environmentally benign, does not contribute to the accumulation of greenhouse gases, and does not compete for valuable and limited hydrocarbon resources. However, these advantages can be fully realized only if the energy comes from a clean, renewable source such as the sun or wind.

When water is used as the feedstock, there is only a small (32.9 kJ/mol N_2) thermodynamic advantage for the direct synthesis of NH_3 compared to a two-stage synthesis involving water splitting followed by H-B. The overall energy saving may, however, become more significant if the H-B process is avoided altogether and direct reductive N_2 fixation is conducted under milder conditions.

The two most important N-containing commodity chemicals are NH_3 and HNO_3. In 2017, their worldwide production was estimated to be 150 (17) and 50 (18) million metric tons , respectively. Presently, nearly all HNO_3 is manufactured using a three-stage process: steam reforming of methane, H-B, and then the Ostwald process (Figure 1), but this approach is energetically wasteful compared to direct oxidative N_2 fixation.

An attractive alternative route to HNO_3, which avoids the NH_3 intermediate, is direct N_2 oxidation to aqueous HNO_3 (eq 1).

$$N_{2(g)} + 2.5O_{2(g)} + H_2O_{(liq)} \rightleftarrows 2H^+_{(aq)} + 2NO_{3^-(aq)} \qquad (1)$$
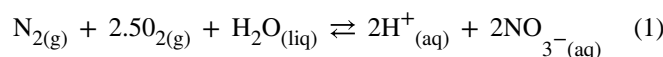
The equilibrium constant for this reaction is $\sim 2.7 \times 10^{-3}$ $M^4/bar^{3.5}$ ($G^0 = 14.6$ kJ/mol N_2) (14–16, 19), which is large enough to drive spontaneous formation of ~0.1 M HNO_3 in any pool of water on the surface of the earth. Moreover, if equilibrium were to be achieved between the earth's atmosphere and the world's oceans, the oceans would contain ~0.02 M HNO_3 and ~90% of atmospheric O_2 would be consumed. Fortunately for life on Earth, under ordinary conditions and in the absence of a catalyst, eq 1 is immeasurably slow in both directions.

Reduction of N_2 to NH_3

Overview.

As discussed in the previous two sections, the most important N_2 reduction reaction is NH_3 synthesis, specifically $N_2 + 3H_2 \rightleftarrows 2NH_3$. Given that this reaction is slightly thermodynamically favorable under ambient conditions, major effort has been devoted to developing alternative and environmentally friendly processes that would allow NH_3 to be produced at distributed sources under more benign conditions rather than the large-scale centralized H-B process. This goal is particularly important in developing countries where the population, and hence the need for food, is increasing rapidly. In these countries, access to fertilizer is hampered by poor transportation infrastructure and insufficient capital to build large chemical plants. For example, there are no large-scale NH_3 production facilities in all of East Africa. To address this need, there has been substantial effort expended to understand N_2 reduction using a variety of catalysts; including: heterogeneous, enzymes, and homogeneous catalysts, and electro- and photocatalysts.

Heterogeneous catalysis.

The commercial H-B process is carried out using a heterogeneous catalyst based on iron and promoted with Al_2O_3 and potassium. Typically, 2500 tons of NH_3 per day are produced in a single plant where natural gas and water are available in large quantities. It is now well accepted that the relative activity of metallic catalysts can be correlated to their binding energies with N-containing species in terms of a volcano-shaped relationship. Metals that bind nitrogen too strongly or too weakly are on either side of the volcano (20). For those having low binding energies, N_2 dissociation is rate-limiting. For those metals exhibiting high binding energies, N_2 dissociation occurs but desorption of the resulting atomic N (and

other N-containing intermediates) is slow, limiting the number of available binding sites and thereby slowing the catalytic rate (21).

Recent calculations suggest that the energies of all intermediates and transition states involved in a conventional NH_3 synthesis reaction network scale with the N binding energy. As shown in Figure 2, these correlations limit the rate of NH_3 synthesis on transition metals to much lower values than would be possible on a material with both a low N_2 dissociation barrier and more moderate intermediate binding energies (22). Clearly, an important challenge is to break this type of scaling relationship, which should lead to the development of catalysts yielding reaction rates that are potentially orders of magnitude higher than the current state of the art.

Advances in the synthesis, characterization, and modeling of non-traditional heterogeneous catalysts, such as intermetallics, alloys containing a single heteroelement, and shape-controlled materials, whose discovery might be driven by computational models, offer the promise for more active catalysts. These combined efforts should lead to catalysts that could potentially operate at lower temperatures and thus reduce the operating pressures of the H-B process. Another opportunity to reduce the CO_2 footprint of the H-B process is to replace the methane reformer with a water-electrolyzer to provide CO_2-free H_2, but this would require cost-effective, large-scale electrolyzers.

Enzyme catalysis.

A range of microbes (bacteria and archaea) living in all major ecosystems are able to reduce N_2 to NH_3 using the enzyme nitrogenase. Nitrogen fixation by these microbes contributes to global supply of NH_3, but it is insufficient to support modern intensive agriculture food production. Exciting frontier areas for the use of microbial N_2 fixation include engineering the nitrogen fixation genes into eukaryotes (23), such as plants, and using nitrogen-fixing microbes in microbial electrocatalysis cells that permit sustained N_2 reduction to NH_3 (24). Such systems offer the promise of providing localized solutions to N_2 reduction, but are not likely to displace the need for large-scale N_2 reduction in the near term.

One important lesson that can be learned from biological nitrogen fixation is understanding how the enzyme nitrogenase accomplishes reduction of N_2 to NH_3 at low temperatures and pressures and without H_2. The first nitrogenase to be purified (and the most widely distributed) is Mo-dependent and, as shown in Figure 3, has a metal-cluster active site containing Mo, Fe, S, C, and homocitrate (FeMo-cofactor).

An important step toward mechanistic understanding of nitrogenase emerged from trapping an intermediate with four H^+ and four e^- accumulated immediately prior to binding N_2. Characterization of this intermediate (termed the E_4 state) has revealed the presence of bridging hydrides (Fe-H-Fe). The E_4 state undergoes reductive elimination of the two hydrides with release of H_2, with concomitant activation of the metal core by two e^- for binding and reduction of N_2 to a metal-bound diazenido species (HN=N-Fe). Although these studies have provided insights into the central catalytic step, which is the cleavage of the N_2 triple bond, many challenges remain before the entire mechanism can be elucidated. These include a molecular level understanding of both the early and late stages of the N_2 reduction

pathways, an understanding of the roles of ATP hydrolysis in driving electron transfer, and then reconciliation of the resulting empirical mechanism with computational studies.

These foregoing challenges primarily involve substrate moieties bound as catalytic intermediates. In parallel, important questions remain about the FeMo-cofactor active site of Mo-dependent nitrogenase. For example, what changes in redox and spin states of the seven Fe centers and the Mo center accompany the stepwise transformations of substrates? Additionally, the FeMo-cofactor contains the first example of a carbide (C^{4-}) in biology. The significance and function of this carbide with respect to mechanism are unknown. Understanding the structure of FeMo-cofactor intermediates and synthetic analogues could provide important clues to guide the design of new homogeneous and heterogeneous catalysts for N_2 reduction (25). Biomimetic approaches could take advantage of not only the coordination chemistry in the FeMo-cofactor, but also the cooperative interactions with nearby acidic amino acid residues in the nitrogenase protein.

Electrochemical techniques offer a powerful alternative method of delivering electrons to nitrogenase without a requirement for ATP hydrolysis, and they also offer new avenues for addressing aspects of the nitrogenase mechanism. Electron transfer from an electrode, previously demonstrated for a number of redox enzymes, has been applied to nitrogenase but only via mediators (i.e., no direct electron transfer) (26–28). As illustrated in a recent study, this approach, in combination with computations (29), provides insights into catalytic nitrogen transformations.

A related frontier area is using nanomaterials to deliver electrons to nitrogenase. For example, it has been recently demonstrated that a CdS nanorod-nitrogenase MoFe protein hybrid achieves light-dependent N_2 reduction to NH_3 using a sacrificial electron donor (30). Such systems offer a means to use light as the exclusive energy source to drive N_2 reduction.

Homogeneous catalysis.

Synthetic homogeneous catalysts designed for N_2 reduction provide well-defined molecular pre-catalysts and intermediates, which can be thoroughly characterized by diverse spectroscopic techniques and thereby provide excellent opportunities for determining mechanistic information about N_2 reduction to NH_3. The reactivity of synthetic inorganic complexes provides insights into molecular reactivity and individual bond-making processes that occur in nitrogenases. The discovery of nitrogenase, along with a transition metal compound that contains N_2 bound to ruthenium (31), initiated a race to prepare NH_3 catalytically under mild conditions via a transition metal complex. Indeed, entire institutes were created in England and Russia in the late 1960s for this purpose. The stoichiometric N_2-to-NH_3 conversion using H_2SO_4 was demonstrated using low-valent Mo-N_2 and W-N_2 complexes in the 1970s (32); typically the electrons required came from the metal complex. In 1985, the synthesis of NH_3 was accomplished by Pickett and Talarmin using an electrochemical route starting from the tungsten complex $[W(N_2)_2(PMe_2Ph)_4]$, with the electrons supplied by the electrode and protons from an added acid (33). The catalytic reduction of N_2 to NH_3 by H^+/e^- was reported in subsequent studies, using, for example, a well-defined Mo-containing catalyst (34). Up to eight equivalents of NH_3 per Mo were formed, along with H_2. Both experiments and calculations support a mechanism involving

the addition of 6H$^+$ and 6e$^-$ to the N$_2$ initially bound to a Mo(III) center. Altogether, eight of these proposed intermediates were prepared and characterized.

Additional Mo pre-catalysts for reduction of N$_2$ using chemical reductants and an acid, a dimolybdenum–dinitrogen complex (35) and a molybdenum nitride (36), were subsequently reported in 2011 and 2015, respectively. In 2013, Fe complexes were reported that catalyze reduction of N$_2$ to NH$_3$ using a strong reducing agent (KC$_8$) and a strong acid at 200 K (37); improvements to the Fe system recently produced as many as 84 equivalents of NH$_3$ per Fe (38). These Fe complexes were designed to reflect the trigonal symmetry of the Fe in the catalytic face of FeMo-cofactor (Figure 3) and to allow variation of an axial ligand, so as to explore tuning of N$_2$ binding/reduction by the unusual carbide at the center of the FeMo-cofactor.

In all these cases it appears that catalytic N$_2$ reduction is a 6-electron process, involving many intermediate chemical species [M-N $_x$H$_y^{n+}$], but unlike nitrogenase without a mechanistic requirement for production of H$_2$. Nonetheless, in all cases N$_2$ reduction is accompanied by production of H$_2$, and at least with the Fe complexes, this has been shown to involve a catalytic process, with H$^+$ reduction competing with N$_2$ reduction.

Much work remains to move this field forward. For example, rational design of potential catalysts will be guided by accurate determination of the bond dissociation free energies (BDFEs) of N-H bonds, including likely intermediates such as M-N=NH, M=N-NH$_2$, and M=N-NH$_3$. Initial experimental and theoretical estimates have shown that N-H BDFEs of coordinated NH$_3$ can vary significantly and demonstrate the importance of metal identity and its oxidation state as well as the possibility of ligand control to tune the stability of potential intermediates. In addition, determination of the energies of these bonds will allow evaluation of energetic requirements of the individual chemical steps that ultimately lead to NH$_3$. It is also important to identify features that tune the reduction potentials of relevant complexes to ensure that the multiple reductions required for catalysis are energetically feasible. Thus, research should focus on exploring complexes designed to simultaneously promote N$_2$ binding and multiple reductions at the metal site.

Electrocatalysis and photocatalysis.

The potential-pH predominance (Pourbaix) diagram for the N$_2$-H$_2$O system shown in Figure 4 reveals that reduction of N$_2$ to NH$_4^+$/NH$_3$ (eq 2 and the N$_2$ reduction line in Figure 4) is thermodynamically possible under moderately reducing conditions.

$$N_{2(g)} + 8H^+_{(aq)}(6H^+_{(aq)}) + 6e- \rightleftarrows 2NH_4^+_{(aq)}(2NH_{3(aq)}) \quad (2)$$
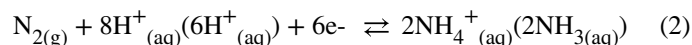
Moreover, with a sufficiently active electrocatalyst, the N$_2$ reduction reaction can, in principle, proceed in a narrow range of negative potentials without interference from water reduction (line a in Figure 4) over the entire pH range. However, at potentials below line a, an extremely selective electrocatalyst would be required to suppress parasitic water reduction. Note that the nitrogen reduction reaction could be paired with a water oxidation half-reaction to supply the H$^+$ and e$^-$ required for a complete electrolysis cell. Such a cell

would essentially combine water splitting with NH_3 formation as depicted by the direct reductive fixation route in Figure 1. Despite the inviting prospect of a scalable NH_3 electrolysis cell running on renewable electricity at or near room temperature, the difficulty of selectively catalyzing the nitrogen reduction reaction has prevented development of an efficient electrochemical system.

At present, only a few examples of pairing the nitrogen reduction reaction with water oxidation at ambient temperature and pressure have been reported, and in all cases, due to competing H_2 evolution, the faradaic efficiencies for NH_3 are so low that even its reliable detection is challenging (39, 40). For example, an efficiency of 0.83% and a production rate of 9.4×10^{-10} mol-NH_3 cm^{-2} s^{-1} were measured at 353 K at an applied cell voltage of 1.2 V using Pt electrodes and a Nafion electrolyte (41). Another electrochemical approach involved an electrochemical cycling process for producing NH_3 (42). The cycling included separate steps of LiOH electrolysis, Li nitridation, and Li_3N hydrolysis, thereby circumventing the parasitic H_2 evolution reaction and leading to higher faradaic efficiencies for NH_3.

Proton-conducting ceramic oxides have been explored as electrodes for nitrogen reduction, and when they operate at higher temperatures both the rate and faradaic efficiency increase (43). For example, efficiencies in excess of 50% and rates in the range of 10^{-9}-10^{-8} mol-NH_3 cm^{-2} s^{-1} have been attained above 673 K using oxide or molten chloride electrolytes and a variety of metal or metal oxide cathodes (43, 44). Note, however, that higher temperatures introduce an additional energy burden and hence compromise the advantage of this approach compared to H-B.

Photochemical reduction of N_2 to NH_3 has also been reported, and there may be guidance in these studies relevant to electrochemistry (45, 46). Photocatalytic routes to NH_3 have been summarized recently (47). One of the biggest challenges for photocatalytic NH_3 synthesis is the discovery of active and stable photoelectrode materials responsive to visible light. Synthetic nitrogenase mimics in the form of chalcogels, composed of Mo and Fe-containing biomimetic clusters, can potentially accomplish photocatalytic N_2 fixation and conversion to NH_3 at ambient temperature and pressure. Both Fe–S and Mo-Fe–S chalcogels have displayed promising activity toward N_2 reduction (48).

Plasma-driven transformations.

The feasibility of using plasmas consisting of ions, electrons, and excited molecular species to drive chemical reactions that are thermally inaccessible has been known for many years (7). For example, NH_3 was synthesized in laboratory-scale, non-thermal $N_2 + H_2$ plasmas at temperatures and pressures lower than those used in H-B as early as the 1970s, and more recently the synthesis has been demonstrated under much milder conditions (1 atm and 140°C) (49). The plasma synthesis of NH_3 has been carried out both homogeneously and in combination with heterogeneous catalysts (7, 49, 50).

Several mechanisms have been proposed to account for enhancements in catalytic activity in the presence of non-thermal plasmas (51–53). However, the fundamental science and practical engineering of plasma-driven NH_3 syntheses lag behind thermal and

electrochemical routes and are therefore ripe for additional research. Further progress in this field will draw on the insights gained from traditional heterogeneous and electrochemical reductions.

Chemical looping.

Chemical looping is perhaps most familiar from combustion where two connected fluidized beds are used to cycle solid particles between an oxidized and a reduced state to combust a carbon-containing fuel with oxygen (54). Chemical looping could also be performed with two fixed beds instead of fluidized beds. Nitrogen can be used instead of oxygen for a similar looping approach in NH_3 synthesis (55). First, N_2 is contacted with a suitable solid-state transition metal to yield a nitride (activation). In the second step, NH_3 is harvested by contacting the nitride with steam or H_2 (56). Recently, lithium has been employed as the parent metal for the nitride, but this approach requires liquid-phase electrolysis to recycle lithium and this step is usually not present in chemical looping (42).

Potential advantages of chemical looping include the ability to independently control process conditions for N_2 activation and product harvest. In this sense chemical looping enables breaking the scaling relationship alluded to in Figure 2. Operation at atmospheric pressure is another major advantage of chemical looping for nitrogen activation (57). Based on results from a pilot-scale plant, chemical looping for combustion, including CO_2 capture, has been compared to conventional combustion and appears to be economically attractive (58). This may be an indication of the possible economic feasibility of chemical looping for nitrogen activation.

Oxidation of N_2

Overview.

The dominance of the H-B process in commercial N_2 fixation is arguably a direct consequence of the ready availability of H_2 from fossil hydrocarbons. As shown in Figure 1, oxidative fixation of N_2 can, in principle, be achieved with a lower energy input than reductive fixation if N_2, H_2O, and O_2 are used as reactants. Other nitrogen oxides are accessible at even lower free energies, especially when coupled with water to form the corresponding oxoacids.

Although H-B and natural processes have motivated substantial research into N_2 reductive fixation, direct N_2 oxidation remains largely unexplored despite its great practical value as a replacement for the Ostwald process. The fact that living organisms have not evolved to consume N_2 and O_2 and produce aqueous HNO_3 suggests fundamental chemical challenges that merit investigation. As a result, there is very little literature on the homogeneous oxidative chemistry of N_2.

Direct oxidation of N_2 with O_2.

NO_x is unavoidably generated at the high temperatures that prevail during combustion in air. NO is the primary combustion-generated component of NO_x, and its formation can be viewed in the context of its equilibrium with N_2 and O_2 (eq 3).

$$N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)} \quad (3)$$
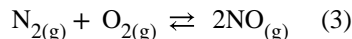
The standard enthalpy of this reaction is 90.3 kJ/mol NO and the entropy is 12.4 J/(mol NO K) (14, 15), indicating that equilibrium is unfavorable for NO production under ambient conditions. Due to the positive entropy, however, the equilibrium NO concentration rises rapidly with temperature, exceeding 100 ppm above 2000 K (59).

The direct bimolecular reaction of N_2 and O_2 to produce NO is symmetry-forbidden and has a negligible rate even at combustion temperatures. Rather, NO is produced during combustion via eqs 4 and 5, where O (and similarly OH) radicals attack N_2, as originally proposed by Zeldovich (60).

$$O + N_2 \rightarrow NO + N \quad (4)$$

$$N + O_2 \rightarrow NO + O \quad (5)$$

Analogous reactions are at play in high-temperature thermal plasmas, as in the original B-E arc process. Thermal plasmas are unlikely to be energy-competitive with the H-B process, even if the latter uses a renewable H_2 source (61), because the overall energy efficiencies of N_2 activation are low and rapid thermal quenching is required to suppress NO decomposition back to N_2 and O_2.

The aforementioned fundamental limitations can be mitigated using low-temperature, non-thermal plasmas generated by either a dielectric barrier discharge or microwave absorption at or below atmospheric pressure, potentially coupled with appropriate catalysts (7). According to current estimates, theoretical energy consumption for N_2 fixation via eq 3 in a non-thermal plasma (~400 kJ/mol N_2) is more than 2.5 times lower than that for the H-B process with methane-derived H_2 (61–63), and the energy efficiencies already attained in the laboratory (600–1200 kJ/mol N_2, assuming 100% efficient plasma generation (62, 63)) are better than the H-B process using H_2 from water electrolysis (~3000 kJ/mol N_2 (61)), 40% of which would go to electrolysis (64). Experiments and kinetic models show that the primary effect of the nonthermal plasma is to accelerate Zeldovich-like reactions involving athermal, vibrationally excited N_2. Practical implementation of non-thermal plasmas is hampered by their relatively low power per unit reactant mass and thus low throughput.

A thermal, heterogeneous N_2 oxidation catalyst would have to activate N_2 and O_2 and be stable at the extreme temperatures at which NO production becomes thermodynamically favored. Because of these stringent demands, non-thermal electro-, photo-, or plasma-assisted oxidation routes likely offer the greatest opportunities for progress. The development of catalytic systems that can effectively couple with these external energy sources will be key to practical advances. Preliminary results with non-thermal plasmas,

especially coupled to catalysts, are promising. There is a pressing need to uncover the fundamental mechanisms that couple plasma chemistry, surface chemistry, catalysts, and theory to guide optimization of plasma and rational development of appropriate catalytic materials.

Electrochemical oxidation of N_2 to HNO_3.

The oxidation line in Figure 4 shows that N_2 is electrochemically unstable toward NO_3^- under moderately oxidizing conditions (eq 6).

$$N_{2(g)} + 6H_2O_{(liq)} \rightleftarrows 2NO_{3^-(aq)} + 12H^+_{(aq)} + 10e^- \quad (6)$$
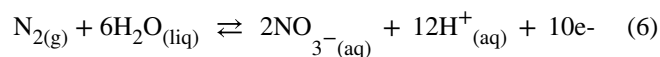
At pH > 1.3, this ten-electron reaction is more thermodynamically favorable than the parasitic four-electron water oxidation to O_2. Thus, it is possible for NO_3^- to be the only product of an anodic process, particularly in neutral and alkaline solutions, if a sufficiently active and selective electrocatalyst for eq 6 can be discovered. The corresponding cell-completing cathodic reaction can be either water reduction to H_2 or O_2 reduction to water. No progress has yet been made in developing such catalysts, but there is no reason to believe that they cannot eventually be discovered given the necessary resources.

By coupling cathodic N2 reduction (eq 2) with anodic N2 oxidation (eq 6), an electrochemical cell consuming only atmospheric N_2 and water as feedstock to yield aqueous NH_4NO_3 (eq 7) can be envisioned.

$$N_{2(g)} + 3H_2O_{(liq)} \rightleftarrows NH_4^+_{(aq)} + NO_3^-_{(aq)} + H_{2(g)} \quad (7)$$
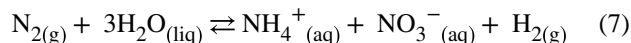
The additional H_2 production is necessary for matching cathodic and anodic currents and maintaining the electrolyte pH constant. Such a cell would require a minimum of 1.08 V to operate in neutral or alkaline electrolyte, which is slightly lower than the minimum water electrolysis voltage of 1.23 V. Advances relating to electrochemical N_2 oxidation will require development of catalysts that are sufficiently active (capable of good current densities at low overpotentials), selective (with respect to water oxidation), and stable (toward deactivation under harsh redox and pH operating conditions).

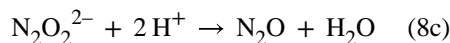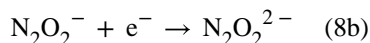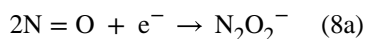## NO_y Reduction and NH_3 Oxidation

Overview.

The redox chemistry of forms of nitrogen other than N_2 is immense and rich, and it is extensively incorporated into biological systems. Both NO_y and NH_3 are environmentally hazardous pollutants generated by industrial and transportation activity, and thus extensive research has gone into developing and applying NO_y reduction and NH_3 oxidation catalysts. As is often the case, the understanding of these catalysts lags their applications

Ammonia oxidation and NO_y reduction are critical to environmental protection and are much less well understood or optimized than the synthesis of NH_3. There are appealing opportunities to apply the experimental and computational tools of modern heterogeneous catalysis to these reactions, both to develop a fundamental understanding of catalytic processes and to identify superior materials and catalytic processes; for example, catalysts that can selectively reduce NO_y to N_2 using hydrocarbon reductants. Environmental applications generally demand high longevity, durability, and tolerance to poisons. Key gaps in understanding include how activity and selectivity can be achieved in relatively cool gas streams, how catalyst structure evolves over long periods of time, how sulfur and other common poisons interfere with reactions, and especially how these effects can be mitigated.

NO_y reduction.

NO decomposition, the reverse of eq 3, is thermodynamically downhill but difficult to catalyze under the oxygen-rich conditions of interest for environmental protection (65). Nevertheless, NO decomposition has been demonstrated using both homogeneous and heterogeneous catalysts. Decomposition appears to involve a two-electron reduction of two NO molecules to a hyponitrite (eq 8).

$$2N = O \ + \ e^- \ \rightarrow \ N_2O_2^- \quad (8a)$$

$$N_2O_2^- \ + \ e^- \ \rightarrow \ N_2O_2^{2-} \quad (8b)$$

$$N_2O_2^{2-} \ + \ 2\,H^+ \ \rightarrow \ N_2O \ + \ H_2O \quad (8c)$$

Coordination complexes of hyponitrites are not uncommon, and a tri-Cu hyponitrite coordination complex has been isolated as an intermediate in the catalytic decomposition of NO to N_2 (66). A Cu dimer is similarly implicated as the active site in a Cu-exchanged zeolite catalyst for NO decomposition (67).

NO_x can be catalytically reduced to N_2 via several routes. Precious metals are active for NO_x reduction by CO and hydrocarbons, but only under conditions in which O_2 concentrations are low (10). Vanadia/titania and metal-exchanged zeolites catalyze selective reduction of NO_x by NH_3 (68). Nitrosamine appears to be the key N_2-forming intermediate in the catalytic pathway (eq 9).

$$NH_3 \ + \ NO \ \rightarrow \ H_2NNO \ + \ H^+ \ + \ e^- \quad (9a)$$

$$H_2NNO \rightarrow N_2 + H_2O \quad (9b)$$
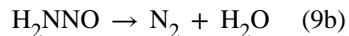
This N_2-forming reaction is exothermic, implying significant, but perhaps not insurmountable, kinetic challenges to reversing the chemistry.

NO_x can also be catalytically reduced with H_2 over Pd and Pt catalysts (13), and N_2 is typically the desired product (65). By suitable selection of promoters and control of the NO/H_2 ratio, however, NH_3 can be produced over Pt catalysts (69). Likewise, NH_3 competes with N_2 as the product of the catalytic reduction of NO_2^- and NO_3^- by H_2 over Pd catalysts (13).

Bacteria analogously reduce NO_3^- and NO_2^- through a series of gaseous intermediates leading ultimately to N_2 in a process called denitrification (eq 10). In these bacteria, NO_y acts as a terminal electron acceptor in an anaerobic respiration process. Electrons flowing through membrane-bound proteins produces a proton gradient that in turn is used to make ATP. Each step in the denitrification process is catalyzed by well-studied metalloenzymes that use some rather unusual metal clusters to achieve their chemistry (70, 71). From a global nitrogen perspective, denitrification by these bacteria functions to convert fixed forms of N (NO_y) into N_2. In some cases, this process is beneficial, such as during waste-water treatment to remove nitrates. In other cases, such as in agriculture, denitrification results in loss of N that was applied to crops as fertilizer.

$$2\,NO_3^- + 10\,e^- + 12\,H^+ \rightarrow N_2 + 6\,H_2O \quad (10)$$
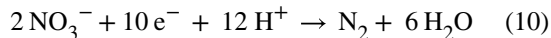
NH_3 oxidation.

Heterogeneous NH_3 oxidation with O_2 is at the heart of the Ostwald process and is practiced in a variety of environmental protection applications. Precious metals remain the workhorse catalysts, and therefore opportunities exist to develop lower-cost materials having equivalent or better activity and selectivity. The preferred NH_3 oxidation products shift from N_2 at low temperatures to NO at higher temperatures, with N_2O being a minor but highly undesirable product. At present, a full mechanistic understanding of this process and of the kinetic origins of selectivity is not available.

NH_3 and/or NO_2^- are fuel for bacteria and archaea that employ multi-electron oxidative reactions to generate reducing equivalents for cellular respiration and to establish a proton gradient for ATP synthesis (72, 73). Ammonia-oxidizing bacteria (AOB) and archaea (AOA) stoichiometrically convert NH_3 to NO_2^-. AOA and AOB first carry out the selective conversion of NH_3 to hydroxylamine (NH_2OH) using an integral membrane Cu monooxygenase called ammonia monooxygenase (AMO) (eq 11). Active AMO has never been purified, and thus this challenging transformation awaits mechanistic elucidation.

$$NH_3 + \frac{1}{2}O_2 \rightarrow NH_2OH \quad (11)$$
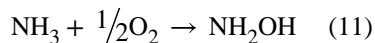
The NH_2OH generated by AMO is oxidized to provide a net electron flow for cellular respiration. How AOA processes NH_2OH is entirely unknown (74). In AOB, this process is carried out by hydroxylamine oxidoreductase (HAO), which contains a rare, covalently modified c-heme, heme P460, to which NH_2OH binds at Fe and undergoes proton-coupled oxidation (72). Recent experiments strongly support NO as the enzymatic product of HAO reactivity, contrary to decades of dogma asserting NO_2^- as the enzymatic product (75). Assuming a 2-electron turnover of AMO, the 3-electron oxidation of NH_2OH by HAO furnishes one net electron for cellular respiration. Stoichiometric production of NO_2^- from NH_3 by AOB likely involves an additional, but as-yet unidentified, third enzyme in the pathway. Cytotoxicity of both NO and NH_2OH may be managed by cytochrome P460, a monoheme enzyme that selectively produces N_2O from the reaction of NH_2OH with Fe-bound NO (76). NO_2^- is itself cellular fuel for nitrite-oxidizing bacteria (NOB) that effect the 2-electron oxidation of NO_2^- to NO_3^- and for recently discovered "complete ammonia oxidation" (COMAMMOX) bacteria that effect the 8-electron oxidation of NH_3 to NO_3^- (77).

Opportunity abounds to extract broadly applicable insights through the study of the oxidative enzymes operative in nitrification. Establishing the mechanism of NH_3 oxidation by AMO remains a grand challenge whose difficulty is exacerbated by the integral membrane nature of the enzyme and the sluggish growth of its host organisms. The end goal is tantalizing technology: selective hydroxylation of relatively inert bonds generalizable beyond N-species, especially considering that enzymes related to AMO, such as particulate methane monooxygenase, effect similar transformations of unactivated alkanes (78).

Mechanistic understanding of NH_2OH and NO_2^- oxidation in turn offers insights into proton-coupled, multi-electron transformations that are crucial to redox catalysis. NH_2OH is an energetic, cytotoxic metabolite that AOB and AOA harness as a source of reducing equivalents. The absence of requisite c-heme biosynthesis pathways in AOA necessitates substitution of HAO for either a non-heme or Cu-based enzyme for NH_2OH oxidation (79). Thus, opportunities exist to fill a "missing link" in the biogeochemical nitrogen cycle while expanding understanding of how transition metals can transduce energy from redox-active small molecules.

Concluding outlook

Since the beginning of the 20th century, both the ability to produce and the need to remediate nitrogen-containing compounds have been coupled to fossil fuels. Demands for greater energy efficiency, smaller and more flexible distributed processes, and environmental protection provide growing impetus to expand the scope of practically viable oxidative and reductive transformations of nitrogen that are not driven by fossil fuels. Opportunities exist to achieve radically improved, new, and different pathways, but progress in this regard will require a molecular-level understanding of nitrogen transformation reactions, as well as the

translation of these core insights to the discovery of new catalytic systems and alternative means of delivering the energy needed to drive those reactions. These understandings will emerge through the collective knowledge and insights to be gained from fundamental research that integrates experiments and theory in hetero- and homogeneous catalysis science, in photon- and electron-driven processes, and in biochemistry and biology.

Acknowledgments

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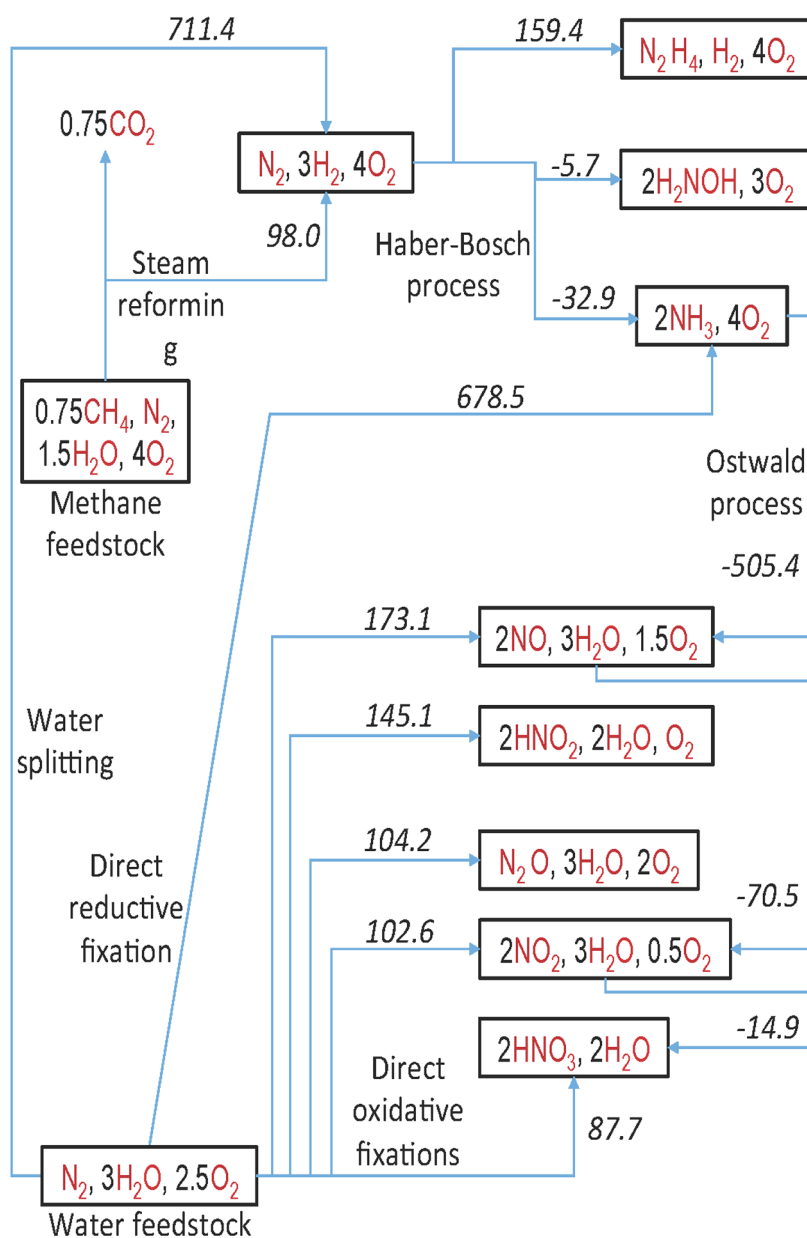
Figure 1.
Atom and energy economy of nitrogen fixation. The numerical values represent standard (for gaseous reactants and products and liquid H_2O, as defined in ref. 14) Gibbs free energies in kJ/mol of fixed N_2 in the direction of the arrows. All thermochemical data are from ref. 15, except for H_2NOH (ref. 16).
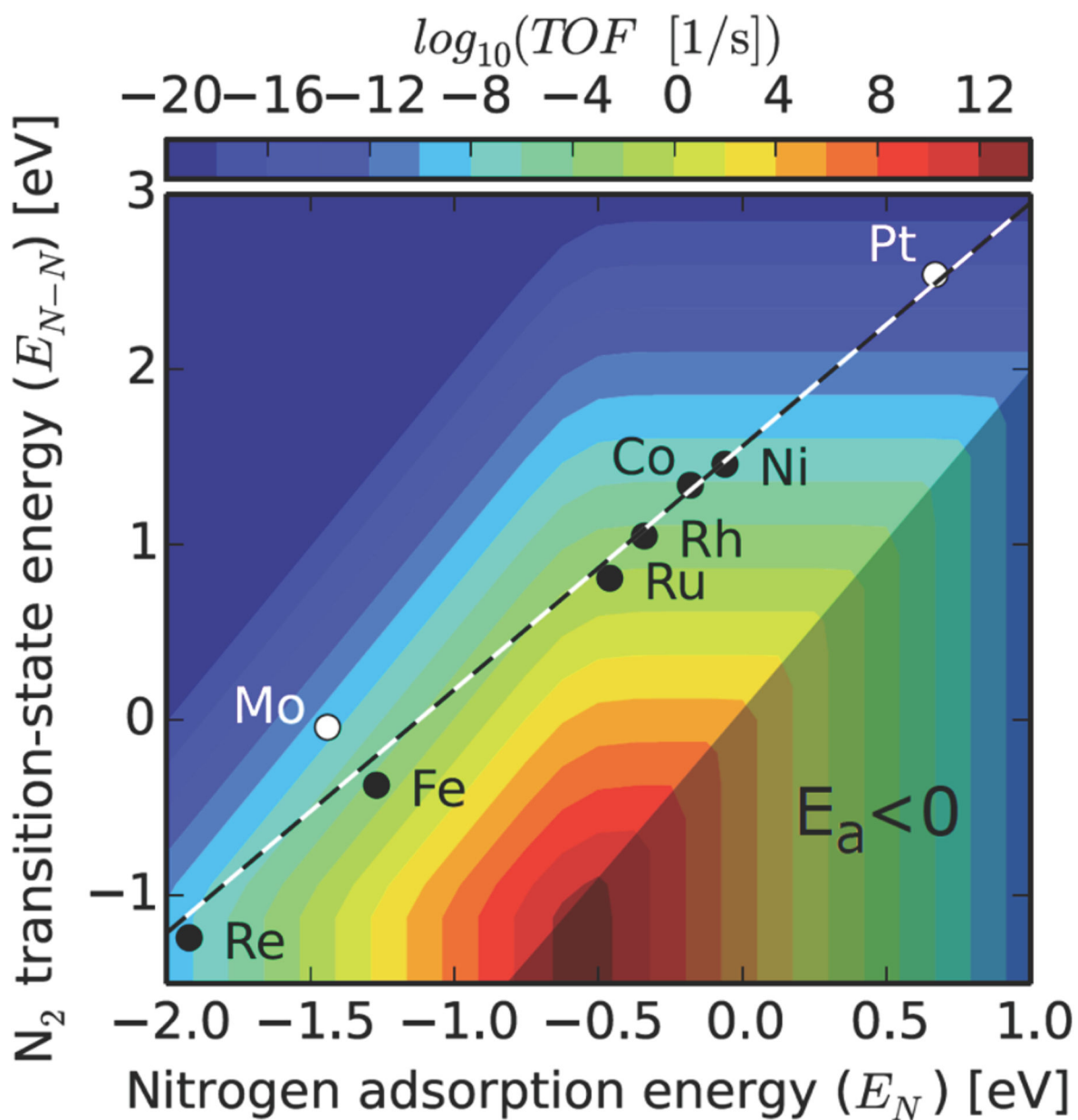
Figure 2.
Linear scaling between nitrogen binding energy and activation barrier for N_2 dissociation.
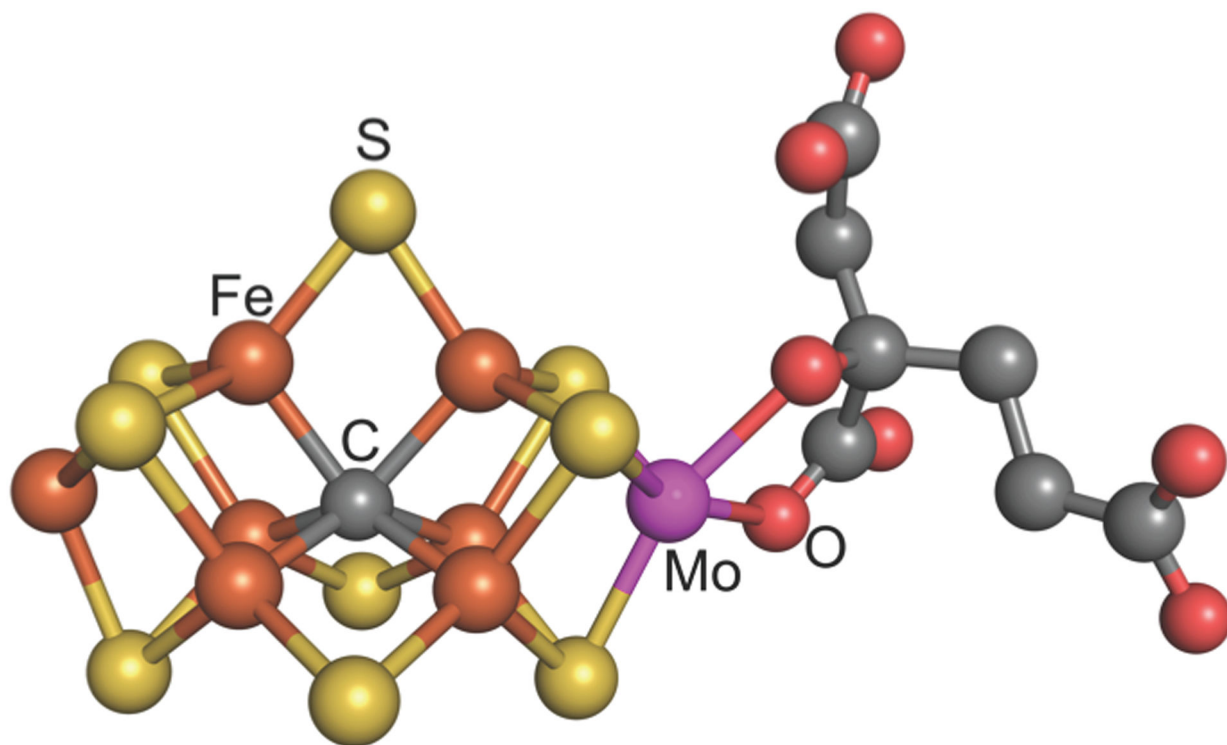TOF = turnover frequency (from ref. 22).

Figure 3.
FeMo-cofactor with Fe in rust, S in yellow, C in gray, Mo in magenta, and O in red. Made
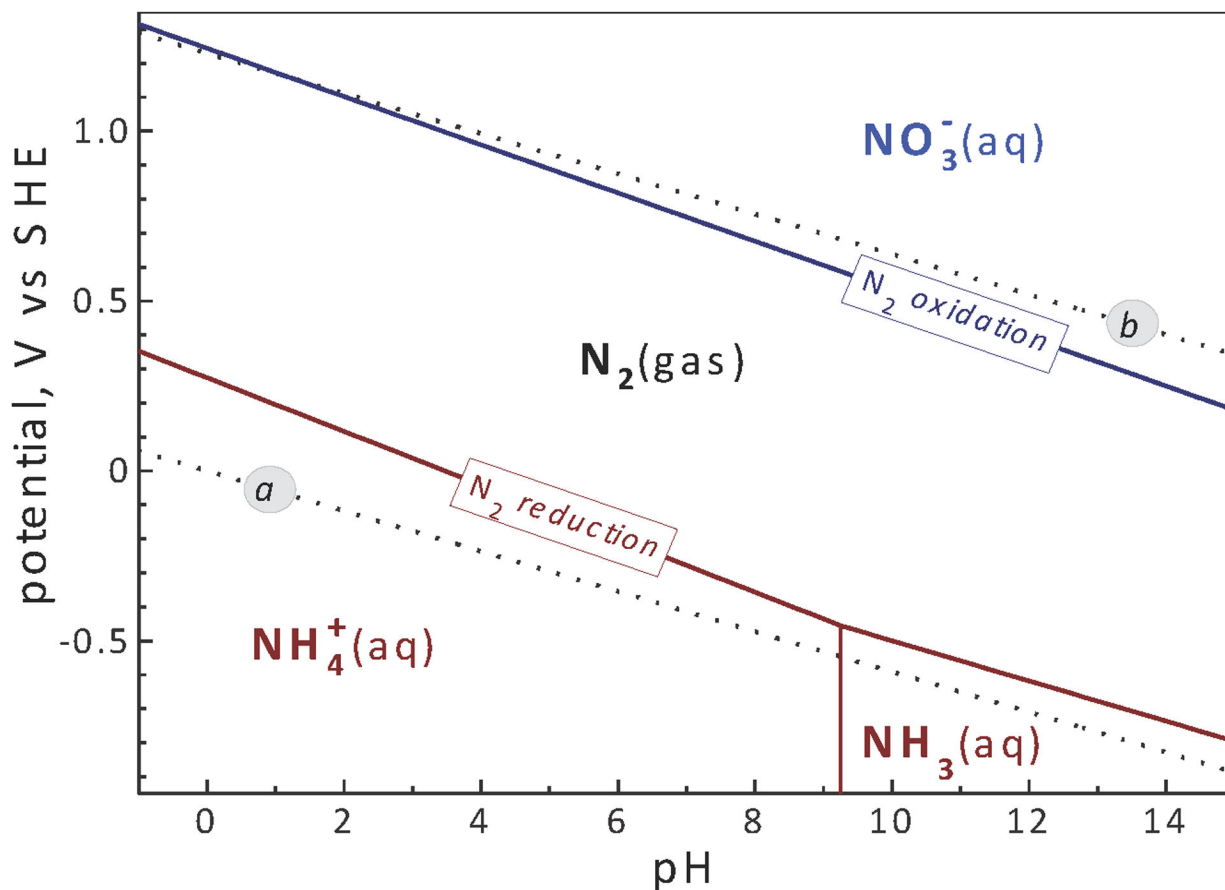from PDB: 1M1N

Figure 4.
Partial Pourbaix diagram for the N_2-H_2O system showing lines corresponding to N_2 reduction to NH_4^+/NH_3 and N_2 oxidation to NO_3^-. Lines *a* and *b* straddle the region of water stability (reduction to H_2 and oxidation to O_2, respectively). See ref. 14 for details and refs. 15 and 19 for primary data.