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Thermodynamics of Ternary Nitride Formation by Ammonolysis: Application to $LiMoN_2$, Na_3WN_3 and Na_3WO_3N

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Abstract

An approximate method for predicting the feasibility of synthesis of ternary nitrides from appropriate oxides and ammonia gas is outlined. The known thermodynamic data for binary oxides and nitrides may be a helpful guide in predicting the formation of ternary nitrides by ammonolysis of ternary oxides. When the difference between the free energy of formation of the ternaries from the binary oxides ($\Delta G_f^{\circ}(O)$) and binary nitrides ($\Delta G_f^{\circ}(N)$) is small, the predictions are expected to be reliable. Such considerations suggest that ternary oxides containing the most electropositive metals (alkaline, alkaline earth, rare earth) will not form ternary nitrides by ammonolysis, but perhaps will form oxynitrides or decompose to the electropositive metal oxide/hydroxide and binary transition metal nitride. When the metals in the ternary oxide are from group V or greater, ternary nitride formation by reaction with ammonia is likely.

We have developed a new high temperature calorimetric procedure for determining the standard enthalpies of formation of ternary nitrides and applied it to: $LiMoN_2$, Na_3WN_3 and Na_3WO_3N. The standard enthalpies of formation: ΔH_f° ($LiMoN_2$) = -386.0 ± 6.4 kJ/mol, ΔH_f° (Na_3WN_3) = -358.7 ± 53.3 kJ/mol and ΔH_f° (Na_3WO_3N) = -1358.8 ± 18.2 kJ/mol were obtained.

Introduction

In recent years, many new and interesting ternary nitrides have been discovered.[1-26] We have been developing novel synthetic strategies using precursors in the synthesis of new ternary nitrides. The advantage of using precursors to synthesize solid state materials is the possibility of using much lower temperatures for synthesis. This results because the desired elements are already mixed at the atomic level making diffusion lengths short. Low temperature synthesis may also lead to new compounds not realized using high temperature methods, if such compounds are unstable at high temperatures.

Specifically, we have investigated the practicality of the ammonolysis of ternary oxides (and to a lesser extent chlorides) to prepare new ternary nitrides. Recently reported $LiMoN_2$[1] and $FeWN_2$[26] are the only known ternary nitrides to be prepared from the ammonolysis of ternary oxides. We have developed a predictive scheme for these ammonolysis reactions using thermodynamic considerations.

High temperature reaction calorimetry has been very useful in understanding ternary oxide formation.[27] For the first time we have applied this methodology to ternary nitrides. The strategy is to devise a thermodynamic cycle involving rapid oxidation of a nitride or oxynitride to a well defined solid or molten oxide. The enthalpies of formation of $LiMoN_2$, Na_3WN_3 and Na_3WO_3N have been measured.

Thermodynamic Calculations to Predict the Feasibility of Nitride Synthesis

Oxide Precursors

Ternary solid state compounds, as well as ionic salts and coordination compounds, are potential precursors to binary and ternary nitrides. For a number of these potential precursors, especially for oxides and chlorides, sufficient thermodynamic data are available to make some reasoned judgments about their suitability as precursors. The standard free energies of formation of oxides (per mole of transition metal) are generally more negative than those of nitrides, making nitrides usually unstable, or at best kinetically stable, under ambient conditions and thus very rare in nature. This fact alone would seem to prohibit the conversion of oxides to nitrides. However, by choosing appropriate oxides, nitrogen sources and reaction conditions, some nitrides can be made from oxides. For example, we have experimentally confirmed literature reports that Nb_2O_5, Ta_2O_5, MoO_3 and WO_3 can be reacted in flowing ammonia gas at 973 - 1123 K to produce NbN, Ta_3N_5, Mo_2N and W_2N, respectively.[28,29] When we discovered that $LiMoN_2$ could be synthesized from Li_2MoO_4 and ammonia gas at 983 K,[1] we entertained the idea of reacting other ternary oxides in the same manner. After several unsuccessful attempts and realizing the variety and large number of ternary oxides available, we sought a semi-quantitative way of predicting the outcome of these types of reactions.

Theory

The main driving force for the reaction of NH_3 with oxides is the production of water and to a lesser extent the free energies of formation of the binary or ternary phases. The general ammonolysis reaction can be written as:

$$MO_x + 2/3x\ NH_3 \longrightarrow MN_y + xH_2O + (x/3 - y/2)\ N_2 \qquad (1)$$

Because nitrides frequently contain the metals in a lower formal oxidation state than oxides, this reaction admits the possibility of reduction of M, and thus the production of nitrogen gas. In order to better predict which ternary oxides might be suitable precursors for ternary nitrides, thermodynamic data for the reactions of binary oxides with ammonia gas are a guide. Figure 1 depicts the free energy

Fig 1

cycle that can be used to predict which ammonolysis reactions are plausible. If $\Delta G_f^b(O)$ and $\Delta G_f^b(N)$ (defined in fig. 1) are similar, then ΔG_T and ΔG_B (defined in fig. 1) will be nearly equal and one can "predict" which ternaries will form by ammonolysis of oxides based on thermodynamic data for the binary oxides alone. Published thermodynamic data allow the calculation of $\Delta G_f^b(O)$ and ΔG_B.[30,31] However, essentially no data exist for $\Delta G_f^b(N)$. Since transition metal oxides exist for a variety of oxidation states, $\Delta G_f^b(O)$ can generally be constructed from reactions in which the oxygen content is fixed by the binary

composition. This is not the case for nitrides, so $\Delta G_f^b(N)$ may include a redox reaction when nitrogen or ammonia is present.

The reactions of binary oxides to form ternaries may be split into two groups, those with "small" $\Delta G_f^b(O)$ (< 40 kJ/mol) and "large" $\Delta G_f^b(O)$ (> 40 kJ/mol) in magnitude. The formation of $FeWO_4$ from the binary oxides (eq. 2) is a representative of small $\Delta G_f^b(O)$.

$$FeO + WO_3 \longrightarrow FeWO_4 \qquad (2)$$

$\Delta G_f^b(O)$ is -37.2 kJ/mol compared to the standard free energy of formation from the elements (ΔG_f°) of -1054 kJ/mol.

$\Delta G_f^b(O)$ is large when the reactants have a high degree of acid/base character. For example, $\Delta G_f^b(O)$ for Li_2MoO_4 (eq. 3) and Na_2WO_4 (eq. 4) are relatively large (-180.0 and -290.0 kJ/mol, respectively)

$$Li_2O \text{ (base)} + MoO_3 \text{ (acid)} \longrightarrow Li_2MoO_4 \qquad (3)$$

$$Na_2O \text{ (base)} + WO_3 \text{ (acid)} \rightarrow Na_2WO_4 \qquad (4)$$

when compared to their standard free energies of formation from the elements (-1410 and -1435 kJ/mol, respectively), or to $\Delta G_f^b(O)$ for $FeWO_4$. It is expected that similar considerations of acid/base character influence $\Delta G_f^b(N)$. However,

no data exist that allow comparison of the magnitude of this effect in nitrides with that in oxides. It is even more difficult to estimate the effect of redox reactions on $\Delta G_f^b(N)$, except that a large contribution is expected from the entropy of the nitrogen or ammonia gas that is consumed or evolved. In any case, if we start with the assumption that $\Delta G_f^b(O)$ and $\Delta G_f^b(N)$ are similar, then we can "predict" which ΔG_T are favorable for the synthesis of nitrides by the ammonolysis of oxides. As thermodynamic data for ternary nitrides become available, the validity of this assumption can be examined.

Thermodynamic data for most binary oxides and nitrides at 298 K are readily found in the literature.[30,31] However, the same cannot be said for elevated temperatures (~1000 K) where the reactions of interest take place. These high temperature data can be estimated from simple thermodynamic relationships, starting with:

$$dG = VdP - SdT \tag{5}$$

where G is the Gibbs free energy. At constant pressure:

$$dG = -SdT \tag{6}$$

Consider reactions of the type:

$$\text{metal(s)} + nO_2(g) \text{ or } nN_2(g) \longrightarrow \text{metal oxide(s) or nitride(s)} \tag{7}$$

The entropy change is:

$$\Delta S_{rxn} = S_{prod} - S_{react} \qquad (8)$$

Since the entropy of a gas is higher than that of solids and the entropy of the product and reactant solids partly cancel, we approximate $(d\Delta S_{rxn}/dT)_{solids} \sim 0$. The entropy of most gases increase only slightly, ~20%, between 298 and 1000 K (see data for N_2 and O_2 in Table I), then

$$\Delta S_{rxn} \approx -nS_{gas} \qquad (9)$$

where S_{gas} is the average molar entropy of the reactant gas between 298 K and the temperature of interest. Hence, equation 6 reduces to:

$$\Delta G_{rxn}(T) - \Delta G°_{rxn}(298\ K) = n\Delta TS_{gas} \qquad (10)$$

In this approximation, the difference in free energy of these reactions in the standard state (298 K) and a higher temperature (T) is due entirely to the entropy of the gas. The calculated changes obtained from equation 10 are usually within 5 - 10% of that experimentally found (when the data is available) indicating that the assumptions are reasonable.

Tables I and II list experimentally determined thermodynamic data for some selected liquids, gases and solids of interest.

Tables I & II

Once the high temperature thermodynamic values for the oxide and nitride binaries are known or estimated, then general ammonolysis reactions (eq. 1) can be considered. Table III lists these reactions along with their

Table III

calculated free energy changes. It is apparent that many binary oxides are suitable precursors for binary nitrides except those of the electropositive metals: the alkali, alkaline earth, and rare earth metals, as well as Zr, Hf and La.

Equation 10 was derived on the basis of a system at constant pressure (strictly, constant fugacity of 1); in the ammonolysis reactions the ammonia (or nitrogen and hydrogen) are assumed to be at constant pressure, 1 atm. However, the water being produced in the usual experimental apparatus is swept away by flowing ammonia gas and thus is at a fugacity well below 1 atm; this leads to a further modification of equation 10.

$$\mu H_2O = \mu^\circ H_2O + RT \ln(fH_2O/f^\circ H_2O) \qquad (11)$$

Assuming ideal gas behavior, the free energy of reaction is further lowered an amount:

$$\delta(\Delta Grxn(T)) = RT \ln(PH_2O) \qquad (12)$$

where PH_2O is the partial pressure of the water produced. Unfortunately, measuring the pressure of the evolved water in such a flow reaction is difficult.

A lower limit to the water pressure is determined by the water in the ammonia source or from "outside" sources (quartz tube, O-ring seals etc.). The water content in the ammonia according to suppliers (Matheson 99.99% purity) is ~10 ppm. If the ammonia is dried with sodium and leaks in the system are small, an estimate of 10^{-6} atm for the water vapor pressure is reasonable.[32] The last column in Table III lists the pressure of water needed to decrease a positive $\Delta G_{rxn}(T)$ to zero, as calculated from equation 12. We assume that if this calculated pressure is less than 10^{-6} atm, the reaction with NH_3 will not proceed. These estimates do not address any kinetic issues and therefore, experiments need to be performed to assess if useful rates of reaction occur at the reaction temperature of interest. A representative example of this water pressure effect is the ammonolysis of TiO_2. At 1000 K the $\Delta G_{rxn}(T)$ for the ammonolysis of TiO_2 is +24.06 kJ/mol (table III). The water pressure required to make $\Delta G_{rxn}(T) = 0$ is 0.235 atm, easily obtainable in the reaction system we use. Indeed, TiN can be synthesized from the ammonolysis of TiO_2 at 973 K in 12 h when particle sizes are small enough that kinetic factors do not significantly reduce the reaction rate.[33,34]

Table III shows that oxides of the electropositive metals, sodium and potassium, are potential candidates to form amides (their nitrides are unknown). However, in these cases there is a competing reaction, the formation of hydroxides, which is more thermodynamically favorable unless the water pressure is quite low, as shown in table IV. Again kinetic considerations are not included here.

Table IV

Chloride and Sulfide Precursors

Although oxides are the largest class of extended structure precursors that can be used to form ternary or higher nitrides, other solid state compounds can also be considered. These include halides, chalcogenides or pnictides. Reaction with NH_3 would produce the desired nitride and the appropriate hydrogen containing gas, such as HCl for chlorides or H_2S for sulfides. However, a thermodynamic analysis similar to the one presented for oxides leads to similar conclusions; that is, if electropositive metals are present, ternary nitrides will not form. Instead, no reaction, or separate phases containing different anions, or a mixed anion phase results. For example, we reacted $LiVS_2$ with NH_3 gas at 973 K and found the binary products Li_2S and VN by X-ray powder diffraction. Hydrogen sulfide is significantly less thermodynamically stable at a 1000 K (-50 kJ/mol) than water (table I), hence the driving force for the sulfide reactions is much less. Table V shows some thermodynamic data for reactions of chlorides

Table V

with NH_3. Comparison with table III again shows that there is no thermodynamic advantage expected in the formation of nitrides from chloride precursors relative to oxide precursors. However, it is possible that there may be kinetic advantages.

In summary, the general expectation is that binary oxides may be used as precursors in the formation of binary nitrides by reaction with ammonia, if the cations are not too electropositive (ΔG_B not too positive). If alkaline, alkaline

earth, rare earth, or group IV metals are present, it is unlikely that pure binary nitrides will be formed. These conclusions are strictly valid when $\Delta G_f^b(O) = \Delta G_f^b(N)$. If $\Delta G_f^b(N) < \Delta G_f^b(O)$, then ternary nitrides will result even if ΔG_B is moderately positive. On the other hand, if $\Delta G_f^b(N) > \Delta G_f^b(O)$, fewer ternary nitrides will result than initially predicted. When formation of a ternary nitride does not occur, one expects either no reaction, disproportionation into binary oxide and binary nitride or an oxynitride product. Examples of the latter include: $BaTaO_2N$,[35] Na_3WO_3N,[36] $LnTaON_2$ (where Ln = lanthanide),[37] and $LaWO_{0.6}N_{2.4}$.[38] In general, we do not expect ΔG_T to be very large.

Since there is no reliable method to predict the composition or structure of new phases, let alone their free energies of formation, only statements of probability of ternary nitride formation in a particular reaction scheme is possible. Once a particular ternary nitride is known to exist, the formation of that phase from suitable oxide precursors, or indeed from any potential precursor, can be experimentally addressed.

Reaction Calorimetry at High Temperature to Measure Enthalpies of Formation of Ternary Nitrides

$LiMoN_2$ is synthesized by the ammonolysis of Li_2MoO_4 at 973 K. Na_3WN_3 is synthesized from W_2N in a sodium amide flux under flowing ammonia gas or in an ammonothermal bomb reaction.[8,9] The oxynitrides, Na_3MO_3N (M = Mo and W), are prepared from the ammonolysis of $1/2Na_2O{\cdot}Na_2MO_4$.[35] In this section we examine the thermodynamic properties of three compounds, as a

beginning in the experimental exploration of the stability of ternary nitrides relative to the respective elements, binary nitrides and ternary oxides.

Thermochemical Measurements

We have developed techniques to measure enthalpies of formation of oxidation resistant ternary nitrides ($LiMoN_2$)[1] and air sensitive ternary nitrides (Na_3WN_3)[8,9] and oxynitrides (Na_3WO_3N).[36] These data will lend a better understanding of why $LiMoN_2$ is formed from the ammonolysis of Li_2MoO_4, even though our previous considerations do not predict this reaction to be likely (see ammonolysis reaction data in table III).

The general goal of these experiments was to find a chemical reaction involving the ternary nitride or oxynitride with oxygen gas, occurring rapidly (not more than an hour) at 973 - 1273 K in a high temperature calorimeter, which leads to well defined products. Then a thermochemical cycle linking that reaction, the enthalpy of which is measured, to other known enthalpies allows the calculation of the standard enthalpy of formation for the ternary nitride or oxynitride.

As far as we know, these experiments represent the first calorimetric studies of heats of formation of ternary nitrides. Although the general operation and calibration of high temperature calorimeters are well established,[27] the approach of utilizing oxidation reactions of nitrides is new. The success or failure of such experiments, and their achievable accuracy, depends critically on establishing well defined chemical reactions for use in the thermochemical

cycles. The procedure and data reported here represents our first reasonably successful experiments, but we expect that further refinements will improve accuracy and make these methods more general.

Thermochemical measurements were made using a high temperature Tian-Calvet type twin microcalorimeter operating at 977 K.[27] Transposed temperature drop calorimetry was employed for the thermochemical study of the oxidation reactions. This means the sample was dropped from room temperature into the hot calorimeter, where it underwent reaction. Oxygen gas was flushed through the system at ~145 mL/hr to provide a driving force for oxidation and to remove nitrogen gas produced during oxidation in the calorimeter(note: oxygen consumed in the oxidation reaction is ~ 10 mL, depending on sample size). Before the start of the experiment, the calorimeter was allowed to reach thermal equilibrium until a stable signal (baseline) from the thermopiles was obtained.

The calorimeter was calibrated by the standard platinum drop method. Small pieces of platinum of known weight and heat content were dropped into the calorimeter from room temperature to obtain a calibration factor relating the peak area to the enthalpy.

To measure enthalpy effects in the calorimeter with the highest possible accuracy, the following conditions must be met. 1) The oxidation of nitride or oxynitride must be complete on the time scale of the calorimetric experiment, 30-60 min. 2) The oxidation product must be either a well crystallized phase

assemblage (with no complication from polymorphism) or a homogeneous liquid. 3) The reaction must not be so violent as to splatter sample above the platinum and silica crucible. 4) Any gases produced must be expelled from the calorimeter in the flowing gas stream.

$LiMoN_2$

The previously described conditions were met by oxidizing this material to a molten mixture of Li_2O and MoO_3 by the reaction

$$LiMoN_2\ (s, 298\ K) + 7/4O_2\ (977\ K) \longrightarrow (1/2Li_2O + MoO_3)\ (l, 977\ K) + N_2\ (977\ K) \qquad (13)$$

Before performing measurements in the calorimeter, we first determined the conditions under which $LiMoN_2$ was most readily oxidized. A first set of experiments was performed in a simple tube furnace at 973 K under flowing oxygen gas. To our surprise, we found that bulk amounts (~0.25 g or more) of $LiMoN_2$ were not completely oxidized under these conditions after ~1/2 hr. Partial oxidation did occur during these reactions because some clear, colorless liquid was formed which, when cooled, proved to be Li_2MoO_4 and MoO_3 by X-ray powder diffraction. However, more than ~75% of the sample remained black in color indicating incomplete oxidation. This suggested that the molten lithium molybdate formed produced an oxygen gas diffusion barrier, drastically reducing the oxidation rate. From these findings it seemed that a small amount of liquid may be beneficial in the oxidation reaction by continually removing

formed oxide product, on the other hand too much liquid would form an oxygen diffusion barrier preventing complete oxidation.

A second set of reactions which more closely simulated the actual calorimetry conditions was performed. A small amount (~50 mg) of Li_2MoO_4/MoO_3 was placed into an alumina cup which was then placed into a 973 K box furnace. A small pellet (~20 mg) of $LiMoN_2$ was dropped into the melt and it was allowed to react under these conditions for 1/2 hr. The molten reaction mixture was quenched to room temperature leaving a slightly off white, crystalline solid. The solid was a mixture of Li_2MoO_4 and MoO_3 as shown by X-ray powder diffraction and mass change. Note that the initial and final compositions of the melt are identical. This experiment showed that the enthalpy measured in the calorimeter under similar reaction conditions would indeed correspond to complete oxidation of $LiMoN_2$ to molten $Li_2O{\cdot}2MoO_3$.

Following the initial experiments in the box furnace, calorimetry proceeded as follows. Pellets (3 mm diameter) of $LiMoN_2$ were prepared (ranging in mass from 7-12 mg) and were dropped into the calorimeter that contained no melt. Under these conditions the oxidation process was quite slow, as indicated by heat being evolved for times greater than 90 min. A second type of experiment was performed in which a pellet (~ 10 mg) consisting of $Li_2MoO_4 + MoO_3$ (equivalent to $Li_2O{:}2MoO_3$ and having the same metals ratio as in $LiMoN_2$) was first dropped into the calorimeter. The liquid present was expected to enhance the oxidation reaction (eq. 13). The oxide mixture was allowed to melt at 977 K (eutectic mp - 803 K)[39] and the calorimeter equilibrated before a pellet of

$LiMoN_2$ was dropped. The $LiMoN_2$ pellet was dropped and produced a relatively rapid oxidation reaction that was complete in ~60 min, when the system had again returned to equilibrium. A second $LiMoN_2$ pellet of similar mass was dropped into the calorimeter yielding results similar to the first $LiMoN_2$ drop. However, when a third $LiMoN_2$ pellet was dropped the reaction was once again slow (> 90 min) and the measured enthalpy was not consistent with the first two $LiMoN_2$ drops. These findings supported our initial idea that a small amount of liquid would promote the oxidation reaction, whereas, after several pellets had been dropped (each producing $1/2Li_2O + MoO_3$) enough melt was present to cover any pellets dropped thereafter, thus slowing the oxidation. We concluded from further drop experiments that a maximum of three drops, one $Li_2MoO_4 + MoO_3$ and two $LiMoN_2$ pellets, could be made to give reliable and reproducible heat of oxidation data.

In order to complete the thermochemical cycle and to calculate the $\Delta H_f°$ for $LiMoN_2$ (see cycle below), the heat content and heat of melting of $Li_2MoO_4 + MoO_3$ was measured when pellets (7-10 mg) of $Li_2MoO_4 + MoO_3$ were dropped in the same calorimetric system to determine the enthalpy for that process (eq. 14). These drops were made after the two $LiMoN_2$ pellet drops, resulting in consistent and reproducible heat of reaction data.

$$(Li_2MoO_4 + MoO_3)\ (s, 298\ K) \longrightarrow (Li_2O + 2MoO_3)\ (l, 977\ K) \qquad (14)$$

<u>Thermochemical cycle to determine $\Delta H_f°$ for $LiMoN_2$.</u>

1) $LiMoN_2$ (s, 298 K) + $7/4O_2$ (g, 977 K) $\longrightarrow$ ($1/2Li_2O$+ MoO_3) (*l*, 977 K) + N_2 (g, 977 K) $\Delta H_{ox\,1}$

2) (Li_2O + $2MoO_3$) (*l*, 977 K) $\longrightarrow$ Li_2MoO_4 (s, 298 K) + MoO_3 (s, 298 K) $-\Delta H_{1.2}$

3) O_2 (g, 298 K) $\longrightarrow$ O_2 (g, 977 K) $\Delta H_{1.3}$

4) N_2 (g, 977 K) $\longrightarrow$ N_2 (g, 298 K) $\Delta H_{1.4}$

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5) $LiMoN_2$ (298 K) + $7/4O_2$ (298 K) $\longrightarrow$ $1/2Li_2MoO_4$ (298 K) + $1/2MoO_3$ (298 K) + N_2 (298 K) $\Delta H_{1.5}$

$$\Delta H_{1.5} = \Delta H_{ox\,1} - 1/2\Delta H_{1.2} + 7/4\Delta H_{1.3} + \Delta H_{1.4}$$

(we used $\Delta H_{1.3}$ = 21.907 kJ/mol O_2 and $\Delta H_{1.4}$ = -20.718 kJ/mol N_2 in our calculation)[30]

$$\Delta H_{1.5} = [1/2\Delta H_f°(Li_2MoO_4) + 1/2\Delta H_f°(MoO_3) + \Delta H_f°(N_2)] - [\Delta H_f°(LiMoN_2) + 7/4\Delta H_f°(O_2)]$$

(we used $\Delta H_f°(Li_2MoO_4)$ = -1520.30 kJ/mol, $\Delta H_f°(MoO_3)$ = -745.09 kJ/mol and $\Delta H_f°(O_2) = \Delta H_f°(N_2) = 0$ at standard state in our calculation)[31]

Na_3WO_3N and Na_3WN_3

Both Na_3WO_3N and Na_3WN_3 are quite air sensitive and are sodium rich. This required modifications in the techniques to measure the heat of oxidation. The following reactions can be expected:

$$Na_3WO_3N\ (s, 298\ K) + 3/4O_2\ (g, 977\ K) \rightarrow (3/2Na_2O + WO_3)\ (l, 977\ K) + 1/2N_2\ (g, 977\ K) \quad (15)$$

$$Na_3WN_3\ (s, 298\ K) + 9/4O_2\ (g, 977\ K) \rightarrow (3/2Na_2O + WO_3)\ (l, 977\ K) + 3/2N_2\ (g, 977\ K) \quad (16)$$

The resulting oxidation products would be sodium oxide rich relative to the ternary oxide Na_2WO_4, hence "free" sodium oxide would be present and the melts could be corrosive and quite reactive with atmospheric water and carbon dioxide. In addition, the excess sodium oxide can react with the platinum crucible in which the oxidation reaction takes place. Therefore, WO_3 was mixed with Na_3WO_3N and Na_3WN_3 in a mortar (in an argon filled glove box) in a ratio of 5/4 WO_3:1 Na_3WO_3N and 5/4 WO_3:1 Na_3WN_3. The expected oxidation products that would result from this mixture are

$$Na_3WO_3N\ (298\ K) + 5/4WO_3\ (298\ K) + 3/4O_2\ (977\ K) \rightarrow (3/2Na_2O + 9/4WO_3)\ (l, 977\ K) + 1/2N_2\ (977\ K) \quad (17)$$

$$Na_3WN_3\ (298\ K) + 5/4WO_3\ (298\ K) + 9/4O_2\ (977\ K) \rightarrow (3/2Na_2O + 9/4WO_3)\ (l, 977\ K) + 3/2N_2\ (977\ K) \quad (18)$$

This keeps the sodium to tungsten ratio less than 2 to 1 so that no attack of the platinum crucible is expected (or observed). Another advantage of adding WO_3 to the system is the low melting point of the resulting oxide mixture (~943 K),[39] which may help the kinetics of the oxidation reaction, as for $LiMoN_2$. Also, at this Na_2O:WO_3 ratio the system is "buffered" enthalpically.[40] In other words, the enthalpy of solution changes very little with slight changes in the mole fraction of WO_3, reducing measurement inconsistencies when slight variations in stoichiometry are present.

As mentioned before, both Na_3WO_3N and Na_3WN_3 are very air sensitive. Typical pellet drop experiments require an air exposure of the sample for ~5 s, too long for either of these compounds. We were able circumvent this problem by sealing the samples (~ 20-30 mg) in thin-walled silica glass capsules (approximately 3.5 mm diameter and 13 mm long) under vacuum. When capsules containing $Na_3WN_3 + 5/4WO_3$ were dropped into the 977 K calorimeter, they exploded after about 5 s, but the capsules containing $Na_3WO_3N + 5/4WO_3$ exploded only some of the time. When these latter capsules did not explode, the silica glass drop tube was lowered to smash them. We believe nitrogen gas is generated by decomposition of the nitride or oxynitride at 977 K. The nitride produces more nitrogen gas than the oxynitride leading to the more violent explosion of the capsules containing the former. Once the capsule is open, the oxidation proceeds rapidly. To optimize calorimetric conditions the following improvements in technique were made. A machined alumina ceramic plug was pressed on top of the platinum crucible to

prevent material from splattering out due to the explosion. For future experiments, the mass ratio of sample to capsule should be adjusted to ensure spontaneous, but not too violent, capsule breakage.

Na_3WO_3N:5/4WO_3 and Na_3WN_3:5/4WO_3 were heated under a flow of oxygen gas at 973 K for ~30 min in a tube furnace to verify that under these conditions both compounds are fully oxidized. X-ray powder diffraction and mass change confirmed that full oxidation was achieved.

Once again, to calculate ΔH_f° for Na_3WO_3N and Na_3WN_3, the heat content of the resulting oxide products had to be determined. An oxide mixture with the stoichiometry 3/2 Na_2O:9/4 WO_3 was prepared by reacting 3/2 Na_2CO_3:9/4 WO_3 at 973 K. This reaction mixture melted after ~ 15 min and it was kept at this temperature until no more CO_2 evolved. The resulting powder consisted of Na_2WO_4 and WO_3 as identified by X-ray powder diffraction. The powder was placed in an open silica glass capsule (approximately the same dimensions used before) and dropped into the calorimeter. The enthalpy for this drop (eq. 19), along with that for an empty silica glass capsule drop (eq. 20) are used in the calculation of the standard enthalpy of formation of Na_3WO_3N and Na_3WN_3 from a thermochemical cycle (see cycle below).

$$3/2Na_2WO_4\ (s, 298\ K) + 3/4WO_3\ (s, 298\ K) \longrightarrow (3/2Na_2O + 9/4WO_3)\ (l, 977\ K) \qquad (19)$$

$$\text{Silica Glass (298 K)} \longrightarrow \text{Silica Glass (977 K)} \qquad (20)$$

Thermochemical cycle used in the calculation of the $\Delta H_f°$ for Na_3WO_3N (an analogous cycle was used for Na_3WN_3).

1) Na_3WO_3N (s, 298 K) + $5/4WO_3$ (s, 298 K) + $3/4O_2$ (g, 977 K) $\rightarrow$ ($3/2Na_2O$ + $9/4WO_3$) (*l*, 977 K) + $1/2N_2$ (g, 977 K) $\Delta H_{ox\,2}$

2) ($3/2Na_2O$ + $9/4WO_3$) (*l*, 977 K) $\rightarrow$ $3/2Na_2WO_4$ (s, 298 K) + $3/4WO_3$ (s, 298 K) $-\Delta H_{2.2}$

3) O_2 (298 K) $\rightarrow$ O_2 (977 K) $\Delta H_{2.3}$

4) N_2 (977 K) $\rightarrow$ N_2 (298 K) $\Delta H_{2.4}$

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5) Na_3WO_3N (298 K) + $5/4WO_3$ (298 K) + $3/4O_2$ (298 K) $\rightarrow$ $3/2Na_2WO_4$ (298 K) + $3/4WO_3$ (298 K) + $1/2N_2$ (298 K) $\Delta H_{2.5}$

$$\Delta H_{2.5} = \Delta H_{ox\,2} - \Delta H_{2.2} + 3/4\Delta H_{2.3} + 1/2\Delta H_{2.4}$$

$$\Delta H_{2.5} = [3/2\Delta H_f°(Na_2WO_4) + 3/4\Delta H_f°(WO_3) + 1/2\Delta H_f°(N_2)] - [\Delta H_f°(Na_3WO_3N) + 5/4\Delta H_f°(WO_3) + 3/4\Delta H_f°(O_2)]$$

(we used $\Delta H_f°(Na_2WO_4)$ = -1548.9 kJ/mol and $\Delta H_f°(WO_3)$ = -842.87 kJ/mol in our calculation)[31]

Ta_3N_5

We have attempted to determine the conditions in which the thermochemical properties of Ta_3N_5 may be measured. This has proved to be very challenging. Ta_3N_5 is one of the few binary transition metal nitrides for which no thermochemical data is reported in the literature. Preliminary oxidation reactions of Ta_3N_5 at temperatures as high as 1773 K in flowing oxygen gas for more than an hour results in incomplete oxidation. The resulting off-white powder has the Ta_2O_5 structure by X-ray powder diffraction, as expected (eq. 21), but the mass gain after the oxidation is about 14% less than expected, indicating incomplete oxidation.

$$2Ta_3N_5 + 15/2O_2 \longrightarrow 3Ta_2O_5 + 5N_2 \qquad (21)$$

We will continue to examine this system to determine appropriate conditions for complete oxidation of Ta_3N_5. Perhaps a suitable solvent can be used to speed the oxidation process.

Results and Discussion

$LiMoN_2$

Seven $LiMoN_2$ pellet drops were used in calculating the heat of oxidation ($\Delta H_{ox\,1}$) for the reaction shown in eq. 13. Five $Li_2MoO_4 + MoO_3$ pellets were dropped to determine the enthalpy of the reaction in eq. 14 ($\Delta H_{1.2}$). These experimentally determined values along with literature data for nitrogen and

oxygen gas, were used in the thermochemical cycle to calculate the standard heat of formation of $LiMoN_2$: These data are shown in table VI.

Table VI

The stability of $LiMoN_2$ becomes evident when the standard enthalpy of formation from the binaries (ΔH_f^b) of $LiMoN_2$ (-224.0 kJ/mol, eq. 22) is

$$1/2Mo_2N + 1/3\ Li_3N + 7/12N_2 \longrightarrow LiMoN_2 \qquad (22)$$

compared to that of Li_2MoO_4 (-180.0 kJ/mol). If the $\Delta H_f^b(N)/\Delta H_f^\circ$ for $LiMoN_2$ was approximately equal to $\Delta H_f^b(O)/\Delta H_f^\circ$ for Li_2MoO_4, the predicted $\Delta H_f^b(N)$ of $LiMoN_2$ would be about -46 kJ/mol. There must be other contributing factors that influence the stability of $LiMoN_2$ relative to the binary nitrides. One obvious difference is that the formation of $LiMoN_2$ involves oxidation of the molybdenum. At this point, we are unable to quantify this effect, but a possible method for approximating this oxidation/reduction contribution would be to measure the enthalpy of reaction between Li_2O and MoO_2 (eq. 23) and compare this to the reaction between Li_2O and MoO_3 to synthesize Li_2MoO_4.

$$Li_2O + MoO_2 + 1/2O_2 \rightarrow Li_2MoO_4 \qquad (23)$$

The ΔH_f° for Li_2MoO_4 is -1520.3 kJ/mol which is almost four times as negative as that for $LiMoN_2$. This alone makes it seem unlikely to that $LiMoN_2$ could be synthesized by the ammonolysis of Li_2MoO_4. If we assume $\Delta G_f^\circ/\Delta H_f^\circ$ is about the same for $LiMoN_2$ and Li_2MoO_4 (so $\Delta G_f^\circ(LiMoN_2)$ can be estimated), then the free energy for the ammonolysis reaction (eq. 24) can be

approximated ($\Delta G_f°(LiMoN_2) \approx -358$ kJ/mol, $\Delta G_f°(Li_2MoO_4) = -1409.6$ kJ/mol). The main driving force for this reaction is

$$Li_2MoO_4 + 7/3NH_3 \longrightarrow LiMoN_2 + 1/2Li_2O + 1/6N_2 + \mathbf{7/2H_2O} \qquad (24)$$

$$\Delta G_{rxn}°(RT) = -21 \text{ kJ/mol } LiMoN_2$$

the production of water (-237.2 kJ/mol). The reaction is further driven to the right by sweeping the product gases away with the flowing ammonia gas. At 1000 K, the ammonolysis reaction temperature, $\Delta G_{rxn}(T)$ should be less than -21 kJ/mol if it is assumed that the change in free energy with increased temperature is a result of the entropy of the gaseous species only. This also argues for a decrease in $\Delta G_{rxn}°(1000\text{ K})$ (ΔG_{rxn} becomes even more negative), since there are 7/3 moles of gaseous reactants, but 11/3 moles of gaseous products.

Na_3WO_3N and Na_3WN_3

Seven sealed silica glass capsules containing $Na_3WO_3N + 5/4WO_3$ were dropped to determine the heat of oxidation ($\Delta H_{ox\,2}$) for the reaction in eq. 17. Seven empty silica glass capsules were dropped so this heat content could be subtracted from $\Delta H_{ox\,2}$ to obtain an enthalpy value for the oxidation reaction only. The value for the silica glass was determined to be 38.61 ± 0.4 kJ/mol. Six open silica glass capsules containing $3/2Na_2O + 9/4WO_3$ were dropped to calculate the enthalpy associated with the heating and melting of the oxide mixture ($\Delta H_{2.2}$, eq. 19). These values, along with literature data for nitrogen

and oxygen gas, were used in the thermochemical cycle to calculate the standard heat of formation for Na_3WO_3N (an analogous thermochemical cycle was constructed for Na_3WN_3). The data for Na_3WO_3N and Na_3WN_3 are shown in table VII.

Table VII

The large magnitude of $\Delta H_f^\circ(Na_3WO_3N)$ (-1358.8 kJ/mol) is not surprising since the compound is more chemically similar to Na_2WO_4 than Na_3WN_3 (i.e. it is primarily an oxide). The $\Delta H_f^b(N)$ for Na_3WO_3N cannot be calculated since Na_3N has not been synthesized and the product is an oxynitride. The feasibility of the ammonolysis of $1/2Na_2O + Na_2WO_4$ can be addressed if again we assume that $\Delta G_f^\circ/\Delta H_f^\circ$ for Na_3WO_3N and Na_2WO_4 are equal ($\Delta G_f^\circ(Na_3WO_3N) \approx -1258$ kJ/mol and $\Delta G_f^\circ(Na_2WO_4) = -1434.53$ kJ/mol, eq. 25). Even though the $\Delta G_{rxn}(RT)$ is positive, the water pressure required

$$1/2Na_2O + Na_2WO_4 + NH_3 \longrightarrow Na_3WO_3N + 3/2H_2O \qquad (25)$$

$$\Delta G_{rxn}(RT) \approx +27 \text{ kJ/mol } Na_3WO_3N$$

to make $\Delta G_{rxn}(RT) = 0$ is 7×10^{-4} atm (see eq. 12). Since P_{H_2O} is estimated to be considerably less in our reaction apparatus, the reaction should proceed. As the temperature increases, so will the entropy change in the ammonolysis reaction (eq. 25). This will cause $\Delta G_{rxn}(RT)$ to decrease and the water pressure at which $\Delta G_{rxn}(RT) = 0$ will increase, making this reaction even more likely at the reaction temperature (1000 K).

The ΔH_f° for Na_3WN_3 is much less negative than the ΔH_f° for Na_3WO_3N, as expected (table VII). Only a 'pseudo' ΔH_f^b can be calculated (eq. 26) for

$$1/2W_2N + 3NaNH_2 \rightarrow Na_3WN_3 + 3H_2 + 1/4N_2 \qquad (26)$$

$$\Delta H_f^b = -238.1 \text{ kJ/mol } Na_3WN_3$$

Na_3WN_3, since Na_3N has not been synthesized. The $\Delta H_f^b(N)$ from eq. 26 does however, lend some insight on the stability of Na_3WN_3 relative to Na_2WO_4. As for $LiMoN_2$, $\Delta H_f^b(N)$ for Na_3WN_3 is relatively large in magnitude compared to that for the analogous ternary oxide ($\Delta H_f^b(Na_2WO_4)$ = -290 kJ/mol). For the case of Na_3WN_3, where tungsten is fully oxidized, the large $\Delta H_f^b(N)$ may indicate the importance of acid/base interactions as previously discussed for ternary oxide formation from binary oxides.

The thermodynamic properties of Na_3WO_3N and Na_3WN_3 were measured to understand why the pure nitride, Na_3WN_3, cannot be synthesized from the ammonolysis of $1/2Na_2O + Na_2WO_4$ (eq. 27). If we consider the

$$1/2Na_2O + Na_2WO_4 + 3NH_3 \longrightarrow Na_3WN_3 + 9/2H_2O \qquad (27)$$

$$\Delta G_{rxn}(RT) \approx +204 \text{ kJ/mol } Na_3WN_3$$

hypothetical ammonolysis reaction of this oxide mixture to synthesize Na_3WN_3, it becomes obvious why only Na_3WO_3N is formed (compare free energies of reaction in eq. 25 and eq. 27)

Conclusion

The results of our calorimetric measurements support our initial predictions concerning the ammonolysis of ternary oxides to synthesize ternary nitrides. That is, if $\Delta G_f^b(O) \geq \Delta G_f^b(N)$ and ΔG_B is not too positive, then ternary nitrides may result from the ammonolysis of ternary oxides. This is likely the case for $LiMoN_2$. If $\Delta G_f^b(O) \leq \Delta G_f^b(N)$ and/or ΔG_B is quite positive, oxynitrides or mixed binary oxides/nitrides will likely result. This is in agreement with what is observed when considering the ammonolysis of $1/2Na_2O{:}Na_2WO_4$ produces Na_3WO_3N instead of Na_3WN_3. Determining what ternary nitrides may be synthesized from the ammonolysis of ternary oxides will become more evident as thermodynamic data becomes available for ternary nitrides. It is interesting and surprising that $\Delta H_f^b/\Delta H_f^\circ$ for $LiMoN_2$ and Na_3WN_3 are much greater than those of the respective ternary oxides, indicating the stability of the ternary nitrides relative to their respective binary nitrides. Changes in oxidation state of the metal, as in the synthesis of $LiMoN_2$ from Li_2MoO_4, may play an important role in the stability of $LiMoN_2$.

We have not addressed the ammonolysis reactions of ternary oxides with "small" $\Delta G_f^b(O)$. The ammonolysis of this class of ternary oxides has only recently received attention[26,41] and will likely lead to new ternary nitrides in

which the thermochemical properties can be measured and compared to those with "large" $\Delta G_f^{\circ}(O)$. Thermodynamic measurements of this class of oxides/nitrides will be the subject of future work.

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Table I. Thermodynamic data for some selected gases of interest.

Element/Compound	T (K)	ΔH_f° (kJ/mol)	S°(J/K mol)	ΔG°(kJ/mol)
N_2	298	0.0	192	0.0
	1000	0.0	228	0.0
O_2	298	0.0	205	0.0
	1000	0.0	244	0.0
H_2O	298	-285.8	69.9	-237.2
	1000	-247.7	233	-192.5
NH_3	298	-46.0	193	-16.4
	1000	-54.8	246	61.9
H_2	298	0.0	131	0.0
	1000	0.0	166	0.0
HCl	298	-92.5	187	-95.4
	1000	-94.6	223	-100.8
H_2S	298	-20.5	206	-33.3
	1000	-90.0	253	-41.0
Cl_2	298	0.0	223	0.0
	1000	0.0	266.9	0.0

Table II. Standard free energies of formation (kJ/mol) for selected binary oxides and nitrides at room temperature.

Oxides		Nitrides	
Compound	ΔG_f°	Compound	ΔG_f°
Li_2O	-560.7	Li_3N	-154.8
Na_2O	-379.5	$NaNH_2$[a]	-64.0
K_2O	-325.1	KNH_2[a]	-66.9
MgO	-569.0	Mg_3N_2	-401.2
CaO	-602.5	Ca_3N_2	-410.0
SrO	-560.6	Sr_3N_2	-322.2
BaO	-518.8	Ba_3N_2	-305.4
La_2O_3	-1707	LaN	-270.3
Al_2O_3	-1573	AlN	-287.0
TiO_2	-891.2	TiN	-309.2
ZrO_2	-1042	ZrN	-336.8
V_2O_5	-1423	VN	-191.2
Nb_2O_5	-1766	NbN	-213.4
Ta_2O_5	-1920	Ta_3N_5	-1151[b]
CrO_3	-506.3	CrN	-92.0
MoO_3	-669.4	Mo_2N	-50.2
WO_3	-756.7	W_2N	-46.0
MnO_2	-464.4	Mn_3N_2	-146.4
Fe_2O_3	-744.8	Fe_2N	+12.6
CoO	-213.8	Co_3N	+8.4[d]
NiO	-211.7	Ni_3N	[c]
CuO	-128.4	Cu_3N	+74.5[d]
ZnO_2	-318.4	Zn_3N_2	-20.9

[a]The nitrides are unknown for these metals, hence the amides are reported here.
[b]The free energy of formation for Ta_3N_5 is not known. The value listed was estimated from the free energy of formation of TaN [$(\Delta G_f^\circ (Ta_3N_5) \approx 5\Delta G_f^\circ (TaN)$].
[c]Niether ΔG_f nor ΔH_f known.
[d]Only ΔH_f known.

Table III. Thermodynamic data for the ammonolysis reactions of binary oxides.

Metal	T (K)	ΔG_f (kJ/mol) oxide	nitride	Reaction	ΔG_{rxn} (T) (kJ)	P_{water} (atm) where ΔG_{rxn} (T) $\rightarrow$ 0
Li	298	-561	-155	$3Li_2O + 2NH_3 \rightarrow$	+715	1.58×10^{-42}
	1000	-469	-31.2	$2Li_3N + 3H_2O$	+640	7.16×10^{-12}
Na	298	-379	-64.0[a]	$Na_2O + 2NH_3 \rightarrow$	+25.1	3.98×10^{-5}
	1000	-281	+50.6[b]	$2NaNH_2 + H_2O$	+65.3	3.90×10^{-4}
K	298	-325	-66.9[a]	same as above	-41.8	d
	1000	-225	+36.7[b]		-18.7	d
Mg	298	-569	-401	$3MgO + 2NH_3 \rightarrow$	+649	1.28×10^{-38}
	1000	-494	-257	$Mg_3N_2 + 3H_2O$	+523	7.83×10^{-10}
Ca	298	-144	-410	same as above	+753	9.94×10^{-45}
	1000	-127	-259[b]		+632	1.0×10^{-11}
Sr	298	-561	-322	same as above	+715	1.58×10^{-42}
	1000	-494	-172[b]		+607	3.18×10^{-11}
Ba	298	-519	-305	same as above	+628	2.14×10^{-37}
	1000	-456	-155[b]		+510	1.48×10^{-9}
La	298	-1707	-270	$La_2O_3 + 2NH_3 \rightarrow 2LaN$	+485	4.39×10^{-29}
	1000	-1464	-195	$+ 3H_2O$	+373	3.18×10^{-7}
Al	298	-1573	-287	same as above	+376	1.05×10^{-22}
	1000	-1351	-212		+223	1.31×10^{-4}
Ti	298	-891	-309	$TiO_2 + 4/3NH_3 \rightarrow TiN$	+117	5.40×10^{-11}
	1000	-761	-243	$+ 2H_2O + 1/6N_2$	+24.1	0.235
Zr	298	-1042	-337	same as above	+213	1.99×10^{-19}
	1000	-910	-272		+142	1.98×10^{-4}
V	298	-1423	-191	$V_2O_5 + 10/3NH_3 \rightarrow$	-33.5	d
	1000	-1125	-131	$2VN + 5H_2O + 2/3N_2$	-406	d
Nb	298	-1766	-213	same as above	+192	1.79×10^{-7}
	1000	-1464	-138[b]		-80.8	d

Table III (cont.)

Ta	298	-1920	-1172[c]	$3Ta_2O_5 + 10NH_3 \rightarrow$	-33.5	d
	1000	-1607	-795[b,c]	$2Ta_3N_5 + 15H_2O$	-282	d
Cr	298	-506	-92.9	$CrO_3 + 2NH_3 \rightarrow CrN +$	-251	d
	1000	-267[b]	-39.5[b]	$3H_2O + 1/2N_2$	-548	d
Mo	298	-669	-50.2	$2MoO_3 + 4NH_3 \rightarrow$	-8.4	d
	1000	-494	+25.1[b]	$Mo_2N + 6H_2O + 3/2N_2$	-615	d
W	298	-766	-46.0	same as above	-33.5	d
	1000	-586	+29.3[b]		-427	d
Mn	298	-464	-146	$3MnO_2 + 4NH_3 \rightarrow$	-71.1	d
	1000	-304[b]	+4.2[b]	$Mn_3N_2 + 6H_2O + N_2$	-636	d
Fe	298	-745	+12.6	$Fe_2O_3 + 2NH_3 \rightarrow Fe_2N$	+83.4	1.29×10^{-5}
	1000	-561	+87.9[b]	$+ 3H_2O + 1/2N_2$	-131	d
Zn	298	-318	-20.9	$3ZnO + 2NH_3 \rightarrow$	+255	1.22×10^{-15}
	1000	-238[b]	+130[b]	$Zn_3N_2 + 3H_2O$	+140	3.63×10^{-3}

[a] Calculations done for the formation of the amide not the nitride.
[b] These free energies of formation were calculated using equation 10.
[c] These values were estimated form those given for TaN.
[d] The pressure of water not determined because $\Delta G_f < 0$.

Table IV. Thermodynamic data for the ammonlysis reactions of Li, Na and K oxides and peroxides.

Metal	T (K)	ΔG_f (kJ/mol) peroxide/oxide	hydroxide	Reaction	ΔG_{rxn} (T) (kJ)	P_{water} (atm) where ΔG_{rxn} (T) $\rightarrow 0$
Li	298	-569	-439	$Li_2O_2 + NH_3 \rightarrow 2LiOH$	-296	a
	1000	-418	-304	$+ 1/2N_2 + 1/2H_2$	-418	a
	298			$Li_2O + NH_3 \rightarrow LiOH +$	+50.2	a
	1000			$LiNH_2$	+118	a
	298			$LiOH + NH_3 \rightarrow LiNH_2$	+131	1.11×10^{-23}
	1000			$+ H_2O$	+66.1	3.52×10^{-4}
	298			$Li_2O + 2NH_3 \rightarrow 2LiNH_2$	+181	1.76×10^{-32}
	1000			$+ H_2O$	+185	2.19×10^{-10}
Na	298	-448	-379	$Na_2O_2 + NH_3 \rightarrow$	-295	a
	1000	-298	-278	$2NaOH + 1/2N_2 +$	-448	a
				$1/2H_2$		
	298			$Na_2O + NH_3 \rightarrow NaOH +$	-51.5	a
	1000			$NaNH_2$	-7.1	a
	298			$NaOH + NH_3 \rightarrow$	+105	3.30×10^{-19}
	1000			$NaNH_2 + H_2O$	+70.7	2.03×10^{-4}
	298			$Na_2O + 2NH_3 \rightarrow$	+25.1	3.98×10^{-5}
	1000			$2NaNH_2 + H_2O$	+65.3	3.90×10^{-4}
K	298	-431	-379	$K_2O_2 + NH_3 \rightarrow 2KOH +$	-310	a
	1000	-276	-279	$1/2N_2 + 1/2H_2$	-474	a
	298			$K_2O + NH_3 \rightarrow KOH +$	-107	a
	1000			KNH_2	-80.3	a
	298			$KOH + NH_3 \rightarrow KNH_2 +$	+98.7	4.92×10^{-18}
	1000			H_2O	+60.2	7.13×10^{-4}
	298			$K_2O + 2NH_3 \rightarrow 2KNH_2$	-41.8	a
	1000			$+ H_2O$	-18.7	a

[a] No water is formed in these reactions.

Table V. Thermodynamic data for the ammonolysis of binary chlorides of some selected metals.

Metal	T (K)	ΔG_f (kJ/mol)		Reaction	ΔG_{rxn} (T)	P_{water} (atm) where
		chloride	nitride		(kJ)	ΔG_{rxn} (T) $\rightarrow$ 0
Na	298	-384	-64.0	$NaCl + NH_3 \rightarrow$	+241	5.72 x 10-43
	1000	-319	+50.6	$NaNH_2 + HCl$	+207	1.60 x 10-11
Ca	298	-749	-410	$3CaCl_2 + 2NH_3 \rightarrow$	+1297	1.28 x 10-38
	1000	640	-259	$Ca_3N_2 + 6HCl$	+937	6.93 x 10-9
La	298	-1029	-270	$LaCl_3 + NH_3 \rightarrow LaN +$	+490	2.50 x 10-29
	1000	-770[a]	-195	$3HCl$	+210	2.24 x 10-4
Ti	298	-728	-309	$TiCl_4 + 4/3NH_3 \rightarrow$	+58.2	2.83 x 10-3
	1000	-573	-243	$TiN + 4HCl + 1/6N_2$	-157	[c]
Ta	298	-745	-1172[b]	$3TaCl_5 + 5NH_3 \rightarrow$	-280	[c]
	1000	-315[a]	-795[a,b]	$Ta_3N_5 + 15HCl$	-383	[c]
Mo	298	-423	-50.2	$2MoCl_5 + 10/3NH_3 \rightarrow$	-105	[c]
	1000	-210	+25.1	$Mo_2N + 10HCl +$	-770	[c]
				$7/6N_2$		
Mn	298	-439	-146	$3MnCl_2 + 2NH_3 \rightarrow$	+632	3.49 x 10-19
	1000	-269[a]	+4.2	$Mn_3N_2 + 6HCl$	+81.2	0.197
Fe	298	-334	+12.6	$3FeCl_3 + 2NH_3 \rightarrow$	+473	1.54 x 10-14
	1000	-195	+87.9	$Fe_2N + 6HCl + 1/2N_2$	-251	[c]
Zn	298	-369	-20.9	$3ZnCl_2 + 2NH_3 \rightarrow$	+548	9.73 x 10-17
	1000	-197[a]	+130	$Zn_3N_2 + 6HCl$	-6.7	[c]

[a] These free energies of formation were calculated using equation 10.
[b]These values were estimated from those given for TaN.
[c] Pressure of water not dtermined because $\Delta G_f < 0$.

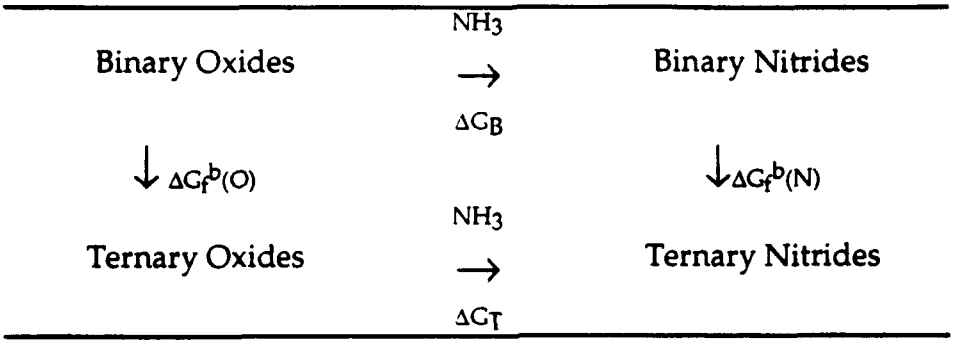
Table VI. Enthalpies of oxidation for $LiMoN_2$ ($\Delta H_{ox\ 1}$, eq. 13) and heat content and enthalpy of melting for $Li_2MoO_4 + MoO_3$ ($\Delta H_{1.2}$, eq. 14). The uncertainties refer $\pm 2\sigma_M$.

$\Delta H_{ox\ 1}$ (kJ/mol $LiMoN_2$)	$\Delta H_{1.2}$ (kJ/[$Li_2MoO_4 + MoO_3$])	$\Delta H_f°(LiMoN_2)$ (kJ/mol)
-628.24	270.77	-386.0 ± 6.4
-628.30	269.75	
-627.98	271.40	
-623.11	274.79	
-642.86	265.96	
-629.38	270.5 ± 2.8	
-623.56		
-629.1 ± 5.0		

Table VII. Enthalpies of oxidation for Na_3WO_3N + 5/4 WO_3 (ΔH_{ox} 2, eq. 17), Na_3WN_3 + 5/4 WO_3 (ΔH_{ox} 3, eq. 18), heat content and enthalpy of melting of 3/2 Na_2WO_4 + 3/4 WO_3 ($\Delta H_{2.2}$, eq. 19) and the standard enthalpy of formation of Na_3WO_3N and Na_3WN_3 (the contribution from the silica glass has been considered in all calculations). The uncertainties refer to ± 2σM.

ΔH_{ox} 2 (kJ/[Na_3WO_3N + 5/4WO_3)	ΔH_{ox} 3 (kJ/[Na_3WN_3 + 5/4WO_3)	$\Delta H_{2.2}$ (kJ/[3/2Na_2WO_4 + 3/4 WO_3])	$\Delta H_f°(Na_3WO_3N)$ (kJ/mol)	$\Delta H_f°(Na_3WN_3)$ (kJ/mol)
-199.50	-1136.72	340.03	-1358.8 ± 18.2	-358.7 ± 53.3
-202.42	-1114.48	334.94		
-213.48	-1186.45	349.74		
-207.31	-1228.66	356.91		
-180.00	-1260.77	332.53		
-224.26	-1272.30	345.40		
-214.70	-1269.97	343.3 ± 7.5		
-206.0 ± 10.7	-1276.33			
	-1218.2 ± 45.8			

Figure 1. A cycle showing the free energy changes to consider for the conversion of binary and ternary oxides to nitrides by ammonolysis.



ΔG_B = free energy of reaction for the ammonolysis of binary oxides.

ΔG_T = free energy of reaction for the ammonolysis of ternary oxides.

$\Delta G_f^b(O)$ = free energy of formation of ternary oxides from the binaries.

$\Delta G_f^b(N)$ = free energy of formation of ternary nitrides from the binaries.