Journal of Alloys and Compounds, 182 (1992) 91–102
JALCOM 107

Thermodynamics of nitride and hydride formation by the reaction of metals with flowing NH_3

Masahiro Katsura
Department of Nuclear Engineering, Faculty of Engineering, Osaka University, 565 Suita Yamada-oka 2-1, Osaka (Japan)

(Received August 12, 1991)

Abstract

The state where the equilibrium dissociation of ammonia, $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$, is not reached can be produced by flowing NH_3. In this case NH_3 must be considered to be in an unstable state. Nitrogen-rich metal nitrides, which cannot be obtained by action of N_2 under normal pressures, can be prepared by use of a stream of NH_3. This suggests that high nitrogen activity may arise from the high instability exhibited by a stream of NH_3.

It may be highly probable that a stream of NH_3 also acts as a hydriding agent with high hydrogen activity.

A thermodynamic analysis was performed with the object of gaining insights into these aspects from the equilibrium point of view.

1. Introduction

Although metal nitrides are usually produced by reaction of metal or metal hydride with molecular nitrogen, NH_3 is often used as a nitriding agent instead of N_2 gas. The Fe–N, Mo–N and U–N systems have been subjected to intensive study by use of flowing NH_3 or NH_3–H_2 mixture.

Schenk *et al.* [1] measured the solubility of nitrogen in iron at pressures up to 1×10^5 Pa (1 atm) and found that it obeyed Sieverts' law. According to Atkinson and Bodsworth [2], the maximum solubility of nitrogen in austenite was only 0.03 wt.% at 10^5 Pa (1 atm) of N_2 gas. They suggested that by subjecting iron at appropriate temperatures to extremely high pressures of N_2 gas, *i.e.* more than 10^9 Pa (10^4 atm), more concentrated solid solutions might be prepared. However, iron nitride, Fe_4N, could be readily prepared at 500 °C with a gaseous NH_3–H_2 mixture [3]. Hägg reported a phase of higher nitrogen content, Fe_2N [4]. This phase was confirmed by Jack, who also prepared Fe_2N by reaction of iron with flowing NH_3 [5].

In an attempt to prepare molybdenum nitrides, several workers carried out the reaction between molybdenum metal and N_2 and that of molybdenum with NH_3 [6–9]. According to the experimental study of Jehn and Ettmayer [10], the N_2 pressure required to prepare Mo_2N was 10^6 Pa (10 atm) at 1020 °C and 10^7 Pa (100 atm) at 1380 °C. On the other hand, a higher

0925-8388/92/$5.00

molybdenum nitride, MoN, could be obtained only by flowing NH_3 over molybdenum powder at temperatures between 700 and 1000 °C [11]. Attempts to prepare MoN with N_2 gas at pressures up to 3×10^7 Pa (300 atm) were not successful.

The *P–T–C* (equilibrium N_2 pressure–temperature–composition) relationships for α-U_2N_{3+x} ($0\leqslant x\leqslant 0.50$) were reported by Bugl and Bauer [12], Tagawa [13], Lapat and Holden [14] and Müller and Ragos [15]. All these authors prepared U_2N_{3+x} by reaction of uranium with N_2 and obtained the *P–T–C* relationship by equilibration of thus-prepared U_2N_{3+x} with N_2. The N:U ratio of U_2N_{3+x} ranged from 1.5 to 1.7. Price and Warren [16] and Trzebiatowski and Troc [17] prepared nitrogen-rich α-U_2N_{3+x} (N:U$\geqslant$1.80) by reaction of uranium with flowing NH_3 gas. Berthold and Hein [18] carried out the reaction of UF_4 with flowing NH_3 and obtained α-U_2N_{3+x} with N:U = 1.90. These results suggest that nitrogen-rich α-U_2N_{3+x}, which cannot be obtained by reaction with N_2 gas under normal pressures, could be prepared with flowing NH_3. Yoshizawa *et al.* [19] showed that highly nitrogen-rich UC–UN solid solutions can be prepared under NH_3 flow and concluded that the nitrogen activity in flowing NH_3 must be enormously high, corresponding to very high N_2 pressure.

As often claimed, NH_3 is considered to be kinetically favourable as a nitriding agent compared with N_2. Two important trends should be pointed out: (1) the use of NH_3 makes the reaction period much shorter and (2) the nitride is formed at considerably lower temperatures. However, the fact that the higher nitrides of iron, molybdenum or uranium can be obtained only by use of flowing NH_3 or NH_3–H_2 gas mixture may suggest that flowing NH_3 possesses extremely high nitrogen activity. By flowing NH_3 through a hot zone at sufficiently high speeds, the dissociation of NH_3 into N_2 and H_2 can be suppressed to some extent. In other words, a state may be created where the dissociation equilibrium $NH_3=\frac{1}{2}N_2+\frac{3}{2}H_2$ is not reached. In this situation NH_3 must be regarded as being in an unstable state with respect to the dissociation equilibrium. The high nitrogen activity exhibited by flowing NH_3 may arise from its instability. In order to discuss thermodynamically nitride formation by reaction of metal with flowing NH_3, it is necessary to evaluate quantitatively the nitrogen activity exhibited by flowing NH_3.

Early workers [3, 20] who studied the reactions of iron with NH_3 or NH_3–H_2 gaseous mixtures tried to estimate the pressure of N_2 required for the formation of higher iron nitrides (Fe_4N and Fe_2N) by reaction of iron with N_2. For this purpose they combined the equilibrium between iron nitrides and NH_3–H_2 mixture with the dissociation equilibrium $NH_3=\frac{1}{2}N_2+\frac{3}{2}H_2$. The estimated nitrogen pressures were of the order of 10^3–10^5 atm.

The relation $K_p=P_{NH_3}{}^{eq}/(P_{N_2}{}^{eq})^{1/2}(P_{H_2}{}^{eq})^{3/2}$, which relates the equilibrium partial pressures of the three gases, $P_{NH_3}{}^{eq}$, $P_{N_2}{}^{eq}$ and $P_{H_2}{}^{eq}$, to the equilibrium constant, has often been used to predict the nitrogen activity of unstable NH_3. One might be inclined to doubt whether the equilibrium constant K_p may be used in the case of an unstable gaseous mixture of NH_3, H_2 and N_2, since the value of K_p at a given temperature must be determined by measurement of equilibrium partial pressures of the gases from a classical thermodynamic point of view. Although many workers dealt thermodynamically with the formation of metal nitrides by reaction of metals with flowing NH_3, the thermodynamic understanding of nitride formation by use of flowing NH_3 must as yet be regarded as not established. Moreover, no exact thermodynamic treatment of why unstable NH_3, which can be prepared by flowing it, exhibits an extremely high nitrogen activity has been reported.

Although Darken and Gurry [21] indicated the possibility of hydride formation by reaction of metal with NH_3, little attention has been paid to hydride formation by use of NH_3. Recently Shohoji *et al.* [23] have suggested that flowing NH_3 might act as an efficient hydriding agent rather than nitriding agent at relatively low temperatures. However, neither theoretical evaluation of hydrogen activity exhibited by flowing NH_3 nor experimental study of hydride formation by reaction of metals with flowing NH_3 has been reported.

Unstable gaseous mixture of NH_3, H_2 and N_2, as prepared by flowing NH_3 through a hot zone, may act either as a nitriding agent or as a hydriding agent and the mixture may possess high nitrogen and hydrogen activities, which increase with increasing instability of the mixture.

This paper describes a thermodynamic analysis of the reaction of metals with flowing NH_3, attention being focused on both nitride and hydride formations. Nitrogen and hydrogen activities exhibited by flowing NH_3 are evaluated as a function of the extent of dissociation. To supplement the thermodynamic analysis, a statistical thermodynamic treatment is also given.

2. Thermodynamic analysis of reactions of metal with NH_3

When a metal is brought into contact with NH_3, the following three reactions are possible, as suggested by Darken and Gurry [21]:

$$NH_3\ (g) = \tfrac{1}{2}N_2\ (g) + \tfrac{3}{2}H_2\ (g) \tag{A}$$

$$NH_3\ (g) = N\ (\text{in nitride}) + \tfrac{3}{2}H_2\ (g) \tag{B}$$

$$NH_3\ (g) = 3H\ (\text{in hydride}) + \tfrac{1}{2}N_2\ (g) \tag{C}$$

Reaction (A) is the dissociation of NH_3 into N_2 and H_2, catalysed by the metal. Reactions (B) and (C) represent nitride formation and hydride formation by action of NH_3 respectively.

At equilibrium NH_3 always coexists with N_2 and H_2 and the partial pressures of the three gases may be determined uniquely by the equilibrium constant of reaction (A) at a given temperature if the total pressure is given. If a metal exists in this atmosphere, either reaction (B) or (C) might occur in parallel with reaction (A). Under these circumstances NH_3 may act either as a nitriding agent or as a hydriding agent according to whether reaction (B) or (C) prevails, and the nitrogen activity of NH_3 must be equal to that of N_2 and the hydrogen activity of NH_3 must be equal to that of H_2, since the equilibrium $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ is established in the gaseous phase. However, a state where the dissociation equilibrium $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ is not reached may be produced. For example, the dissociation of NH_3 can be suppressed to a great extent by using a flow method.

Next the following situation will be considered. NH_3 gas is passed into a reaction tube, in the centre of which a metal specimen is placed. The temperature distribution in the reaction tube is such that the temperature at the centre is highest and the temperature decreases from the centre to the two ends. Although by flowing NH_3 gas its extent of dissociation into N_2 and H_2 may be kept below the equilibrium dissociation degree, complete suppression of NH_3 dissociation is impossible. In other words, a certain degree of dissociation of NH_3 is unavoidable; the extent depends upon several experimental conditions such as the temperature of the hottest zone, the temperature distribution, the flow rate of NH_3, the surface properties of the walls of the reaction tube and the specimen and the geometric construction of the whole system. As the flow rate is reduced, the extent of dissociation approaches its equilibrium value. Consequently, a mixture of NH_3, N_2 and H_2 with an arbitrary gas composition can be prepared by flowing NH_3 at an appropriate flow rate. However, the thus-prepared gas mixture must be in an unstable state with respect to the stable equilibrium $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$, since this reaction would proceed to the right, resulting in a decrease in the relative amount of NH_3, if the time during which the mixture stays in a hot region were longer. If the metal has a tendency to form a nitride, the nitridation reaction (B) may proceed in parallel with the catalytic decomposition of NH_3. Eventually a steady state may be established where the respective partial pressures of NH_3, H_2 and N_2 in the gas phase and the composition of the nitride are all uniquely determined and are independent of time. It should be emphasized that although the above state resembles equilibrium in its invariance with time, it differs from equilibrium in that NH_3 continues to flow in the system and consequently entropy is being produced. In this situation the gas phase of NH_3, H_2 and N_2 is not in equilibrium but a partial equilibrium between the nitride and the gas phase is established. Of the two reactions (A) and (B) which may occur within the system, reaction (A) is constrained to an unstable non-equilibrium state by flowing NH_3 but reaction (B) may proceed to the right with sufficient speed until partial equilibrium is reached between the nitride and the gas phase, where the nitrogen activity exhibited by the gas phase must be equal to that of the nitride.

Reaction (B) represents a partial equilibrium between flowing NH_3 and a metal nitride. At partial equilibrium the following relation must hold:

$$\mu(NH_3) = \mu(\text{N in nitride}) + \tfrac{3}{2}\mu(H_2) \tag{1}$$

where μ denotes chemical potential and

$$\mu(NH_3) = \Delta G_f^\circ(NH_3) + RT\ln(P_{NH_3}) \tag{2}$$

$$\mu(H_2) = RT\ln(P_{H_2}) \tag{3}$$

Here P_{NH_3} and P_{H_2} are expressed in atmospheres and $\Delta G_f^\circ(NH_3)$ is the standard free energy of formation of NH_3, namely the difference in free energies of NH_3, N_2 and H_2 at 1 atm pressure, *i.e.* $G^\circ(NH_3) - \frac{1}{2}G^\circ(N_2) - \frac{3}{2}G^\circ(H_2)$. It is also assumed that NH_3 and H_2 behave ideally. This may be valid since the pressure of flowing NH_3 is considered to be equal to atmospheric pressure.

Substituting eqns. (2) and (3) into eqn. (1) yields

$$\mu(\mathrm{N}) = \Delta G_f^\circ(\mathrm{NH_3}) + RT\ln\left(\frac{P_{\mathrm{NH_3}}}{P_{\mathrm{H_2}}{}^{3/2}}\right) \tag{4}$$

By passing NH_3 rapidly through a hot zone, a gas mixture of H_2, N_2 and unstable NH_3 is obtainable. In this case $P_{\mathrm{NH_3}}$ is always larger than that at equilibrium, $P_{\mathrm{NH_3}}{}^{\mathrm{eq}}$, and $P_{\mathrm{H_2}}$ and $P_{\mathrm{N_2}}$ are smaller than $P_{\mathrm{H_2}}{}^{\mathrm{eq}}$ and $P_{\mathrm{N_2}}{}^{\mathrm{eq}}$ respectively. At partial equilibrium the chemical potential of nitrogen in the gas phase must be equal to that of the nitride, $\mu(\mathrm{N})$. Therefore $\mu(\mathrm{N})$ also expresses the chemical potential of nitrogen in the gas phase. It should be noted that $\mu(\mathrm{N})$ is controlled only by $P_{\mathrm{NH_3}}/(P_{\mathrm{H_2}})^{3/2}$ and that the pressure of coexisting N_2, $P_{\mathrm{N_2}}$, makes no contribution to $\mu(\mathrm{N})$. Equation (4) implies that as the value of $P_{\mathrm{NH_3}}/(P_{\mathrm{H_2}})^{3/2}$ becomes larger, $\mu(\mathrm{N})$ becomes higher. The chemical potential $\mu(\mathrm{N})$ of an unstable mixture of NH_3, H_2 and N_2 is much larger than that of N_2 at 1 atm, while $\mu(\mathrm{N})$ of a mixture of these gases at equilibrium is smaller than it.

The chemical potential $\mu(\mathrm{N})$ is related to the nitrogen activity a_{N} by the relation

$$\mu(\mathrm{N}) = RT\ln(a_{\mathrm{N}}) \tag{5}$$

From eqns. (4) and (5) the following relation is obtained:

$$a_{\mathrm{N}} = \frac{P_{\mathrm{NH_3}}}{(P_{\mathrm{H_2}})^{3/2}}\exp\left(\frac{\Delta G_f^\circ(\mathrm{NH_3})}{RT}\right) \tag{6}$$

Since the free energy of formation is related to the equilibrium constant K_p by

$$\Delta G_f^\circ(\mathrm{NH_3}) = -RT\ln(K_p) \tag{7}$$

the nitrogen activity a_{N} is given by

$$a_{\mathrm{N}} = \frac{1}{K_p}\frac{P_{\mathrm{NH_3}}}{(P_{\mathrm{H_2}})^{3/2}} \tag{8}$$

When the partial equilibrium between the unstable gas phase produced by flowing NH_3 and a metal hydride prevails, the following relation must hold:

$$\mu(\mathrm{H}) = \tfrac{1}{3}\mu(\mathrm{NH_3}) - \tfrac{1}{6}\mu(\mathrm{N_2}) \tag{9}$$

In a similar way to that in which eqn. (4) has been derived, the chemical potential of hydrogen of flowing NH_3, $\mu(\mathrm{H})$, can be expressed as

$$\mu(\mathrm{H}) = \tfrac{1}{3}\left[\Delta G_f^\circ(\mathrm{NH_3}) + RT\ln\left(\frac{P_{\mathrm{NH_3}}}{(P_{\mathrm{N_2}})^{1/2}}\right)\right] \tag{10}$$

The hydrogen activity a_{H} exhibited by an unstable gaseous mixture of NH_3, H_2 and N_2 is readily obtained as

$$a_H = \left(\frac{1}{K_p} \frac{P_{NH_3}}{(P_{N_2})^{1/2}} \right)^{1/3} \tag{11}$$

Again it should be emphasized that a_H is controlled only by $(P_{NH_3})^{1/2}/(P_{N_2})^{1/6}$, *i.e.* P_{H_2} makes no contribution to a_H.

Figures 1 and 2 show a_N and a_H respectively as a function of the extent of dissociation, α, at several temperatures. As can be seen from these figures, if appropriate conditions of temperature and extent of dissociation (which depends on flow rate) can be established, high nitrogen activity and high hydrogen activity may be obtained by suppressing the dissociation of NH_3.

3. Statistical thermodynamic analysis

According to Fowler and Guggenheim [23], the chemical potential of NH_3 is given by the following equation when the state of the gaseous nitrogen atom at rest and that of the gaseous hydrogen atom at rest are taken as the respective reference states:

$$\mu_{NH_3} = -\tfrac{1}{2}D^\circ(N_2) - \tfrac{3}{2}D^\circ(H_2) + \Delta H^\circ_{f,0}(NH_3) + RT\ln(P_{NH_3}) + A(T) \tag{12}$$

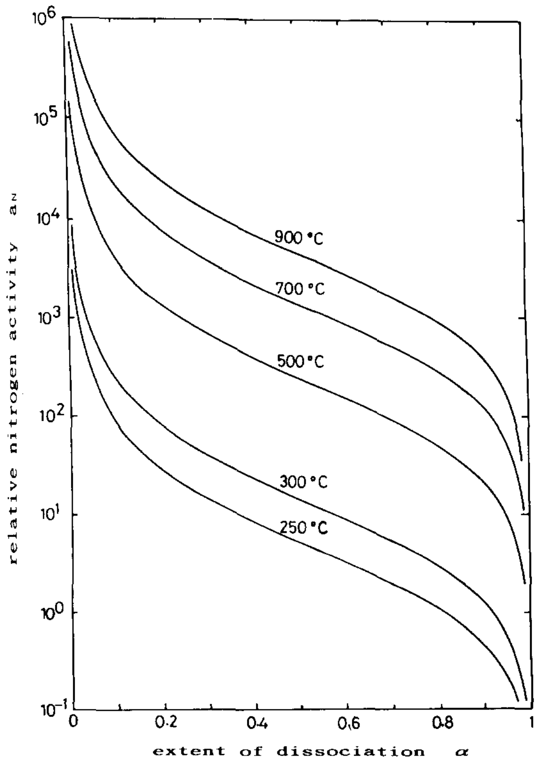

Fig. 1. Relative nitrogen activity (a_N) exhibited by flowing NH_3 as a function of extent of dissociation (α) at several temperatures.

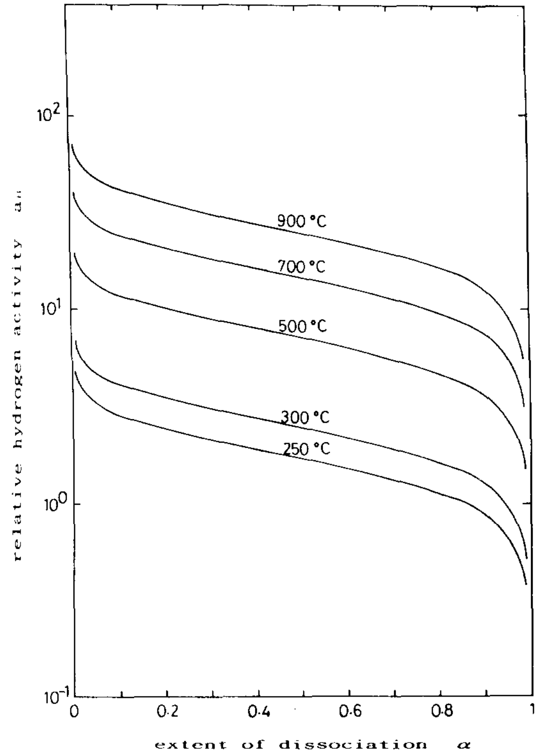

Fig. 2. Relative hydrogen activity (a_H) exhibited by flowing NH_3 as a function of extent of dissociation (α) at several temperatures.

where $D°(N_2)$ and $D°(H_2)$ are the dissociation energies of N_2 and H_2 at 0 K respectively and $\Delta H^{\circ}_{f,\,0}(NH_3)$ is the enthalpy of formation of NH_3 at 0 K. The last term on the right-hand side of eqn. (12), $A(T)$, which is dependent only on temperature, is given by

$$A(T)=RT\left\{-4\ln(T)+\ln(\Sigma_v)\ln\left[1-\exp\left(\frac{-\Theta_v(NH_3)}{T}\right)\right]-j_{NH_3}-\ln[\rho_N(\rho_H)^3]\right\} \tag{13}$$

where $\Theta_v(NH_3)$ is the characteristic temperature for vibration of NH_3 and ρ_N and ρ_H are the nuclear spin weights of nitrogen and hydrogen respectively. The symbol j_{NH_3}, is given by

$$j_{NH_3}=\ln\left(\frac{(2\pi m_{NH_3})^{3/2}k^{5/2}}{h^3}\,\frac{8\pi^2(2\pi k)^{3/2}(I_A I_B I_C)^{1/2}}{h^3}\,\frac{v_o(NH_3)}{\sigma(NH_3)}\right) \tag{14}$$

where k, h, m_{NH_3}, $v_o(NH_3)$ and $\sigma(NH_3)$ denote the Boltzmann constant, the Planck constant, the mass of the NH_3 molecule, the electronic weight of the normal state of NH_3 and the symmetry number of the NH_3 molecule respectively. I_A, I_B and I_C are the principal moments of inertia.

The chemical potential of H_2 is given by

$$\mu_{H_2} = -D^{\circ}(H_2) + RT\ln(P_{H_2}) + B(T) \tag{15}$$

where $B(T)$ is a function dependent only on temperature and is expressed as

$$B(T) = RT\left\{-\tfrac{7}{2}\ln(T) + \ln\left[1-\exp\left(\frac{-\Theta_v(H_2)}{T}\right)\right] - j_{H_2} - 2\ln(\rho_H)\right\} \tag{16}$$

Similarly, the chemical potential of N_2 is given by

$$\mu_{N_2} = -D^{\circ}(N_2) + RT\ln(P_{N_2}) + C(T) \tag{17}$$

and

$$C(T) = RT\left\{-\tfrac{7}{2}\ln(T) + \ln\left[1-\exp\left(\frac{-\Theta_v(N_2)}{T}\right)\right] - j_{N_2} - 2\ln(\rho_N)\right\} \tag{18}$$

Here the reference states are those of the respective gaseous atoms at rest and j_{H_2} and j_{N_2} are given by

$$j_{A_2} = \ln\left(\frac{(2\pi m_{A_2})^{3/2}k^{5/2}}{h^3}\,\frac{8\pi^2 I_{A_2}k}{h^2}\,\frac{v_o(A_2)}{\sigma(A_2)}\right) \tag{19}$$

where A_2 stands for H_2 or N_2. The meanings of the symbols appearing in eqns. (15)–(19) are obvious by analogy with eqns. (12) and (13).

Substituting eqns. (12) and (14) into eqn. (1) yields

$$\mu_N = -\tfrac{1}{2}D^{\circ}(N_2) + \Delta H^{\circ}_{f,0}(NH_3) + A(T) - \tfrac{3}{2}B(T) + RT\ln\left(\frac{P_{NH_3}}{(P_{H_2})^{3/2}}\right) \tag{20}$$

The absolute nitrogen activity λ_N exhibited by the gas phase prepared by flowing NH_3 is related to μ_N by

$$\mu_N = RT\ln(\lambda_N) \tag{21}$$

The standard state with respect to which the chemical potential of nitrogen is evaluated is usually taken as the state of N_2 at 1 atm. The chemical potential of N_2 at 1 atm, $\mu_{N_2}{}^0$, can readily be obtained by substituting $P_{N_2} = 1.01325\times10^5$ Pa (1 atm) in eqn. (17):

$$\mu_{N_2}{}^0 = 2RT\ln(\lambda_N{}^0) = -D^{\circ}(N_2) + RT\ln(1.01325\times10^5) + C(T) \tag{22}$$

where $\lambda_N{}^0$ denotes the nitrogen activity of N_2 at 1 atm. The chemical potential of nitrogen exhibited by an unstable gaseous mixture of NH_3, H_2 and N_2 is then given by

$$\begin{aligned}\mu_N - \tfrac{1}{2}\mu_{N_2}{}^0 &= RT\ln\left(\frac{\lambda_N}{\lambda_N{}^0}\right) = RT\ln(a_N)\\ &= \Delta H^{\circ}_{f,0} + A(T) - \tfrac{3}{2}B(T) - \tfrac{1}{2}C(T)\\ &\quad - RT\ln(1.01325\times10^5) + RT\ln\left(\frac{P_{NH_3}}{(P_{H_2})^{3/2}}\right)\end{aligned} \tag{23}$$

where P_{NH_3} and P_{H_2} are expressed in atmospheres and a_N is the relative nitrogen activity of the flowing gas with respect to $\frac{1}{2}N_2$ at 1 atm.

The equilibrium $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ must be controlled by the relation

$$\mu_{NH_3} = \frac{1}{2}\mu_{N_2} + \frac{3}{2}\mu_{H_2} \tag{24}$$

Substituting eqns. (12), (15) and (17) into eqn. (24), one obtains

$$RT \ln\left(\frac{P_{NH_3}}{(P_{N_2})^{1/2}(P_{H_2})^{3/2}}\right) = -[\Delta H^{\circ}_{f,\,0}(NH_3) + A(T) - \tfrac{3}{2}B(T) - \tfrac{1}{2}C(T) - RT\ln(1.01325\times10^5)] \tag{25}$$

where the pressures of the three gases are expressed in atmospheres. Therefore $P_{NH_3}/(P_{N_2})^{1/2}(P_{H_2})^{3/2}$ must be equal to the equilibrium constant K_p. Comparison of eqn. (25) with eqn. (23) leads to the same relation as eqn. (8):

$$a_N = \frac{1}{K_p}\frac{P_{NH_3}}{(P_{N_2})^{3/2}} \tag{8}$$

Equation (11), which expresses the hydrogen activity of the gas phase of H_2, N_2 and unstable NH_3 as a function of P_{NH_3} and P_{N_2}, can be easily obtained in a similar way.

4. Discussion

The experimental results of the reactions of iron, molybdenum and uranium with flowing NH_3 or NH_3–H_2 gas mixture reported in the literature imply that extremely high nitrogen activities may be obtained by flowing NH_3 or NH_3–H_2 mixture. Although the nitride formations of these three metals by use of flowing NH_3 or NH_3–H_2 mixture have been thermodynamically dealt with, characterizing thermodynamically nitride formation by reaction of metal with NH_3 is a complicated task not sufficiently appreciated by many investigators. It was in the early 1920s that Noyes and Smith [20] showed the possibility of calculating the dissociation pressure of Fe_2N and Fe_4N by applying the equilibrium constant K_p for $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$. They obtained P_{N_2} values varying between 2×10^4 and 5×10^5 atm based on their own experimental results at 460 °C. Although their treatment was a step in the right direction for understanding why unstable NH_3 could exhibit extremely high nitrogen activity, there was some confusion as to the theoretical development. In addition, $1/K_p = P_{NH_3}/(P_{N_2})^{1/2}(P_{H_2})^{3/2}$ does not hold unless all these gases behave ideally. N_2 gas at such high pressures as 10^4–10^5 atm cannot be treated as an ideal gas at all. Atkinson and Bodsworth [2] have carried out reaction experiments of iron with flowing NH_3–H_2 gas mixture and analysed thermodynamically the results obtained. Although they evaluated the nitrogen activity of formed iron nitride by using the relation $a_N = (1/K)P_{NH_3}/(P_{H_2})^{3/2}$ derived by themselves, where K is a given constant, they determined K experimentally in rather a complicated manner. It seems that they did not recognize the equality between K and K_p. As clarified in the thermodynamic and statistical thermodynamic developments for obtaining eqn. (8), the equilibrium constant K_p for $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ can be used to evaluate the nitrogen activity a_N and it is not necessary to appeal to experiment in order to obtain K. If the relation $1/K_p = (P_{N_2})^{1/2}(P_{H_2})^{3/2}/P_{NH_3}$ is substituted into eqn. (8), a simple relation $a_N = (P_{N_2})^{1/2}$ is obtained.

Figure 1 indicates that if the extent of dissociation of NH_3, α, could be maintained much less than the equilibrium dissociation degree, extremely high nitrogen activities would be obtained and the relation $a_N = (P_{N_2})^{1/2}$ could give an enormously high N_2 pressure. As already indicated, it is rather meaningless to evaluate the precise value of the N_2 pressure that would be required to prepare the same nitrogen activity produced by flowing NH_3, since eqn. (8) has been derived on the assumption that all three gases, NH_3, H_2 and N_2, behave ideally. In other words the relation $1/K_p = (P_{N_2})^{1/2}(P_{H_2})^{3/2}/P_{NH_3}$, which is valid only at equilibrium, can be used to estimate roughly how high an N_2 pressure would be needed if one tried to prepare nitrogen-rich nitrides, as formed by use of unstable NH_3, by reaction of metal with N_2. The value of $P_{NH_3}/(P_{H_2})^{3/2}$ in the gas mixture prepared by flowing NH_3 through a hot zone is always much higher than that at equilibrium at the temperature in question.

The equilibrium constant K_p enters eqns. (8) and (11), which express the nitrogen activity and hydrogen activity respectively of the unstable non-equilibrium gas phase prepared by flowing NH_3. It is interesting to note that the non-equilibrium gas phase of NH_3, H_2 and N_2 is still governed by the equilibrium constant. In other words, K_p determines how high a nitrogen activity or P_{N_2} would be required to maintain a high value of $P_{NH_3}/(P_{H_2})^{3/2}$ in the unstable non-equilibrium gas phase as prepared by flowing NH_3 through a hot region.

As already mentioned, when a partial equilibrium between an unstable gas mixture of NH_3, H_2 and N_2 as prepared by flowing NH_3 and a nitride is attained, the nitrogen activity of the nitride must be equal to that of the gas mixture, which is controlled by $P_{NH_3}/(P_{H_2})^{3/2}$. In this case N_2 gas existing in the gas mixture has nothing to do with the nitride formation. In other words, there exist two nitriding agents in the gas mixture, one being N_2 and the other the combination of NH_3 and H_2. Since the nitrogen activity of the latter is much higher than that of the former, N_2 does not play any significant role in the nitride formation. The thus-formed nitrides must be unstable nitrides with respect to N_2 under normal pressure. According to the present author's experience, nitrogen-rich U_2N_{3+x} with an N:U ratio of more than 1.80 prepared by use of flowing NH_3 is pyrophoric and, in handling nitrogen-rich U_2N_{3+x}, it is necessary to be extremely careful to exclude O_2 from the system.

On the other hand, in dealing with the hydride formation by action of flowing NH_3, the hydrogen activity is controlled by $(P_{NH_3})^{1/3}/(P_{N_2})^{1/6}$ (see eqn. (11)). Although two hydriding agents, H_2 and the combination of NH_3

and N_2, exist in the gas phase, H_2 does not take part in the hydride formation.

It may be worthwhile emphasizing that an unstable mixture of NH_3, H_2 and N_2 prepared by flowing NH_3 may function either as a nitriding agent or as a hydriding agent according to whether the metal in question can form nitride or hydride under a given condition.

Although metal–hydrogen systems have been studied extensively and intensively, no information about hydride formation by reaction of metal with NH_3 is available. The present thermodynamic analysis shows clearly that flowing NH_3 may act as a potential hydriding agent. It is strongly hoped that the experimental work giving support to the theoretical analysis will be performed.

As can be seen from Fig. 1, the relative nitrogen activity a_N becomes enormously larger at smaller values of the extent of dissociation, α, particularly at higher temperatures. It is also recognized that the value of a_N is larger at higher temperatures if the comparison is made at the same value of the extent of dissociation. This may reflect the fact that it becomes much more difficult to maintain the same extent of dissociation at higher temperatures, *i.e.* a gas mixture with given partial pressures of NH_3, H_2 and N_2 is more unstable with respect to the equilibrium dissociation $NH_3=\frac{1}{2}N_2+\frac{3}{2}H_2$. The extent of dissociation of NH_3 can be a measure of the instability of NH_3. A similar tendency can be observed for the hydrogen activity a_H exhibited by flowing NH_3, although the suppression of decomposition of NH_3 is less effective for obtaining high hydrogen activity than for obtaining high nitrogen activity (see Fig. 2). Moreover, at a given temperature the nitrogen activity varies much more markedly with the extent of dissociation than the hydrogen activity does.

It might be interesting to note an implication of the molecular formula of NH_3, namely that three hydrogen atoms are necessary to fix one nitrogen atom while one nitrogen atom can fix three hydrogen atoms. This might reflect the fact that the suppression of dissociation of NH_3 gives more effectively a higher nitrogen activity compared with the case of hydriding.

5. Concluding remarks

When NH_3 is passed through a region held at high temperature at an appropriate flow rate, the extent of dissociation of NH_3 into H_2 and N_2 can be kept less than the equilibrium degree of dissociation at the temperature in question, the state of which may be considered an unstable state. Thus a gaseous mixture of N_2, H_2 and unstable NH_3 with the desired relative amounts can be prepared with proper precautions. These gaseous mixtures as prepared by flowing NH_3 can provide an extremely high nitrogen activity because of its high instability if suitable experimental conditions are selected. Therefore the use of a stream of NH_3 makes it possible to prepare a nitrogen-rich metal nitride, which cannot be obtained by N_2 at normal pressure. Strong experimental evidence giving support to the above consideration exists in the literature.

Although little work has been done on hydride formation by reaction of a metal with a stream of NH_3, in principle it is possible that a stream of NH_3 may act as a hydriding agent with high hydrogen activity under suitable conditions.

Why extremely high nitrogen activity or high hydrogen activity is provided by flowing NH_3 should be explained from the equilibrium viewpoint rather than the kinetic viewpoint.

The thermodynamic analysis explains well why high nitrogen and hydrogen activities can be attained by flowing NH_3. Moreover, it may be possible to evaluate these activity values if the partial pressures of NH_3, H_2 and N_2 in the gas phase participating in the nitriding or hydriding reaction by use of a stream of NH_3 are known. Equivalent results can also be deduced from statistical thermodynamic considerations.

References

1 V. H. Shenk, M. G. Frohberg and F. Reinders, *Stahl Eisen, 83* (2) (1963) 93.
2 D. Atkinson and C. Bodsworth, *J. Iron Steel Inst., 208* (June 1970) 587.
3 P. H. Emmett, S. B. Hendricks and S. Brunauer, *J. Am. Chem. Soc., 52* (1930) 1456.
4 G. Hägg, *Nature, 122* (1928) 826.
5 K. H. Jack, *Proc. R. Soc. A, 195* (1948) 56.
6 P. Hägg, *Z. Phys. Chem. Abt. B, 7* (1930) 339.
7 N. Schönberg, *Acta Metall., 2* (1954) 427.
8 N. Schönberg, *Acta Chem. Scand., 8* (1954) 204.
9 P. Ettmayer, *Monatsch. Chem., 101* (1970) 127.
10 H. Jehn and P. Ettmayer, *High Temp.-High Press., 8* (1976) 83.
11 H. Jehn and P. Ettmayer, *J. Less-Common Met., 58* (1978) 85.
12 J. Bugl and A. A. Bauer, in J. T. Waber, P. Chiotti and W. N. Miner (eds.), *Int. Symp. on Compounds of Interest in Nuclear Reactor Technology*, Edwards, Ann Arbor, MI, 1964, p. 215.
13 H. Tagawa, *J. Nucl. Mater., 51* (1974) 78.
14 P. E. Lapat and R. B. Holden, in J. T. Waber, P. Chiotti and W. N. Miner (eds.), *Int. Symp. on Compounds of Interest in Nuclear Reactor Technology*, Edwards, Ann Arbor, MI, 1964, p. 225.
15 F. Müller and H. Ragos, *Thermodynamics of Nuclear Materials*, IAEA, Vienna, 1968, p. 257.
16 C. E. Price and I. H. Warren, *Inorg. Chem., 4* (1965) 115.
17 W. Trzebiatowski and R. Troc, *Bull. Acad. Pol. Sci., Ser. Sci. Chim., X* (86) (1962) 395.
18 H. J. Berthold and H. G. Hein, *Angew. Chem., 81* (22) (1969) 910.
19 H. Yoshizawa, N. Shohoji, M. Katsura, T. Sano and T. Yato, *Technol. Rep. Osaka Univ., 27* (1977) 363.
20 A. Noyes and L. B. Smith, *J. Am. Chem. Soc., 43* (1921) 475.
21 L. Darken and R. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953, p. 372.
22 N. Shohoji, T. Marcelo and M. Katsura, *Solid State Ionics, 38* (1990) 187.
23 R. Fowler and A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, Cambridge, 1965, p. 87.