TWO IRON NITRIDES.

By Shun-ichi SATOH.

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I. Introduction. Compounds of iron and nitrogen, so far as is known in literature, are $Fe_{12}N$(1), Fe_8N(2), Fe_6N(2), Fe_4N(3), Fe_7N_2(4), Fe_6N_2(4), Fe_5N_2(5), Fe_2N(6), Fe_3N_2(7) and FeN(8). Of these, Fe_4N and Fe_2N are definitely known compounds. Fe_2N is obtained by passing gaseous ammonia over iron powder at 450°C. It is a paramagnetic substance(10) forming a hexagonal close packed lattice(9). Its heat of formation is 3040 cal.(11) Fe_4N is obtained by heating Fe_2N in vacuo at 440°–550°C. It forms a face centred cubic lattice(12), being a ferromagnetic substance(10). Its heat of formation is not yet determined. The equilibrium diagram of iron and nitrogen system was studied by C. B. Sawyer(13) (thermal analyses), T. Murakami and S. Iwaizumi(14) (magnetic analyses), A. Fry(10) (microscope and magnetic analyses) and by E. Lehrer(15) (magnetic analyses and X-ray). Fig. 1 shows a most reliable equilibrium diagram obtained by E. Lehrer(15).

The equilibrium between iron, iron nitride, ammonia and hydrogen at a high temperature was studied by E. Baur and G.L. Voerman(16), A.A. Noyes

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(1) N. Tschischewski, *J. Iron and Steel Inst.*, **92** (1915), 77.

(2) A. A. Noyes and L. B. Smith, *J. Am. Chem. Soc.*, **43** (1921), 480.

(3) C. Charpy et L. Bonnerot, *Compt. rend.*, **158** (1914), 996; A. Fry, *Stahl und Eisen*, **43** (1923), 1272.

(4) A. W. F. Rogstadius, Dissertation Upsala, (1860).

(5) H. Braune, *Stahl und Eisen*, **26** (1906), 1360.

(6) G. J. Fowler, *J. Chem. Soc.*, **79** (1901), 288.

(7) A. H. White and L. Kirschbraun, *J. Am. Chem. Soc.*, **28** (1906), 1347.

(8) A. Guntz, *Compt. rend.*, **135** (1902), 739.

(9) G. Hägg, *Nova acta regiae societates scientiarum Upsaliensis*, IV, **7**, No. 1; A. Osawa and S. Iwaizumi, *Z. Kryst.*, **69** (1928), 26.

(10) A. Fry, loc. cit.

(11) G. Fowler, Ph. J. Hartog, *J. Chem. Soc.*, **79** (1901), 299.

(12) R. Brill, *Naturw.*, **16** (1928), 593; A. Osawa and S. Iwaizumi, loc. cit.; O. Eisenhut und E. Kaupp, *Z. Elektrochem.*, **36** (1930), 392. G. Hägg, loc. cit.

(13) C. B. Sawyer, *Tran. Am. Inst. Min. Met. Eng.*, **69** (1923), 810.

(14) T. Murakami and S. Iwaizumi, *Kinzoku no Kenkyu*, **5** (1928), 159.

(15) E. Lehrer, *Z. Elektrochem.*, **36** (1930), 460.

(16) E. Baur und G. L. Voerman, *Z. physik. Chem.*, **52** (1905), 471.

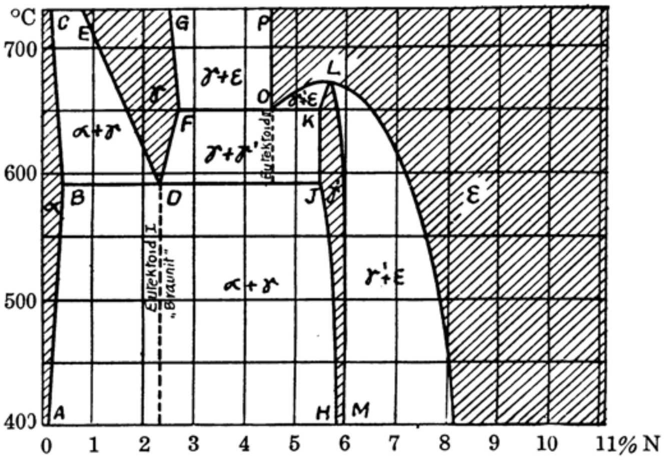

Fig. 1.

Equilibrium diagram of iron and nitrogen according to E. Lehrer.

and L.B. Smith⁽¹⁾, E. Lehrer⁽²⁾, P.H. Emmett, S.B. Hendricks, S. Brunauer⁽³⁾ and S. Brunauer, M.E. Jefferson, P.H. Emmett, S.B. Hendricks⁽⁴⁾. The authors of the first two papers did not clearly determine the composition of the solid phase that takes part in equilibrium, but E. Lehrer⁽²⁾ determined that Fe_2N and Fe_4N as well as Fe_4N and Fe could coexist but Fe and Fe_2N could not coexist to take part in equilibrium.

The author measured the heat of formation of Fe_4N by means of calorimeter. Then he obtained the equilibrium equations of the systems iron, iron nitrides, ammonia and hydrogen from the observed heat of formation of Fe_4N and compared them with the experimental data obtained at high temperatures. Next, he studied the electrochemical properties of iron nitrides.

II. Specimens. The author prepared iron nitride with the apparatus shown in one of his previous papers⁽⁵⁾ as Fig. 1. Iron oxide, which he obtained by igniting iron oxalate, was reduced with electrolytic hydrogen. Pure iron thus obtained was treated with gaseous ammonia at 450°C. for 40 hrs. Gaseous ammonia was obtained by evaporating liquid ammonia; it was purified through solid potassium hydroxide, calcium oxide, barium

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(1) A. A. Noyes and L. B. Smith, loc. cit.

(2) E. Lehrer, *Z. Elektrochem.*, **36** (1930), 388.

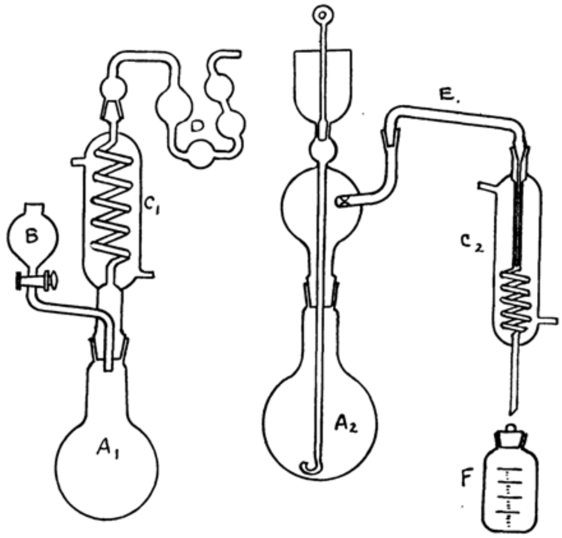
(3) P. H. Emmett and others, *J. Am. Chem. Soc.*, **52** (1930), 1456.

(4) S. Brunauer and others, *J. Am. Chem. Soc.*, **53** (1931), 1778.

(5) S. Satoh, this Bulletin, **5** (1930), 291.

oxide and molten metallic sodium. Iron nitride which was produced in this way, contains 10.65% nitrogen; it is paramagnetic substance and called ε. Then he decomposed ε in vacuo at 500°C., at which Fe_4N does not decompose, and obtained nitrides which contain respectively 6.15% and 6.53% nitrogen and which are called $\varepsilon+\gamma'$. Next, he decomposed $\varepsilon+\gamma'$ in vacuo at 550°C., at which Fe_2N decomposes, and obtained nitride, containing 5.52% nitrogen, which is called $\gamma'+\alpha$. The decomposition was carried out by means of the apparatus referred to as Fig. 2 in the previous paper(1). Iron nitride which contains 6.53% nitrogen was used in the calorimetric investigation; the other nitrides were used to study their electrochemical properties.

The author analysed the nitrides, employing the method adopted by F. Wüst and J. Duhr(2). A fused silica tube specially made was used for distillation to prevent yielding alkalies in the distillate. By analysing oft-sublimated ammonium chloride, reliable results were obtaind. The apparatus is shown in Fig. 2.



A. Flask.
B. Dropping funnel.
C. Condenser.
D. Bulb neck.
E. Transparent quartz tube.
F. Receiver.

Fig. 2. Apparatus used for analysis of nitrogen in iron.

The powder photograms were taken with two cameras, diameters of which were respectively 60.1 and 60.4 mm. Fe-K-radiation was used from a tube of Siegbahn type, which was run with about 30,000 volts and 4 milli-

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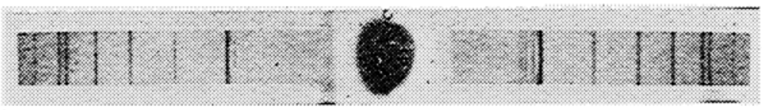
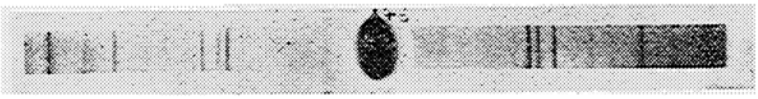
(1) S. Satoh, this Bulletin, **5** (1930), 291.

(2) F. Wüst und J. Duhr, *Mitt. Kaiser Wilhelm Inst. Eisen fors.*, **2** (1921), 39.

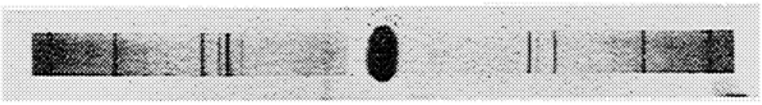
amperes. Powder photograms are indicated in Fig. 3. The $\sin^2\theta$ values which the author has obtained from the photograms, using Hadding's correction:



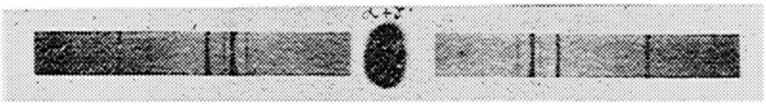
ε (10.65% N_2)



ε + γ′ (6.53% N_2)



ε + γ′ (6.15% N_2)



γ′ + α (5.52% N_2)

α (0% N_2)

Fig. 3. Powder photograms of iron nitrides.
Fe-K-radiation.

$$2\gamma_{\text{corr.}} = 2\gamma_0 - \rho(1 \pm \cos 2\theta)$$

are given in Tables 1–5, together with the calculated values. The calculated values of $\sin^2\theta$ in Table 1 were obtained by the formula:

Table 1. Powder photograms of iron nitride (ε) (10.65% N_2).
Fe-K-radiation.

Film dia. 60.4 mm.

Intensity	Radiation	*h k l.*	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
St.	α	100	0.1622	0.1626	Hex.
M.	β	101	0.1728	0.1731	,,
St.	α	002	0.1908	0.1914	,,
St.	α	101	0.2101	0.2105	,,
W.	β	102	0.2905	0.2911	,,
St.	α	102	0.3527	0.3540	,,
W.	β	110	0.4009	0.4011	,,
St.	α	110	0.4866	0.4878	,,
St.	α	103	0.5917	0.5932	,,
W.	α	200	0,6487	0.6504	,,
St.	α	112	0.6767	0.6791	,,
St.	α	201	0.6967	0.6982	,,
W.	α	004	0.7623	0.7655	,,

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4}{3}\cdot\frac{h^2+hk+k^2}{a^2}+\frac{l^2}{c^2}\right]$$

where λ is the wave-length of the iron radiation $-K_\alpha = 1.932$ Å. and $K_\beta = 1.753$ Å; a and c are elementary dimensions $- a = 2.767$ Å. and $c = 4.417$ Å. The calculated values of $\sin^2\theta$ of ε-phase in Tables 2 and 3 were obtained by the above formula where $a = 2.713$ Å. and $c = 4.376$ Å. The calculated values of $\sin^2\theta$ of γ'-phase in Tables 3 and 4 were obtained by the formula:

Table 2. Powder photograms of iron nitride ($\gamma' + \varepsilon$) (6.53% N_2).
Fe-K-radiation.

Film dia. 60.4 mm.

Intensity	Radiatian.	*h k l.*	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
W.	β	111	0.1599	0.1606	F. C. C.
v. w.	α	100	0.1689	0.1691	Hex.
v. w.	β	101	0.1817	0.1792	,,
St.	α	111	0.1940	0.1952	F. C. C.
St.	β	200	0.2185	0.2141	,,
St.	α	200	0.2607	0.2603	,,
M.	α	102	0.3644	0.3641	Hex.
W.	β	220	0.4273	0.4282	F. C. C.
W.	α	110	0.5084	0.5073	Hex.
St.	α	220	0.5212	0.5206	F. C. C.
W.	β	311	0.5868	0.5888	,,
M.	α	103	0.6094	0.6079	Hex.
W.	α	112	0.7029	0.7023	,,
St.	α	311	0.7134	0.7146	F. C. C.
W.	α	201	0.7252	0.7252	Hex.
St.	α	222	0.7796	0.7795	F. C. C.

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2) .$$

where the side of elementary cube a is 3.789 Å. The calculated values of $\sin^2\theta$ of pure iron in Table 5 were obtained by the above formula where $a = 2.86$ Å. The accordance between the observed and calculated values of $\sin^2\theta$ is very good. From the above experiment it may be clearly seen that ε-phase only forms a hexagonal close packed lattice and it contains neither a face centred cubic lattice of Fe_4N nor a body centred cubic lattice of iron, that $\varepsilon+\gamma'$-phase is a mixture of a hexagonal close packed lattice of Fe_2N and a face centred cubic lattice of Fe_4N and does not contain a body centred cubic lattice of iron, and that similarly $\gamma'+\alpha$-phase does not contain a hexagonal close packed lattice of ε-phase.

Table 3.

Powder photograms of iron nitride ($\gamma'+\varepsilon$) (6.15% N_2)
Fe-K-radiation.

Film dia. 60.1 mm.

Intensity	Radiation	*h k l.*	Sin²θ obs.	Sin²θ calc.	Lattice
W.	β	111	0.1626	0.1606	F. C. C.
St.	α	111	0.1965	0.1952	,,
M.	β	200	0.2175	0.2141	,,
St.	α	200	0.2624	0.2603	,,
W.	α	102	0.3630	0.3641	Hex.
W.	β	220	0.4298	0.4282	F. C. C.
W.	α	110	0.5029	0.5073	Hex.
St.	α	220	0.5224	0.5206	F. C. C.
W.	β	311	0.5885	0.5888	,,
W.	α	103	0.6039	0.6079	Hex.
v. w.	β	222	0.6428	0.6424	F. C. C.
W.	α	112	0.6951	0.7023	Hex.
St.	α	311	0.7150	0.7146	F. C. C.

Table 4.

Powder photograms of iron nitride ($\alpha+\gamma'$) (5.52% N_2)
Fe-K-radiation.

Film dia. 60.1 mm.

Intensity.	Radiation	*h k l.*	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
M.	β	111	0.1605	0.1606	F. C. C.
St.	α	111	0.1940	0.1952	,,
W.	β	200	0.2151	0.2141	,,
St.	α	200	0.2599	0.2603	,,
W.	β	220	0.4281	0.4282	,,
St.	α	220	0.5224	0.5206	,,
W.	β	311	0.5894	0.5888	,,
v. w.	β	222	0.6428	0.6424	,,
St.	α	311	0.7142	0.7146	,,

Table 5.

Powder photograms of iron. (α)
Fe-K-radiation.

Film dia. 60.40 mm.

Intensity	Radiation	*h k l.*	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
W.	β	110	0.1876	0.1878	B. C. C.
St.	α	110	0.2272	0.2282	,,
W.	β	200	0.3743	0.3756	,,
M.	α	200	0.4547	0.4564	,,
W.	β	211	0.5598	0.5633	,,
St.	α	211	0.6800	0.6846	,,
v. w.	β	110	0.7465	0.7511	,,

III. Determination of the Heat of Formation of Fe_4N. When iron nitride is dissolved in dilute sulphuric acid, it is decomposed and yields salts of iron and of ammonium, hydrogen being evolved at the same time. This reaction offers a convenient method for the determination of the heat of formation of the nitride. The equation corresponding to the reaction is as follows:

$$2[Fe_4N] + (10H_2SO_4Aq) = (8FeSO_4Aq) + (2NH_4HSO_4Aq) + 5H_2$$

The concentration of acid was 1.022 normal. Six hundred grams were introduced into a glass calorimeter, a very thin glass beaker of about 19 gr. in weight, provided with a cover and supported on three corks inside a Dewar's vessel. The liquid was agitated by a glass screw-stirrer revolving about four times a second, and a regular current of hydrogen was led through the calorimeter to prevent the oxidation of the ferrous sulphate formed. The calibrated Beckmann's thermometer was used. The apparatus is shown in Fig. 4.

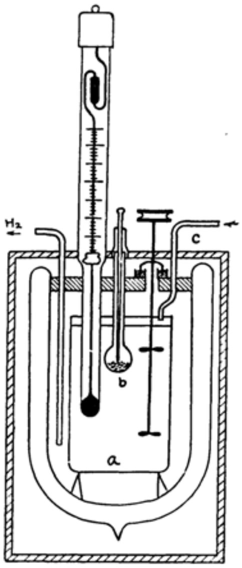


Fig. 4. Apparatus for measurement of heat of solution of iron nitride.

The thermometer was carefully observed until the rate of change was steady. Then the iron nitride, contained in *b*, was introduced into the calorimeter by breaking *b* by a glass rod and readings were taken every minute until the rate of change was steady. The reaction was a slow one; the time needed to accomplish each experiment was about 4 hrs. The correction was calculated graphically and the agreement of four results shows that the determinations are satisfactory. The solution yielded almost no coloration with potassium thiocyanate at the conclusion of the experiments.

The specific heat of the final solution was taken to be equal to that of the solution of sulphuric acid used. The specific heat was taken from the experiments of G. Agde and H. Holtmann(1), which gives 0.9598. The specimen used contains 6.53% nitrogen : mixture of 12.04% Fe_2N and 87.96% Fe_4N. The heat of solution of Fe_2N in dilute sulphric acid was taken from the determination of G. Fowler, Ph. J. Hartog(2) as 81.56 Cal. for 125.7 gr. of Fe_2N.

The details of the experiments are shown in Table 6.

Table 6. Details of the calorimetric experiments.

Number of experiment.	60	61	62	63	Mean
Composition of the nitride % N_2	6.53	6.53	6.53	6.53	
Water equivalent of calorimeter and contents. (including acid, stirrer, part of thermometer immersed etc.)	580.0	580.3	580.3	580.4	

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(1) G. Agde und H. Holtmann, *Z. anorg. allgem. Chem.*, **158** (1926), 316.
(2) G. Fowler, Ph. J. Hartog, loc. cit.

Table 6.—(*Continued.*)

Number of experiment.	60	61	62	63	Mean
Weight of substance dissolved (gr.)	1.0005	1.0046	1,0032	1.0023	
Rise of temperature. (°C.)	0.930	0.954	0.927	0.937	
Cooling correction. (°C.)	0.031	0.034	0.028	0.023	
Total number of calories evolved. (Cal.)	0.5574	0.5734	0.5542	0.5572	
Calories evolved by the solution of Fe_2N. (Cal.)	0.0782	0.0785	0.0784	0.0783	
Calories evolved by the solution of 1gr. Fe_4N. (Cal.)	0.5446	0.5600	0.5392	0.5432	0.5468
Thermal value of the reaction in calories.	129.74				

If we start from a given initial system and pass to a given final system by two different cycles of transformations, we may assume that the total heat evolved is in both cases the same.

We take as the initial system $4[Fe]+N+10H+5[S]+20O+Aq.$
We take as the final system $(4\,FeSO_4Aq)+(NH_4HSO_4Aq)+5H.$

Cycle I — Thermal value of reaction.

$4[Fe]+N=[Fe_4N]$ — x

$5\{H_2+[S]+2O_2\}+Aq=(5H_2SO_4Aq)$ — $5a_1$

$[Fe_4N]+(5SO_4H_2)+Aq=(4SO_4FeAq)+(NH_4HSO_4Aq)+5H$ — 129.74

Cycle II

$4[Fe]+4[S]+16O+Aq=(4SO_4FeAq)$ — $4a_2$

$N+10H+[S]+4O+Aq=(NH_4HSO_4Aq)+5H$ — a_3

$(FeSO_4Aq)+(NH_4HSO_4Aq)=(FeSO_4Aq)+(NH_4HSO_4Aq)$ — 0

We have the equation $x+5a_1+129.74=4a_2+a_3$
According to Berthelot, $a_1=210.1$ Cal, $a_2=234.9$ Cal,
$a_3=245.1$ Cal, we find $x=4.46$ Cal, i.e.,

$$4[Fe]+N=[Fe_4N]+4460\ \text{cal.}$$

IV. Discussion of the Results. By combining the measured heat of formation of Fe_4N:

$$4[Fe] + N = [Fe_4N] + 4460 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

with the heat of formation of ammonia:

$$2NH_3 = N_2 + 3H_2 - 22000 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

the author obtained the following result:

$$8[Fe] + 2NH_3 = 2[Fe_4N] + 3H_2 - 13080 \quad \ldots\ldots \quad (4)$$

Similarly by combining the heat of formation of Fe_2N measured by G. Fowler, Ph. J. Hartog⁽¹⁾

$$2[Fe] + N = [Fe_2N] + 3040 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

with (1) and (3), he obtained the following result:

$$2[Fe_4N] + 2NH_3 = 4[Fe_2N] + 3H_2 - 18760 \quad \ldots\ldots \quad (5)$$

The author obtained the equilibrium equations of the reaction (4) and (5) by the use of the Nernst's heat theorem in order to compare them with the observed equilibrium data obtained by E. Lehrer⁽²⁾ at high temperatures. Lehrer's data are not obtained from pure Fe_2N, Fe_4N, Fe but from solid solutions ε, γ', α. However, γ' and α may be regarded as almost same as pure Fe_4N and Fe respectively, therefore the author found it convenient to compare these data with his equation. ε can not be regarded as equal to pure Fe_2N but the author dared to compare his equation with these experimental data in the following way: Considering that the atomic heat of nitrogen is of course less than 6.4, he calculated the atomic heat of nitrogen from the observed molecular heats of some nitrogen compounds according to Neumann and Kopp's law assuming the atomic heat of oxygen to be 4, that of hydrogen to be 2.3 and those of other elements to be 6.4 each.

Nitrogen compounds.	Calculated atomic heat of nitrogen.
NO_3Na	3.4
$(NO_3)_2Ba$	3.75
$(NO_3)_2Sr$	3.95
NH_4Cl	4.4
NO_3K	5.7
	4.24 (mean).

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(1) G. Fowler, Ph. J. Hartog, loc. cit.

(2) E. Lehrer, loc. cit.

The mean atomic heat (4.24) thus obtained was used as the atomic heat of nitrogen in calculating the molecular heats of iron nitrides. From the above mentioned observed result, the heat of formation of Fe_4N (W_1) is expressed in the following equation:

$$4[Fe_4N] = 8[Fe]+N_2-W_1 \qquad 17°C. \dots\dots\dots\dots\dots \quad (6)$$

where $W_1 = 8920$. On the assumption that W_1 varies with the temperature, W_1 may be expressed by a series containing only integral powers of T:

$$W_1 = W_{01}+3.5\,T+\alpha T^2 .$$

Differentiating with respect to T,

$$\frac{dW_1}{dT} = \sum nC_p = 3.5+2\,\alpha T . \qquad \text{where} \quad \sum n = 1 .$$

Assuming the atomic heat of iron to be 6.0, the molecular heat of gaseous nitrogen to be 6.9 and that of Fe_4N to be $6\times 4+4.24 = 28.24$, we obtain

$$\alpha = \frac{6.9+8\times 6-2\times 28.24-3.5}{2\times 290} = -0.008759 .$$

Therefore $\qquad W_1 = 8642+3.5\,T-0.008759\,T^2$

The equiliblium equation of the reaction (6) can readily be obtained as shown below: The chemical constant of nitrogen is 2.6. Accordingly,

$$\sum m = 1 , \qquad \sum mI = 2.6$$

Therefore,

$$\log P_{N_{2(1)}} = -\frac{8642}{4.571\,T}+1.75\log T-\frac{0.008759T}{4.571}+2.6\dots\dots\dots \quad (7)$$

According to F. Haber⁽¹⁾, the variation of the equilibrium constant of ammonia is expressed by the following equation:

$$\log K_p = -\frac{4196}{T}+5.0176\log T+0.0002012\,T-0.372\times 10^{-6}T^2-4.2 \quad (8)$$

From (7) and (8), the equilibrium equation of the reaction (4) can readily be obtained as shown below:

$$\log K_{p_1} = -\frac{2305}{T}+3.2676\cdot\log T+0.0021174\,T-3.72\times 10^{-7}T^2-6.8 \quad (9)$$

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(1) F. Haber, *Z. Elektrochem.*, **20** (1914), 597.

According to G. Fowler, Ph. J. Hartog⁽¹⁾, the heat of formation of Fe_2N is expressed in the following equation:

$$2\,[\mathrm{Fe}] + \mathrm{N} = 2\,[\mathrm{Fe_2N}] + 3040 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

From (1) and (2), we obtain

$$4\,[\mathrm{Fe_2N}] = 2\,[\mathrm{Fe_4N}] + \mathrm{N_2} - 3240 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

$$3240 = W_2$$

On the assumption that W_2 varies with the temperature, W_2 may be expressed similarly as in the case of W_1 as follows:

$$W_2 = W_{02} + 3.5\,T + \alpha T^2 \,.$$

Similarly, $$\frac{dW_2}{dT} = \sum nC_p = 3.5 + 2\,\alpha T\,, \qquad \text{where} \quad \sum n = 1\,.$$

Assuming the molecular heat of Fe_4N to be 28.24, that of gaseous nitrogen to be 6.9 and that of Fe_2N to be $6 \times 2 + 4.24 = 16.24$, we obtain

$$\alpha = \frac{6.9 + 2 \times 28.24 - 4 \times 16.24 - 3.5}{2 \times 290} = -0.008759\,.$$

Therefore $$W_2 = 2962 + 3.5\,T - 0.008759\,T^2$$

The equilibrium equation of the reaction (10) can similarly be obtained. As previously shown,

$$\sum m = 1\,, \qquad \sum mI = 2.6\,.$$

Therefore,

$$\log P_{\mathrm{N2(2)}} = -\frac{2962}{4.571\,T} + 1.75 \log T - \frac{0.008759\,T}{4.571} + 2.6 \;\ldots\ldots\ldots \quad (11)$$

From (11) and (8), the equilibrium equation of the reaction (5) can readily be obtained as before:

$$\log K_{p_2} = -\frac{3548}{T} + 3.2676 \cdot \log T + 0.0021174\,T - 3.72 \times 10^{-7} T^2 - 6.8 \quad (12)$$

The agreement of the equilibrium constants at high temperatures between the calculated values according to the equations (9) and (12) and those observed by E. Lehrer⁽²⁾ is quite satisfactory as shown in Table 7 and Fig. 5.

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(1) G. Fowler, Ph. J. Hartog, loc. cit.

(2) E. Lehrer, loc. cit.

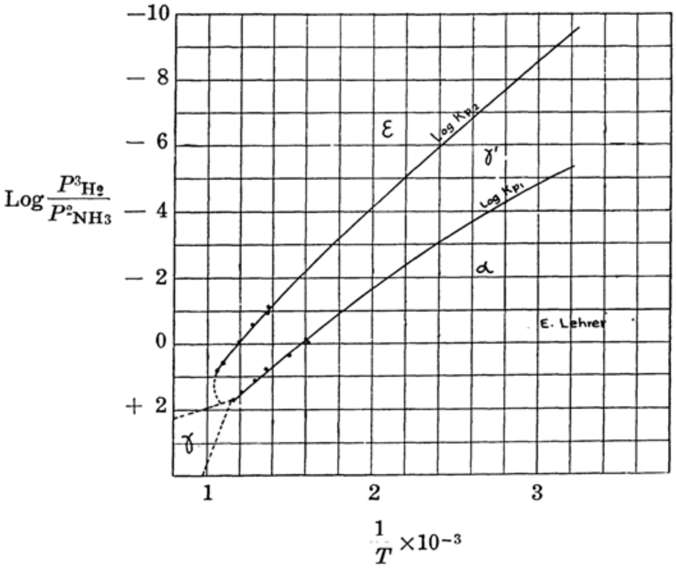

Fig. 5. Variation of equilibrium constants of
$8\,Fe + 2NH_3 = 2Fe_4N + 3H_2$ (Log K_{p1})
$2\,Fe_4N + 2NH_3 = 4\,Fe_2N + 3H_2$ (Log K_{p2})
with temperature.

Table 7. Equilibrium constants of reactions:
$8Fe+2NH_3 = 2Fe_4N+3H_2$
$2Fe_4N+2NH_3 = 4Fe_2N+3H_2$
at various temperatures.

T°K	$8Fe+2NH_3 = 2Fe_4N+3H_2$ Log $\frac{P^3_{H_2}}{P^2_{NH_3}}$		T°K	$2Fe_4N+2NH_3 = 4Fe_2N+3H_2$ Log $\frac{P^3_{H_2}}{P^2_{NH_3}}$	
	Log K_{p_1} (Author)	Log K_{p_1} (Lehrer)		Log K_{p_2} (Author)	Log K_{p_2} (Lehrer)
618	−0.243	−0.0637	729	−0.966	−1.123
623	−0.195	−0.1154	730	−0.957	−0.968
668	+0.228	+0.346	783	−0.444	−0.589
734	+0.779	+0.752	835	+0.007	−0.060
773	+1.070	+1.107	905	+0.553	+0.600
827	+1.445	+1.473	940	+0.802	+0.845
862	+1.669	+1.675			

The author deduced the following two empirical equations from the measured heat of formation at an ordinary temperature, in order to see whether these equations could express the observed data of E. Lehrer⁽¹⁾ or not:

$$\log K_{p'_1} = -\frac{13080}{4.571\,T} + 4.775$$

$$\log K_{p'_2} = -\frac{18760}{4.571\,T} + 4.775$$

At 734° K and 773° K, the observed equilibrium constants of the reaction (4) are +0.752 and +1.107 respectively while the corresponding calculated values are +0.876 and +1.073 respectively ($\log K_{p'_1}$). And at 730° K and 835° K, the observed data of the reaction (5) are −0.968 and −0.06 respectively while the corresponding calculated values are −0.847 and −0.140 ($\log K_{p'_2}$). In this case the agreement between the observed and calculated values is fairly good.

V. Electrochemical Properties of Iron Nitrides. As described in the previous paper⁽²⁾, single potential of nitrified iron in ferrous sulphate solution is greatly influenced by the presence of ferric ion. The author measured the single potential of ε, which was confirmed by X-ray to contain no iron.

ε-phase immersed in the ferrous sulphate solution (1 normal) free from ferric ion showed the potential of

$$\varepsilon_h = -0.448 \text{ volt.}$$

which corresponds to the potential of powdered iron, but that immersed in the same solution containing 7 per cent. ferric ion showed the potential of

$$\varepsilon_h = +0.5708 \text{ volt.}$$

It is clear that the presence of ferric ion or oxygen changes the iron nitride into the passive state and that the single potential of iron nitride reported by F. Hanaman⁽³⁾ is nothing more than that of the passive iron nitride.

If the iron nitride does not show the passive state in the ammonia solution, cells may be constructed by suitable combination of nitrides and hydrogen electrode, and by measuring the electromotive force of these cells, equilibrium constants of the reactions:

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(1) E. Lehrer, loc. cit.

(2) S. Satoh, *Am. Inst. Min. Met. Eng., Tech. Publ.*, No. 447 (1932).

(3) F. Hanaman, Dissertation Berlin, (1913).

$$8\,[\mathrm{Fe}]+2\mathrm{NH_3} = 2\,[\mathrm{Fe_4N}]+3\mathrm{H_2}\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$2\,[\mathrm{Fe_4N}]+2\mathrm{NH_3} = 4\,[\mathrm{Fe_2N}]+3\mathrm{H_2}\ldots\ldots\ldots\ldots \quad (5)$$

could be directly measured.

ε-phase immersed in 1-normal ammonia solution shows the potential of

$$\varepsilon_h = +0.199 \text{ volt},$$

as shown in Fig. 6, but that immersed in the same solution free from oxygen shows the potential of

$$\varepsilon_h = -0.713 \text{ volt}.$$

As may be seen, iron nitride shows no sign of changing into the passive state in the oxygen free ammonia solution.

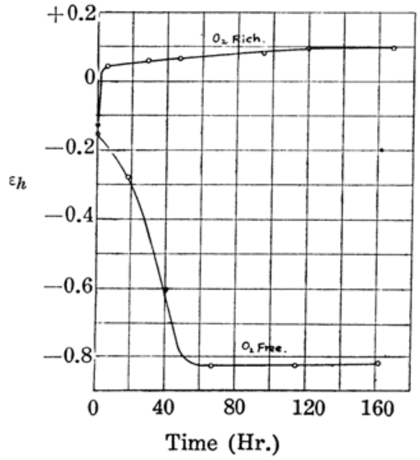

Fig. 6. Potential measurement of iron nitride 1-normal ammonia solution which contained oxygen or not.

If $P_{\mathrm{H_2}}$ denoted the partial pressure of hydrogen over ammonia solution and $P_{\mathrm{NH_3}}$ that of ammonia, and K_{p_1}, K_{p_2} the equilibrium constants of reactions (4) and (5) respectively, the electromotive force of the cells:

$$\mathrm{Fe}\,|\,\mathrm{Fe}+\mathrm{Fe_4N}--\mathrm{NH_3}--|\,[\mathrm{PtPt}]\,\mathrm{H_2}$$

$$\mathrm{Fe_2N}+\mathrm{Fe_4N}\,|\,\mathrm{Fe_2N}--\mathrm{NH_3}--|\,[\mathrm{PtPt}]\,\mathrm{H_2}$$

could be expressed in the following equations :

$$E_1 = \frac{RT}{nF}\left(\log K_{p_1} - \log \frac{P^3_{\mathrm{H}_2}}{P^2_{\mathrm{NH}_3}}\right)$$

$$E_2 = \frac{RT}{nF}\left(\log K_{p_2} - \log \frac{P^3_{\mathrm{H}_2}}{P^2_{\mathrm{NH}_3}}\right)$$

where $n = 6$ and $T = 308$. The values of log K_{p_1} and log K_{p_2} calculated from (9) and (12) are respectively —5.534 and —9.57. The partial pressure of ammonia over 1-normal ammonia solution obtained from the curve based on the measurements of W. Gaus⁽¹⁾, R. Abegg and H. Riesenfeld⁽²⁾ is 22.1 mm. at 35°C. Therefore, the values of P_{NH_3} can be calculated by the formula of J. Lock and J. Forssall⁽³⁾ as follows :

$$P_{\mathrm{NH}_3} = \frac{22.1 \times n + 0.18\, n^2}{760} = 0.03095 \text{ at.},$$

where $n = 1.055$.

According to E. P. Perman⁽⁴⁾, the partial pressure of water over 1.055 normal ammonia solution can be calculated by the following formula :

$$p_0 = P \cdot (1 - x) = 41.43 \text{ mm.},$$

in which p_0 are the partial pressures of water over the solutions, P are the pressures of pure water at the same temperature, and x is the fractional amount of ammonia in 1 gr. of the solution.

Therefore, the values of P_{H_2} can be calculated by the following formula :

$$P_{\mathrm{H}_2} = \frac{760 - P - p_0}{760} = \frac{695.1}{760} = 0.9146 \quad \text{at.}$$

Therefore,

$$E_1 = \frac{0.0001983 \times 308}{6}(-5.534 - 2.90) = -0.0859 \text{ volt.}$$

$$E_2 = \frac{0.0001983 \times 308}{6}(-9.57 - 2.90) = -0.1269 \text{ volt.}$$

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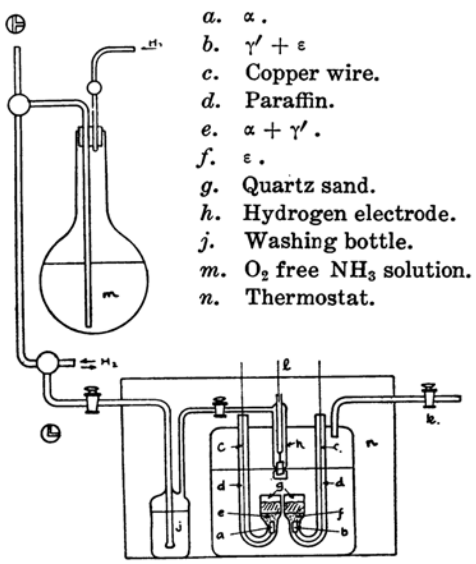
(1) W. Gaus, *Z. anorg. Chem.*, **25** (1900), 236.

(2) R. Abegg, H. Riesenfeld, *Z. physik. Chem.*, **40** (1902), 90.

(3) J. Lock and J. Forsall, *Am. Chem. J.*, **31** (1904), 268.

(4) E. P. Perman, *Trans. Chem. Soc.*, **79** (1901), 718 ; **83** (1903), 1168.

With the object of ascertaining these results, the author made experiments with the apparatus shown in Fig. 7. ε, $\varepsilon + \gamma'$, $\gamma + \alpha$, and α, the compositions of which were determined by chemical analyses and X-ray, were used as specimens. α and $\varepsilon+\gamma'$, compressed in cylindrical form, were soldered at their ends with copper wire. The soldered ends of the specimens α and $\varepsilon+\gamma'$ were inserted into a glass tube *a* and *b* respectively, filled with solid paraffin to prevent the solution from entering into the soldered part. In *e* and *f* the powders of $\gamma' + \alpha$ and ε were introduced respectively. And *g* was filled with quartz sand purified with aqua regia. *h* is a hydrogen electrode and the purified hydrogen was passed through the tube *i*, and



a. α.
b. $\gamma' + \varepsilon$
c. Copper wire.
d. Paraffin.
e. $\alpha + \gamma'$.
f. ε.
g. Quartz sand.
h. Hydrogen electrode.
j. Washing bottle.
m. O_2 free NH_3 solution.
n. Thermostat.

Fig. 7. Apparatus for measurement of the E. M. F. of the iron nitride cell.

through a solution of ammonia of the same concentration as was contained in the cell. *l*, *c* being connected with Leeds and Northrup potentiometer, the electromotive force of the cell was measured. The oxygen free ammonia solution was poured into the cell through *m*. The temperature of the cell was kept constant (35° ± 0.2°C.) by means of the air thermostat. The results obtained are shown in Table 8, and the time voltage curves are shown in Figs. 8 and 9.

As may be seen from the curves, very constant voltage was obtained in each case and the final constant voltages were shown as below :

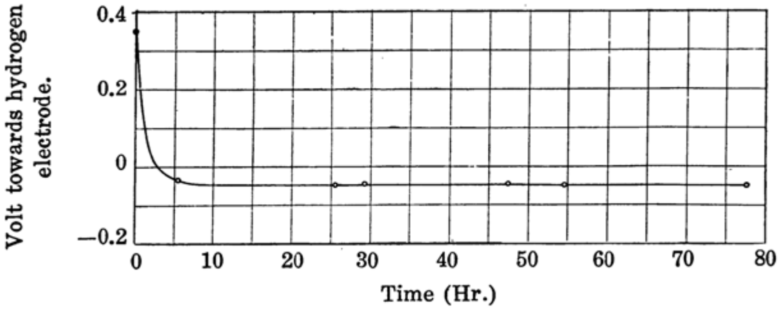


Fig. 8. Time voltage curve of iron nitride cell.
$\underset{-}{\alpha} \mid \alpha+\gamma'-1.055\,n\cdot NH_3- \mid [PtPt]\,\underset{+}{H_2}$ at 35°C.

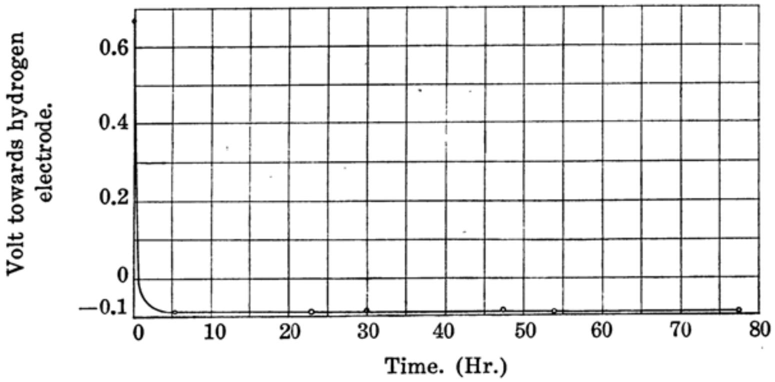


Fig. 9. Time voltage curve of iron nitride cell.
$\underset{-}{\gamma'+\varepsilon} \mid \varepsilon-1.055\,n\cdot NH_3- \mid [PtPt]\,\underset{+}{H_2}$ at 35°C.

Table 8.

Potential measurement of iron nitride cells.

Temp. (°C.)	Time in NH_3 solution. (Hr.)	$\underset{-}{\alpha} \mid \alpha+\gamma'-1.055\,n\cdot NH_3- \mid [PtPt]\,\underset{+}{H_2}$ volt.	$\underset{-}{\gamma'+\varepsilon} \mid \varepsilon-1.055\,n\cdot NH_3- \mid [PtPt]\,\underset{+}{H_2}$ volt.
35	0	—0.3501	—0.6693
,,	5.5	0.03232	0.08595
,,	23	0.04965	0.08447
,,	30	0.04564	0.08145
,,	47.5	0.04507	0.07974
,,	54.	0.04911	0.08309
,,	77.5	0.04800	0.08270

$$\underset{(-)}{\alpha} \mid \alpha+\gamma' -\!- 1.055\,\text{n-NH}_3 -\!- \mid [\text{PtPt}]\underset{(+)}{\text{H}_2}, \quad E_1' = -0.048\ \text{volt},$$

$$\underset{(-)}{\gamma'+\varepsilon} \mid \varepsilon -\!- 1.055\,\text{n-NH}_3 -\!- \mid [\text{PtPt}]\underset{(+)}{\text{H}_2}, \quad E_2' = -0.0827\ \text{volt}.$$

These values do not agree with the calculated ones. Differences between the observed and calculated values are about 0.04 volt at 35°C. and about 0.07 volt at 0°C. Although E_1-E_2 and $E_1'-E_2'$ seem to agree fairly well, this cell could not be regarded as a reversible iron nitride cell. The author tested various solutions such as ammonical methyl alcohol, ammoniacal ethyl alcohol, Diver's solution and liquid ammonia containing potassium amide, but was not able to obtain the reversible iron nitride cell.

Summary.

1. The heat of formation of Fe_4N was determined by means of calorimeter.

2. The molecular heats of Fe_2N and Fe_4N were calculated by applying the Neumann and Kopp's law and obtained the equilibrium equations of the systems: Fe, Fe_4N, NH_3, H_2 and Fe_4N, Fe_2N, NH_3, H_2 from the observed heat of formation of Fe_4N by using the Nernst's heat theorem. The calculated values by these equations agree well with the equilibrium data obtained at high temperatures.

3. Various iron nitrides were prepared and their compositions were accurately determined by X-ray.

4. The electrochemical properties of the iron nitrides were studied and the passive state of iron nitride was made clear.

5. The reversible property of the iron nitride cell was examined.

Research Laboratory, Mitsubishi Zosen Kaisha Ltd.
Komagome, Hongo, Tokyo.