Solubility of Nitrogen in Austenitic Iron under High Nitrogen Pressure and Thermodynamic Properties of Iron-Nitrogen Interstitial Solid Solution

Solubility of Nitrogen in Austenitic Iron under High Nitrogen Pressure and Thermodynamic Properties of Iron-Nitrogen Interstitial Solid Solution*

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Synopsis

Studies on the equilibrium between austenitic iron and nitrogen under various conditions of the maximum pressure of 920 kg/cm² and the temperature range from 950° to 1300°C were carried out by using a high temperature and high pressure equipment. It was shown that the concentration of nitrogen in austenite deviated from Sieverts' law with increasing pressure. The casue for such discrepancy was considered thermodynamically and statistically. That is, the experimental result can reasonably be explained from the geometrical consideration that the chemical potential of a nitrogen atom in austenite, in case of a high nitrogen content deviates remarkably from that in an idial random interstitial solid solution, since each intestitial atom added excludes other interstitial atoms from the seven adjacent sites. Thus, the activity of nitrogen in austenitic iron can be expressed by the following equations:

$$\log a_{\mathrm{N}} = \log \frac{N_{\mathrm{N}}}{1 - 9 N_{\mathrm{N}}} + 3.34 - \frac{427}{T}$$ for the standard state of nitrogen gas 1 atm pressure, $a_{\mathrm{N}} = f_{\mathrm{N}_2}^{1/2}$.

$$\log a_{\mathrm{N}} = \log \frac{N_{\mathrm{N}}}{1 - 9 N_{\mathrm{N}}}$$ for the standard state of infinitely dilute solid solution.

I. Introduction

Nitrogen atom, like carbon, dissolves interstitially in the iron lattice and has various effects on the properties of iron. The thermodynamic properties of the iron-carbon interstitial solid solution have been statistically and thermodynamically investigated by many investigators. In contrast, studies of thermodynamic properties of the iron-nitrogen interstitial solid solution have been limited only in the low concentration of nitrogen because of the low solubility of nitrogen at 1 atmospheric pressure. Attempts of further investigations in the high concentration of nitrogen should inevitably encounter extreme difficulties incidental to the experimental techniques in the highly compressed nitrogen gas.

Studies of the nitrogen solubility in austenitic iron have mostly been made under a pressure below 760 mm Hg (1 atm). The pressure dependence of the

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nitrogen solubility was first studied by Sieverts,[1] with an eventual establishment of Sieverts' law which asserts that the solubility of nitrogen is proportional to the square root of pressure. This theory has further been confirmed by the relevant studies of Mori et al.[2] and of Schenck et al.[3]

Recently, Schenck et al.[4] have reported the validity of Sieverts' law in the pressure range up to 65 atm, but in their cases the atomic fraction of nitrogen in austenitic iron was only about 0.005. So, in the present study, the solubility of nitrogen in austenitic iron was measured in the range of temperature from 950° to 1300°C and pressure up to 920 kg/cm². Measurements were made using the high temperature and high pressure equipment described in the previous report[5] and the statistical thermodynamic discussions were made on the iron-nitrogen interstitial solid solution.

II. Materials and experimental procedures

The pure iron ingot prepared by electron beam melting of electrolytic iron was hot-forged and swaged, and made into a bar of 10 mm in diameter by use of the centerless grinding. This bar was refined by zone melting once in argon and four times in the hydrogen gas at the rate of 1 mm/min, and then cold-swaged and drawn into wires of 0.3 and 0.5 mm in diameter. In the final process, these wires were annealed in a dry hydrogen gas at 1000°C for one hour. The chemical compositions of the iron are shown in Table 1.

Table 1. Chemical compositions of iron used.

	C	Si	Mn	P	S	Cu	W	O	H
High pure iron	<0.001	Tr	0.001	0.002	Tr	0.005	0.001	0.0011	<0.0001

The high pressure and high temperature equipment employed in the present study was the furnace of direct heating type reported in the previous paper.[5] The wire specimen was made in a shape of spiral of an outside diameter of 4 mm and heated by flowing an electric current directly. The temperature was measured by the Pt-Pt·Rh thermocouples (0.03 mmϕ) spot-welded at two points of spiral. The accuracy of temperature measurement was about ±5°C at low pressure and about ±10°C at high pressure, and the error of pressure measurement was less than 0.3%.

(1) A. Sieverts, Z. Phys. Chem., **A155** (1931), 211.

(2) T. Mori, K. Shinmyo, E. Ichise and S. Koyama, J. Japan Inst. Metals, **29** (1965), 1001 (in Japanese).

(3) H. Schenck, M.G. Froberg and F. Reinders, Stahl u. Eisen, **83** (1963), 93.

(4) H. Schenck, M.G. Froberg and W. Kranz, Arch. Eisenhütt., **34** (1963), 825.

(5) T. Masumoto, M. Naka and Y. Imai, J. Japan Inst. Metals, **34** (1970), 188 (in Japanese).

After the pressure was attained to a desired level and the residue of oxygen was eliminated from the nitrogen gas by heating sodium metal, the specimen was heated for a required time at a desired temperature. The heating time was settled at about 5 times of the equilibrium time estimated from the diffusibility of nitrogen in iron (e.g., 30 min at 1300°C to 5 hr at 1000°C). After heating, the electric current was switched off and the specimen was cooled (the cooling rate was about 500°C/sec between 300° and 1300°C, and higher at higher pressures). The nitrogen content in the specimen was determined by averaging the results of analyses repeated for several times. The denitrogenization during cooling was examined by observing the state of dispersion of nitrides in specimen aged at low temperatures. The experimental result revealed that the structure was uniform at the surface and the interior, showing that the denitrogenization was almost negligible. The analysis of nitrogen in iron was carried out by the micro-Kjeldahl method, i.e., the dissolution of the specimen in sulfuric acid followed by the distillation and Nessler color comparison. The accuracy of analysis was about ±0.01 wt% for 0.2 wt% of nitrogen

III. Experimental results

By the above-mentioned methods, the solubility of nitrogen in austenitic iron was measured in the temperature range from 950° to 1300°C and the pressure up to maximum 920 kg/cm². The results are shown in Table 2. The relationships

Table 2. Experimenal results of nitrogen contents in iron under various conditions of pressure and temperature.

Temperature °C	Pressure kg/cm²	Nitrogen wt%	Temperature °C	Pressure kg/cm²	Nitrogen wt%
950	50	0.196		700	0.549
	95	0.238		920	0.659
	250	0.370			
	300	0.400	1050	100	0.208
	350	0.444			
	400	0.483	1100	50	0.180
	450	0.470		100	0.205
	500	0.508		200	0.278
	550	0.482		300	0.345
	600	0.536			
	650	0.534	1150	100	0.209
	700	0.623			
	800	0.656	1200	50	0.127
				95	0.199
1000	40	0.136		200	0.305
	100	0.224			
	205	0.341	1250	100	0.240
	320	0.393			
	400	0.452	1300	50	0.159
	500	0.516		100	0.211
	500	0.486			
	600	0.527			

between the nitrogen content in iron and the square root of nitrogen pressure at 950°, 1000° and 1100°C are shown in Figs. 1, 2 and 3, respectively. In Fig. 4 is shown the temperature dependence of the nitrogen content in austenitic iron under various pressures. The dashed lines in Fig. 1 to Fig. 3 represent the extrapolation of values obtained from the experimental results at 1 atm by Darken et al.,[6]
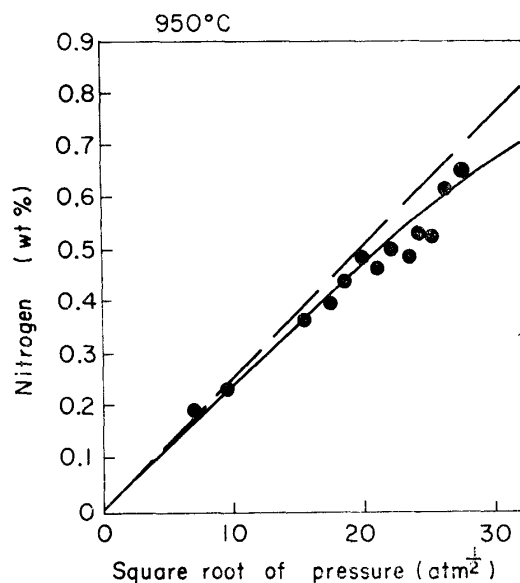

Fig. 1. Relationship between the introgen content and the square root of nitrogen pressure for iron at 950°C
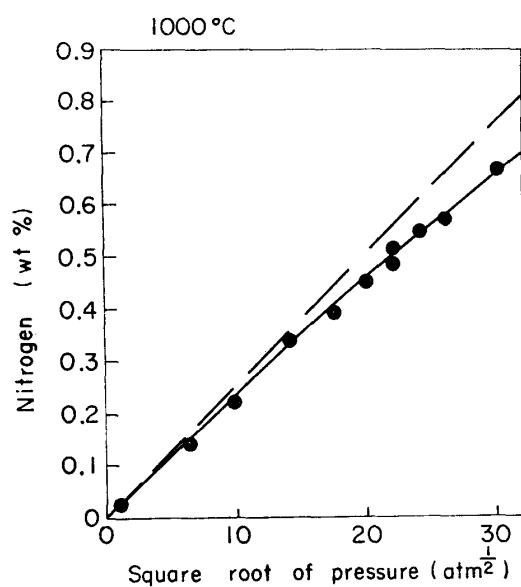

Fig. 2.   Fig. 3.

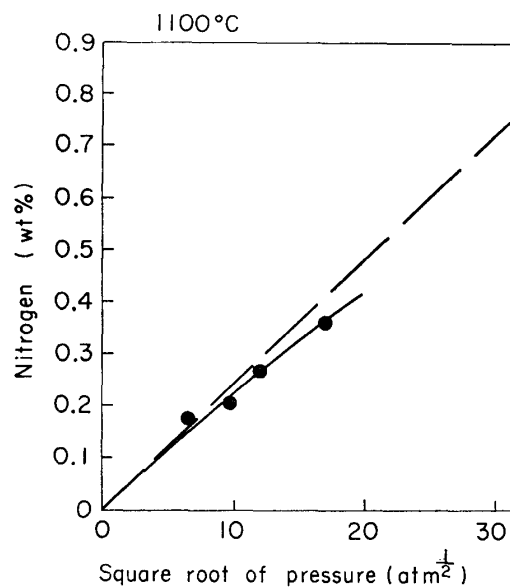Fig. 2. Relationship between the nitrogen content and the square root of nitrogen pressure for pure iron at 1000°C.

Fig. 3. Relationship between the nitrogen content and the square root of nitrogen pressure for pure iron at 1100°C.

(6)   L.S. Darken, R.P. Smith and C.W. Filer, Trans. Met. Soc. AIME, **191** (1951), 1174.

i.e., $\log[\%N]/\sqrt{\overline{P_{N_2}}}=0.0404-1.2\times10^{-5}\,T$. The data plotted in these figures show the tendencies of distinct deviation from the extrapolated line from the nitrogen solubility below 1 atm to the lower nitrogen side with increasing pressure. Fig. 4 also shows the temperature dependence of the nitrogen solubility. This dependence is approximately linear without the influence of pressure, suggesting that the enthalpy of solubility of nitrogen in austenitic iron would not be affected by pressure.
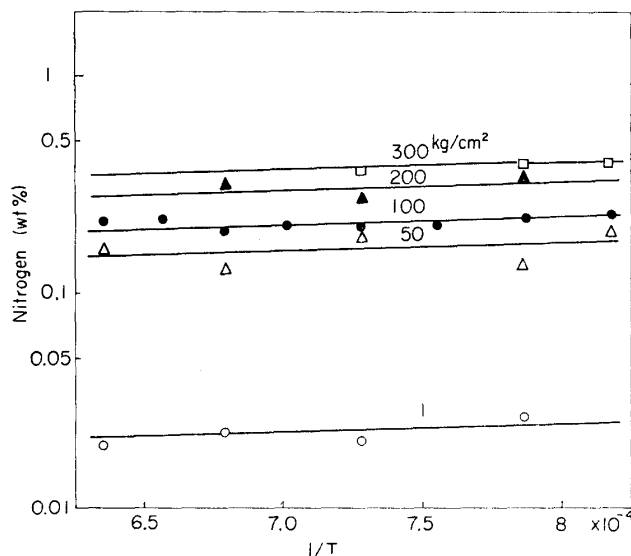

Fig. 4. Temperature dependence of nitrogen content in austenite of iron under various pressures.

IV. Discussion

The experimental results show that the deviation from Sieverts' law becomes greater with increasing pressure. For the reason of this deviation, the following three factors may be taken into consideration.

(1) Variation of the solubility of nitrogen in iron due to compression.

(2) Deviations from ideal state of gas at high pressures.

(3) Interaction between solute nitrogen atoms in high concentrated solid solution.

These factors are discussed in the following descriptions.

1. Variation of the solubility of nitrogen in solid due to compression

At a constant temperature and pressure, the equilibrium between the nitrogen gas and the austenite phase can be expressed as

$$\mu_N^{\gamma} = 1/2\mu_{N_2}^g \tag{1}$$

where μ_N^{γ} is the chemical potential of a nitrogen atom in austenitic iron and $\mu_{N_2}^g$ the chemical potential of a nitrogen molecule in nitrogen gas.

Then, the chemical potential of a nitrogen atom in the austenite can be also written as

$$\mu_N^\gamma = \mu_N^{o\gamma} + RT \ln \gamma_N N_N \tag{2}$$

where $\mu_N^{o\gamma}$ is the chemical potential of a nitrogen atom in the standard state of imaginary solid solution when the atomic fraction of nitrogen N_N and the activity coefficient of nitrogen in the solid solution γ_N would be 1. From Eqs. (1) and (2), the following equation can be derived;

$$\ln \gamma_N N_N = \frac{1}{RT} \left(\frac{1}{2} \mu_N^g - \mu_N^{o\gamma} \right) \tag{3}$$

If the pressure is changed keeping an equilibrium state, this equation becomes as

$$\left(\frac{\partial \ln \gamma_N N_N}{\partial P} \right)_{T,eq} = \frac{1}{RT} \left[\frac{1}{2} \left(\frac{\partial \mu_{N_2}^g}{\partial P} \right)_T - \left(\frac{\partial \mu_N^{o\gamma}}{\partial P} \right)_T \right] \tag{4}$$

If γ_N would not vary with pressure, $(\partial \mu_N^{o\gamma}/\partial P)_T = \bar{v}_N^\gamma$ and $(\partial \mu_{N_2}^g/\partial P)_T = v_{N_2}$, where $\bar{v}_N^\gamma$ is the partial molar volume of nitrogen in austenite, and v_{N_2} is the molar volume of nitrogen gas. Hence Eq. (4) can be written

$$\left(\frac{\partial \ln N_N}{\partial P} \right)_T = \frac{1}{RT} \left(\frac{v_{N_2}}{2} - \bar{v}_N^\gamma \right) \tag{5}$$

The decrease of the nitrogen content at 1000°C and 1000 atm which is calculated by Eq. (5) on the assumption that $\bar{v}_N^\gamma$ is equal to $\bar{v}_C^\gamma$ (4.47 cc at 725°C) of the partial molar volume of carbon in austenite,[7] is about 0.0016 wt% of nitrogen. This fact indicates that the effect of pressure on the solubility up to an order of 1000 atm can be ignored.

2. Deviations from ideal state of gas at high pressure

Considering the deviation from ideal gas state at high pressures, the fugacity (f) must be taken into account in place of pressures in the thermodynamic equations dealing with the equilibrium state. Of the various methods for obtaining the fugacity, the most simple Newton's law[8] was employed in this study.

By the rule of corresponding states, the activity coefficient of gas (f/P) can be represented as the common function of the reduced variables instead of pressures and temperatures in all gases. Accordingly, the fugacity of nitrogen at various temperatures and pressures were obtained, using the Newton's curves relating the activity coefficient of gas to the reduced temperature (Tr) and the reduced pressure (Pr), which are ratios to the critical pressure and temperature of nitrogen, respectively. The results represented in Table 3 show that the values of fugacity are higher than those of observed pressure at each temperature, and that the chemical potential of the actual gas is higher than that of the ideal one. It is,

(7) J.E. Hillard, Trans. Met. Soc. AIME, **227** (1963), 429.

(8) R.H. Newton, Ind. Eng. Chem., **27** (1935), 302.

Table 3. Activity coefficient of nitrogen and fugacity calculated
from experimental results.

Temperature °C	Pressure atm	Activity Coef.	Fugacity atm	Temperature °C	Pressure atm	Activity Coef.	Fugacity atm
950	48	1.01	49		310	1.10	341
	92	1.02	94		387	1.12	433
	242	1.08	261		484	1.16	561
	290	1.09	316		581	1.19	691
	339	1.11	376		677	1.22	826
	387	1.13	437		890	1.30	1157
	436	1.15	501				
	484	1.17	566	1100	48	1.01	49
	532	1.18	628		97	1.03	100
	581	1.20	697		194	1.05	204
	629	1.21	761		290	1.07	310
	677	1.24	839				
	774	1.27	983	1200	48	1.01	49
					92	1.02	94
1000	39	1.00	39		194	1.05	204
	97	1.03	100		48		
	198	1.06	210	1300	97	1.00	48
						1.02	99

therefore, considered that the deviations from ideality cause to increase the nitrogen content in iron. In actual cases, however, the solubility in iron decreases with increasing pressure in contradistinction to the indications of fugacity.

3. Interaction between solute nitrogen atoms in high concentrated solid solution

The thermodynamic properties of the high concentrated solid solution deviate from ideality, because the interaction between solute atoms in the solid solution becomes significant with the increase of solute atoms. Such instances of the deviation from Sieverts' law have shown in the experiments of high concentrated hydrogen-metal solid solutions.[9] These effects of increased solute atoms are discussed in the following.

In view of the non-ideality of compressed gas, the effects of nitrogen pressure illustrated in Figs. 1 and 2 are re-expressed as functions of the fugacity (f) in Figs. 5 and 6, respectively, (the dashed line denotes the extrapolation of nitrogen solubility from 1 atm to higher pressure).

In discussing the deviations of solid solution from ideal behavior, there are two models that can be divided into the geometric and energetic considerations. The former group applied by Saito,[10] Takeuchi,[11] Darken,[12] and Machlin[13]

(9)   A.D. McQuillan, *Phase Stability of Metals and Alloys*, (1966), 375.
(10) K. Saito, *Application of Statistical Thermodynamics to Metallurgy*, (1964), 175 (in Japanese).
(11) S. Takeuchi and S. Kachi, J. Japan Inst. Metals, **14** (1950), 7 (in Japanese).
(12) L.S. Darken, J. Amer. Chem. Soc., **68** (1946), 1163.
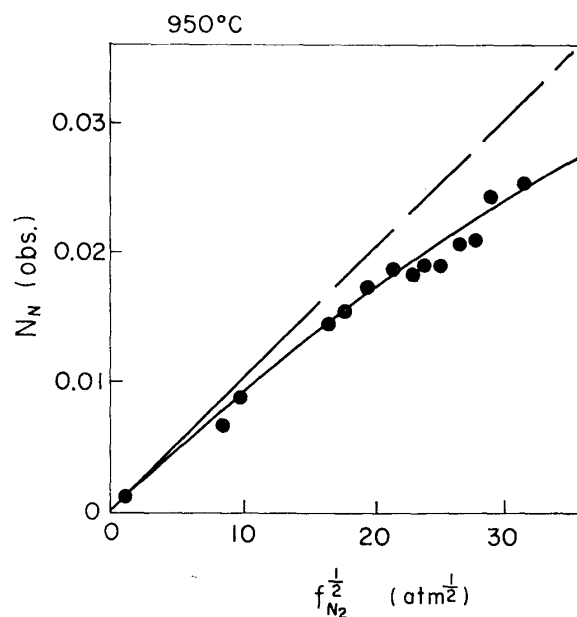(13) E.S. Machlin, Trans. Met. Soc. AIME, **242** (1968), 1845.

Fig. 5. Relationship between the atomic fraction of nitrogen and the square root of fugacity for pure iron at 950°C.
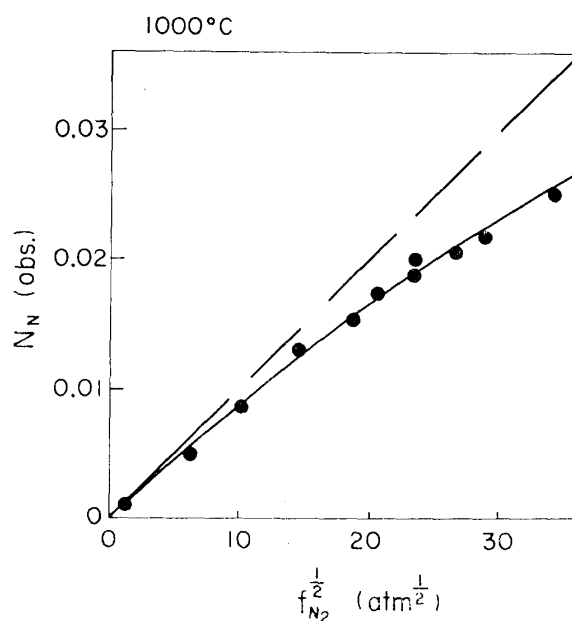

Fig. 6. Relationship between the atomic fraction of nitrogen and the square root fugacity for pure iron at 1000°C.

represents the statistical thermodynamic treatment of the assumed concentration dependence of partial energy of solute atoms and the latter group applied by Spesier,[14] Mclellan[15] and Bodsworth[16] represents the treatment on the

(14) R. Speiser and J.W. Spretnak, Trans. ASM, **47** (1955), 493.

(15) R.B. Mclellan, J.L. Garrard, S.J. Horowitz and J.A. Sprague, Trans. Met. Soc. AIME, **239** (1967), 528.

(16) C. Bodsworth, I.M. Davidson and D. Atkinson, Trans. Met. Soc. AIME, **242** (1968), 1136.

assumed concentration dependence of non-random configurational entropy in the solid solution. Even in Darken's energetic model, there was a repulsive force between carbon atoms in austenite which was presumed to reduce the number of C-C pairs in the Fe-C system below that corresponding to a random distribution. Alternatively, the deviation from ideality was also explained from the concentration dependence of non-random configurational entropy in the Fe-C system by Mclellan et al.[15] and in the βZr-H, Nb-H and Ta-H system by Oates et al.[17] The discussion in the present study is mainly based on the geometric model.

Supposing that interstitial solute atoms occupy only the octahedral interstitial sites in the fcc lattice[18] and that the occupancy of an interstitial site by a nitrogen atom excludes (Z-1) in the number of surrounding octahedral sites from being occupied by other nitrogen atoms because of the repulsion between nitrogen atoms, the number of configurations W, according to Speiser and Spretnak,[14] is

$$W = \frac{n_{Fe}(n_{Fe}-Z)(n_{Fe}-2Z)\cdots\cdots(n_{Fe}-(n_N-1)Z)}{n_N!} \tag{6}$$

where n_{Fe} and n_N are the numbers of iron atoms and nitrogen atoms, respectively. The configurational entropy of the system of n_{Fe} and n_N being $S=-k\ ln\ W$, the partial molar configurational entropy of a nitrogen atom, $\bar{S}_N^c$, can be obtained by differentiation with respect to n_N at a constant n_{Fe} and by rewriting into the atomic fraction, $N_N = n_N/(n_{Fe}+n_N)$, as follows:

$$\bar{S}_N^c = -k\ ln\ \frac{N_N}{n-(n+Z)N_N} \tag{7}$$

The configurational entropy of a perfectly random interstitial solid solution can be obtained only by putting $Z=1$ in Eq. (7), $\bar{S}_N^c$ in other cases generally deviating from that of the ideal solution. If $\bar{E}_N$ and $\bar{S}_N^v$ respectively represent the partial energy of a nitrogen atom and the partial non-configurational entropy of a nitrogen atom, $\bar{E}_N$ and $\bar{S}_N^v$ can be considered to be constant in a dilute solid solution, independent of the solute concentration. Therefore, the chemical potential of a nitrogen atom in the solid solution, μ_N^γ can be expressed as

$$\mu_N^\gamma = \bar{E}_N - T\bar{S}_N^v - \frac{\partial S^c}{\partial N_N}$$

$$= \bar{E}_N - T\bar{S}_N^v - kT\ ln\ \frac{1-(1+Z)\ N_N}{N_N} \tag{8}$$

On the other hand, a_N as the activity of nitrogen in the solid solution and μ_N^g as the chemical potential of a nitrogen atom in the gas phase are given by

(17)   W.A. Oates, J.A. Lambert and P.T. Gallagher, Trans. Met. Soc. AIME, **245** (1969), 47.

(18)   K.H. Jack, Proc. Roy. Soc., **A208** (1951), 200.

$$\mu_{\mathrm{N}}^{'} = \mu^{\circ\infty} + kT \, ln \, a_{\mathrm{N}}$$

and $$\mu_{\mathrm{N}}^{g} = \mu_{\mathrm{N}}^{\circ g} + kT \, ln \, f_{\mathrm{N}_2}^{1/2} \qquad (9)$$

where $\mu_{\mathrm{N}}^{\circ\infty}$ and $\mu_{\mathrm{N}}^{\circ g}$ are the chemical potential of the infinitely dilute solution and that of nitrogen gas at the standard state of $f_{\mathrm{N}_2} = 1$ atm, respectively. Since $\mu_{\mathrm{N}}^{\gamma} = \mu_{\mathrm{N}}^{g}$ is given in equilibrium, the following equations can be derived from Eqs. (8) and (9):

$$a_{\mathrm{N}} = \frac{N_{\mathrm{N}}}{1-(1+Z)\,N_{\mathrm{N}}} \exp\left(\frac{\Delta G}{kT}\right)$$

and $$\Delta G = \bar{E}_{\mathrm{N}} - T\bar{S}_{\mathrm{N}}^{v} - \mu_{\mathrm{N}}^{\circ} \qquad (10)$$

When $a_{\mathrm{N}} = f_{\mathrm{N}_2}^{1/2}$ is used as the activity at the standard state of the nitrogen gas at 1 atm, $\Delta G = \bar{E}_{\mathrm{N}} - T\bar{S}_{\mathrm{N}}^{v} - \mu_{\mathrm{N}}^{\circ g}$. Eq. (10) is the expression of Mclellan's[15] model applied to the case of a low concentration of nitrogen ($N_{\mathrm{N}} \approx 0.03$) as assumed free from such an overlap of excluded sites as at a high concentration of nitrogen. Since $(\mu_{\mathrm{N}}^{\circ g})$ 1 atm $= (\mu_{\mathrm{N}}^{\gamma})$ 1 atm is given at 1 atm of nitrogen pressure, the following equation can be derived from Eqs. (8) and (9):

$$f_{\mathrm{N}_2}^{1/2} = \frac{N_{\mathrm{N}}}{1-(1+Z)N_{\mathrm{N}}} \left(\frac{1-(1+Z)\,[N_{\mathrm{N}}]_{1\,\mathrm{atm}}}{[N_{\mathrm{N}}]_{1\,\mathrm{atm}}}\right) \qquad (11)$$

where $[N_{\mathrm{N}}]_{1\,\mathrm{atm}}$ is the concentration of nitrogen in solid solution at 1 atm of nitrogen pressure. The activity of nitrogen under the standard condition of infinitely dilute solid solution is set as a_{N}^{∞}. As $\lim\limits_{N\to 0} \dfrac{\partial S^c}{\partial N_{\mathrm{N}}} = 0$ at $N \to 0$, the term of the partial configurational entropy vanishes and $\mu_{\mathrm{N}}^{\circ\infty} = \bar{E}_{\mathrm{N}} - T\bar{S}_{\mathrm{N}}^{v}$ with eventual $\Delta G = 0$ is given for the chemical potential of a nitrogen atom at the standard state of the infinitely dilute solution. Thus, the following equation can be formulated:

$$a^{\infty} = \frac{N_{\mathrm{N}}}{1-(1+Z)N_{\mathrm{N}}} \qquad (12)$$

Using the values of $f_{\mathrm{N}_2}^{1/2}$ and N_{N} measured in the present study, the values of Z were calculated with Eq. (11). The calculated values at 950°C, that have been derived from relatively numerous numbers of observed values, are shown in Table 4.

Although the scattering of the calculated value Z is large, the average value at 950°C and 1000°C is $Z = 8$. The results of $A = \log\left(\dfrac{1-(1+Z)[N_{\mathrm{N}}]_{1\,\mathrm{atm}}}{[N_{\mathrm{N}}]_{1\,\mathrm{atm}}}\right)$ calculated at 950° to 1300°C are shown in Table 5, where the values of Darken et al.[6] were used for $[N_{\mathrm{N}}]_{1\,\mathrm{atm}}$. The relation between these values of A and temperatures can be obtained by a least square method to be approximated by

$$A = 3.34 - \frac{427}{T} \qquad (13)$$

Table 4. Numbers of interstitial sites blocked by a nitrogen atom.

$f_{N_2}{}^{1/2}$	9.7	16.2	17.8	19.4	20.9	22.4	23.8
N_N	0.00943	0.0146	0.0158	0.0175	0.0185	0.0190	0.0197
Z	4.9	7.6	8.0	6.2	7.7	9.4	9.2
$f_{N_2}{}^{1/2}$	25.1	26.4	27.6	29.0	31.4	Average value	
N_N	0.0190	0.0210	0.0210	0.0244	0.0257	$\bar{Z}=8$	
Z	13.4	9.9	12.7	6.5	7.1		

Table 5. Calculated A.

Temperature °C	950	1000	1100	1200	1300
$[N_N]_{1atm}$	0.00102	0.00100	0.00095	0.00091	0.00086
A	2.986	2.996	3.018	3.040	3.064

$$A = \log \left(\frac{1-(1+Z)[N_N]_{1atm}}{[N_N]_{1atm}} \right)$$

Accordingly the following equation can be derived from Eqs. (11) and (13)

$$\log f_N^{1/2} = \log \frac{N_N}{1-9N_N} + 3.34 - \frac{427}{T} \tag{14}$$

The relation between the calculated values, $f_{N_2}^{1/2}$(cal), and these observed values, $f_{N_2}^{1/2}$(obs), are represented in Fig. 7, which shows that both are in agreement with each other.
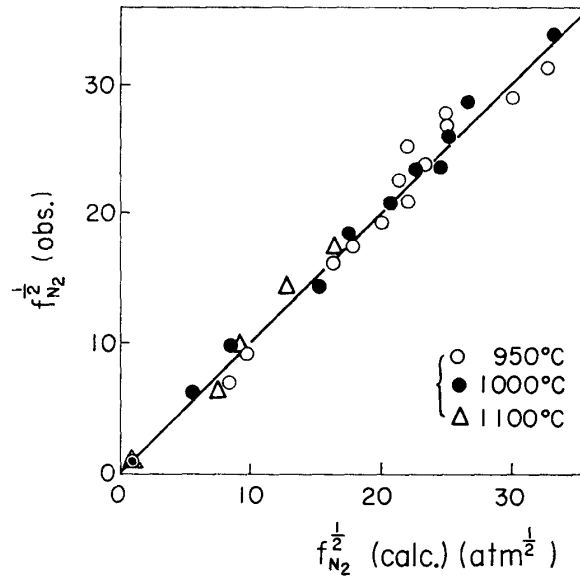

Fig. 7. Comparison between observed value and calculated value of fugacity.

The values of the activity of nitrogen relative to the infinitely dilute solid solution as the standard state were calculated by Eq. (12) to determine again the values of Z. The reaction of nitrogen gas dissolved into the austenite phase and the equilibrium constant of the reaction, K_f are expressed as

$$1/2\, N_2 \rightleftharpoons N(\gamma), \quad K_f = a_N / \sqrt{f_{N_2}} \qquad (15)$$
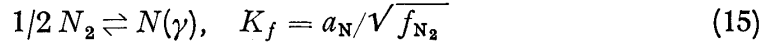
Therefore, $a_N^\infty = K_f^\infty \cdot \sqrt{f_{N_2}}$, $K_f^\infty = [N_N / \sqrt{f_{N_2}}]_{N_N \to 0}$. K_f^∞ was obtained by least-

$$a_N^\infty \,(\text{calc.}) = \frac{N_N}{1 - 9\,N_N}$$
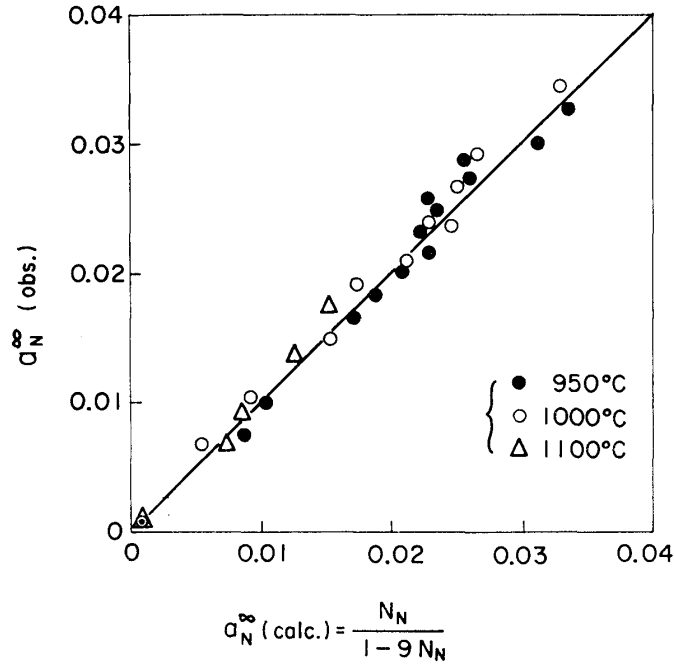
Fig. 8. Comparison between a_N^∞ obtained from experimental results and a_N^∞ calculated using Eq. (12).
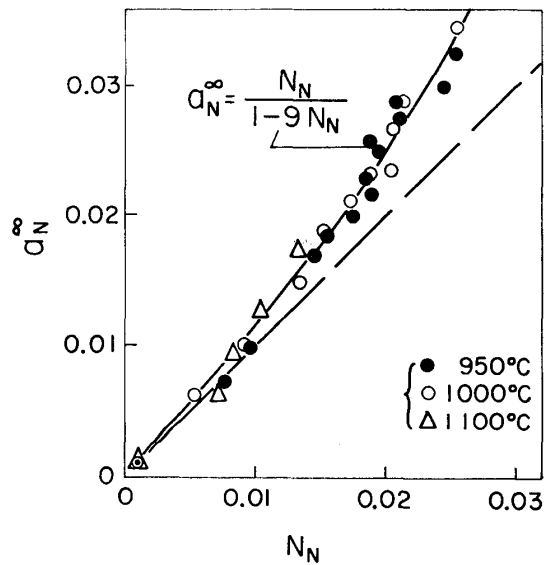
Fig. 9. Relationship between the atomic fraction of nitrogen and the nitrogen activity in austenite (Infinitely dilute solid solution standard state).

squaring the logarithm of the apparent equilibrium constant extrapolated to $N_N \rightarrow$ 0. Substituting the a_N^∞(obs) and N_N into Eq. (12), the value of Z calculated by the least square method was about 8. At $Z=8$, the values of a_N^∞(cal) calculated with Eq. (12) are shown in relation to the observed values of a_N^∞(obs) in Figs. 8 and 9. Using the values respectively calculated with Eqs. (11) and (14) at composition C, pressure P, and temperature T, the relationships of P to C, P to T, and T to C are shown in Figs. 10, 11 and 12, respectively. These all remarkably agree with the
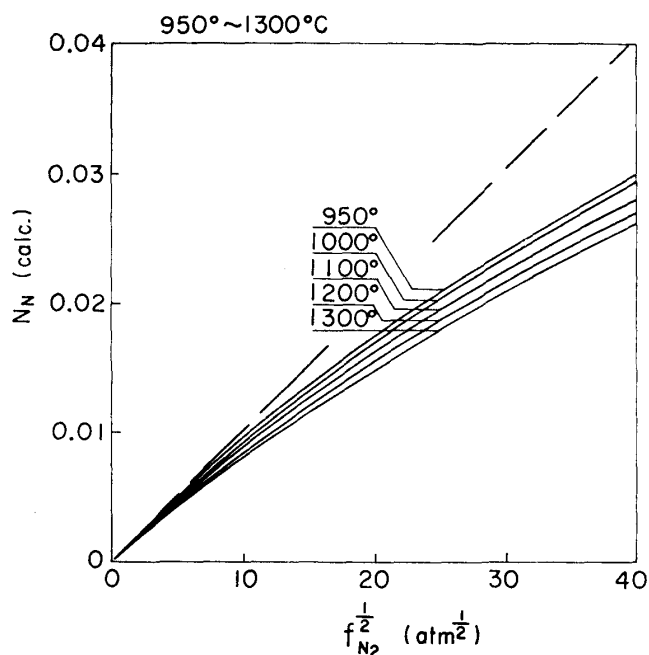
Fig. 10. Relationship between the atomic fraction of nitrogen calculated using Eq. (14) and the square root of fugacity for pure iron in the range of 950° to 1300°C.
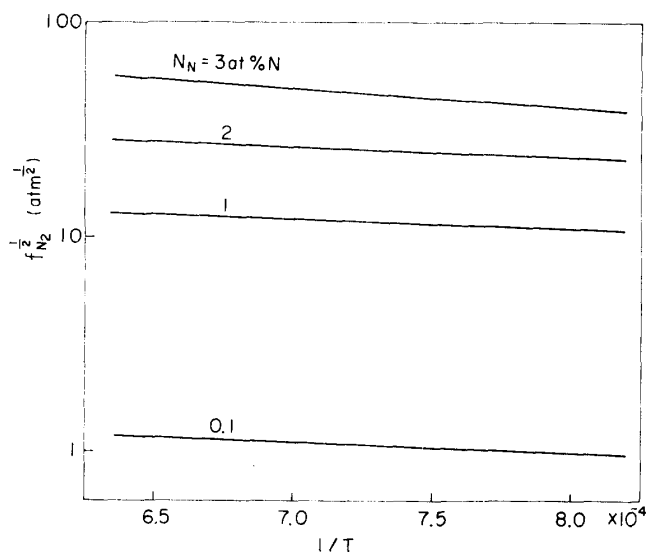

Fig. 11. Temperature dependence of fugacity calculated using Eq. (14) for austenite of iron.

experimental values. Using the data of the previous report,[5] the nitrogen solubility in austenitic iron at 1400°C is compared with the value obtained with Eq. (14) in Fig. 13. These also agree with each other.

The interstitial sites blocked by a nitrogen in the iron-nitrogen austenite are eight ($Z=8$), and so, each nitrogen atom excludes seven surrounding interstitial sites from being occupied by other nitrogen atoms. As shown in Fig. 14, only one interstitial atom can be accomodated in every other unit cell in the octahedral
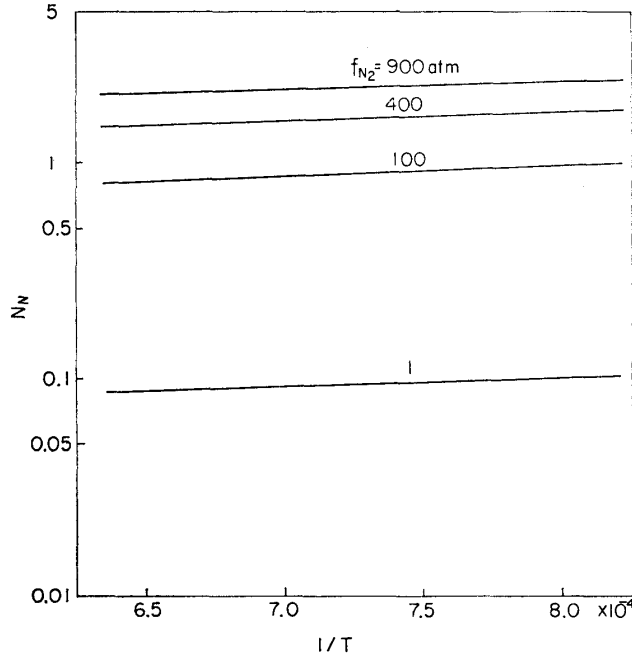
Fig. 12. Temperature dependence of nitrogen content in austenite of iron under various pressure. (Calculated using Eq. (14))
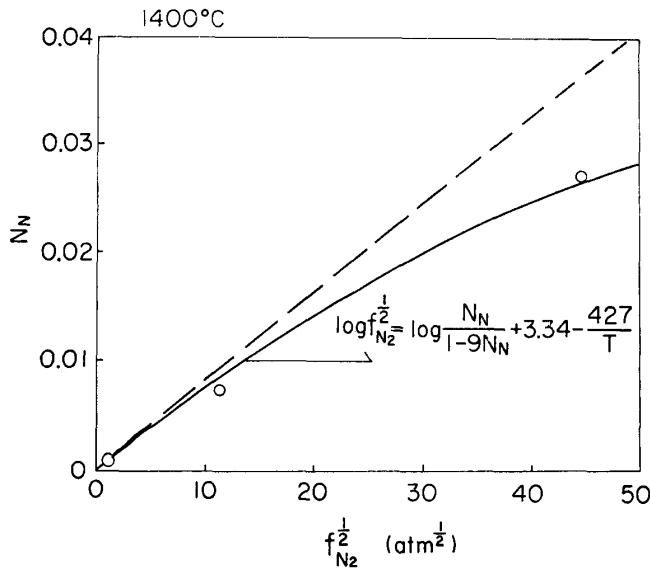

Fig. 13. Relationship between the atomic fraction of nitrogen and the square root of fugacity for pure iron at 1400°C (by data of previous report[5]).

interstitial sites, namely each nitrogen atom excludes six of the first neighbor sites and one of the second nearest-neighbor sites, which signifies that all the first and the second nearest neighbor atoms are repulsed. In Fig. 14, if nitrogen atoms enter in the all sites of the solid circle, then the concentration of nitrogen becomes 12 at%N, i.e. almost equalling to the maximum concentration of solution in austenite of the Fe-N.
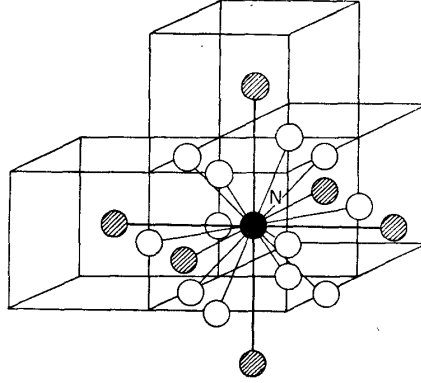
Fig. 14. Blocking configuration for face centered cubic lattices with Z=8
$\bigcirc$: Site of the nearest neighbor octahedral position.
⬤: Site of the second neighbor octahedral position.

In the above-mentioned discussions, the present experimental results were explained in terms of the interstitial blocking model giving the simple and useful semiempirical equation of the nitrogen solubility. However, this model is a rough approximation, that is, the deviation from the behavior of Sieverts' law arises only from the dependence of the non-random configurational entropy on the concentration of solute atoms.

Then, the thermodynamic properties of Fe-N solid solution will be discussed with the quasi-chemical treatment taking into account both the dependences of partial energy and the configurational entropy on the concentration of solute atoms. This discussion is based on the statistical thermodynamic treatment by Takeuchi and Kachi[11], which has been applied to Fe-C interstitial solid solution.

The complete partition function Γ_{FeN} for Fe-N interstitial solid solution is

$$\Gamma_{FeN} = K(T)^{n_{Fe}}(q_N(T) j_N)^{n_N} W(n_{Fe}, n_N, \bar{X}_{NN}) \exp\left(\frac{Z_{FeN} n_N \mathcal{E}_{FeN} + \bar{X}_{NN} \mathcal{E}_{NN}}{kT}\right)$$

(16)

where $q_N(T)$ and j_N are the vibrational and the internal partition functions, respectively, and $K(T)$ is the partition function for an iron atom; W is the number of physically different states that have the same internal energy when the number of N-N paris is $\bar{X}_{NN}$. $\mathcal{E}_{NN}$ is the number of N-N paris depending on the N-N pair interaction energy $\mathcal{E}_{NN}$.

$\mathcal{E}_{FeN}$ is the interaction energy of Fe-N pairs. Z_N is the coordination number of

interstitial sites in a sublattice. Z_{FeN} is the number of the lattice points around an interstitial site. $\bar{X}_{NN}$ is obtained from the quasi-chemical theory.

$$\frac{\text{(no. of interstitial vacant site pairs) (no. of N-N pairs)}}{\text{(no. of interstitial vacant site—N pairs)}} = \exp\left(\frac{-\varepsilon_{NN}}{kT}\right)$$

$$\frac{\bar{X}_{NN}\left(\frac{1}{2}n_{Fe}Z_N - N_N Z_N + \bar{X}_{NN}\right)}{\left(\frac{1}{2}n_N Z_N - \bar{X}_{NN}\right)^2} = \exp\left(-\frac{\varepsilon_{NN}}{kT}\right) \tag{17}$$

and the chemical potential of a nitrogen atom is

$$\mu^\gamma = -kT\left(\frac{\partial \ln \Gamma_{FeN}}{\partial n_N}\right)_{n_{Fe},T} \tag{18}$$

$$= kT \ln \frac{N_N}{1-2N_N} + \frac{2N_N}{1-N_N}\delta(\alpha)Z_N kT + \varepsilon_{FeN} + kT \ln q_N(T)j_N \tag{19}$$

where $\delta(\alpha)Z_N = \frac{1}{4}\{(1-\alpha)^2(2-\alpha)-2\alpha \ln \alpha\}Z_N$ \qquad (20)

The values of μ_N^γ and ε_{NN} can be determined in the same way as in the previous discussion and ε_{NN} was estimated to be 2.35 kcal/mol at 950°C and 3.11 kcal/mol at 1000°C. The interaction energy of N-N pair may have a positive value in austenitic iron because of the strain field around a nitrogen atom.

The configurational entropy of Fe-N system is also obtained to compare with various different models.

(1) For random ideal solid solution,

$$\frac{S^c}{k} = n_{Fe}\ln\frac{n_{Fe}}{n_{Fe}-n_N} - n_N \ln \frac{n_N}{n_{Fe}-n_N} \tag{21}$$

(2) For non-random blocking solid solution,

$$\frac{S^c}{k} = n_{Fe}\ln\frac{n_{Fe}/Z}{n_{Fe}/Z-n_N} - n_N \ln \frac{n_N}{n_{Fe}/Z-n_N} \tag{22}$$

(3) For non-random quasi-chemical solid solution

$$\frac{S^c}{k} = n_{Fe}\ln\frac{n_{Fe}}{n_{Fe}-n_N} - n_N \ln \frac{n_N}{n_{Fe}-n_N} - \frac{1}{4}\frac{n_N^2}{n_{Fe}}(1-\alpha)^2(2-\alpha)Z_N \tag{23}$$

The partial molar configurational entropy of a nitrogen atom is obtained by differentiating S^c with respect to n_N, holding n_{Fe} constant.
Therefore,

$$\frac{\bar{S}_{N}^{c}}{k} = -\ln\frac{N_{N}}{1-2N_{N}} \qquad \text{for random ideal solid solution} \qquad (24)$$

$$\frac{\bar{S}_{N}^{c}}{k} = -\ln\frac{N_{N}}{1-(1+Z)N_{N}} \qquad \text{for non-random blocking solid}$$
$$\text{solution} \qquad (25)$$

and

$$\frac{\bar{S}_{N}^{c}}{k} = -\ln\frac{N_{N}}{1-2N_{N}} - \frac{6N_{N}}{1-N_{N}}(1-a)^{2}(2-a) \qquad \text{for non-random}$$
$$\text{quasichemical solid solution} \qquad (26)$$

Fig. 15 shows the $\bar{S}_{N}^{c}$ calculated at 1000°C substituting the blocking number $Z=8$ and $\varepsilon_{NN}=3.11$ kcal/mol (1000°C) into the above equations. Only for the quasi-chemical model, $\bar{S}_{N}^{c}$ has the temperature dependence and is in the middle of values for the blocking model and for the ideal model, signifying that the discrepancy from the ideal solution may be due to both the concentration dependences of the non-random configurational entropy and the partial energy of solution. The departure from the random ideal solution, $(\Delta\bar{S}_{N}^{c}=\bar{S}_{N}^{c}-\bar{S}_{N}^{c}(\text{random}))$, is shown in Fig. 16.
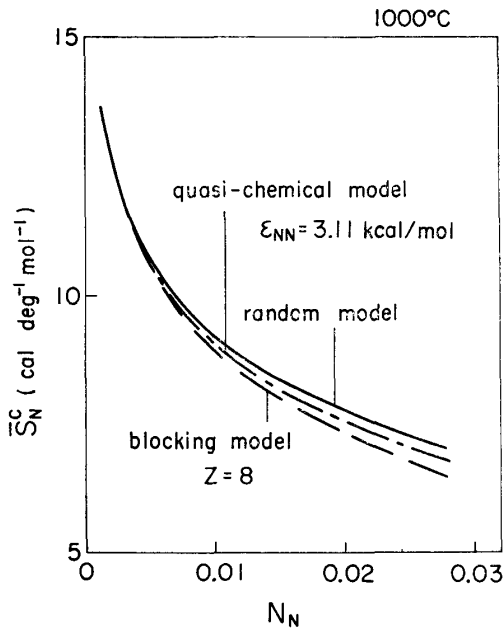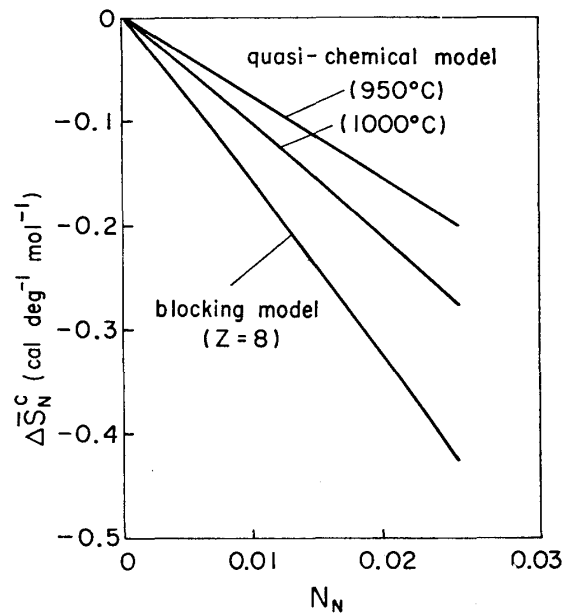

Fig. 15.   Fig. 16.

Fig. 15. Partial molor entropy of a nitrogen atom in the iron-nitrogen austenite, at 1000°C.
Fig. 16. Difference of the partial molar entropy of a nitrogen atom between value in quasi-chemical model, blocking model and values in random model.

The activity coefficient relative to the Henry's standard state is $f_{N}^{(N)}=K/$ $([\text{wt}\%N]/\sqrt{f_{N_2}})$; K is the value of $[\text{wt}\%N]/\sqrt{f_{N_2}}$ with $[\text{wt}\%N]$ approaching to zero. Therefore, with experimental values, the first order interaction coefficient

is $e_N^{(N)} = \partial \log f_N^{(N)}/\partial [\%N] = 0.0144$ (950°C), 0.176 (1000°C). The interaction parameter $\varepsilon_N^{(N)} = \partial \log \gamma_N^{(N)}/\partial N$ was obtained as $\varepsilon_N^{(N)} = 9.06$ (950°C), 10.9 (1000°C) using the correlation formula of Schenck et al.,[19] and $\varepsilon_N^{(N)} = (230\,e_N^{(N)}-1)\,M_N/M_{Fe}+1$ (where M_{Fe} and M_N are atomic weight of iron and that of nitrogen, respectively). As for the influence of carbon on the nitrogen solubility, the values have been reported as $e_N^{(C)} = 0.127$ (1000°C), $\varepsilon_N^{(C)} = 7.0$ (1000°C) by Mori et al.,[20] and $\varepsilon_N^{(C)} = 6.2$ (1200°C) by Schenck et al.[3] These values are a little smaller than our first order interaction $e_N^{(N)}$ and the interaction parameter $\varepsilon_N^{(N)}$ for nitrogen. This is reasonably explained by Schenck' discussion that $\varepsilon_N^{(C)}$ become smaller than $\varepsilon_N^{(N)}$ according to the change of the atomic number.

V. Conclusion

The solubility of compressed nitrogen gas in pure austenitic iron under the pressures up to maximum 920 kg/cm² was measured in the temperature range from 950° to 1300°C.

(1) The nitrogen solubility in austenite was observed deviating from the values corresponding to Sieverts' law which asserts that the nitrogen solubility is proportional to the square root of pressure. The reason for this deviation was discussed statistically and thermodynamically on the geometric and energetic models for the interstitial solid solution.

(2) The thermodynamic properties of the iron-nitrogen austenitic solid solution were observed to deviate greater from ideality with the higher concentration of nitrogen. The experimental results could be favorably explained by considering one nitrogen atom repulsing other nitrogen atoms from entering the seven adjacent interstitial sites.

The activities of nitrogen in austenite were given as the following equations.

$$\log a_N = \log \frac{N_N}{1-9N_N} + 3.34 - \frac{427}{T}$$

(Standard state of nitrogen gas at 1 atm pressure, $a_N = f_{N_2}^{1/2}$)

$$\log a_N = \log \frac{N_N}{1-9N_N}$$

(Standard state of infinitely dilute solid solution)

(19) H. Schenck, M.G. Froberg and E. Steinmentz, Arch. Eisenhütt., **31** (1960), 671.
(20) T. Mori, E. Ichise, Y. Niwa and M. Kuga, J. Japan Inst. Metals, **31** (1967), 887 (in Japanese.