

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

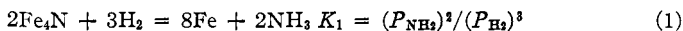
## EQUILIBRIA IN THE IRON-NITROGEN SYSTEM

BY STEPHEN BRUNAUER, M. E. JEFFERSON, P. H. EMMETT AND S. B. HENDRICKS

RECEIVED FEBRUARY 28, 1931

PUBLISHED MAY 6, 1931

In a previous paper<sup>1</sup> the values of the equilibrium constants for the reaction



were reported at various temperatures and with their help the dissociation pressures of  $\text{Fe}_4\text{N}$  were calculated. While these experiments were being extended to iron nitrides of higher nitrogen content, Lehrer,<sup>2</sup> Eisenhut and Kaupp<sup>3</sup> and Lehrer<sup>4</sup> published exhaustive studies of both the iron- $\text{NH}_3$ -iron nitride- $\text{H}_2$  and the iron-nitrogen system by magnetometric and x-ray methods. The investigations in the present paper have been restricted to (1) the extension of our equilibrium data on the above reaction to 400 and 575°; (2) a determination of the equilibrium constants for the conversion of  $\text{Fe}_4\text{N}$  into the higher nitrides by  $\text{NH}_3$ - $\text{H}_2$  mixtures at 400, 444 and 500°; and (3) a study of the equilibria at 400 and 444° within the solid solutions formed by the higher nitrides. Some additional information has also been obtained relative to the purity of the Fe and  $\text{Fe}_4\text{N}$  phases involved in reaction (1). In the designation of the solid phases we have adopted the nomenclature of Hägg.<sup>5</sup> Iron containing only as much nitrogen as may dissolve in it below the  $P_{\text{NH}_3}$ - $P_{\text{H}_2}$  ratio necessary for its conversion into  $\text{Fe}_4\text{N}$  constitutes the  $\alpha$ -phase. The nitride approximating  $\text{Fe}_4\text{N}$  in composition over the temperature range studied is the  $\gamma'$ -phase. The  $\epsilon$ -phase is the series of solid solutions ranging in composition from approximately that of  $\text{Fe}_3\text{N}$  to that of  $\text{Fe}_2\text{N}$  in our experiments.

### Apparatus and Experimental Procedure

A dynamic system similar to that described in our previous paper was used. Hydrogen-ammonia mixtures of definite compositions were passed over a sample of iron at a fixed temperature. The gases were obtained and purified in the manner previously described.<sup>1</sup> Calibrated water-jacketed flowmeters permitted mixing the two gases accurately in any desired proportion immediately before passing them over the sample. All readings were corrected to the temperature and pressure at which the flowmeters were originally calibrated.

The iron used was obtained by the reduction in hydrogen of c. p. ferric

<sup>1</sup> Emmett, Hendricks and Brunauer, *THIS JOURNAL*, **52**, 1456 (1930).

<sup>2</sup> Lehrer, *Z. Elektrochem.*, **36**, 383 (1930).

<sup>3</sup> Eisenhut and Kaupp, *ibid.*, **36**, 392 (1930).

<sup>4</sup> Lehrer, *ibid.*, **36**, 460 (1930).

<sup>5</sup> Hägg, *Nature*, **121**, 826 (1928).

oxalate. Iron reduced from ferric oxide has also been tried, but it cracked ammonia appreciably at 444°.

The glass reaction vessel was similar to that described in the previous paper. An attached side tube which was kept outside the furnace had three arms: one for taking samples for x-ray powder photographs, one for samples for chemical analysis, and one for mixing x-ray samples with reference substances. The reaction tube was heated by a nichrome wound furnace controlled by hand adjusted rheostats. An aluminum block was used inside the furnace as a temperature equalizer. The variation in temperature was not more than  $\pm 1.5^\circ$  during a run. In the experiments carried out at 444° the furnace was replaced by a sulfur bath; the temperature in these runs was constant within  $\pm 0.5^\circ$ . All temperatures were determined with chromel-alumel thermocouples in conjunction with a Leeds and Northrup Type K potentiometer. The thermocouples were calibrated against a platinum-platinum-rhodium thermocouple, calibrated by the U. S. Bureau of Standards.

In a typical experiment a charge of about 20 g. of ferric oxalate was completely reduced in the reaction tube in a stream of hydrogen at about 450°. Various mixtures of ammonia-hydrogen were then passed over the iron for definite periods of time at a fixed temperature. The composition of the gaseous mixture was checked by titration before and after it passed over the iron. At a flow of approximately 100 cc. of gas per minute no cracking occurred at 400 and 444°; slight cracking took place, however, with high  $P_{\text{NH}_3}$ - $P_{\text{H}_2}$  ratios from 500 to 575°. Equilibrium was usually reached in ten to twenty hours at 400°, in five to ten hours at 444° and in five hours or less at 500° and higher temperatures.

At the end of each experiment pure nitrogen was run over the hot sample for a few seconds to flush out the  $\text{NH}_3$ - $\text{H}_2$  mixtures; the reaction tube was then removed from the furnace and the sample cooled quickly with the stream of nitrogen still passing over it. When the tube was cool an x-ray sample was taken and three samples were sealed off for analysis. These samples were then dissolved without exposure to air by breaking their containers under sulfuric acid. The nitrogen and iron contents of the samples were then determined by the Kjeldahl and the Jones reductor methods, respectively.

The x-ray data were obtained from powder diffraction photographs taken with iron K radiation in a camera of about 3.46 cm. radius. For determining the lattice dimensions the nitride samples were mixed with sodium chloride. In each case measurements were made on at least three photographs.

### Results and Discussion

**A. Equilibrium Runs.**—The equilibrium runs for the Fe-Fe<sub>3</sub>N system at 400 and 575° are given in Table I. From them it can be concluded that

at 1 atmosphere pressure an  $\text{NH}_3\text{-H}_2$  mixture need not contain more than 37%  $\text{NH}_3$  to convert Fe into  $\text{Fe}_4\text{N}$  at 400, and 14.5% at 575°.

TABLE I

SUMMARY OF EQUILIBRIUM RUNS IN THE SYSTEM  $\text{Fe-NH}_3\text{-Fe}_4\text{N-H}_2$  AT 400 AND 575°

Run	Temp., °C.	$\text{NH}_3$ in $\text{NH}_3\text{-H}_2$ gas mixture, %	$\text{N}_2$ by weight in samples (average), %	X-ray diffraction pattern
M1	400	35	0.09	No photograph
M2		37	.14	No photograph
M3		39	.17	No $\text{Fe}_4\text{N}$ , only Fe
M4		41	.48	$\text{Fe}_4\text{N}$ present
P1		37	.09	Presence of $\text{Fe}_4\text{N}$ doubtful
P2		37	.10	Very faint $\text{Fe}_4\text{N}$
P3		37	.11	Very faint $\text{Fe}_4\text{N}$
A3	575	11.5-13	.13	Only Fe
A4		12-14	.13	Only Fe
A5		14-15	.31	Very faint $\text{Fe}_4\text{N}$
A6		14.6-16	2.46	Strong $\text{Fe}_4\text{N}$

The results of the equilibrium runs in the system  $\gamma'\text{-NH}_3\text{-}\epsilon\text{-H}_2$  are given in Table II. The equilibrium constants were determined at 400, 444 and 500°. At temperatures of 550° and higher the cracking of ammonia made the determination of the constants impracticable.

TABLE II

SUMMARY OF EQUILIBRIUM RUNS IN THE SYSTEM  $\gamma'\text{-NH}_3\text{-}\epsilon\text{-H}_2$

Run	Temp., °C.	Starting material	$\text{NH}_3$ in $\text{NH}_3\text{-H}_2$ gas mixture, %	$\text{N}_2$ by weight in samples (average), %	X-ray diffraction pattern
P6	400	$\gamma'$	75	5.91	Only $\text{Fe}_4\text{N}$
P8		$\gamma'$	77	5.93	Only $\text{Fe}_4\text{N}$
P11		$\gamma'$	79	6.15	Presence of $\epsilon$ besides $\text{Fe}_4\text{N}$
F1		$\epsilon$	79	8.78	No photograph
F2		$\epsilon$	77	8.47	Only $\epsilon$
F3		$\epsilon$	75	8.22	Only $\epsilon$
F4		$\epsilon$	75	8.07	Presence of $\text{Fe}_4\text{N}$ besides $\epsilon$
III 4	444	$\gamma'$	75	6.83	Presence of $\epsilon$ and $\gamma'$
III 5		$\epsilon + \gamma'$	70	5.99	Presence of $\epsilon$ and $\gamma'$
III 12		$\gamma'$	70	6.03	Only $\text{Fe}_4\text{N}$
III 13		$\gamma'$	72	5.85	Only $\text{Fe}_4\text{N}$
III 14		$\gamma'$	72	6.14	Faint lines of $\epsilon$ besides $\text{Fe}_4\text{N}$
IV 2		$\gamma'$	70	6.05	Very faint lines of $\epsilon$
IV 3		$\gamma'$ (trace $\epsilon$ )	70	6.13	Very faint lines of $\epsilon$
IV 4		$\gamma'$ (trace $\epsilon$ )	72	6.20	$\epsilon$ lines stronger
B2	500	$\epsilon$	59	7.89	Only $\epsilon$
B3		$\epsilon$	58	7.89	Only $\epsilon$
B4		$\epsilon$	56	7.63	Distinct $\text{Fe}_4\text{N}$ lines
B5		$\epsilon$ (some $\gamma'$ )	54	7.30	No photograph
B6		$\epsilon + \gamma'$	58	7.45	No photograph

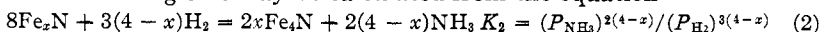
The errors in these experiments consist of those involved (1) in obtaining a constant and definite  $\text{NH}_3\text{-H}_2$  mixture, (2) in measuring the temperature of the reacting material, and (3) in determining the composition and amounts of the solid phases at the end of each run. Errors (1) and (2) are considerably less than in the previous paper because of (1) the correction for variation of pressure and temperature of the flowmeter capillaries from the temperature and pressure at which they were calibrated, and (2) better temperature regulation. The ammonia percentages given are accurate to  $\pm 0.5$ ; we accordingly estimate that the percentage of ammonia in an  $\text{NH}_3\text{-H}_2$  mixture at 1 atm. necessary to convert Fe to  $\text{Fe}_4\text{N}$  is  $37 \pm 2$  at 400, and  $14.5 \pm 1$  at  $575^\circ$ . The equilibrium percentage of ammonia for the conversion of  $\text{Fe}_4\text{N}$  into the  $\epsilon$ -phase is  $77 \pm 2$  at 400,  $70 \pm 2$  at 444, and  $57 \pm 1.5$  at  $500^\circ$ .

It should be pointed out that the "equilibrium" values deduced from Table I above, as well as those presented in Table I of the previous publication from this Laboratory, for the Fe- $\text{Fe}_4\text{N}$  system in reality represent only the upper limit of the true equilibrium values for two reasons. In the first place, because of the sluggishness with which  $\text{NH}_3\text{-H}_2$  mixtures slightly below equilibrium reduced the nitride, experiments approaching equilibrium from the high nitride side were impracticable. Furthermore, any thermal decomposition of the  $\text{Fe}_4\text{N}$  formed in these experiments would tend to increase the apparent percentage ammonia necessary to convert Fe into  $\text{Fe}_4\text{N}$ . The thermal decomposition rate of the nitride samples used was very low. No satisfactory method of correctly estimating the influence of this factor on the equilibrium constant has as yet been devised. The slowness of the thermal decomposition compared to the rate of nitride formation makes it highly probable, however, that this influence is small.

The equilibrium measurements on the  $\gamma'\text{-}\epsilon$  system were approached from both the high and low nitride sides. These values, however, are still susceptible to any influence that the thermal decomposition of the  $\epsilon$ -phase may have on them, and must in a strict sense also be regarded as upper limits of the true equilibrium values.

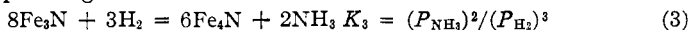
In Fig. 1 curve A is a plot of  $\log K_1$ , the equilibrium constant for reaction (1), against  $1/T$ . Of the six points in the plot, four were reported in the previous paper, two were determined in the present experiments. The dotted line shows the curve obtained by Lehrer<sup>2,4</sup> in this region by the magnetometric method. The agreement between the two sets of experiments seems well within the combined experimental errors.

The equilibrium constant for the conversion of  $\text{Fe}_4\text{N}$  into a nitride of the solid solution region  $\epsilon$  may be calculated from the equation



In the temperature region studied the composition of the nitride of lowest nitrogen content of the  $\epsilon$ -phase is such as to make the value of  $x$  approxi-

mately equal to 3. Consequently as a convenient means of comparing our results with those of Lehrer we have plotted in Fig. 1, curve B,  $1/T$  against  $\log K_3$  corresponding to the reaction



The dissociation pressure of  $\text{Fe}_4\text{N}$  into Fe and nitrogen is as previously pointed out approximately 5000 atmospheres at about  $450^\circ$ . Similar calculations from data of Table II indicate that the dissociation pressure of the  $\epsilon$ -phase containing about 7.9% nitrogen into  $\text{Fe}_4\text{N}$  and nitrogen is of the order of  $3 \times 10^5$  atmospheres at  $450^\circ$ .

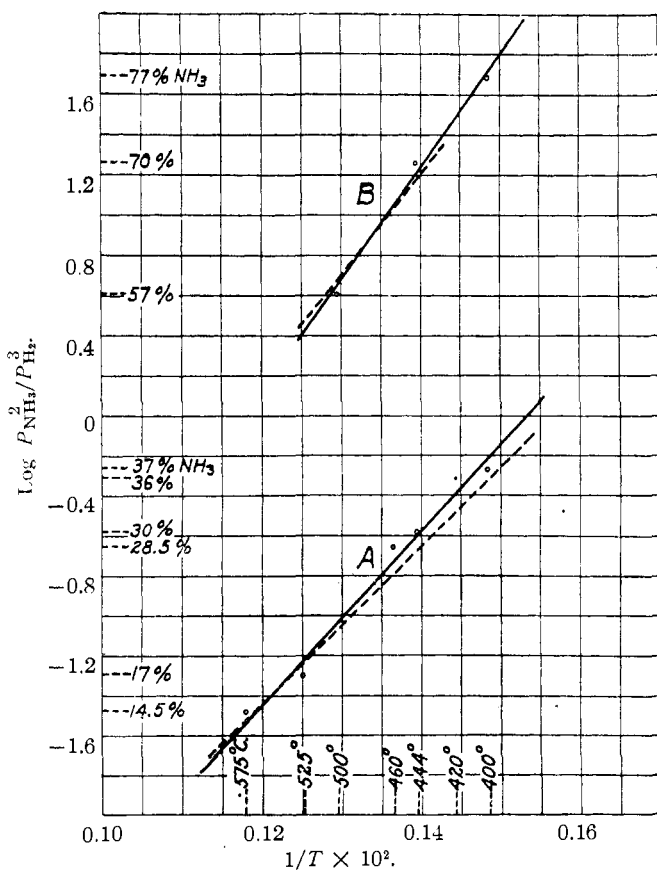


Fig. 1.—Variation of  $\log K_1$  and  $\log K_3$  with  $1/T$ .

### B. Composition of the Phases

**The  $\alpha$ -Phase.**—An exhaustive investigation of the amount of nitrogen taken up by iron when exposed to  $\text{NH}_3$ - $\text{H}_2$  mixtures containing less ammonia than corresponds to the Fe- $\text{Fe}_4\text{N}$  equilibrium has not been included in the present experiments. However, in twelve experiments at tempera-

tures between 400 and 575° and at ammonia concentrations only a few per cent. below equilibrium, no more than 0.2% nitrogen could be put into the iron samples in five to ten hours' exposure. The probable error in the analytical determination was  $\pm 0.02\%$  nitrogen. X-Ray diffraction patterns obtained did not show a change in the lattice constant of  $\alpha$ -iron taking up 0.2% nitrogen.

**The  $\gamma'$ -Phase.**—In agreement with the results of Eisenhut and Kaupp our experiments indicate a variation in the composition of the  $\gamma'$ -phase from about 5.65 to 5.95% nitrogen. The probable analytical error in this region was  $\pm 0.05\%$  nitrogen. The magnitude of the error in this narrow solid solution region made it impracticable to determine accurately the variation of composition of the  $\gamma'$ -phase as a function of the  $P_{\text{NH}_3}/P_{\text{H}_2}$  ratio used in its formation. X-Ray diffraction patterns did not show a variation in the lattice constant of the  $\gamma'$ -phase with increasing nitrogen content.

**The  $\epsilon$ -Phase.**—The variation in the composition of the  $\epsilon$ -phase with increasing  $P_{\text{NH}_3}/P_{\text{H}_2}$  ratios was investigated at 400 and 444°. The summary of these experiments is given in Table III. At temperatures of 500° and higher an appreciable decomposition of the nitride prevented us from making similar investigations.

TABLE III

COMPOSITION OF THE  $\epsilon$ -PHASE IN EQUILIBRIUM WITH VARIOUS  $\text{NH}_3\text{-H}_2$  MIXTURES

NH <sub>3</sub> in NH <sub>3</sub> -H <sub>2</sub> gas mixtures, %	Composition of the $\epsilon$ -phase, % N <sub>2</sub> by weight in nitride					
	High nitride side	Low nitride side	Best average value	High nitride side	Low nitride side	Best average value
72	..	..	..	7.9	..	7.9
75	..	..	..	8.1	..	8.1
80	8.4	..	8.4	8.8	..	8.8
85	..	..	..	9.2	..	9.2
90	9.45	9.25	9.4	9.7	9.7	9.7
95	10.15	10.15	10.15	10.25	10.4	10.35
98	..	..	..	10.95	10.85	10.9
100	11.05	..	11.05	11.2	..	11.2

The probable analytical error varied between  $\pm 0.06\%$  nitrogen for the lower limit of the  $\epsilon$ -phase to  $\pm 0.10\%$  nitrogen for the upper limit. As the table shows, equilibrium was approached from both high and low nitride sides whenever the reaction rate permitted it. This was possible only with gas mixtures containing over 85% of ammonia. Below this value equilibrium could be conveniently approached from the high nitride side only.

Figure 2 represents the variation in the composition of the various iron nitrides with increasing  $P_{\text{NH}_3}/P_{\text{H}_2}$  ratios at 400 and 444°. The slopes of the curves representing the variation in the composition of the phases  $\alpha$  and  $\gamma'$  are uncertain; for this reason they were drawn with dotted lines.

Errors in the determination of the lattice dimensions of the  $\epsilon$ -phase by means of x-ray powder photographs might arise from systematic errors

inherent in the method and from accidental errors of measurements. The technique ordinarily used consists in mounting a small sample coaxial with a cylindrical film. If the sample is too thick, the diffraction cones will not have apexes on the same line. If the sample is not accurately centered, each line on the film will be at a different distance from it. Divergence of the x-ray beams also introduces an error into the measurements. For a cubic substance these errors can partially be corrected for by extrapolating to  $\theta = 90^\circ$  a curve obtained by plotting the values of  $A_K$ , the measured values of  $a_0$ , against the corresponding values of  $\theta$ .<sup>6</sup> The determination by this method of two parameters defining the dimensions of a hexagonal lattice must depend upon a relationship between them. In either case considerable error can be introduced by the extrapolation, particularly so if values of  $A_K$  are not determined for large values of  $\theta$ . This method was used by Eisenhut and Kaupp<sup>3</sup> in the determination of  $a$  and  $c$  for various samples of the  $\epsilon$ -phase.

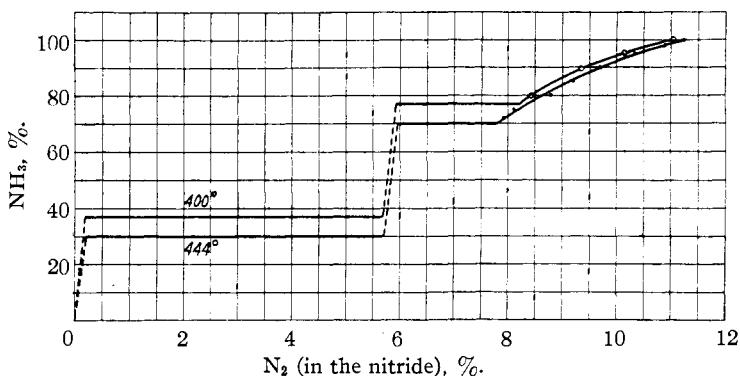


Fig. 2.—Equilibrium diagram showing the variation of the percentage nitrogen in the iron nitrides with the percentage ammonia in the ammonia-hydrogen mixtures.

In our work we effectively eliminated these sources of error by reducing the sample to very small cross sectional area, approximately the half value thickness, and by using only those films that had constant radii, determined from the sodium chloride reference lines. This method approximates the ideal case given by Kettmann.<sup>6</sup> The probable limits of error for the  $a$  values given in Table IV are  $\pm 0.002 \text{ \AA.}$ , for the  $c$  values  $\pm 0.003 \text{ \AA.}$

The x-ray data obtained from the  $\epsilon$ -phase are summarized in Table IV. The values of  $a$  and  $c$  corresponding to various compositions of the solid phase are listed in this table and are shown in Fig. 3 in comparison with the values of Eisenhut and Kaupp and Hägg.<sup>7</sup> The three sets of results, although closely similar, show variations that we believe to be greater than

<sup>6</sup> Kettmann, *Z. Physik*, 53, 198 (1929).

<sup>7</sup> Hägg, *Z. physik. Chem.*, 8B, 455 (1930).

TABLE IV  
SUMMARY OF X-RAY DATA FOR THE  $\epsilon$ -PHASE

Plane	1 100% NH <sub>3</sub> 400°	2 95% 444°	3 95% 400°	4 90% 444°	5 90% 400°	6 85% 444°	7 80% 444°	8 80% 400°
(100)	2.397	2.383	2.380	2.393	2.372	2.369	2.359	2.358
(002)	2.202		2.202		2.197			2.194
(101)	2.108	2.096	2.096	2.091	2.090	2.082	2.079	2.074
(102)	1.624	1.621		1.619	1.610	1.606	1.604	1.599
(110)	1.384	1.374	1.389	1.371	1.368	1.365	1.361	1.359
(112)	1.172	1.166	1.164	1.163	1.162	1.160	1.157	1.156
(103)	1.256	1.249	1.248	1.246	1.246	1.244	1.242	1.241
(201)	1.156				1.144	1.142	1.138	1.138
(004)	1.105	1.101					1.095	
$a_0$	2.764	2.750	2.746	2.742	2.737	2.732	2.723	2.722
$c_0$	4.424	4.402	4.400	4.391	4.397	4.386	4.382	4.376
% N	11.06	10.35	10.14	9.65	9.4	9.3	8.8	8.47
At. Fe /At. N	2.02	2.16	2.25	2.35	2.42	2.44	2.60	2.73

our experimental error. Eisenhut and Kaupp indicated that both  $a$  and  $c$  of the  $\epsilon$ -phase are linear functions of the nitrogen concentration expressed

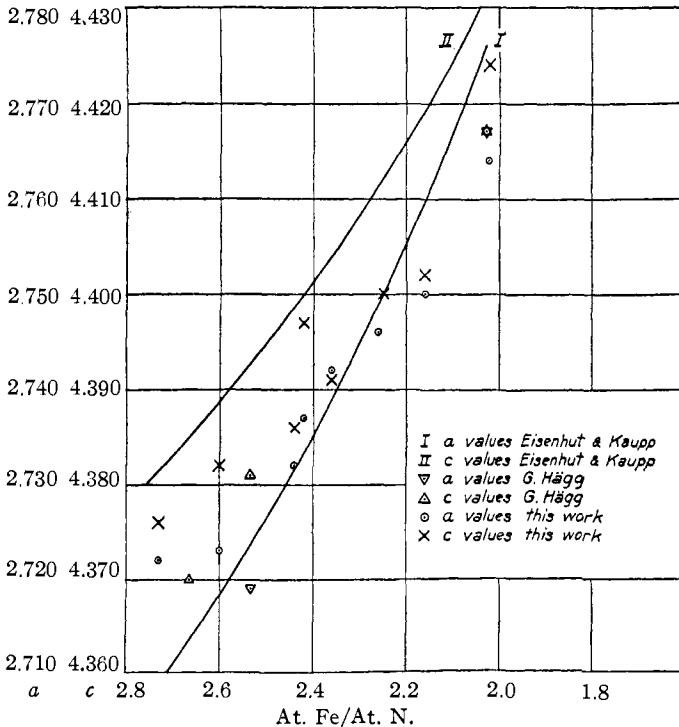


Fig. 3.—Variation in the lattice constants  $a$  and  $c$  of the  $\epsilon$ -phase with increasing atomic ratios Fe:N.



as per cent. by weight. Within the limits of our experimental error it is possible for  $a$  to be a linear function either of the nitrogen concentration expressed as per cent. by weight, or of the ratio of the number of iron to nitrogen atoms. The values of  $c$ , however, are not linear functions of either of these variables. We do not believe that any of the results thus far obtained are sufficiently accurate to warrant the deduction of empirical equations expressing either  $a$  or  $c$  as functions of the nitrogen concentration.

We wish to acknowledge the excellent coöperation of Miss Ellen Z. Kibbe, who analyzed all the nitride samples, and Mr. Leonardo Testa, glass blower.

### Summary

1. The equilibrium data for the reaction  $2\text{Fe}_4\text{N} + 3\text{H}_2 = 8\text{Fe} + 2\text{NH}_3$  have been extended to 400 and 575°; they indicate that the percentage of  $\text{NH}_3$  in an  $\text{NH}_3\text{-H}_2$  mixture at 1 atmosphere necessary to convert Fe to  $\text{Fe}_4\text{N}$  is  $37 \pm 2$  at 400, and  $14.5 \pm 1$  at 575°.

2. The percentages of ammonia in an  $\text{NH}_3\text{-H}_2$  mixture in equilibrium with the solid phases  $\gamma'$  and  $\epsilon$  were found to be  $77 \pm 2$  at 400,  $70 \pm 2$  at 444 and  $57 \pm 1.5$  at 500°.

3. The composition and lattice dimensions of the  $\epsilon$ -phase in equilibrium with various  $\text{NH}_3\text{-H}_2$  mixtures have been determined at 400 and 444°.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

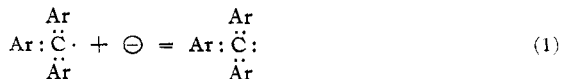
## THE ELECTRON AFFINITY OF FREE RADICALS. II. DIPHENYL- ALPHA-NAPHTHYLMETHYL, DIPHENYLBIPHENYL AND PHENYLBIPHENYL-ALPHA-NAPHTHYLMETHYL

BY HENRY E. BENT

RECEIVED MARCH 2, 1931

PUBLISHED MAY 6, 1931

The work to be described in this paper is a continuation of the study of the effect of various groups on the electron affinity of organic free radicals.<sup>1</sup> The type reaction may be represented by the equation



Ar, in general, being an aromatic group.

The details of the method and experimental procedure are described in the first paper on triphenylmethyl, in which it was shown that its electron affinity in the gaseous state is 59 kg. cal. with an uncertainty of the order of magnitude of 5 kg. cal. The reaction studied experimentally is the addition of sodium to the free radical to give the negative ion in ether solution



<sup>1</sup> H. E. Bent, *THIS JOURNAL*, **52**, 1498 (1930).