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REVIEW AND EVALUATION OF RATE DATA FOR GAS PHASE REACTIONS OF THE N-H SYSTEM

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REVIEW AND EVALUATION OF RATE DATA FOR GAS PHASE REACTIONS OF THE N-H SYSTEM*

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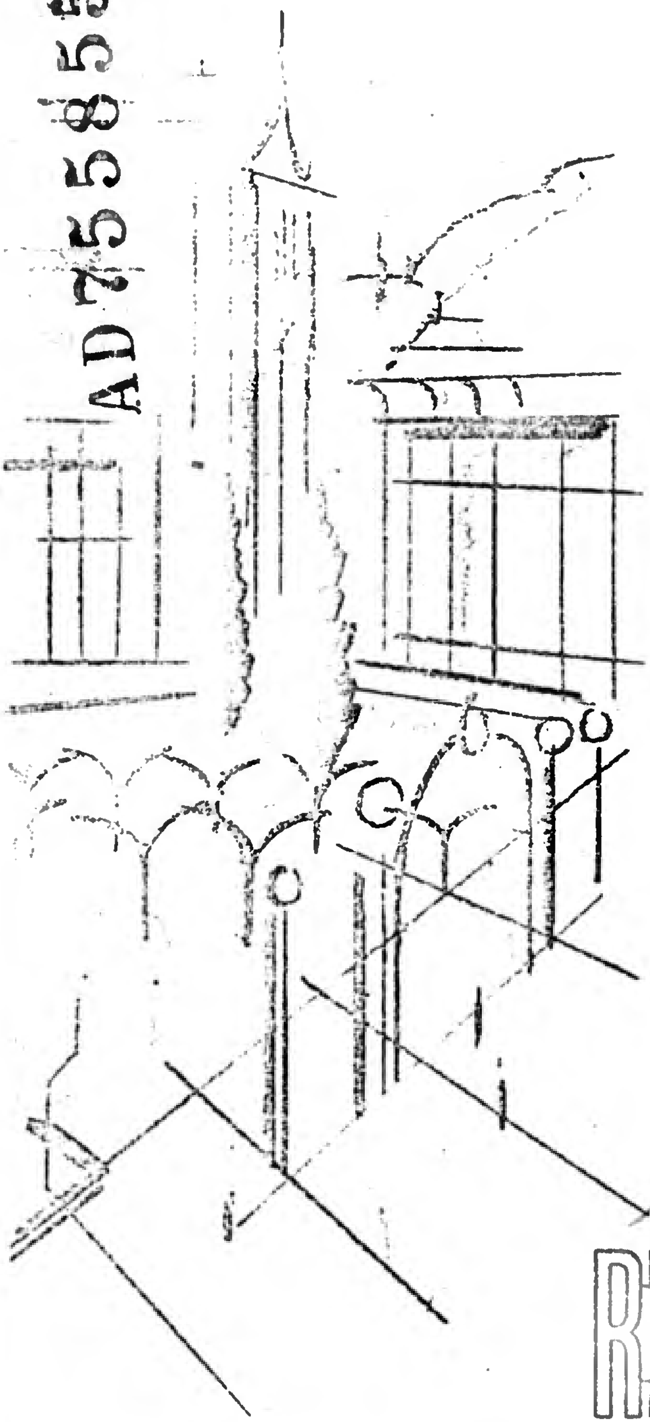

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13. ABSTRACT

While a number of recent reviews of rate data have been undertaken, there is not a current review of data relating to the N-H system. Reaction rate data for gas phase reactions between species containing nitrogen and hydrogen have been compiled and reviewed. Where sufficient data are available from a number of sources a suggested best-fit reaction rate constant has been derived. Data for these reactions are summarized graphically and discussed separately with general features of the available data noted and needed experimental extensions of the data emphasized. Available data for all reactions considered in the review are tabulated. Motivation for the review is the concurrent experimental investigation of ammonia decomposition using a high temperature flow reactor being developed.

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Discussion of Selected Reactions

Reactions discussed below are those for which the relatively greater abundance of data and absence of discussion in other recent reviews warrent more specific consideration. Reactions in this group have been widely discussed in examining the elementary kinetics of reaction systems containing nitrogen and hydrogen. Following the discussion the available results pertinent to each reaction are presented graphically in Figures 1-6 with a tabular compilation appearing in Appendix A.

$NH_3 + M \rightarrow NH_2 + H + M$

Reported results for thermally breaking the NH_2 - H bond are derived from shock tube studies in which this reaction is taken to be the initiating step in a chain mechanism for ammonia decomposition. All of these studies are at temperatures in excess of 2000°K and most focus on the early time of the overall ammonia decomposition process. The studies between 2000 and 3000°K (4, 7, 13) use argon as diluent and are in fair agreement. Bradley, et. al. (4) followed the progress of the reaction by tracing NH emission. The study is part of an extensive series (58, 40, 2, 4) of studies of reactions in shock heated ammonia and hydrazine. Michel and Wagner (13) also reported on this reaction in a shock tube study concerned primarily with hydrazine decomposition. Ammonia composition was followed in this case by the decay of uv absorption. The NH radical was also detected in this study. Data on ammonia decomposition were also obtained by Takayama and Miyama (17) in investigating oxidation of ammonia. Ammonia was again followed by uv absorption.

A study at much higher temperature (2900 - 9600°K) and using Xenon as a diluent differs primarily in the prexponential factor from the argon shock tube results.(5) This suggests a lower third body efficiency for Xenon as compared to argon. The activation energy in this case is more nearly the NH_2 - H bond dissociation energy. Reaction progress was followed in this case by recording NH emission.

Some discussion of this reaction is also included in the studies of the overall reaction

$$NH_3 + M \rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2$$

These results are summarized on page A-5.

There is need for further study of the elementary reaction

$$NH_3 + M \rightarrow NH_2 + H + M$$

at temperatures below 2000°K and by some means other than shock tube to corroborate the agreement of the higher temperature shock tube results. Rate data for this reaction is reviewed graphically in Figure 1. The best-fit value of the rate constant is

$$k = 10^{14.52} \exp \left(\frac{-\ 84.2\ \text{Kcal/mole}}{RT}\right) \text{cc/mole-sec}$$

$\underline{N_2H_4 \rightarrow NH_2 + NH_2}$

The unimolecular decomposition of hydrazine has been studied quite extensively over a wide range of conditions with good agreement. A long standing difficulty in interpreting data on hydrazine decomposition is in determining the regime of the reaction. At high pressure the unimolecular decomposition seems controlling whereas at low pressure the reaction is characterised as bimolecular following a Lindemann mechanism.

Szwarc (51) studied hydrazine decomposition in a flow reactor with toluene as a carrier gas. His conclusion that the reaction at atmospheric pressure was unimolecular was later reinterpreted by Gilbert (42). Gilbert showed that the reaction was in the low pressure bimolecular region by examining the details of flow in the apparatus used by Szwarc. Independent data of Gilbert also supported the bimolecular mechanism at low pressure in a flow reactor.

An extensive investigation of the pressure dependence of the decomposition of hydrazine was done by Wagner, et. al. (13, 56). A shock tube study over a wide pressure range (56) distinguished the high pressure unimolecular reaction. It was also suggested that Szwarc obtained a higher rate constant for the bimolecular reaction because of the higher collision efficiency of toluene. The later study by Wagner (13) was in substantial agreement with results of McHale, Knox and Palmer (44).

A best fit of the data for unimolecular decomposition of hydrazine gives a rate constant of

$$k = 10^{12.5} \exp \left(\frac{-\ 51.2\ \text{Kcal/mole}}{RT} \right)$$

$\underline{NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3}$

This reaction has been discussed most frequently as a chain propagation reaction in the hydrazine decomposition mechanism. The direct experimental observation of the reaction is not known. It was initially suggested as part of a mechanism due to Adams and Stocks (46) although these authors gave no rate data for the reaction. Moberly (15) suggested a preexponential factor of 10^{12} in interpreting shock tube data for hydrazine decomposition. Michel and Wagner (13) obtained data for the reaction by a steady state analysis of the initial phase of the decomposition of hydrazine in a shock tube. Similarly, Eberstein and Glassman (31) found rate data for the propagation reaction by agreement with experimental results for a flow reactor investigation of hydrazine decomposition.

A summary of data for the reaction is given on page A-7 and Figure 3.

The selected best fit rate constant is

$$k = 10^{12.86} \exp\left(\frac{-\ 9.56\ \text{Kcal/mole}}{RT}\right)$$

$NH_2 + NH_2 \rightarrow NH_3 + NH$

A shock tube study of hydrazine decomposition by Diesen (41) provided data on disproportionation of NH_2 radicals. Concentrations of stable species (NH_3, N_2H_4, N_2, H_2) and the NH_2 radical were followed by time of flight mass spectrometry at low pressure (0.04 - 0.25 atm.) and temperatures between 1200 and 2500°K. It was concluded that the reaction

$$NH_2 + NH_2 \rightarrow NH + NH_3$$

was more important at low pressure than the recombination of NH_2

$$NH_2 + NH_2 \rightarrow N_2H_4$$

Saltzman and Bair (39) examined the reaction of NH_2 over a wider range of pressure with results in qualitative agreement with the conclusion of Diesen. In this study NH_2 was generated by photolysis in ammonia and the low pressure disproportionation reaction was distinguished from the higher pressure recombination of NH_2. Recent experimental results of Wolfrum (61) yet to be published are also included in Figure 4 and on page A-8. Empirical calculations (43, 45) have also been made of the rate constant.

Agreement of the reported data is not good even with some data reported under similar conditions. The suggested value for the rate constant is

$$k = 10^{12.60} \exp\left(\frac{-\ 5.56\ \text{Kcal/mole}}{RT}\right)$$

$H + NH_3 \rightarrow NH_2 + H_2$

No unambiguous data on the reaction of H atoms with ammonia can be obtained from the literature. Experimental results from low temperature studies yield activation energies above 10 Kcal/mole while the calculated data give considerably lower values (2.0 - 3.4 Kcal/mole).

An electric discharge flow system was used by Sciavello and Valpi (26) to generate H atoms at 420°K. Stable species were followed with a mass spectrometer and rate data for H atoms reacting with ammonia were inferred from the experiment. In a later study (24) at higher temperature (590-690°K) the reaction rate was characterized using the explosion limit method. Ammonia was added to flames of H_2/O_2 and CO/O_2 and data interpreted from ammonia inhibition of the combustion. The reaction

$$NH_3 + H \rightarrow NH_2 + H_2$$

was taken as competing with the chain branching step

$$H + O_2 \rightarrow OH + O$$

by removing H atoms and producing less reactive NH_2. Electron spin resonance was used to follow H atom concentration. Calculated values for the rate constant are also available (43, 45) which do not agree with the experimental results giving reaction rates much too high at low temperature.

Data are needed for the reaction at higher temperature where the reaction should remain slow enough to follow by conventional means. The selected best fit rate constant from available data summarized in Figure 5 is

$$k = 10^{12.0} \exp\left(\frac{-6.23 \text{ Kcal/mole}}{RT}\right)$$

$\underline{H + NH_2 \rightarrow NH + H_2}$

Rate data for this H atom exchange reaction are all calculated results. Most estimates of the activation energy range between 2.0 and 4.4 Kcal/mole with the value of Bahn (63) very much higher (21.469 Kcal/mole). The calculated rate data are all for high temperature systems between 1000 and 4000°K. A number of the estimates (21, 28, 45) are due to Mayer and Schieler with other authors.

The available estimates of the rate constant are summarized on page A-8 and in Figure 6. The best fit to the data from the literature suggests a rate constant

$$k = 10^{10.92} \exp\left(\frac{-\ 5.60\ \text{Kcal/mole}}{RT}\right)$$

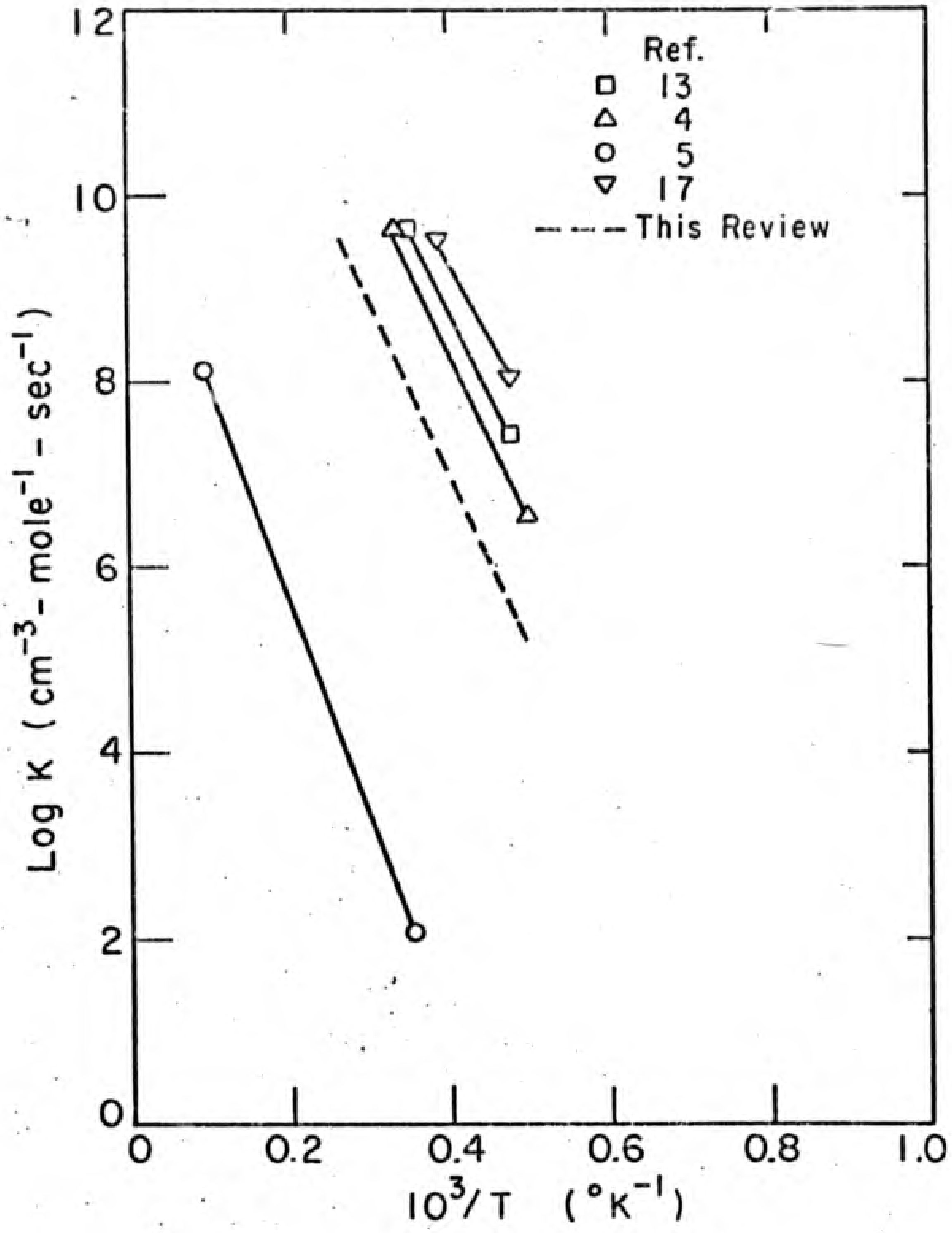

Figure 1

$NH_3 + M \longrightarrow NH_2 + H + M$

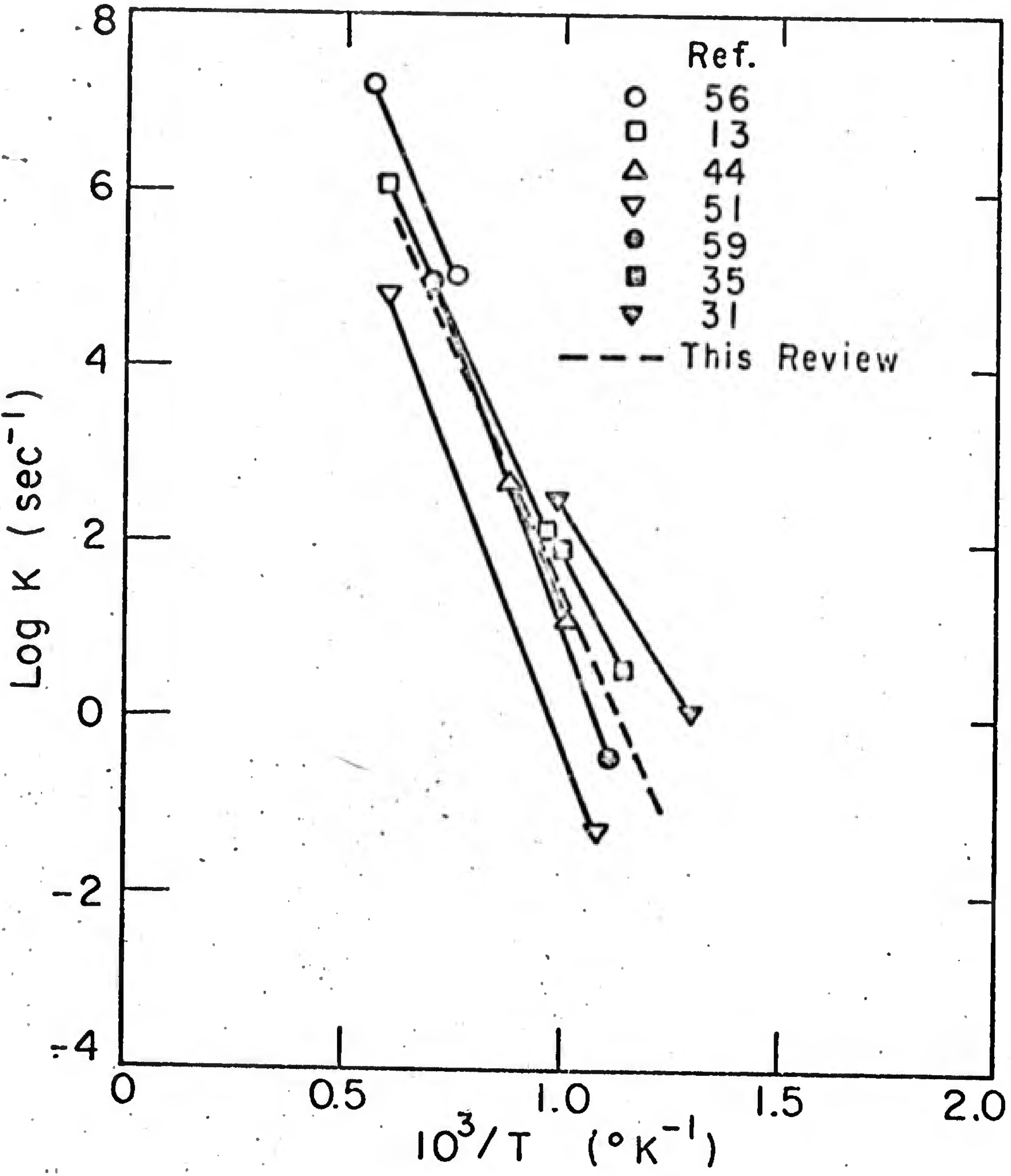

Figure 2

$N_2H_4 \longrightarrow NH_2 + NH_2$

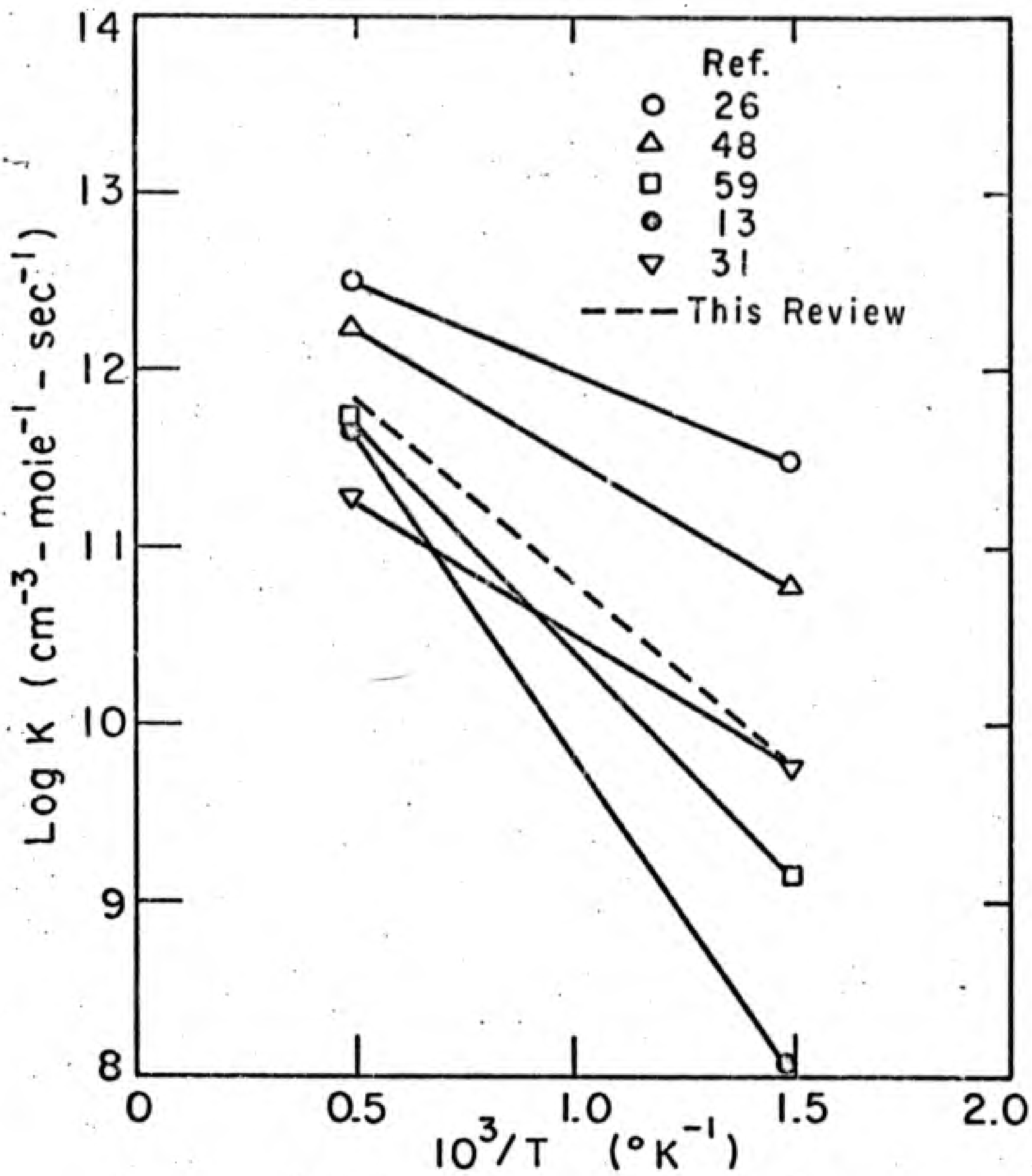

Figure 3

$NH_2 + N_2H_4 \longrightarrow NH_3 + N_2H_3$

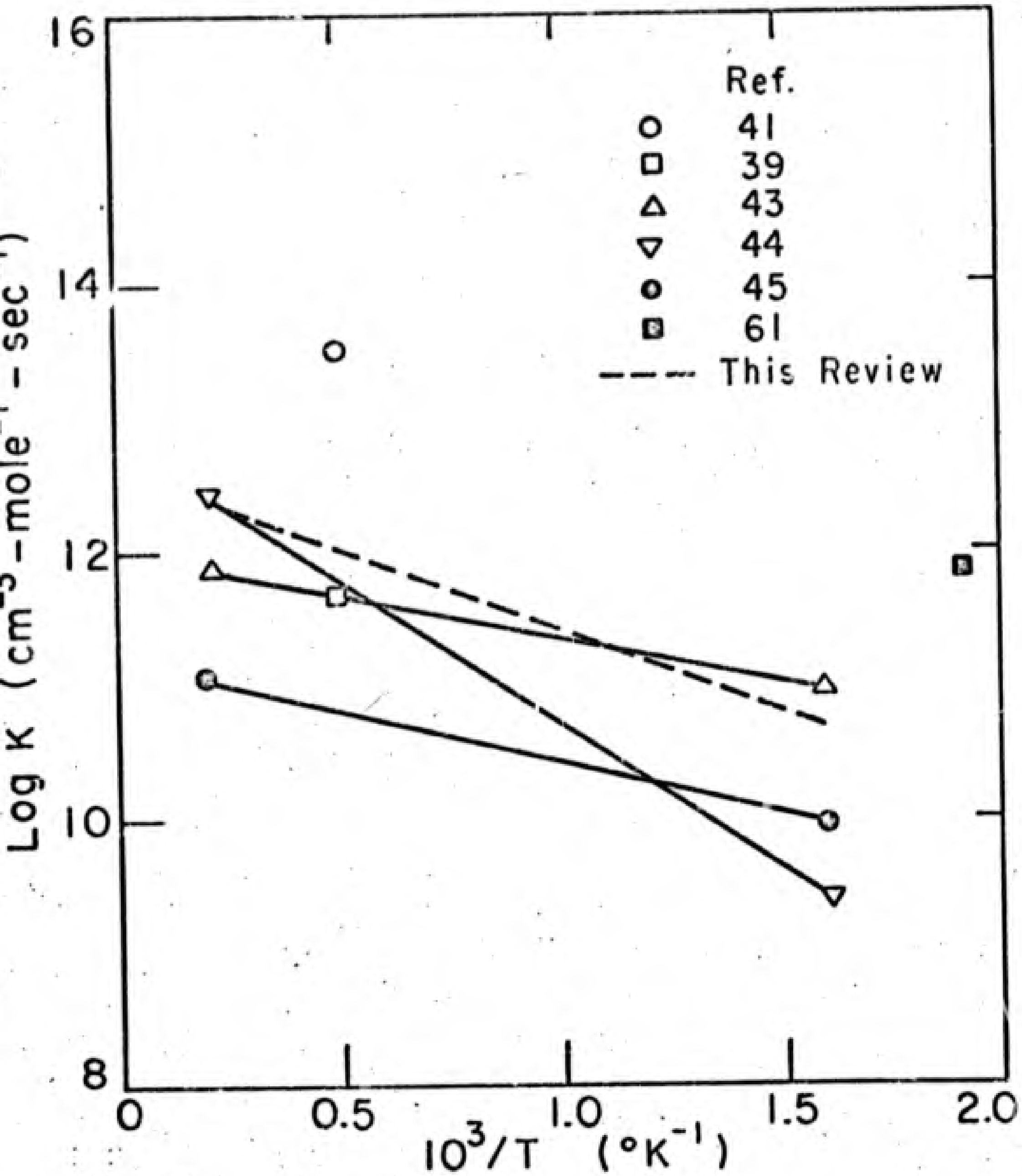

Figure 4

$NH_2 + NH_2 \longrightarrow NH_3 + NH$

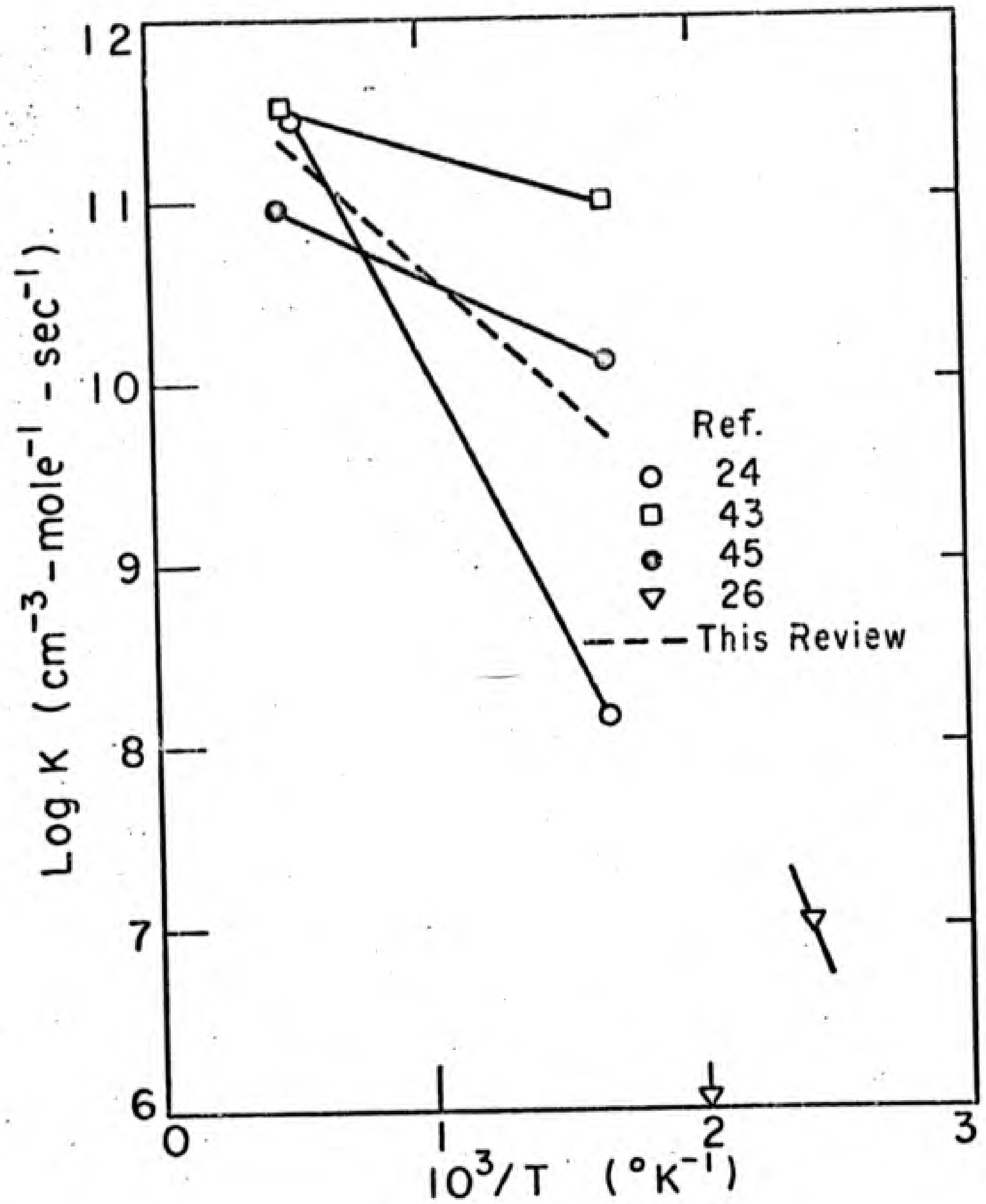

Figure 5

$H + NH_3 \longrightarrow NH_2 + H_2$

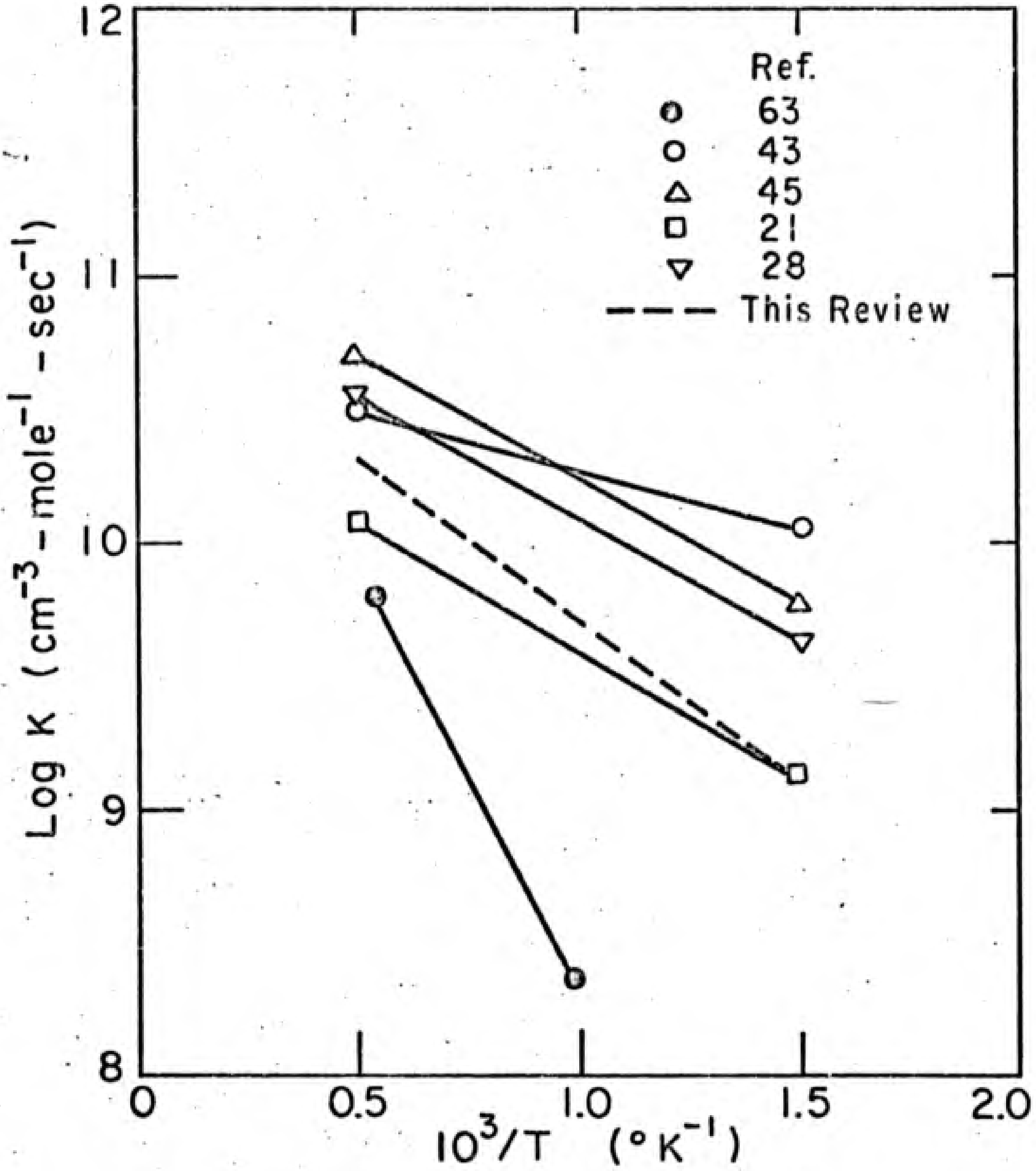

Figure 6

$NH_2 + H \longrightarrow NH + H_2$

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APPENDIX A

Rate Data for Reactions in the Gaseous N-H System

1. Introduction

The following compilation includes reaction rate data for reactions in the gas phase involving species containing only nitrogen and hydrogen. The reactions are all indexed with the reaction written in the endothermic direction. Data listed for each reaction include forward (k_f) and reverse (k_r) reaction rate constants where available or activation energy (E) or pre-exponential factor (A) for the available experimental and theoretical determinations. Also included is the heat of reaction at 298°K for each reaction calculated from enthalpies of formation provided by Reference 62 and recorded in Table A2. A number of reactions for which the only available data are the calculated values given in the tabulation by Bahn (63) have not been included. The present review was assisted by a bibliography provided by the National Bureau of Standards (57).

The order in which the reactions are listed is determined generally by the abundance of data for the reaction with the most frequently studied reactions presented first. Concentration units are moles/cc and activation energy is kcal/mole. If m is the total reaction order then the rate constant k has units

$$k = \frac{1}{\text{sec}} \left[\frac{\text{moles}}{\text{cc}}\right]^{(1-m)}$$

Table A1. Bond strengths.

Bond	Bond Strength (kcal/mole at 298°K)	Reference
H - H	104.20	JANAF (62)
N ≡ N	225.94	"
N - H	84.07	"
$H - NH_2$	103.14	"
$H_2N - NH_2$	57.39	"
H - NH	95.00	"
$H - N_2H_3$	93.03	"
HN = NH	111.10	"
$HN = NH_2$	(79.07)	est
$H - N_2H_2$	(61.00)	est

Table A2. Heats of formation.

Species	Heat of Formation (kcal/mole at 298°K)	Reference
NH_2	40.07	JANAF (62)
H	52.10	"
N	112.97	"
NH	81.00	JANAF (62)
N_2H_3	(42)	est
NH_3	-10.97	JANAF (62)
N_2H_4	22.75	"
N_2H_2	50.90	"
N_2, H_2	0.00	"

2. Index of Reactions

Reaction	Page
$N_2H_2 + H_2 = NH_2 + NH_2$	A-12
$NH_2 + NH_2 \rightarrow H + N_2H_3$	A-12
$N_2H_3 \rightarrow N_2 + H_2 + H$	A-12

3. Rate Data

Reaction and Rate Constant	Temperature	Comment	Ref
$NH_3 + M = NH_2 + H + M$	103.14 kcal/mole		
$k_f = 3.6\times10^{15} \exp(-\frac{83.0}{RT})$	2000-3000°K	Shock Tube M = Ar	4
$k_f = 4.1\times10^{15} \exp(-\frac{79.5}{RT})$	2100-2900°K	Shock Tube M = Ar	13
$k_f = 2.4\times10^{10} \exp(-\frac{107.31}{RT})$	2900-9600°K	Shock Tube M = Ar	5
$k_f = 10^{15.36\pm0.15} \exp(-\frac{71.1\pm9.2}{RT})$	2100-2600°K	Shock Tube M = Ar	17
$NH_3 + M = \frac{1}{2} N_2 + \frac{3}{2} H_2 + M$ (Overall)	10.97 kcal/mole		
k_f: $E = 77.0$	2190-3860°K	$\frac{3}{2}$ order Shock Tube M = Ar	2
k_f: $E = 103.0$	2190-2800°K	"	2
k_f: $E = 79.0$	2800-3860°K	"	2
$k_f = 2.5\times10^{16} \exp(-\frac{77.7}{RT})$	2000-3000°K	1/2 order in Ar 3/2 order in NH_3	8
$k_f = 10^{10} \exp(-\frac{83.7}{RT})$	2400-3000°K	zero order in Ar 1st order in NH_3	11
$k_f = 10^{11.7} \exp(-\frac{102.0}{RT})$	2400-3000°K	"	11
k_f: $E = 52$	2000-3000°K	oxygen impurity	7
k_f: No reaction	1323°K	flow reactor	10
Discussion:			64

Reaction and Rate Constant	Temperature	Comment	Ref
$N_2H_4 = NH_2 + NH_2$	57.39 kcal/mole		
$k_f = 10^{13.0} \exp(-\frac{54.000}{RT})$	970-1120°K	k_∞	44
$k_f = 4\times10^{12} \exp(-\frac{60.000}{RT})$			51
$k_f = 10^{14} \exp(-\frac{60.000}{RT})$			56
$k_f = 10^{12.8} \exp(-\frac{52.200}{RT})$	1100-1600°K	at 7.5×10^{-5} moles/cc	13
$k_f = 10^{12} \exp(-\frac{47.500}{RT})$	1100-1600°K	at 2.5×10^{-5} moles/cc	13
$k_f = 10^{10.33} \exp(-\frac{36.170}{RT})$	750-1000°K	overall, 1st order	31
$k_f = 10^{13.9} \exp(-\frac{55.000}{RT})$	1280-1580°K	k_∞, 1st order	59
$k_f = 10^{11.7} \exp(-\frac{54.150}{RT})$	887-1034		35
$k_r = 2.33\times10^{12}$			33
$k_r = 2.5\times10^{12}$			39
$k_r = 10^{13}$			48
$k_r = 10^{12.5}$			31
$N_2H_4 + M = NH_2 + NH_2 + M$	57.39 kcal/mole		
$k_f = 10^{19} \exp(-\frac{60.000}{RT})$		via N_2H_4*	49
$k_f = 10^{15.6} \exp(-\frac{41.000}{RT})$	1280-1580	k_o	56
Discussion:		1,6,27,41,42,46	

Reaction and Rate Constant	Temperature	Comment	Ref
$NH_3 + \frac{1}{2} N_2 + \frac{1}{2} H_2 = N_2H_4$ (Overall)		33.72 kcal/mole	
$k_r = 9\times10^{12} \exp(-\frac{37.400}{RT})$	950-1160°K	3/2 order w.r. to N_2H_4 p = 2.8-5.4 atm	36
k_r: $E_a = 40.3$			
Discussion:		46,49,52,53,54,59	
$NH_3 + N_2H_3 = NH_2 + N_2H_4$		31.79 kcal/mole	
$k_r = 10^{12} \exp(-\frac{7.000}{RT})$			31
$k_r = 10^{13} \exp(-\frac{4.600}{RT})$	400°K		26
$k_r = 10^{13} \exp(-\frac{12.000}{RT})$			59
$k_r = 10^{13.5} \exp(-\frac{17.000}{RT})$			13
$k_r = 10^{13} \exp(-\frac{7.000}{RT})$			48
k_r: $A = 10^{12}$			15
$k_r = (7.9 \pm .7) \times 10^{10}$			41
Discussion:			6

Reaction and Rate Constant	Temperature	Comment	Ref
$NH_3 + NH = NH_2 + NH_2$		9.11 kcal/mole	
$k_r = 2.5\times10^{13}$	1900-2300°K	Shock tube	41
$k_r = 0.46\times10^{12}$		Flash Photolysis	39
$k_r = 10^{12.8} \exp(-\frac{10.000}{RT})$			44
$k_r = 10^{12} T^{0.5} \exp(-\frac{3.000}{RT})$			43
$k_r = 1.7\times10^{11} T^{.632} \exp(-\frac{3.600}{RT})$		Calculated	45
$k_r = 7\times10''$			61
Discussion:		40,5,29,30,37,38	
$NH_2 + H_2 = H + NH_3$		1.06 kcal/mole	
k_r: $\sim10^7$ $E = 10.0$, $E = 15.0$ kcal/mole	420°K		26
$k_r = 5\times10^{11} T^{.5} \exp(-\frac{2.000}{RT})$		Estimated	43
$k_r = 1.9\times10^{11} T^{.673} \exp(-\frac{3.400}{RT})$		Calculated	45
$k_r = (.113\pm.03)\times10^{13} \exp(-\frac{13.700\pm.600}{RT})$	~800°K	cal. + Expt.	24
Discussion:			27
$H_2 + NH = H + NH_2$		11.17 kcal/mole	
$k_r = .35\times10^{11} T^{.79} \exp(-\frac{4.400}{RT})$	1000-4000°K	Calculated AC Theory	21
$k_r = .95\times10^{11} T^{.67} \exp(-\frac{4.300}{RT})$		Calculated	28
$k_r = .5\times10^{11} T^{0.5} \exp(-\frac{2.000}{RT})$		Estimated	43
$k_r = 1.4\times10^{11} T^{.67} \exp(-\frac{4.300}{RT})$		Calculated	43,45
$k_f = 3.996\times10^{11} T^{.4941} \exp(-\frac{21.469}{RT})$	~2000°K	Estimated	63

Reaction and Rate Constant	Temperature	Comment	Ref
$NH + M = N + H + M$		84.07 kcal/mole	
$k_r = 3\times10^{16}\ T^{-0.5}$		Estimated	43
$k_r \geq (4.87\pm0.8)\times10^{14}$	298°K		20
$k_f = 3\times10^{5}\ sec^{-1}$	2000-8000°K	$E_a \approx 0$ via $NH+N_2^{*}\rightarrow NH^{*}+N_2$	58
$k_f = 6.905\times10^{11}T^{0.5}\exp(-\frac{89.293}{RT})$	~2000°K	Estimated	63
$N_2H_3 + M = NH + NH_2 + M$		79.07 kcal/mole	
$k_f = 10^{12.8}\ \exp(-\frac{18.000}{RT})$			48
$k_f = 10^{12.9}\ \exp(-\frac{18.000}{RT})$			31
Discussion:			46, 4, 55
$H_2 + N = H + NH$		20.13 kcal/mole	
$k_r = 10^{12}T^{.68}\ \exp(-\frac{1.900}{RT})$	1000-4000°K	calculated- AC Theory	9
k_f: $< 10^{8}$, $E > 15.000$ kcal/mole	300°K		12
k_f: No reaction			58
$H_2 + N_2 + NH_3 = N_2H_3 + NH_2$		93.04 kcal/mole	
$k_r = 10^{12.5}$			31
k_r: $A = 10^{12}$			15

Reaction and Rate Constant	Temperature	Comment	Ref
$NH_2 + M = N + H_2 + M$		12.03 kcal/mole	
k_r: E large, slow reaction			12
$k_r = 1.66\times10^{-10}\ cm^6 mole^{-2} sec^{-1}$			22
Discussion:			23
$N_2H_3 = H + N_2H_2$		61.00 kcal/mole	
k_f: $E \simeq 42$ kcal/mole			13
$k_f = 1.373\times10^{19} T^{-.4926} \exp(-\frac{67.559}{RT})$		Estimated	63
$k_r = 1.402\times10^{15} T^{0.5}$		Estimated	63
$H_2 + H_2 + N_2 = H + N_2H_3$		94.10 kcal/mole	
$k_r = 10^{15}$			31
k_r: $A = 10^{12}$			15
$NH_2 + NH_3 = H_2 + N_2H_3$		12.9 kcal/mole	
k_r: $E_a \sim 27$ kcal/mole			4
$k_f = 2.117\times10^{10} T^{.5} \exp(-\frac{21.567}{RT})$	~2000°K	Estimated	63
$H_2 + H_2 = N_2H_2$		50.90 kcal/mole	
$k_r = 10^{14}$	2000°K		41
$k_r = 3.6\times10^{11} T^{.55} \exp(-\frac{1.900}{RT})$		Calculated	28
Discussion:			40

Reaction and Rate Constant	Temperature	Comment	Ref
$N_2H_3 + H_2 = N_2H_4 + H$	32.85 kcal/mole		
$k_r = 3.5\times10^{11} \exp(-\frac{2.000}{RT})$	295-455°K		26
$k_r = 1.3\times10^{13} \exp(\frac{-2.50}{RT})$	298°K		61
Discussion:			1,6,19,27
$N + NH_2 = NH + NH$	8.96 kcal/mole		
$k_f = 1.8\times10^{11}T^{.67} \exp(-\frac{15.100}{RT})$	1000-4000°K	Calculated	21
$NH + N_2H_4 = NH_2 + N_2H_3$	21.65 kcal/mole		
$k_f = 10^{14} \exp(-\frac{10.000}{RT})$			31
$N + NH_3 = NH + NH_2$	19.07 kcal/mole		
$k_f = 5\times10^{11}T^{.5} \exp(-\frac{2.000}{RT})$		Estimated	43
$k_f = 2.092\times10^{11}T^{.5} \exp(-\frac{13.161}{RT})$		Estimated	63
$NH_2 + M = NH + H + M$	93.03 kcal/mole		
$k_f = 2.102\times10^{10}T^{.5} \exp(-\frac{94.555}{RT})$		Estimated	63
$k_r = 2\times10^{16}\ T^{.5}$		Estimated	43
$NH_2 + NH_3 = H + N_2H_4$	45.75 kcal/mole		
$k_r = 10^{13} \exp(-\frac{7.000}{RT})$			1
$k_r = 1.2\times10^{8} \exp(-\frac{2.600}{RT})$			32

Reaction and Rate Constant	Temperature	Comment	Ref
$N_2 + NH_3 + NH_3 = N_2H_3 + N_2H_3$	105.95	kcal/mole	
$k_{\underset{r}{f}} \geq 3\times10^{12}$	423°K		26
$k_{\underset{r}{f}} = 10^{12.3}$			48
$k_{\underset{r}{f}} = 10^{12.0}$			31
$N_2H_2 + H_2 = NH_2 + NH_2$	29.24	kcal/mole	
$k_r = 10^{13.6}\ \exp(-\frac{12.000}{RT})$			25,44
$NH_2 + NH_2 = H + N_2H_3$	13.96	kcal/mole	
$k_f = 6.793\times10^{10}T^{0.4345}\ \exp(-\frac{20.425}{RT})$		Estimated	63
$k_r = 1.7\times10^{12}$			61
$N_2H_3 = N_2 + H_2 + H$	10.10	kcal/mole	
K_f : $A = 10^{12}$			15