The Vanadium-Nitrogen System: A Review

O. N. CARLSON, J. F. SMITH, and R. H. NAFZIGER

This paper is a critical review of the available phase equilibria, crystallographic, and thermodynamic data for the vanadium-nitrogen system. Three nitride phases, $\beta V_2 N_{1-y}$, δVN_{1-x}, and $\delta' VN_{1-x}$, have been identified and their crystal structures, ranges of homogeneity, and melting or decomposition temperatures determined. The solvus boundary for the vanadium-rich solid solution is placed at 3.8 at. pct N at 550 °C and increases to 11 at. pct N at 1500 °C. A break in the solvus observed at 550 °C is associated with the formation of a metastable phase, $V_{16}N$. Other metastable phases have been identified, but their exact stoichiometries and structures have not been unambiguously determined. The enthalpies and free energies of formation, heat capacities, and dissociation pressures for the subnitride and mononitride are evaluated and correlated.

I. INTRODUCTION

THE existence of a mononitride phase in the V-N system was first reported by Roscoe in 1868 and later by Whitehouse in 1907.[1] In 1925 Friederich and Sittig[2] prepared this compound and determined its melting point. Likewise a subnitride phase was reported as early as 1858[1] and tentatively identified as V_2N by Muthmann et al. in 1907.[3] The earliest attempt to determine the V-N phase diagram was that of Hahn[1] who studied the solid solubility of nitrogen in vanadium and determined the structures of VN and V_2N by use of X-ray diffraction. Since that time there have been numerous studies on the solid solubility in vanadium and the composition ranges, structures, dissociation pressures, and thermodynamic properties of the intermediate phases in the V-N system.

II. PHASE RELATIONS

In spite of the extensive amount of work on the V-N system there remains much uncertainty over the number and stability of the phases occurring in the system. Two intermediate phases, fcc δVN_{1-x} and hcp βV_2N_{1-y}, having wide ranges of homogeneity, have been well established. These are shown in the proposed diagram of Figure 1. An ordered phase having a stoichiometry of $V_{32}N_{26}$ has also been reported. There appears to be substantial evidence for its existence, and it is shown in the equilibrium diagram as $\delta' VN_{1-x}$. Other intermediate phases with the stoichiometries of $V_{16}N$, $V_{13}N$, V_9N, V_8N, V_9N_2, and V_4N have also been reported, but it is believed that these phases are metastable if indeed they do exist. These latter phases are therefore not shown in the equilibrium diagram in Figure 1.

The solid solubility of nitrogen in vanadium has been investigated rather extensively by a variety of techniques. There is considerable variation in the results, but agreement is generally within ± 1 at. pct at a given temperature.

The various regions of the equilibrium diagram are discussed in detail in the succeeding sections along with an attempt to make sense out of the confusing plethora of metastable phases.

A. Vanadium Terminal Solid Solution (V)

The results of the different investigations of the solid solubility of nitrogen in vanadium are presented in Figure 2. The earliest attempt to determine the solid solubility of nitrogen in vanadium was that of Hahn.[1] From room temperature lattice parameter measurements, he concluded that vanadium exhibits very little solubility for nitrogen.

Hörz[4] determined the solubility in the temperature range 600 °C to 1200 °C by X-ray parameter and resistivity methods, and Henry et al.[5] determined it for the same range by X-ray and metallographic techniques. As can be seen from Figure 2, their results are in rather poor agreement. Subsequent work by Potter et al.[6] was in better accord with the data of Henry (see Figure 2) as were later results of Hörz.[7] Recent results of Nouet et al.[8] place the solvus somewhat closer to the original Hörz curve.[4] There appears to be general agreement, however, that the heat of solution for the β nitride phase in vanadium is approximately 16 kJ/mol.[7]

Monroe and Cost[9] determined the solubility between 275 °C and 575 °C by internal friction. Their data indicate that there is a break in the solvus at ~ 575 °C with a measurably higher heat of solution, 23.0 kJ/mol, at the lower temperatures. These differences are due to the precipitation of a metastable phase, $V_{16}N$, in the lower temperature[6] range. Hörz[7] also observed the precipitation of an interstitially ordered phase during aging of a quenched 6 at. pct N alloy between 280 °C and 350 °C. A more detailed discussion of this and other metastable phases appears in a later section of this paper.

The vanadium-rich solvus shown in Figure 1 in the range of 575 °C to 1500 °C is that of Hörz.[7] His study appears to be the most comprehensive to date and was based on a combination of X-ray parameter, electrical resistance, and hardness measurements. The V of his investigation was reported to be of "particularly high purity".

The vanadium solidus is based on some recent observations by the present authors. The melting temperature for a series of alloys containing 2 to 14 at. pct N was determined by an optical pyrometer method, the results of which are plotted in Figure 1. These data indicate a minimum in the solidus at 3 to 4 at. pct N as is seen from the diagram.
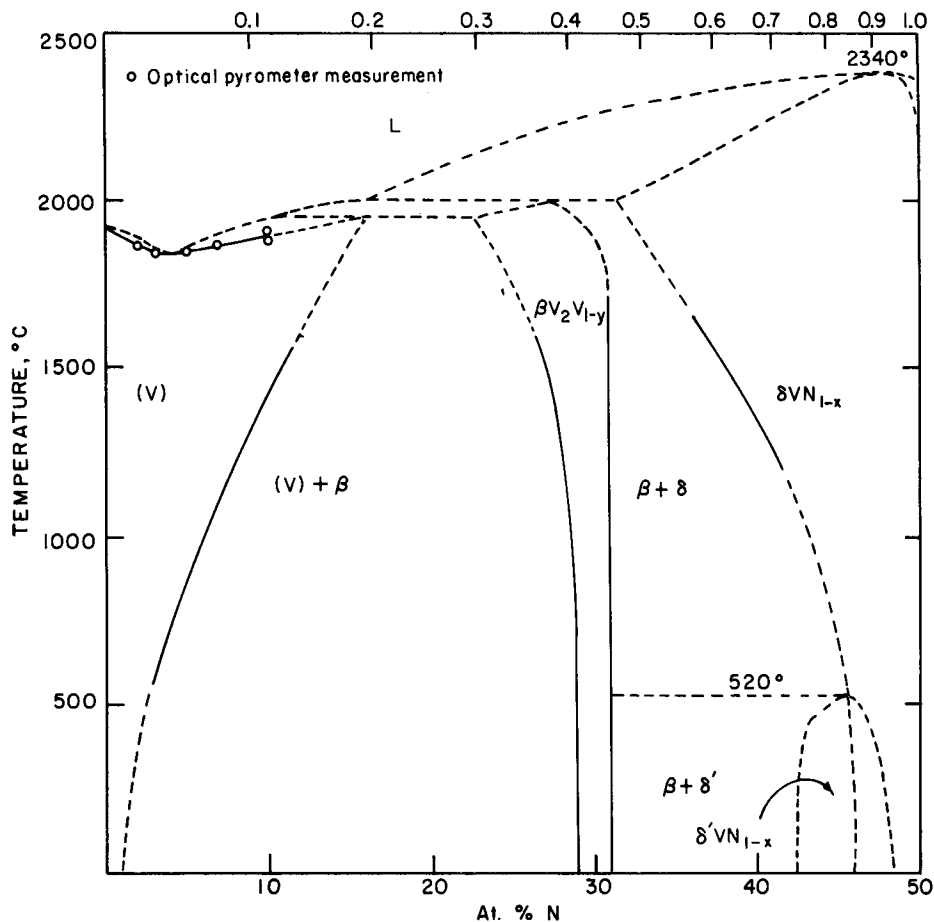
Fig. 1 — Proposed equilibrium diagram for V-N system.

B. $\beta V_2 N_{1-y}$ Phase

The existence of a hexagonal subnitride phase is well established, but there is still some uncertainty over its exact stoichiometry or composition range. Hahn[1] was the first to investigate the structure of this subnitride. From X-ray lattice parameter data he determined the range of homogeneity as extending from $VN_{0.37}$ to $VN_{0.43}$ ($0.26 \geq y \geq 0.14$). The temperature associated with these boundaries was not specified. Potter and Geils[10] investigated the structure of this phase by use of selected area electron diffraction and obtained a hexagonal structure with lattice parameters and c/a ratio similar to those reported by Hahn. Christiansen and Lebech[11] determined the structure of this phase by neutron diffraction and showed it to be isomorphous with hexagonal εFe_2N.[12]

Arbuzov et al.[13] determined the phase boundaries of $\beta V_2 N_{1-y}$ between 700 °C and 1500 °C from lattice parameter-composition measurements on quenched alloys. They obtained a value of 31.0 ± 0.6 at. pct N ($VN_{0.46}$; $y = 0.08$) for the nitrogen-rich boundary with very little temperature dependence. This is corroborated by the work of Khaenko and Fak[14] who placed the boundary at 31.3 at. pct at both 700 °C and 1500 °C. This is somewhat lower than the earlier results of Brauer and Schnell[15] who placed the boundary at 32.8 at. pct N, close to stoichiometric V_2N composition. X-ray diffraction evidence by Arbuzov et al.[13] indicates that the range of homogeneity does not extend to the composition of V_2N; hence, the β phase is represented by substoichiometric designation $V_2 N_{1-y}$.

The position of the vanadium-rich boundary is somewhat less certain. Hahn[1] and Brauer and Schnell[15] place it somewhere between 28 and 30 at. pct at 1500 °C, Arbuzov et al.[13] at approximately 25 at. pct, Fromm and Gebhardt[16] at 27 at. pct, and Khaenko and Fak[14] at 26.7 at. pct at this temperature, increasing to 28.7 at. pct N at 700 °C. Agreement among the data supports the boundary of Khaenko and Fak and has been so constructed in Figure 1. No data are available on the melting or decomposition temperature of $V_2 N_{1-y}$. Brauer and Schnell[15] measured the vapor pressure of $VN_{0.43}$ ($y = 0.14$) between 1375 °C and 1600 °C. In view of the relatively low dissociation pressures in this temperature regime, it can be assumed that this phase should be stable to relatively high temperatures under 1 atm N_2 pressure. This phase has been shown in the diagram as undergoing peritectic melting similar to that postulated by Levinskii[17] for βNb_2N in the Nb-N system.

C. δVN_{1-x} and $\delta' VN_{1-x}$ Phases

The mononitride phase, δVN_{1-x}, has the NaCl-type B1 structure and exists over a wide range of compositions. Brauer and Schnell[15] placed the room temperature boundaries at $VN_{0.72}$ and $VN_{1.00}$ from lattice parameter measurements. These boundaries are in good accord with the earlier work of Hahn.[1] Recent X-ray parameter data of Kieda et al.[18] indicate that the range of homogeneity at temperatures between 1200 °C and 1500 °C extends from $VN_{0.68}$ (40.5 at. pct N) to $VN_{0.98}$ (49.5 at. pct N). Kozheurov

et al.[19] determined the vanadium-rich boundary from dissociation pressure measurements between 1300° and 1650 °C, and Onozuka[20] determined the boundary at 575° and 650 °C from X-ray diffraction data. The data of Kozheurov *et al.*[19] extrapolated to lower temperatures have been used to construct the vanadium-rich boundary of Figure 1. The nitrogen-rich boundary is placed at 50 at. pct N (VN) in accord with the findings of other investigators.[13,15,20] Al-
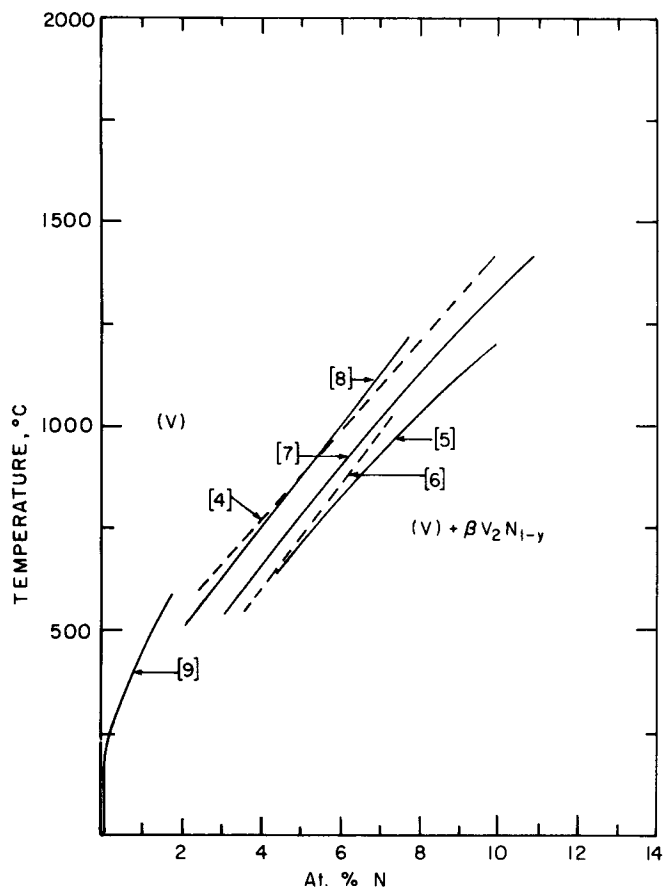
though Kieda *et al.*[18] did not reach this composition in their study, they concluded that it could have been attained if a higher nitrogen pressure or lower temperature had been used.

Several investigators[1,13,15,21] have reported a continuous linear relationship between lattice constant and nitrogen content across the entire δVN_{1-x} region, but Onozuka[20] has found two linear segments with a slope discontinuity near $VN_{0.84}$, as is seen from Figure 3. This was cited as evidence for an ordered phase, $\delta' VN_{1-x}$, occurring below 520 °C. Onozuka noted that all of the previous lattice parameter measurements were made on samples that were annealed and quenched from above 520 °C.

The melting point of the mononitride phase was reported as 2025 °C in the early work of Friedrich and Sittig,[2] but later work by Ettmayer *et al.*[22] places it as 2340 ± 10 °C at 1 atm N_2 pressure. Ettmayer *et al.* determined the melting point of δVN_{1-x} at pressures of 0.5 to 60 atm and found it to be nearly independent of nitrogen pressure or composition over the range of $V_{0.81}$ to $V_{0.95}$. This is the basis for the flat maximum shown for this phase in the proposed diagram.

Onozuka[20] identified a cubic superlattice, indicated here as $\delta' VN_{1-x}$, between $VN_{0.74}$ and $VN_{0.82}$ after prolonged annealing at 500 °C. Evidence for this are the break in the lattice parameter-composition curve previously noted, electron diffraction patterns that show extra reflections, and λ points in heat capacity curves near 500 °C. Other evidence for the phase are discontinuities in electrical resistivity between 350 °C and 500 °C[23] and indications of N ordering from neutron diffraction[24] at a composition of $VN_{0.74}$ and from NMR at a composition of $VN_{0.75}$.[25]

Khaenko and Fak[14] identified δVN_{1-x} as the only phase in a $VN_{0.90}$ alloy that had been annealed at 350 °C. This places the V-rich boundary below this composition. In Figure 1, this boundary has been extrapolated from that of Reference 19 to room temperature in preference to the sharp inflection of Reference 20 just above the 520 °C peritectoid horizontal.

D. *Metastable Phases*

Rostoker and Yamamoto[26] were the first to report an intermediate phase between the V terminal solid solution, (V),

Fig. 2—Nitrogen solid solubility in vanadium reported by various investigators.
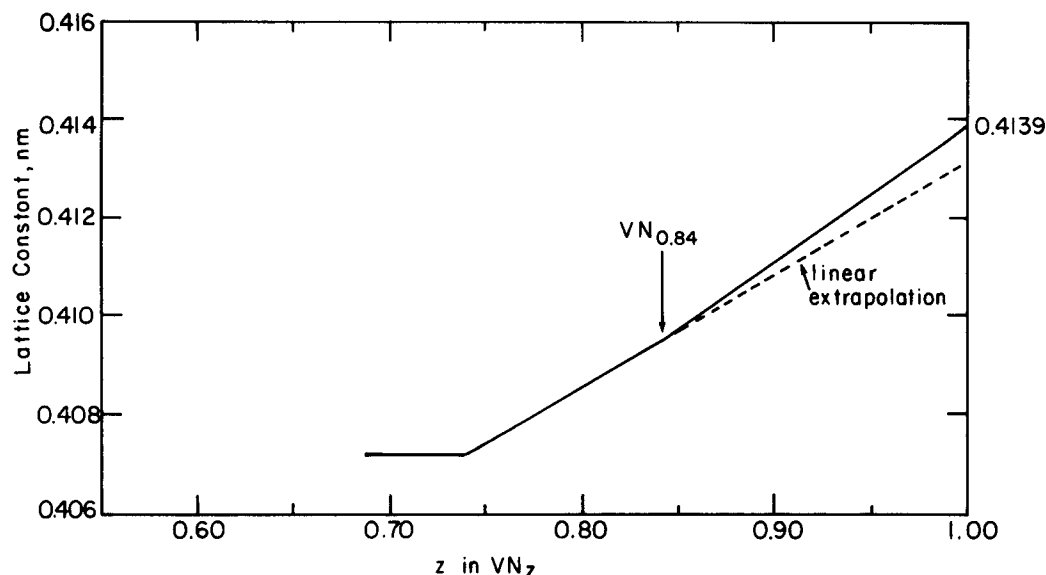

Fig. 3—Plot of lattice parameter *vs* composition for VN_{1-x} phase field from Onozuka.[20]
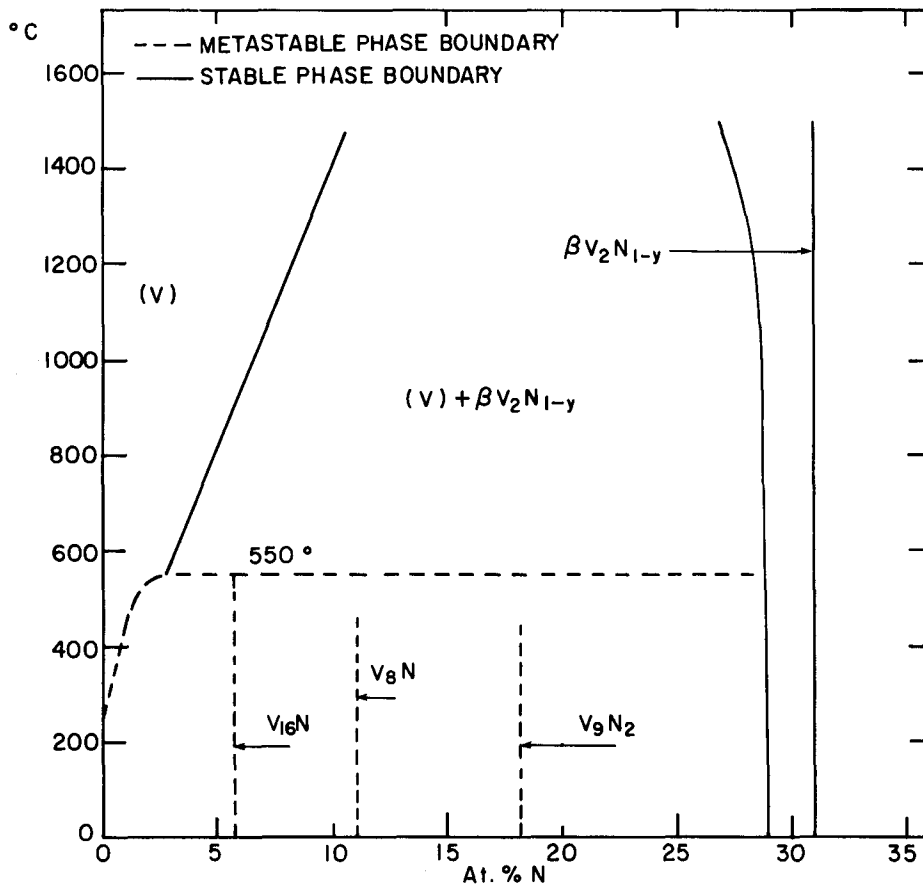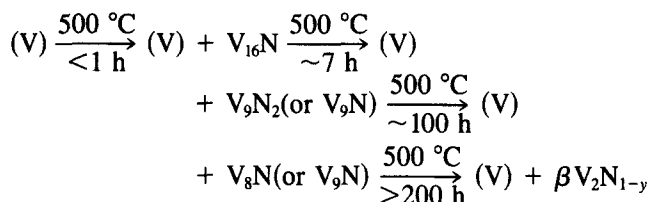
Fig. 4—Metastable phases in vanadium-rich end of V-N system.

and the $\beta V_2 N_{1-y}$ phase. This intermediate phase was indicated to be body-centered tetragonal with $a = 0.2970$ nm and $c = 0.3395$ nm and was formed from an arc-cast and annealed 16 at. pct N alloy. Subsequently, a wide variety of intermediate phases has been reported in this region.[5,6,8,27–36] Reported stoichiometries range through the list previously noted, and the indicated crystal structures are diverse. However, all of the structures that have been reported to date involve ordering of interstitial N atoms in one or another distortion of the lattice of elemental V.

None of these intermediate phases occurs above ~550 °C, and below that temperature the occurrence depends upon time and upon the thermal history of the specimen. A typical sequence of appearance that has been observed[6,30] during aging of a supersaturated terminal solution (V) is as follows:

$$(V) \xrightarrow[<1\ h]{500\ °C} (V) + V_{16}N \xrightarrow[\sim 7\ h]{500\ °C} (V)$$

$$+ V_9N_2(\text{or } V_9N) \xrightarrow[\sim 100\ h]{500\ °C} (V)$$

$$+ V_8N(\text{or } V_9N) \xrightarrow[>200\ h]{500\ °C} (V) + \beta V_2N_{1-y}$$

The inference of metastability for these phases is based on the time dependence, even though cooling to low temperatures can cause persistence for prolonged periods of time. Electron microscopic studies indicate that there are characteristic morphologies associated with the individual phases, and extensive twinning occurs in some of them. This com-

plicates the interpretation of diffraction patterns and has led to some reports of rather large multiple lattice parameters.

Differing thermal histories, aging times, and sample compositions have all contributed to the diverse reports concerning the numbers, structures, and stoichiometries of these metastable phases. For example, Nouet et al.[8] and Potter et al.[6] observed a bct phase in a 10 at. pct N alloy (~V_9N) quenched from 1100 °C or above.

A proposed metastable equilibrium diagram for the vanadium end of the system is given in Figure 4. The solvus representing metastable equilibrium between (V) and $V_{16}N$ is that of Monroe and Cost.[9] The peritectoid horizontal at 550 °C is based on the results of Henry et al.[5] and Epstein et al.[30] in preference to the Hörz[7] value of 500 °C. Three metastable phases, $V_{16}N$, V_8N, and V_9N_2, are represented on the diagram although no attempt is made to designate the temperature ranges over which the latter two exist.

III. CRYSTALLOGRAPHY

A. (V) Phase

Pure V crystallizes in a bcc array with two atoms per unit cell and with $a = 0.30321$ nm.[37] N dissolves interstitially in this structure to expand the lattice. Though the terminal solubility at room temperature is quite limited, lattice parameter measurements on quenched alloys have allowed determination of the compositional dependence over several atomic percent. Results from three investigations are shown

Table I. Coefficients for the Linear Relationships Found by Different Investigators for the Compositional Dependence of the Lattice Parameter for the Terminal Solid Solution of N in V: $a_0 = mc + b$, with a_0 in nm and c in At. Pct N

Comp. Range (At. Pct.)	10^4 m	b	Ref.
0 to 5	4.8	0.30255	7
0 to 8	3.8	0.30273	6
0 to 7	3.2	0.30265	5

Table II. Values of the Slope and Intercept as Found by Various Investigators for the Linear Composition Dependence of the Lattice Parameter of δVN_{1-x}: a_0 (nm) $= mx + b$

Comp. Range (1−x)	Comp. Range (x)	−m	b	Ref.
0.68 to 0.98	0.32 to 0.02	0.0230	0.4137	18
0.72 to 1.00	0.28 to 0.00	0.02629	0.41398	15, 27
0.70 to 1.00	0.30 to 0.00	0.0207	0.4134	1*
0.785 to 0.99	0.215 to 0.01	0.0233	0.4134	38
0.84 to 1.00	0.16 to 0.00	0.0275	0.4139	20

*Hahn's values have been converted from kX units rather than from Å.

in Table I. From the table it may be noted that in all three investigations the compositional trends were found to be linear. The data of Hörz[7] are preferred because of the purity of his material. However, in none of the investigations is the intercept value at pure V as low as the commonly accepted value. This leaves open to question whether there may be some curvature in the lattice parameters vs composition relationship at very low N contents such as was reported by Brauer and Schnell[15] or if this disparity in intercept values may be due to the presence of other impurity species.

B. $\beta V_2 N_{1-y}$

Hahn[1] used X-ray diffraction to examine this phase and found the V sublattice to be adequately described as a hexagonal close-packed array. Weak extra lines from the N sublattice showed that it was necessary to rotate the primary unit cell 30 deg and to expand the a_{hcp} parameter such that $a_\beta = \sqrt{3}\, a_{hcp}$ with $c_\beta = c_{hcp}$. Hahn reported the phase to have a range of homogeneity of $VN_{0.37}$ to $VN_{0.43}$ ($0.26 \geqq y \geqq 0.14$) with $a_\beta = 0.4920$ nm and $c_\beta = 0.4550$ nm at the N-rich boundary and $a_\beta = 0.4913$ nm and $c_\beta = 0.4542$ nm at the V-rich boundary; the temperature for these bounds was not specified. Lattice parameters at intermediate compositions could be fit within experimental scatter by linear dependence upon composition. Hahn's choice of a unit cell has been corroborated by subsequent X-ray,[13,14] electron,[10] and neutron[11] diffraction. With regard to the boundaries of the phase, Khaenko[14] has reported the N-rich composition to be near $VN_{0.46}$ ($y = 0.08$) with little dependence upon temperature, and the V-rich composition was found to vary from near $VN_{0.40}$ ($y = 0.20$) at 700 °C to near $VN_{0.36}$ ($y = 0.28$) at 1500 °C. These boundaries are based upon lattice parameter measurements of quenched specimens with $c_\beta = 0.4547$ nm and $a_\beta = 0.4913$ nm along the N-rich boundary at both 700 °C and 1500 °C and with $c_\beta = 0.4547$ nm and $a_\beta = 0.4907$ nm at 700 °C and $c_\beta = 0.4547$ nm and $a_\beta = 0.4892$ nm at 1500 °C along the V-rich boundary.

The neutron diffraction investigation[11] produced the best resolution of the N atomic positions, and the structure that resulted from this investigation is based upon $\overline{P3}1m$ space group symmetry with

6V in 6(k): $x = 0.323$ $y = 0$ $z = 0.272$

1N in 2(d): $x = \frac{1}{3}$ $y = \frac{2}{3}$ $z = \frac{1}{2}$

2N in 1(a): $x = 0$ $y = 0$ $z = 0$

This structure is of the εFe_2N-type. Deviation from ideal stoichiometry occurs through a defect mechanism with vacant N sites.[13]

C. δVN_{1-x}

There is general agreement that at high temperatures this phase crystallizes with the cubic NaCl-type structure.[1,15,18,20,21,38,39] Composition variation results from variation in the number of vacancies on sites in the N sublattice[13] with x being the fraction of sites vacant. The lattice parameter has been found by all investigators to depend linearly upon composition, and data in Table II illustrate the level of scatter that has been observed among a number of independent investigations. The close agreement of the experimental measurements of Ajami and MacCrone[21] with the earlier measurements of Brauer and Schnell[15] leads to a preference for the relationship

$$a_0 = -0.02629x + 0.41398$$

where a_0 is in nm and x is the value in VN_{1-x}. The temperature dependence of the lattice parameter has been measured for the composition $VN_{0.93}$ by Bogdanov et al.[40] over a temperature range from room temperature to 600 °C. They found

$$a_0(VN_{0.93}) = 0.41293 + 2.886 \times 10^{-6}t + 1.330 \times 10^{-9}t^2$$

with a_0 in nm and t in °C. From this relationship, an expression for the temperature dependence of the linear coefficient of thermal expansion may be derived:

$$\alpha_t(VN_{0.93}) = 6.988 \times 10^{-6} + 6.441 \times 10^{-9}t$$

with α in units of $°C^{-1}$ and t in °C.

D. $\delta' VN_{1-x}$

In Table II it may be noted that the data of Onozuka[20] span only the composition range $0.16 \geqq x \geqq 0.00$. In the range $0.26 \geqq x \geqq 0.16$ he found the lattice parameter to be described by the relationship

$$a_0 = -0.0220x + 0.4130.$$

Thus his plot of a_0 vs x showed a distinct change in slope at $VN_{0.84}$ ($x = 0.16$). Electron diffraction showed that the V-rich region between $0.26 \geqq x \geqq 0.16$ had an ordered arrangement of N atoms that required a doubling of the lattice parameter of the ordinary NaCl-type structure. This result has also been confirmed by X-ray diffraction.[39] Onozuka has proposed a crystal structure based upon space group $P4_2/nmc$ with a total cell occupancy in the eightfold multiple cell of 32 V atoms and 26 N atoms. The proposed positions of the atoms are as follows:
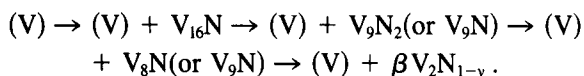
4V in 4(c) with $z = \frac{1}{4}$ 2α N in 2(a)

4V in 4(d) with $z = \frac{1}{4}$ 2β N in 2(b)

8V in 8(e) 4γ N in 4(d) with $z = 0$

8V in 8(g) with $x = \frac{1}{4}$ 8δ N in 8(f) with $x = \frac{1}{4}$

        $z = 0$

                     8η N in 8(g) with $x = \frac{1}{4}$

                            $z = 0$

8V in 8(g) with $x = \frac{1}{4}$

        $z = \frac{1}{2}$

                     8ξ N in 8(g) with $x = \frac{1}{4}$

                            $z = \frac{1}{2}$

Here α, β, γ, δ, η, and ξ represent the occupation probabilities of N atoms on each site and obey the constraint that $\alpha + \beta + 2\gamma + 4\delta + 4\eta + 4\xi = 16(1 - x)$. From the diffraction intensities, values of $\alpha = \xi = 1$, $\beta = \frac{3}{4}$, $\gamma = \delta = \frac{7}{8}$, and $\eta = \frac{1}{2}$ were derived for a composition of $VN_{0.81}$ ($x = 0.19$). Heat capacity anomalies near 520 °C were observed in alloys of compositions in the range $VN_{0.69}$ to $VN_{0.78}$ ($0.31 \geq x \geq 0.22$) but became less distinct in alloys with greater N content. For $x < 0.22$ the temperature associated with an anomaly decreased with increasing N content, and the anomalies no longer were observable with N content above $VN_{0.85}$ ($x \leq 0.15$). Entropy changes inferred from the 520 °C anomalies were found in semiquantitative accord with entropy changes to be expected from the disordering of the proposed ordered structure to produce a disordered NaCl-type structure.

It should be emphasized that, for low values of x, the disordered δVN_{1-x} phase with the NaCl-type structure persists to room temperature and below. A variety of physical measurements indicates that the high-temperature disordered structure is easily retained at room temperature and below for all values of x. Thus, even for higher x values, the ordering kinetics are diffusion controlled and are not rapid.

E. Metastable Phases

In the earlier section on Phase Relations, it was noted that a typical aging sequence below 550 °C of a supersaturated solid solution (V) was as follows:

$$(V) \rightarrow (V) + V_{16}N \rightarrow (V) + V_9N_2(\text{or } V_9N) \rightarrow (V)$$
$$+ V_8N(\text{or } V_9N) \rightarrow (V) + \beta V_2N_{1-y}.$$

Potter et al.[27,28,29] have examined the most V-rich metastable phase in this sequence, and the assignment of stoichiometry of $V_{16}N$ is from their reports. With a phase composition of $\sim$7.4 at. pct N, they found that X-ray patterns indicated a body-centered tetragonal V sublattice with $c_V = 0.300$ nm and $a_V = 0.308$ nm, $c/a = 0.97$. It was further found that the c/a ratio was composition dependent and increased with decreasing N content passing through unity near 6 at. pct N.[27] Electron diffraction studies indicated that ordering of N atoms interacted with the V sublattice to produce twinned arrays with an overall unit cell 16 times larger than the sublattice cell. This supercell was face-centered orthorhombic with $a_S = 1.2140$ nm $\cong 4a_V$, $b_S = 1.2504$ nm $\cong 4a_V$, and $c_S = 0.3035$ nm $\cong c_V$. From

the composition and symmetry, the N atoms were inferred to occupy the 000 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ superlattice sites. Thus the superlattice cell contains 16 subcells with 32 V atoms and 2 N atoms for a net stoichiometry of $V_{16}N$.

Potter and Altstetter[29] have made electron microscopic studies that indicate that formation of this metastable phase was responsible for the deviant solubility boundary observed by Monroe and Cost.[9] It also seems likely that the $V_{13}N$ phase reported by Henry[5] is the $V_{16}N$ phase. Further, it may be noted that the $V_{16}N$ structure is built from an ordering of N atoms in the V sublattice that is only slightly distorted from the elemental structure; this appears to be the case for all of the metastable phases for which any meaningful structural information is available.

Epstein et al.[30] have used electron diffraction to study the structure of the second metastable phase in the foregoing sequence. They found the phase to be body-centered cubic with a V sublattice parameter of $a_V = 0.3046$ nm, which, when combined with the N sublattice, required a supercell with $a_S = 0.9139 \cong 3a_V$. Further investigation[6] of this phase indicated space group symmetry I432. Within symmetry constraints, there are three possibilities for the location of N atoms. One possibility utilizes tetrahedral sites and results in a stoichiometry of V_9N_2. The other two possibilities utilize octahedral sites but result in appreciably different stoichiometries, one with V_9N and the other with V_9N_2. Though there is appreciable difference in the total scattering power from the two different stoichiometries, it proved impossible to select from among the three structures because of the effect on the weak diffraction intensities from displacement fields of the V atoms surrounding each interstitial atom. Epstein et al.[30] have pointed out that there is a phase Ta_9N_2 with N atoms in tetrahedral sites analogous to one of the three possible V_9N_2 structures. Since V and Ta are from the same group in the periodic chart, isomorphism would not be surprising.

The third metastable phase in the foregoing sequence has been examined by Potter et al.[6] with electron and X-ray diffraction and with electron microscopy. They found the base structure to have body-centered tetragonal lattice parameters of $a = 0.3132$ nm and $c = 0.2970$ nm. In consideration of morphological and crystallographic features being analogous to V_9O and with an area fraction analysis indicating a probable composition of 9 to 10 at. pct N, this phase was tentatively assigned a stoichiometry of V_9N. This may be a separate and distinct metastable phase. An alternative possibility, however, for this third metastable phase is one or the other of the V_8N structures that are discussed subsequently.

A variety of other structures and stoichiometries has also been reported. This presumably results from the dynamic nature of the N ordering with dependence upon time, temperature, and composition. Part of the diversity among the reports may be attributable to the proclivity of these structures to twinning and to the development of antiphase boundaries, and part may be due simply to differences in sensitivity of measurement and in the weighting of weak diffraction intensities. As an example, Khaenko and Frenkel[34,36] have observed in quenched and aged alloys in the composition range 5 to 8.5 at. pct N both a tetragonal structure and an orthorhombic structure. Their lattice parameters for the orthorhombic structure nicely match those of Potter et al.[27,28,29] for the phase designated as $V_{16}N$, but

for the tetragonal supercell Khaenko and Frenkel have chosen $a_S = 2\sqrt{2}\ a_V$ and $c_S = c_V$; this looks suspiciously like a difference in the degree of twinning.

On the other hand, Cambini[31] studied specimens that were slowly cooled from 1150 °C rather than quenched and aged. Cambini used X-ray and electron diffraction in combination with electron microscopy and failed to find $V_{16}N$. He did find, however, a precipitate phase with a stoichiometry believed to be V_8N that was dimorphic. His results indicated that both polymorphic forms were based upon a triclinically distorted, pseudo-tetragonal V sublattice with $a_V = b_V = 0.3114$ nm, $c_V = 0.2994$ nm, $\alpha = \beta = 90.5$ deg and $\gamma = 90$ deg. The superlattice parameters of one polymorphic form were $a_S = b_S = 2\sqrt{2}\ a_V$, and $c_S = 2c_V$; the second polymorphic form appeared to be a periodically twinned modification of the first form. Cambini refers to the twinning in this latter structure as "strain-ordered." It may be noted that Galkin et al.[32,35] also have reported an ordered phase with $a_S = b_S = 2\sqrt{2}\ a_V$ and with $c_S = c_V$ but did not report a triclinic deviation from tetragonality. This latter work was done by neutron diffraction, and the structure that was proposed was based upon space group $P4_2/mnm$ with 8V in 8(i) with $x = 0.625$ and $y = 0.125$; 4V in (f) with $x = 0.165$; 4V in 4(f) with $x = 0.379$; and 2N in 2(a) for a net stoichiometry of V_8N.

Nouet et al.[8] have proposed a still different structure for a stoichiometry of V_8N. This structure is based upon X-ray and electron diffraction combined with electron microscopy and has the same lattice parameters as the V_8N structure of Galkin and Vavilova,[32] but the N atoms are located statistically in a fourfold set. Nouet et al.[8] have also reported a phase with V_4N stoichiometry with pseudo- orthorhombic symmetry. When lattice parameters and composition are taken into consideration, their indexing of this orthorhombic cell looks suspiciously like an orthorhombic representation of the hexagonal cell of βV_2N_{1-y}, particularly since they indexed βV_2N_{1-y} on the basis of the V sublattice with $a_V = 0.282$ nm and $c_V = 0.457$ nm, rather than with $a_\beta = 0.488$ nm with $c_\beta = 0.456$ nm.

IV. THERMODYNAMICS

A. δVN_{1-x} Phase

Thermodynamic data for δVN_{1-x} from the period prior to 1975[1,10,15,19,26,41-50] have been reviewed by Chase et al.[51] For the enthalpy of formation of the phase at the stoichiometric limit ($x = 0$), they selected

$$\Delta H^\circ_{f,298} = -108.6 \pm 2.5 \text{ kJ/mol atoms,}$$

and $\quad \Delta H^\circ_{f,0} = -108.1 \pm 2.5$ kJ/mol atoms;

for the absolute entropy at 298 K they selected

$$S^\circ_{298} = 18.64 \pm 0.21 \text{ J/K mol atoms.}$$

It should be noted that the unit of reference is a mole of atoms (g-atom) and not the gram formula weight. The selected values for the enthalpies of formation are based primarily upon the combustion calorimetric measurements of Mah[45] though a second-law value of $\Delta H^\circ_{f,298} = -109.0 \pm 3.1$ kJ/mol atoms from high-temperature effusion-mass spectrometric studies[50] is in good accord. Values for the

enthalpy of formation from an early dissociation pressure measurement,[41] from dissociation pressure measurements off stoichiometry,[15,19] and from emf measurements[48] were not weighted. Modification of $\Delta H^\circ_{f,298}$ to $\Delta H^\circ_{f,0}$ was done with the low temperature heat capacity data of Shomate and Kelley,[43] and the evaluation of S°_{298} was also based on those data. Combination of the absolute entropy, S°_{298}, with absolute entropies for solid V[37] and N_2 gas[52] yields an entropy of formation of $\Delta S^\circ_{f,298} = -44.68 \pm 0.38$ J/(K · mol atoms). Combination of the values for the enthalpy and entropy of formation yields a value for the Gibbs energy of formation of $\Delta G^\circ_{f,298} = -95.3 \pm 2.5$ kJ/mol atoms.

Heat capacity measurements above room temperature have been conducted by King[42] through the range 408 to 1611 K and are the basis for the tabulated values of Chase et al.[51] These tabulated values have been fitted to within the precision of measurement by the relation

$$C_p = 22.589 + 4.718 \times 10^{-3}T$$
$$- 446273T^{-2} \quad \text{J/(K · mol atoms).}$$

Subsequently, Litvinenko et al.[54] measured relative enthalpies by drop calorimetry at several compositions within the range of homogeneity of the phase and at temperatures through the range 400 to 1500 K. Their data have been fitted during the present assessment to the relation

$$H^\circ_T - H^\circ_{298} = (2 - x)^{-1}e^{-0.428x}$$
$$\cdot (43.376T + 5.535 \times 10^{-3}T^2$$
$$+ 772785T^{-1} - 16016) \quad \text{J/mol atoms}$$

and the derivative with respect to temperature is

$$C_p = (2 - x)^{-1}e^{-0.428x}(43.376 + 11.071 \times 10^{-3}T$$
$$- 773785T^{-2}) \quad \text{J/(K · mol atoms).}$$

In these expressions, the value of x is the x in VN_{1-x}. Numerical values from this last expression with $x = 0$ accord within ~1 pct or better at all temperatures of measurement with values from the earlier expression that is based upon King's data. On this basis, the Litvinenko data are accepted as valid for the complete phase field.

Combination of the Litvinenko data for the C_p of VN_{1-x} with C_p data for V[37] and N_2 gas[52] leads to the following:

$$\Delta C_p = (2 - x)^{-1}[e^{-0.428x}(43.376 + 11.071 \times 10^{-3}T$$
$$- 7.738 \times 10^5T^{-2}) - (24.134$$
$$+ 6.196 \times 10^{-3}T - 1.389 \times 10^5T^{-2}$$
$$- 0.7305 \times 10^{-6}T^2) - (1 - x)$$
$$\cdot (11.575 + 6.314 \times 10^{-3}T - 1.147$$
$$\times 10^5T^{-2} - 1.469 \times 10^{-6}T^2)]$$

J/(K · mol atoms) for the temperature range 298 to 900 K, and

$$\Delta C_p = (2 - x)^{-1}[e^{-0.428x}(43.376 + 11.071 \times 10^{-3}T$$
$$- 7.738 \times 10^5T^{-2}) - (25.9$$
$$- 0.125 \times 10^{-3}T + 40.8 \times 10^5T^{-2})$$
$$- (1 - x)(11.575 + 6.314$$
$$\times 10^{-3}T - 1.147 \times 10^5T^{-2}$$
$$- 1.469 \times 10^{-6}T^2)$$

J/(K · mol atoms) for the temperature range 900 to 2000 K. The first relation can be used to convert the 298 K values for ΔH_f° and ΔS_f° at stoichiometry (x = 0) to $\Delta H_{f,900}^\circ$ = −106.9 kJ/mol atoms and $\Delta S_{f,900}^\circ$ = −41.8 J/(K · mol atoms).

A number of measurements have been made of the dissociation pressure for N_2 over δVN_{1-x} at various temperatures and compositions.[15,18–20,44,55] The data are not in complete agreement as can be seen from Figure 5 where values of temperature are plotted vs composition for a dissociation pressure of 1 atm (~1 bar). In this plot the data of Turkdogan and Fenn[44] fall well below the rest of the data. The single point of Onozuka[20] and the single point of Brauer and Schnell[15] are in reasonable accord with the data of Pompe,[55] and the composite line through the points from the three investigations falls very nearly midway between the
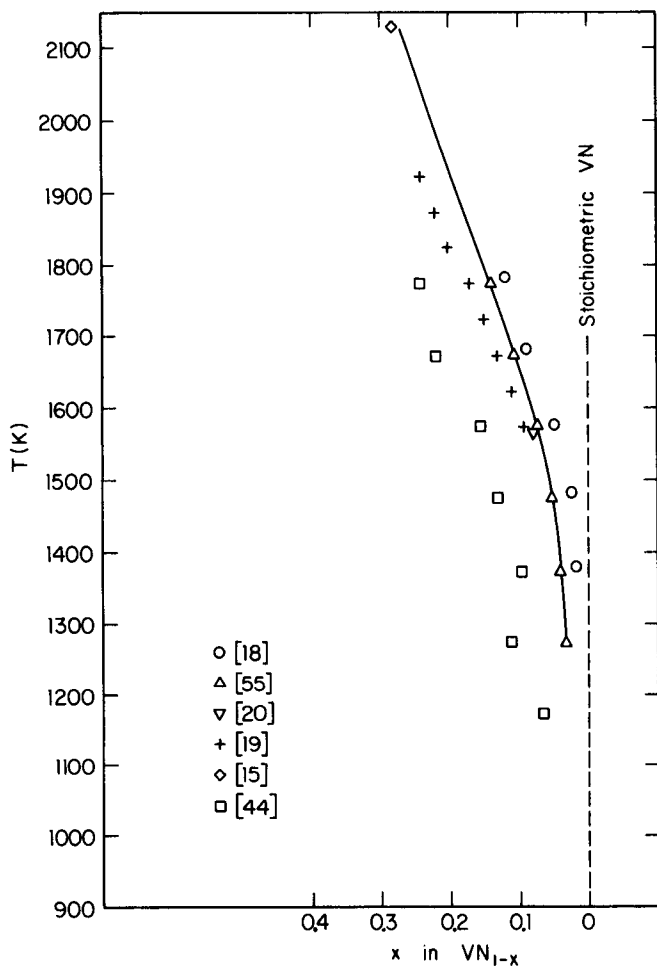

Fig. 5—Comparison of experimental temperature-composition values at which dissociation pressure of δVN_{1-x} is 1 atm (~1 bar).

results of Kieda et al.[18] and of Kozheurov et al.[19] On this basis the data of Pompe are preferred. With $\Delta \overline{G}_N$ = ½RT ln P_{N_2} in the VN_{1-x} solution region, Pompe plotted $\Delta \overline{G}_N$ vs 1/T for a number of compositions to find values of $\Delta \overline{H}_N$ in the temperature range 1223 to 1873 K and in the composition range 0.208 ≧ x ≧ 0.036. His plots showed $\Delta \overline{H}_N$ to be nearly independent of composition and temperature with a value of −155 ± 4 kJ/mol N. Combination of this value with $\Delta G_{f,T}^\circ$ for stoichiometric VN, together with approximation of the entropy of mixing x vacancies and (1 − x) N atoms as ideal, allows estimation of $\Delta G_{f,T}(VN_{1-x})$ at off-stoichiometric compositions:

$$\Delta G_{f,T}(VN_{1-x}) = \Delta G_{f,T}^\circ(VN) + (x/2)155000 + (RT/2)$$
$$\cdot [x \ln x + (1 - x) \ln(1 - x)] \quad J/mol \text{ atoms.}$$

The δVN_{1-x} phase becomes superconducting at low temperatures, and this has led to the measurement of the heat capacities of $VN_{0.74}$ and $VN_{0.89}$ in the temperature range 1.8 to 20 K by Lovtchinov et al.[56] and of VN by Hulm et al.[53] and by Geibel.[57] For all three stoichiometries, it was found that the heat capacity in the normal range could be described by the relation

$$C_p = \gamma T + \beta T^3,$$

and the experimental values of γ and β with the derived densities of electronic states, N_0, and derived Debye temperatures, θ_D, are shown together with the superconducting transition temperatures, T_c, and electron-phonon coupling constants, λ, in Table III.

B. βV_2N_{1-y} Phase

Thermodynamic data for V_2N_{1-y} from the period prior to 1975[15,50,58] have also been reviewed by Chase et al.[51] For the enthalpy of formation of the phase at a stoichiometry of $VN_{0.465}$, Chase et al. selected values of

$$\Delta H_{f,298}^\circ = -90.2 \pm 1.7 \quad kJ/mol \text{ atoms,}$$

$$\Delta H_{f,0}^\circ = -88.8 \pm 1.7 \quad kJ/mol \text{ atoms,}$$

and for the absolute entropy at 298 K they selected

$$S_{298}^\circ = 18.23 \pm 0.03 \quad J/(K \cdot mol \text{ atoms}).$$

Their selected values for the heat capacity in the range 298 to 2800 K can be fitted to better than 0.2 pct at all tabulated points by the relationship

$$C_p = 20.517 + 9.413 \times 10^{-3}T - 3.120 \times 10^5T^{-2}$$
$$- 0.617 \times 10^{-6}T^2$$

in units of J/(K · mol atoms). These selected values are based almost exclusively on the measurements of Pankratz

Table III. Low-Temperature Heat Capacity Parameters and Related Quantities

Stoichiometry	γ mJ/(K^2 mol Atoms)	$10^3\beta$ mJ/(K^4 mol Atoms)	T_c (K)	λ	θ_D (K)	N_0 States/eV per V Atom	Ref.
$VN_{0.74}$	5.95	8.65	1.8	0.440	608	0.88	56
$VN_{0.89}$	7.4	24.1	6.0	0.607	432	0.98	56
VN	8.60	26.2	8.5	0.614	420	1.13	53
VN	9.1	21.3	9.2	—	450	—	57

et al.,[58] who performed low-temperature heat capacity measurements, high-temperature enthalpy measurements, and combustion calorimetric measurements on samples of the same material. The composition of this material was determined by chemical analysis as $VN_{0.465}$ and was indicated to be the nitrogen-rich boundary of the phase. The selected value for the absolute entropy when combined with data for V^{37} and for N_2 gas[52] yields

$$\Delta S^{\circ}_{f,298} = -33.24 \quad J/(K \cdot \text{mol atoms}),$$

and union of this value of $\Delta S^{\circ}_{f,298}$ with the foregoing value of $\Delta H^{\circ}_{f,298}$ produces $\Delta G^{\circ}_{f,298} = -80.3$ kJ/mol atoms. Furthermore, combination of the above heat capacity relationship with corresponding values for V^{37} and for $N_2{}^{52}$ yields for $VN_{0.465}$,

$$\Delta C_p = 0.369 + 3.237 \times 10^{-3}T - 2.535 \times 10^5 T^{-2}$$
$$-11.382 \times 10^{-6}T^2,$$

in units of $J/(K \cdot \text{mol atoms})$ for the temperature range 298 to 900 K and,

$$\Delta C_p = -0.836 + 8.319 \times 10^{-3}T - 3.483 \times 10^5 T^{-2}$$
$$-64.03 \times 10^{-6}T^2,$$

in the temperature range 900 to 2000 K, again in units of $J/(K \cdot \text{mol atoms})$. For convenience, the first expression has been used to convert values of ΔH°_f and ΔS°_f from 298 K to 900 K: $\Delta H^{\circ}_{f,900} = -92.0$ kJ/mol atoms and $\Delta S^{\circ}_{f,900} = -36.3$ J/(K $\cdot$ mol atoms). These values lead to $\Delta G^{\circ}_{f,900} = -59.3$ kJ/mol atoms, which can be extended to $\Delta G^{\circ}_{f,1073} = -53.1$ kJ/mol atoms. This latter value implies that the value of $\Delta G^{\circ}_{f,1073} = -31.3$ kJ/mol atom for $VN_{0.42}$ from Gridnev *et al.*[59] is insufficiently negative.

The only thermodynamic measurements on this phase at a stoichiometry other than $VN_{0.465}$ or $VN_{0.42}$ are those of Brauer and Schnell[15] who measured the dissociation pressure of $VN_{0.43}$ in the temperature range 1300 to 1600 °C. The relationship for the dissociation pressure,

$$\ln P(\text{atm}) = -(2.18 \times 10^4/T) + 4.57,$$

can be generated from their graph of dissociation pressure *vs* reciprocal temperature. Comparison of dissociation pressures from this relationship with dissociation pressures found by Kozheurov *et al.*[19] along the V-rich boundary of the δVN_{1-x} phase shows the Brauer and Schnell values to be about an order of magnitude lower than those of Kozheurov *et al.* When it is recognized that the data of Kozheurov *et al.* are themselves higher than most other data for δVN_{1-x} and that the dissociation pressures for the two phases must be equal in the intermediate two-phase region, the comparison furnishes additional support for selecting the Pompe data[55] for the dissociation pressures of VN_{1-x}.

C. *Liquid*

Revyakin and Kozina[60] have reported nitrogen pressures over liquid solutions of nitrogen in V at 1930 °C (2203 K) for compositions below 23 at. pct N. Their results can be converted to partial molar Gibbs energies through the relation $\Delta \overline{G}_N = \frac{1}{2}RT \ln P_{N_2}$. From their published graph, the data in Table IV have been inferred. Comparison of these nitrogen pressures with those of Farber and Srivastava[50]

Table IV. Nitrogen Pressures and Partial Molar Gibbs Energies at 1930 °C (2203 K) for Liquid Alloys of N in V.[60]

Comp. (At. Pct N)	$P_{N_2}^{1/2}$ (atm$^{1/2}$)	$-\Delta \overline{G}_N$ (kJ/mol N)
2.5	0.019	73
5.0	0.039	59
7.5	0.057	52
10.0	0.075	47
12.5	0.118	39
15.0	0.161	33
20.0	0.251	25

imply that either these pressures are high or the Farber-Srivastava data are low, with the difference being about one order of magnitude.

REFERENCES

1. H. Hahn: *Z. Anorg. Chem.*, 1949, vol. 258, pp. 58-68.
2. E. Friederich and L. Sittig: *Z. Anorg. Chem.*, 1925, vol. 143, pp. 303-07.
3. W. Muthmann, L. Weiss, and R. Riedelbauch: *Justus Liebigs Ann. Chem.*, 1907, vol. 355, pp. 59-99.
4. G. Hörz: *Z. metallkd.*, 1971, vol. 62, pp. 208-16.
5. J. L. Henry, S. A. O'Hare, R. A. McCune, and M. P. Krug: *J. Less-Common Met.*, 1971, vol. 25, pp. 39-47.
6. D. I. Potter, H. D. Epstein, and B. M. Goldstein: *Metall. Trans.*, 1974, vol. 5, pp. 2075-82.
7. G. Hörz: *J. Less-Common Met.*, 1974, vol. 35, pp. 207-25.
8. G. Nouet and J. Vicens: *Phys. Status Solidi (a)*, 1980, vol. 62, pp. 449-57.
9. R. M. Monroe and J. R. Cost: *Trans. AIME*, 1969, vol. 245, pp. 1079-82.
10. D. Potter and R. Geils: *Scr. Metall.*, 1972, vol. 6, pp. 395-98.
11. A. N. Christensen and B. Lebech: *Acta Cryst.*, 1979, vol. B35, pp. 2677-78.
12. W. B. Pearson: *Handbook of Lattice Spacings and Structures of Metals*, Pergamon Press, New York, NY, 1967, vol. 2, p. 447.
13. M. P. Arbuzov, B. V. Khaenko, and O. A. Frenkel: *Inorg. Mater.*, 1975, vol. 11, pp. 236-41.
14. B. V. Khaenko and V. G. Fak: *Inorg. Mater.*, 1978, vol. 14, pp. 1011-16.
15. G. Brauer and W. D. Schnell: *J. Less-Common Met.*, 1964, vol. 6, pp. 326-32.
16. E. Fromm and E. Gebhardt: *Gase und Kohlenstoff in Metallen*, Springer-Verlag, Berlin, 1976, pp. 444-46.
17. Yu. V. Levinskii: *Izv. Akad, Nauk SSSR, Metall.*, 1974, vol. 1, pp. 52-55.
18. N. Kieda, K. Uematsu, N. Mizutani, and M. Kato: *J. Less-Common Met.*, 1984, vol. 99, pp 131-35.

19. V. A. Kozheurov, V. M. Zhikharev, V. I. Shishkov, and G. V. Gritshina: *Izv. Vyssh. Ucheb. Zaved., Chern. Met.*, 1972, vol. (8), pp. 10-13.
20. T. Onozuka: *J. Appl. Cryst.*, 1978, vol. 11, p. 132.
21. F. I. Ajami and R. K. MacCrone: *J. Phys. Chem. Solids*, 1975, vol. 36, pp. 7-15.
22. P. Ettmayer, R. Kieffer, and F. Hattinger: *Metall.*, 1974, vol. 28, pp. 1151-55.
23. L. Glasser and J. Hoy: *J. Phys. Chem.*, 1966, vol. 70, p. 281.
24. E. Q. Vintaikin, V. B. Dimitriev, I. A. Tomlin, and A. G. Shchurik: *Dokl. Akad. Nauk SSSR*, 1970, vol. 193, pp. 1022-24.
25. A. F. Shevakin, I. A. Tomlin, and V. I. Serrak: *Phys. Met. Metall.*, 1971, vol. 32, pp. 85-89.
26. W. Rostoker and A. Yamamoto: *Trans. Am. Soc. Met.*, 1954, vol. 46, pp. 1136-63.
27. D. Potter and C. Altstetter: *Acta Metall.*, 1971, vol. 19, pp. 881-86.
28. D. Potter and C. Altstetter: *Acta Metall.*, 1972, vol. 20, pp. 313-18.
29. D. Potter and C. Altstetter: *Mater. Sci. Eng.*, 1972, vol. 9, pp. 43-46.
30. H. Epstein, B. Goldstein, and D. Potter: *Scr. Metall.*, 1973, vol. 7, pp. 717-20.
31. M. Cambini: *Mater. Res. Bull.*, 1974, vol. 9, pp. 1469-80.
32. L. N. Galkin and V. V. Vavilova: *Dokl. Akad. Nauk SSSR*, 1977, vol. 233(1), pp. 106-07.
33. B. V. Khaenko: *Dopov. Akad. Nauk Ukr. RSR*, 1977, vol. A(3), pp. 275-79.
34. B. V. Khaenko and O. A. Frenkel: *Phys. Met. Metall.*, 1977, vol. 44, pp. 84-94.
35. L. N. Galkin, V. V. Vavilova, and L. Ye. Fykin: *Phys. Met. Metall.*, 1979, vol. 45, pp. 67-71.
36. B. V. Khaenko: *Phys. Met. Metall.*, 1979, vol. 45, pp. 188-90.
37. J. F. Smith: *Bull. Alloy Phase Diagrams*, 1981, vol. 2, pp. 40-41, 172.
38. L. E. Toth, C. P. Wang, and C. M. Yen: *Acta Metall.*, 1966, vol. 14, pp. 1403-08.
39. B. V. Khaenko: *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1979, vol. 15, p. 1952. Engl. Transl: *Inorg. Mater.*, 1979, vol. 15, pp. 1535-43.
40. V. S. Bogdanov, V. S. Neshpor, Yu. D. Kondrashev, A. B. Goncharuk, and A. N. Pityulin: *Poroshk. Metall.*, 1982, no. 5, p. 79; Engl. Transl., 1982, vol. 233, pp. 412-16.
41. R. E. Slade and G. T. Higson: *J. Chem. Soc. (London)*, 1919, vol. 115, pp. 215-16.
42. E. G. King: *J. Am. Chem. Soc.*, 1949, vol. 71, pp. 316-17.
43. C. H. Shomate and K. K. Kelley: *J. Am. Chem. Soc.*, 1949, vol. 71, pp. 314-15.
44. E. T. Turkdogan and E. M. Fenn: *J. Iron and Steel Inst. London*, 1955, vol. 181, pp. 343-44.
45. A. D. Mah: U.S. Bur. of Mines Rep. Invest. No. 6177, 1963.
46. E. K. Storms: U.S. Gov't. Rep. No. LA-2942, 1964, pp. 136-41.
47. A. D. Mah: U.S. Bur. of Mines Rep. Invest. No. 6727, 1966.
48. V. V. Voleinik and B. A. Shabdenov: *Fiz. Khim. Electrokhim. Rasplov. Solei, Shlavkov*, 1969, vol. (1), pp. 157-62.
49. V. A. Kozheurov, V. M. Zhikharev, and V. I. Shishkov: *Izv. Vyssh. Ucheb. Zaved. Chern., Met.*, 1972, vol. (12), pp. 76-80.
50. M. Farber and R. D. Srivastava: *J. Chem. Soc., London, Faraday Trans.*, 1973, vol. 69, pp. 390-98.
51. M. W. Chase, J. L. Curnutt, H. Prophet, R. A. McDonald, and A. N. Syverud: "JANAF Thermodynamic Tables 1975 Supplement," *J. Phys. Chem. Ref. Data*, 1975, vol. 4, pp. 117-19.
52. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman: *Selected Values of the Thermodynamic Properties of the Elements*, ASM, Metals Park, OH, 1973, pp. 318-22.
53. J. K. Hulm, M. S. Walker, and N. Pessall: *Physica*, 1971, vol. 55, pp. 60-68.
54. V. F. Litvinenko, A. S. Bolgar, V. I. Kas'yan, L. K. Shvedova, and J. J. Timofeeva: *Poroshk. Metall.*, 1980, no. 2, p. 46; Engl. Transl., 1980, vol. 206, pp. 109-12.
55. R. Pompe: *Thermochim. Acta*, 1982, vol. 57, pp. 273-81.
56. V. Lovtchinov, H. Madge, and A. N. Christensen: *Phys. Status Solidi (b)*, 1980, vol. 97, pp. 457-61.
57. C. Geibel: Ph.D. Thesis, Univ. of Karlsruhe, 1981; quoted in H. L. Luo, S. A. Wolf, W. W. Fuller, A. S. Edelstein, and C. Y. Huang: *Phys. Rev.*, 1984, vol. B29, pp. 1443-46.
58. L. B. Pankratz, J. M. Stuve, H. O. Poppleton, L. L. Oden, and A. D. Mah: U.S. Bur. Mines Rep. Invest. No. 7585, 1971.
59. V. N. Gridnev, V. G. Ivanchenko, and V. K. Sulzhenko: *Russ. Metall.*, 1983, vol. (3), pp. 184-87.
60. A. V. Revyakin and L. N. Kozina: *Russ. Metall.*, 1973, vol. (2), pp. 51-53.