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The Radiation Chemistry of Gaseous Ammonia

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The Radiation Chemistry of Gaseous Ammonia

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RICHARD W. ROBERTS, *Director*

Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or G values (molecules formed or destroyed per 100 eV). Various indirect methods based on G values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

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H_2 and N_2 are the only significant products of radiolysis of gaseous ammonia under static conditions at dose rates less than about $10^{19} eV \cdot g^{-1} s^{-1}$; and $G(H_2) = 5.0 \pm 1.0$ and $G(N_2) = 1.7 \pm 0.3$ for irradiation at 20°C and pressures near one atmosphere. Yields do not appear to depend significantly upon LET (linear energy transfer); and they are independent of dose up to at least $8 \times 10^{22} eV/g$. In static systems at dose rates $\geq 10^{26}$ $eV \cdot g^{-1} s^{-1}$, and in flow systems, N_2H_4 is also a product.

At dose rates less than $10^{19} eV \cdot g^{-1} s^{-1}$, $G(-NH_3)$ increases markedly with temperature and reaches a plateau value of about 10 at temperatures near 150 – 200°C. At very high dose rates ($\geq 10^{26} eV \cdot g^{-1} s^{-1}$) $G(-NH_3)$ increases significantly at higher temperatures (value depends upon dose rate) and $G(-NH_3)$ does not appear to be leveling off at the highest temperature studied (460°C). In both dose rate regions the increase in $G(-NH_3)$ is attributed primarily to the increasing importance of $NH_3 + H \rightarrow NH_2 + H_2$ with increasing temperature. $G(-NH_3)$ also appears to increase with decreasing dose rate. However, the effect is less pronounced than the effect of temperature, and the experimental evidence is not unequivocal.

NH and NH_2 have been observed spectroscopically in pulse radiolysis of NH_3 and such studies lead to $g(NH) = 0.4$. However, this value of $g(NH)$ is low because of errors in dosimetry. $g(NH_2)$ was not obtained directly because the absorptivity of NH_2 was not available. A number of additives has been employed in attempts to determine primary yields of other species involved in radiolysis; however, results with different additives and from different laboratories are in good agreement only in the case of $g(H_2)$ (0.7 – 0.8) and $g(NH_4^+)$ (3.3 – 3.9). The best value of $g(H)$ appears to be 10.4 ± 0.6; and this is the preferred value. $g(NH_2)$ is obtained from the material balance, $g(H) + 2g(H_2) = g(NH_2) + 2g(NH)$. The preferred value of $g(NH)$ is 0.75, i.e., $g(NH) = g(H_2)$ and this leads to $g(NH_2) = 10.4$.

Key words: Ammonia; chemical kinetics; data compilation; *G*; *g*; gas; radiation chemistry; rates; review.

1. Introduction

This compendium provides a comprehensive summary of data relevant to the radiation chemistry of gaseous ammonia. A complete mechanism for the radiolysis of ammonia cannot be written at present. However, probable contributing processes are discussed in some detail and the supporting evidence is examined critically when possible. Specific rates and/or energies of activation for these elementary processes are given when available but in general such data are not critically evaluated. Properties such as bond energies, ionization energies and electron affinities are tabulated for the major intermediates (app. 1). Such data have for the most part been taken from authoritative reference sources and are presented without critical comment. Preferred values are given for yields of both products (sec. 3) and intermediates (sec. 2.2.1 and 2.2.2).

Throughout the text and tables references are cited by Radiation Chemistry Data Center serial number; in many cases, the authors, or first author only, are included with serial number for easy identification of the work. When only a first author is cited, that name is followed by periods corresponding to the number of co–authors, as Nishikawa..68–0505. The bibliography is a listing of references by serial number; the first two digits of the number represent the year, so that the

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listing is approximately chronological. The literature has been covered through the first half of 1970; however, a few selected papers published later are included.

Symbols and Units

Radiation yields are in units of molecules per 100 eV and are designated G(X) when X is a reaction product. $G(-NH_3)$ represents molecules of ammonia converted to reaction products per 100 eV of energy absorbed. Various conventions have been used for reporting yields of intermediates. In this review such yields (in molecules per 100 eV) will be designated by use of the symbol g.

Other symbols used to designate properties, and the units in which values of the properties have been reported in this review, are listed below. A list of conversion factors is also included when non–SI (Système International) units have been used.

D, bond dissociation energy, kcal/mol.
E_a, activation energy, kcal/mol.
E.A., electron affinity, eV.
$\Delta H_f°$, standard heat of formation, kcal/mol.
I.P., ionization potential, eV.
k, specific rate, second order processes in $dm^3 mol^{-1} s^{-1}$.
P, pressure, atm or torr.
P.A., proton affinity, eV.
t, temperature, °C
Φ, quantum yield.

Conversion factors:

1 kcal = 4.184 kJ
1 atm = 101 325 N/m^2
1 torr = 133.32 N/m^2
1 eV = 1.602×10^{-19} J

2. Mechanism

2.1. Elementary Processes

Because the relative importance of various elementary processes involved in radiolysis of gaseous ammonia depends upon such factors as dose rate, temperature and pressure, it is not possible to write a single mechanism which will be applicable under all conditions. The significant elementary processes that should be considered in mechanisms for radiolysis of gaseous ammonia are summarized in table 2.1.

Formation and reaction of NH_4 are not included. There is some evidence for this species from mass spectrometric studies (67–9004) and its possible formation via $NH_3 + H + M$ in photochemical systems has been discussed (44–7000, 34–7002). Simic and Johnson (68–0659) have considered it as a possible intermediate in radiolysis of NH_3. At this time, however, evidence is very limited.

2.1.1. Elementary Processes Involving Ions and Excited Neutrals

There is considerable experimental evidence in support of the general assumption that ions and excited neutrals produced in reactions (1) and (2) (table 2.1) lead principally to NH_2 and H; NH and H_2 are also produced but in relatively small yields. (See table 2.2.1.)

TABLE 2.1. *Elementary processes*

Reaction	Specific rate[a]	Comments
(1) $NH_3 \rightsquigarrow NH_3^+ + e^-$ $\rightsquigarrow NH_2^+ + H + e^-$ $\rightsquigarrow NH^+ + H_2 + e^-$	—	Accounts for ~ 97% of total ionization at 2×10^{-7} torr for 100 eV e^-; relative abundances are NH_3^+: NH_2^+: NH^+ = 100.0: 40.9: 4.5 (66–0298).
(2) $NH_3 \rightsquigarrow NH_3*$	—	NH_3* represents totality of electronically excited states produced.
(3) $NH_3* \rightarrow NH_2 + H$	—	Only primary process in photolysis when $\lambda > 160$ nm (69–7017, 68–7168, 62–7002, 62–0132). NH_2 has been obs. spectrophotometrically in pulsed radiolysis (71–0169).
(4) $NH_3* \rightarrow NH + H_2$ (5) $NH_3* \rightarrow NH + 2H$	— —	In photolysis (4) accounts for about 12% of primary dissociation 147 nm[b] (64–7003) and 14% at 123.6 nm[b] (62–0132). $g(4) \cong 0.64$[c] (68–0051). NH observed spectrosocopically in pulse radiolysis; $g(NH) \cong 0.4$ (68–0101). Also observed spectroscopically in photochemistry at $\lambda < 160$ nm (67–7484, 63–6002, 63–0149, 62–7002).
(6) $NH_3* + NH_3 \rightarrow 2NH_3$	—	Importance of (6) depends upon lifetime of excited state. Spectral and photochemical evidence indicates that excitation between 217 and 166 nm leads to predissociation (35–9001, 64–7008).
(7) $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	6–11 x 10^{11} [d]	k_7 decreases with increasing translational energy of ion (70–0563).
(8) $NH_2^+ + NH_3 \rightarrow NH_3^+ + NH_2$	1.1 x 10^{11} (66–0298, 63–0150); 2.4 x 10^{11} (70–0563)	—
(9) $NH_2^+ + NH_3 \rightarrow NH_4^+ + NH$	3.9 x 10^{11} (66–9068, 67–9079); 6.5 x 10^{11} (70–0563)	k_8/k_9 depends upon translational energy of ion (70–0563).
(10) $NH^+ + NH_3 \rightarrow N_2H_2^+ + H_2$	1.8 x 10^9 (66–0298)[e]	—
(11) $NH_4^+ + e^- \rightarrow NH_3 + H$	(1.5 ± 0.3) x 10^{16} (71–0002). (See also 66–0201).	$g(NH_4^+) \cong 3.9$ estimated from studies with SF_6 as additive[f]. NH_4^+ accounts for ~ 99% of + ions at 1 torr in radiolysis with 100 eV e^- (66–0298).
(12) $NH_4^+ + e^- \rightarrow NH_2 + H_2$	—	Limiting value of $G(H_2)$ in presence of H–scavengers leads to *upper limit* of ~ 0.8 for $g(12)$[g]. Studies with CCl_4 indicate $g(12) \cong 0.1$[h].
(12) $NH_4^+ + e^- \rightarrow NH_2 + 2H$	—	At normal temperatures and pressures (12′) is endothermic by ~ 40 kcal because of solvation of NH_4^+ (69–0326, 67–0546).
(13) $NH_2 + H + M \rightarrow NH_3 + M$	~ 1.2 x 10^{10} (63–9010)[g] 1.8 x 10^{10} (71–0216)[i] 1.2 x 10^{11} (71–0169)	Pseudo–second order > 1000 torr (71–0169).
(13′) $NH_2 + H \rightarrow NH + H_2$	~ 2.9 x 10^9 (71–0216)[i]	Exothermic by 14 kcal.
(14) $NH_2 + NH_2 + (M) \rightarrow N_2H_4 + (M)$	~ 2.5 x 10^9 (64–7002)[i] ~ 1.8 x 10^9 (71–0216)[i]	Pseudo–second order above ~ 0.45 torr (63–9010). N_2H_4 is significant product in flow systems (67–0271) and in static systems at $\geqslant 10^{20} eV \cdot g^{-1} s^{-1}$ (68–0101, 69–0272) See also 71–0169.
(15) $NH_2 + NH_2 \rightarrow NH + NH_3$	4.6 x 10^8 (64–7002)[i,j]; 5 x 10^8 (71–0216)[i]	—
(16) $NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3$	10^9 exp(–7,000/RT) (65–9044)[k]	—
(16′) $NH_2 + H_2 \rightarrow NH_3 + H$	—	Endothermic by 0.1 kcal. Failure to observe dose dependence indicates (16′) unimportant under usual conditions (see section 3.2.1).
(17) $NH + NH_3 \rightarrow N_2H_4$	1.0 x 10^{10} (68–7214)[l]	—
(17′) $NH + NH_3 \rightarrow 2\,NH_2$	—	Exothermic by 14 kcal.

TABLE 2.1. *Elementary processes* – Continued

Reaction	Specific rate[a]	Comments
(18) $NH + NH \rightarrow N_2H_2^* \rightarrow N_2 + H_2$	7×10^{11} (68–0101)[m]; 5×10^{10} (71–0216)[t]	—
(19) $NH + N_2H_4 \rightarrow NH_2 + N_2H_3$	10^{11} exp(−10,000/RT) (65–9044)[k]	—
(20) $NH + NH_2 + (M) \rightarrow N_2H_3 + (M)$	—	Exothermic by ~ 73 kcal.
(21) $NH + H + (M) \rightarrow NH_2 + (M)$	—	Exothermic by 90 kcal.
(22) $H + N_2H_4 \rightarrow H_2 + N_2H_3$	3.5×10^8 exp(−2000/RT) (62–0131)[n]	Hydrazine has been used as a radical scavenger in NH_3 (See table 2.2.2).
(22′) $H + N_2H_4 \rightarrow NH_3 + NH_2$	10^{10} exp (−7000/RT) (65–9044)[k]	
(23) $H + NH_3 \rightarrow H_2 + NH_2$	4.1×10^{10} exp(−13,700 ± 600)/RT (65–0555)[o]	Values of 4×10^9 exp(−10,500/RT) and 8×10^7 exp(−7200/RT) have been calculated from kinetic analysis of yields from pulse radiolysis of pure NH_3 at very high dose rates (71–0216).
(24) $H + H + M \rightarrow H_2 + M$	1.4 – 9.3×10^9 $dm^6\ mol^{-2}s^{-1}$ when M = H_2.[p]	Specific rate should be higher for M = NH_3.
(25) $N_2H_3 + NH_2 \rightarrow N_2H_2 + NH_3$	—	Estimate $k_{25} \cong k_{14}$ (65–9044).[k] Exothermic by ~ 50 kcal.
(26) $N_2H_3 + H \rightarrow N_2H_2 + H_2$	—	Very fast (65–9044). Exothermic by ~ 50 kcal.
(27) $N_2H_3 + N_2H_3 \rightarrow 2\ NH_3 + N_2$	$\geqslant 3 \times 10^9$ at 150°C (62–0131)[n]	May involve intermediate formation of tetrazane (N_4H_6).[q]
(28) $N_2H_3 + N_2H_3 \rightarrow N_2H_2 + N_2H_4$	$k_{28}/k_{27} = 4$ (70–7065); $k_{27} \gg k_{28}$ (62–0131)[n]	No obvious reason for contradictory specific rate data.[r]
(29) $N_2H_2 \rightarrow N_2 + H_2$	—	Exothermic by ~ 49 ± 5 kcal.
(30) $N_2H_2 + N_2H_2 \rightarrow N_2 + N_2H_4$	—	65–9048

a. Unless otherwise indicated specific rates are in units of $dm^3 \cdot mol^{-1}s^{-1}$ and apply to temperatures near 25°C.

b. Based on limiting $\Phi(H_2)$ in presence of C_2D_4.

c. CCl_4 reduces $G(H_2)$ to 0.64 CCl_4 assumed to scavenge both e− and H and thus (4) is only significant source of H_2 in NH_3–CCl_4. (See sec. 2.1.1.)

d. Values reported are 6.0 (66–9068, 67–9079), 7.8 (66–0298), 9.0 (63–0150) and 10.9 (70–0563) in units of 10^{11} $dm^3 \cdot mol^{-1}s^{-1}$.

e. See also 63–0150.

f. See table 2.2.1.

g. See table 2.2.3.

h. Based on difference between $G(H_2)$ for $NH_3 + CCl_4$ (see *c* above) and $G(H_2)$ from $NH_3 + C_3H_6$ (68–0051).

i. Determined by following decay of NH_2 absorption following r.f. discharge through NH_3. Based on limited data and subject to uncertainties in absorptivity of NH_2.

j. At 2000 K, $k_{15} \cong 2.5 \times 10^{10}$ $dm^3 \cdot mol^{-1}s^{-1}$ (63–0167); $k_{14} \cong k_{15}$ has also been reported from studies at room temperature (absolute rate data not reported) (67–9109).

k. From analysis of the overall energy of activation of decomposition of N_2H_4 on the basis of an assumed mechanism involving (16).

l. Determined by kinetic spectroscopy in flash photolysis of NH_3.

m. Upper limit. Based on kinetic spectroscopy in pulse radiolysis of NH_2; $k_{18} \cong 10^{11}$ $dm^3 \cdot mol^{-1}s^{-1}$ at 2000 K (63–0167).

n. H atoms from microwave discharge flowed into N_2H_4 vapor; reaction followed by mass spectrometry; temp. range 25° to 150°C.

o. Also, $k_{23} \cong 10^4$ $dm^3 \cdot mol^{-1}s^{-1}$ at 150°C and $E_a \cong 10$–15 kcal/mol (62–0131).

p. Values reported are 1.35 (68–5013), 3.4 (64–0288), 5.0 (38–9001), 5.5 (35–0002), 8.5 (34–0005), 8.9 (63–9014), 9.3 (61–9008) in units of 10^9 $dm^6 \cdot mol^{-2}s^{-1}$. See also 65–9041, 67–9108 and 70–9010. Bennett and Blackmore (68–5013) give a critical comparison of specific rates of H + H with H_2 as third–body.

q. $N_4H_6 \rightarrow NH_3 + NH{=}N{-}NH_2$; $HN{=}N{-}NH_2 \longleftrightarrow NH_2{-}N{=}NH$; $N_3H_3 \rightarrow NH_3 + N_2$ (70–7065, 54–9005).

r. Conclusion that $k_{27} \gg k_{28}$ is based on simple observation that NH_3 and N_2 in 2:1 ratio are only products when H atoms flow into N_2H_4 (see *n* above). $k_{28}/k_{27} = 4$ is based on a more complicated analysis of isotopic nitrogens from reaction of H atoms with isotopically labeled hydrazines.

s. Estimated from collision theory.

t. Value calculated by kinetic analysis of product yields from pulse radiolysis of NH_3 on basis of an assumed mechanism.

Photochemical studies indicate that (3) is

$$(3)\ NH_3* \rightarrow NH_2 + H$$

the only dissociation process at wavelengths greater than 160 nm (ref. in table 2.1). At shorter wavelengths (4) and (5) also occur, however reactions (3) and (5) account for 80% of the dissociation.

$$(4)\ NH_3* \rightarrow NH + H_2$$
$$(5)\ NH_3* \rightarrow NH + 2H$$

The spectra of both NH_2 (71–0169) and NH (68–0101) have been observed in pulsed radiolysis. Primary positive ions from (1) undergo rapid ion–molecule reactions (7) – (10) and are thereby converted almost exclusively to NH_4^+ (66–0298). The relative importance of possible modes of neutralization of NH_4^+ (11), (12), and (12′) has been investigated by addition of electron scavengers. In pure ammonia, NH_4^+ is neutralized by e^- since negative ion formation is negligible (66–0298, 34–9002). In the presence of electron scavengers, NH_4^+ is neutralized by the negative ion formed in the scavenging process.

Nishikawa and co-workers (67–0263, 68–0051) have studied the system NH_3 – CCl_4. They assume CCl_4 scavenges electrons in a dissociative attachment that leads to CCl_3 and Cl^-, and that neutralization of NH_4^+ with Cl^- yields NH_4Cl. Because CCl_4 also scavenges H atoms, the limiting value of $G(H_2)$ in the presence of CCl_4 should be the primary yield of non–scavengable H_2 from processes other than (12).

$$(12)\ NH_4^+ + e^- \rightarrow NH_2 + H_2$$

Comparison of this limiting yield of 0.64 with the total non–radical yield of 0.75 (see table 3.2.1) leads to the conclusion that $g(12) \sim 0.1$.

Neutralization of NH_4^+ to give NH_2 and 2H (12′) is endothermic by about 40 kcal (69–0326, 67–0546) if, as seems reasonable, NH_4^+ is solvated at normal temperature and pressures (68–0032, 66–9067, 64–9015). Thus, it appears that neutralization of NH_4^+ in pure ammonia proceeds almost exclusively by reaction (11). In support of such a conclusion, Gordon, Mulac, and Nangia (71–0169) have found that the initial concentration of NH_2 measured spectrophotometrically, is unchanged when SF_6 is added to NH_3.

Gordon, Mulac and Nangia (71–0169) also conclude from the comparison of results for pure NH_3 and NH_3 – SF_6 that 45 percent of the hydrogen atoms are produced by ion–neutralization as opposed to dissociation of excited states. This can be compared with the results of Nishikawa and co-workers (67–0263, 68–0051) who reported that approximately 42 percent of the hydrogen (H_2) is the result of ion–neutralization. The latter estimate is based upon a comparison of hydrogen yields from NH_3 and NH_3 – N_2O. It is assumed that ion–neutralization does not produce hydrogen atoms in the presence of N_2O; and thus, the reduction in $G(H_2)$ by addition of N_2O is taken to be the yield of hydrogen from ion–neutralization. The two estimates are not necessarily directly comparable because the former refers to hydrogen atoms while the latter refers to H_2.

2.1.2. Free Radical Processes

Many important details of the mechanism by which H, NH_2 and NH lead to observed products are uncertain because of the lack of good specific rate data for many of the possible elementary processes.

Evidence from radiolysis of NH_3 in the presence of radical–scavengers indicates that most of the observed yield of H_2 results from processes involving free radicals. Non–radical processes yield only about 0.8 molecule of H_2 per 100 eV (table 2.2.1). At temperatures near 20°C radical sources of H_2 include reactions (13′), (22), (24) and possibly (28) followed by (29). At higher temperatures (23) is also important (see sec. 3.2.3).

N_2H_4 is produced by combination of NH_2 radicals but the observed yield is negligible in static systems except at very high dose rates ($> 10^{20} eV \cdot g^{-1}s^{-1}$) because of reactions (16), (22) and (22′). At high dose rates radical–hydrazine reactions compete less favorably with radical–radical reactions and N_2H_4 is observed in significant yields (71–0216, 69–0272, 68–0101). N_2H_4 is also an important product in flow–systems (see sec. 3.2.6).

Reactions (27) and (29) are likely sources of N_2 but their relative importance is uncertain. Competition between (27) and (28) is an important consideration but contradictory values have been reported for k_{27}/k_{28}. Volpi and Schiavello (62–0131) have found NH_3 and N_2 in a 2:1 ratio are the only products when H atoms from a microwave discharge flow into hydrazine vapor; and have concluded that $k_{27} \gg k_{28}$. Stief (70–7065) on the other hand has reported $k_{28} = 4k_{27}$ on the basis of a study of the reaction of H atoms with isotopically labeled hydrazines. There is no apparent reason for this contradiction.

2.2. Yields of Intermediates

2.2.1. Neutral Species

Yields of intermediates involved in radiolysis of gaseous ammonia are summarized in tables 2.2.1 – 2.2.3. Values cited refer to the total yield of intermediates from both primary and secondary processes (i.e., from process 1 and from both primary and secondary reactions of the ions and excited molecules produced in processes 1 and 2 (table 2.1)). In ammonia, secondary reactions of ions include rapid ion–molecule reactions with NH_3 and subsequent neutralization. Dissociation (3,4,5) is apparently the only important reaction of excited ammonia molecules. Most of these yields have been inferred from studies with additives. Although the imaginative use of additives has been an invaluable source of information about mechanism, the significance of such information is often compromised by assumptions that must be made about the role of the additive.

A summary of values of g(H) obtained with a variety of additives is given in table 2.2.2. Presumably in all cases the additive, AH, reacts with H to produce H_2,

$$AH + H \rightarrow H_2 + A.$$

In most cases, the limiting value of $G(H_2)$ calculated on the basis of energy absorbed in ammonia is assumed equal to $g(H) + g(H_2)$. Results are in reasonably good agreement except for those obtained with propane as additive. Eyre and Smithies (70–0479) have recently shown that $G(H_2)$ from mixtures of propane and ammonia decreases with dose at doses in excess of about 5×10^{18} eV/g, presumably because of the build–up of propylene. They suggest that the lower values reported in earlier studies with mixtures of ammonia and propane (68–0659, 69–0326) may be low for that reason.

The value $g(H) = 12.5$ reported by Jones and Sworski (67–0270) is significantly higher than the other values in table 2.2.2. Their limiting value of $G(H_2)$ is in agreement with that reported by Eyre and Smithies (70–0479) for the $NH_3–N_2H_4$ system; but Jones and Sworski obtain a higher g(H) because of a relatively large correction for the reactions $NH_2 + H \rightarrow NH_3$ and $N_2H_3 + H \rightarrow N_2H_4$. The magnitude of this correction, which is obtained by a kinetic analysis of $G(H_2)$, seems quite large in view of the relatively high rate for $H + N_2H_4 \rightarrow H_2 + N_2H_3$ (table 2.1). In any event, such a correction should be unnecessary for the other studies in table 2.2.2 except 69–0272 and 70–0216, because of the much lower dose rates involved (for dose rates see tables 3.1.1 and 3.1.2).

If the high value of Jones and Sworski and the low values obtained in the earlier studies with propane are disregarded, an average value of 10.4 is obtained for g(H), and this is the preferred value. Table 2.2.2 does not include results obtained with D_2 as additive. Jones and Sworski (67–0270) find $g(H) = 12.5$ at 200 torr in good agreement with their results from $NH_3 - N_2H_4$; however, at 600 torr the analysis leads to $g(H) = 90 \pm 66$. Studies of the $NH_3–D_2$ system by Johnson and Simic (68–0659) indicate a chain reaction is involved in the formation of HD.

TABLE 2.2.1. *Yields of intermediates in radiolysis of gaseous ammonia*

Species	Yield[a] (g)	Radiation	Method of Determination	Comments	Reference
H	5.1–12.5	—	—	Preferred value is 10.4. See table 2.2.2 and section 2.2.1.	—
NH_2	10.4	1.0–1.7 MeV e^-	Anal. of yields from NH_3	Calculated on the basis of an assumed mechanism. Pulse radiolysis, very high dose rate (10^{27} eV·$g^{-1}s^{-1}$).	Boyd..71–0216
NH_2	8.4	2 MeV e^-	$g(NH_2) = g(NH_4^+)$/(fraction of NH_2 from NH_4^+)	Assume $g(NH_4^+) = 100/W$; estimate fraction of NH_2 from NH_4^+ by studies of $NH_3 - SF_6$. Pulse radiolysis.	Gordon..71–0169
NH_2	14	1 MeV e^-	Assume $g(NH_2) = 2g(H_2) + g(H)$	Value probably too high. Based on the unlikely assumption that reaction (12) is exclusive source of non–radical H_2 (see section 2.2.2.) and $g(H) = 12.5$ (from $NH_3 - N_2H_4$).	Jones.67–0270
NH_2	$11.9 - 2 \cdot g(NH)$	$^{60}Co-\gamma$	Based on material balance: $g(NH_2) + 2g(NH) = g(H) + 2g(H_2)$.	$g(H) = 10.4$[b]; $g(H_2) = 0.75$. Assuming $g(NH) = g(H_2)$, preferred value is $g(NH_2) = 10.4$.	Eyre.70–0479
NH	0.74	1.0 – 1.7 MeV e^-	Anal. of yields from NH_3	See comments for NH_2. Preferred value is $g(NH) = 0.75$	Boyd..71–0216
NH	0.4	250 keV e^-	UV spectroscopy	Pulse radiolysis. Yield is low. Used N_2O as dosimeter and assumed $G(N_2) = 9.68$. Accepted value at dose rate $< 10^{19}$ eV·$g^{-1}s^{-1}$ is $G(N_2) = 10.0$ (66–0434); $G(N_2)$ is 12.4 at 10^{27} eV·$g^{-1}s^{-1}$ (68–0318). Dose rate employed here was ~ 10^{26} eV·$g^{-1}s^{-1}$.	Meaburn.68–0101
H_2	0.7 – 0.8	—	—	See table 2.2.3. Preferred value is 0.75.	—
NH_4^+	3.9	$^{60}Co-\gamma$	Decrease in $G(H_2)$ when SF_6 (0.2%) is added to $NH_3 + C_3H_8$ (1.5%).	Agrees well with value calculated from $W = 26.5$ eV per ion pair for e^-–radiation (64–0177) if essentially all positive ions converted to NH_4^+ before neutralization.	Johnson.68–0659, 67–0369
NH_4^+	3.5	$^{60}Co-\gamma$	Decrease in $G(H_2)$ when SF_6 is added to NH_3 – isopropanol (0.5%).	—	Eyre.70–0479
NH_4^+	3.3	$^{60}Co-\gamma$	Decrease in $G(H_2)$ when N_2O is added to NH_3 – isopropanol (0.5%).	—	Eyre.70–0479
NH_4^+	4.0	$^{60}Co-\gamma$	Decrease in $G(H_2)$ when CCl_4 is added to NH_3 – isopropanol (0.5%).	—	Eyre.70–0479

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[a] Unless otherwise indicated yields were measured at ~ 20°C and ~ 1 atm. Yields are in ions, radicals or molecules per 100 eV and refer to the total yield of the intermediate from reaction 1 and from primary and secondary reactions of the ions and excited states produced in reactions 1 and 2 (table 2.1).

[b] Eyre and Smithies (70–0479) distinguish between H atoms produced by ion neutralization and those produced by other reactions (such as 3 and 5). No such distinction is made in this paper and the value 10.4 refers to the total yield of H atoms (calculated from $g(H)$ and $g(e^-)$ values reported by Eyre and Smithies).

TABLE 2.2.2. *Yield of H–atoms*[a]

Yield(g)	Radiation	Method	Comments	Reference
12.5	1 MeV e^-	Kinetic anal. of $G(H_2)$ from $NH_3 - N_2H_4$.	Assume $H + N_2H_4 \rightarrow H_2 + N_2H_3$; calculation of $g(H)$ allows for $NH_2 + H \rightarrow NH_3$ and $H + N_2H_3 \rightarrow N_2H_4$.[b]	Jones.67–0270
10.4	1.0 – 1.7 MeV e^-	Kinetic anal. of product yields from pure NH_3.	Pulse radiolysis. Very high dose rate ($\geq 10^{26}$ $eVg^{-1}s^{-1}$).	Boyd..71–0168
10.8	^{60}Co–γ	$G(H_2)$ from $NH_3 - N_2H_4$; $g(H) = G(H_2) - g(H_2) = 11.6 - 0.8$.[c]	Assume all H react with N_2H_4 to give H_2.	Eyre.70–0479
10.6	^{60}Co–γ	$G(H_2)$ from $NH_3 - N_2H_4$	As above.	Carstensen67–0701
10.4	^{60}Co–γ	Kinetic anal. of $G(H_2)$ from NH_3 – methanol; $g(H) = G(H_2) - g(H_2) = 11.2 - 0.8$.[c]	Assume $H + CH_3OH \rightarrow H_2 + CH_2OH$ scavenges all H.	Eyre.70–0479
9.5	^{60}Co–γ	Kinetic anal. of $G(H_2)$ from NH_3–methanol.	As above.	Carstensen67–0701
10.6	^{60}Co–γ	$G(H_2)$ from NH_3–cyclohexane; $g(H) = G(H_2) - g(H_2) = 11.4 - 0.8$.[c]	Assume $H + C_6H_{12} \rightarrow H_2 + C_6H_{11}$ scavenges all H.	Eyre.70–0479
10.6	^{60}Co–γ	$G(H_2)$ from NH_3–isopropanol; $g(H) = G(H_2) - g(H_2) = 11.4 - 0.8$.[c]	Assume all H react with isopropanol to give H_2	Eyre.70–0479
10.0	^{60}Co–γ	$G(H_2)$ from NH_3–propane; $g(H) = G(H_2) - g(H_2)$ $10.8 - 0.8$.[c]	Assume $H + C_3H_8 \rightarrow H_2 + C_3H_7$ scavenges all H. $G(H_2)$ decreases with dose above $\sim 5 \times 10^{18}$ eV/g.	Eyre.70–0479
7.2	^{60}Co–γ	As immediately above but $g(H) = 8.0 - 0.8$.[c]	Lower value may be result of dose effect (dose not stated). See comment immediately above.	Johnson.68–0659, 67–0369
5.1	^{60}Co–γ	As immediately above but $g(H) = 5.8 - 0.7$.[c]	See comment immediately above.	Nishikawa..69–0326[d]
10.4	1.0 – 1.7 MeV e^-	Kinetic anal. of product yields from pure NH_3.	Pulse radiolysis. Very high dose rate ($\geq 10^{26}$ $eV \cdot g^{-1}s^{-1}$).	Boyd..71–0216

a. Unless otherwise indicated yields were measured at ~ 20°C and ~ 1 atmosphere. Yields are in atoms per 100 eV and refer to the total yield of H from reaction 1 and from primary and secondary reactions of the ions and excited states produced in reactions 1 and 2 (table 2.1).

b. Correction based on kinetic analysis of $G(H_2)$ data. Correction should be unnecessary for other work in this table except 71–0216.

c. See table 2.2.3.

d. See also 68–0505. These authors have also used C_3H_8 to obtain $g(H)$ at high pressure (68–0505, 69–0026).

The limiting value of $G(H_2)$ for pure ammonia at dose rate less than $10^{20}eV \cdot g^{-1}s^{-1}$ and at temperatures near 200°C (see section 3.2.3) has also been used to estimate $g(H)$ (67–0270, 68–0659, 70–0479). It is assumed that when the limiting value of $G(H_2)$ is reached, all H atoms react with either NH_3 or N_2H_4 to produce H_2. Depending upon the origin of the yield of non–scavengable H_2, it is assumed that $G(H_2) = g(H) + g(H_2)$ or $G(H_2) = g(H) + 2g(H_2)$. Combination of the high temperature plateau value of $G(H_2)$, 15, with a $g(H_2)$ of 0.8 (table 2.2.3.), leads to $g(H) =$ 13–14, a value significantly higher than has been obtained by any of the scavenger techniques. However, this estimate involves the important assumption that H_2 is not produced by reaction of N_2H_3 or N_2H_2. Eyre and Smithies (70–0479) have suggested that thermal decomposition of N_2H_3 and/or N_2H_2 may increase with increasing temperature, and thus lead to an increased yield of H_2. They assume that at temperatures near 20°C, N_2H_3 and N_2H_2 lead to N_2 but not to H_2 (see table 2.1).

Additives known to act as efficient thermal hydrogen atom scavengers have been used to determine the yield of molecular hydrogen (see table 2.2.3). In general, the limiting yield of hydrogen in the presence of such scavengers can be used to obtain $g(H_2)$ if proper allowance is

TABLE 2.2.3. *Primary yield of* H_2[a]

Yield(g)	Radiation	Method	Comments	Reference
0.81	^{60}Co–γ	Limiting value of $G(H_2)$ in presence of propylene.	Assume[b] $H + C_3H_6 \rightarrow C_3H_7$, $NH_2 + C_3H_6 \rightarrow C_3H_6NH_2$. $G(N_2)$ reduced from 1.45 to ~ 0.3.	Eyre.70–0479
0.80	^{60}Co–γ	As above.	$G(N_2)$ reduced from 1.9 to ≤0.3.	Johnson.68–0659
0.70 – 0.82	^{60}Co–γ	As above.	—	Nishikawa..67–0263
0.84	250 keV e^-	As above.	Pulse radiolysis.	Meaburn.68–0101
1.4	Fast e^-	As above.	High value may be result of failure to correct for H_2 from C_3H_6.	Sorokin.65–0523
0.74	1.0 – 1.7 MeV e^-	Kinetic analysis of product yields from pure NH_3.	Pulse radiolysis. Very high dose rate ($\leq 10^{26} eV \cdot g^{-1} s^{-1}$)	Boyd..71–0216
0.75	1 MeV e^-	Limiting value of $G(H_2)$ in presence of ethylene.	Acts similarly to propylene. $G(N_2)$ reduced from 1.5 to ≥ 0.6.[c]	Jones67–0270
0.74	^{60}Co–γ	As immediately above.	Also used C_2D_4.	Nishikawa.68–0051, 67–0263
0.84	^{60}Co–γ	Limiting value of $G(H_2)$ in presence of benzene.	Assume[d] $H + C_6H_6 \rightarrow C_6H_7$. $G(N_2)$ reduced from 1.45 to ~ 0.3.	Eyre.70–0479
1.0	^{60}Co–γ	As immediately above.	$G(N_2)$ reduced from 1.4 to 1.0. Aniline not detected.	Carstensen67–0701
0.8	^{60}Co–γ	As immediately above.	—	Johnson.68–0659

a. Unless otherwise indicated yields were measured at ~ 20°C and ~ one atmosphere. Yields are in molecules per 100 eV and refer to total yield of H_2 from reaction 1 and from primary and secondary reactions of the ions and excited states produced by reactions 1 and 2 (table 2.1).

b. Charge exchange between NH_3^+ and C_3H_6 is energetically possible but should be negligible at concentrations involved. Proton transfer from NH_4^+ to C_3H_6 ruled out on basis of proton affinities: ~ 9.2 and 6.6 eV for NH_3 and C_3H_6, respectively (62–9017).

c. N_2 determined mass spectrometrically. Presence of C_2H_4 led to analytical difficulties.

d. Charge exchange between NH_3^+ and C_6H_6 is energetically possible but should be negligible at concentrations involved. Proton transfer from NH_4^+ is probably ruled out on basis of proton affinities: ~ 9.2 and ≤ 6.3 eV (62–9017).

made for energy absorbed in the additive. Results with a variety of additives are in good agreement and lead to $g(H_2) = 0.75$.

Relatively few values of $g(NH_2)$ have been reported. Gordon, Mulac, and Nangia (71–0169) estimate $g(NH_2) = 8.4$ from $g(NH_4^+)$ and the fraction of NH_2 produced by neutralization of NH_4^+. They assume $g(NH_4^+) = 100/W$ (W is the energy in eV to produce an ion pair) and estimate the fraction of NH_2 produced by neutralization of NH_4^+ from a comparison of results of irradiation of pure NH_3 and of NH_3 in the presence of SF_6. Jones and Sworski (67–0270) have suggested $g(NH_2) = g(H) + 2g(H_2)$ on the basis of the unlikely assumption that non–radical H_2 arises exclusively via reaction (12). As noted earlier (sec. 2.1.1) studies of mixtures of NH_3 and CCl_4 indicate $g(12) \sim 0.1$ (68–0051) whereas $g(H_2) = 0.75$. Reaction (4) probably accounts for a significant fraction of non–scavengable H_2. In photochemistry 12 – 14% of the dissociation at 147 and 123.6 nm (64–7003, 62–0132) is attributed to (4),

$$(4)\ NH_3{*} \rightarrow NH + H_2$$

and NH has been observed spectroscopically by Meaburn and Gordon (68–0101) in pulse radiolysis of NH_3. Meaburn and Gordon estimate $g(NH) \sim 0.4$, but this is probably low because of an error in dosimetry (table 2.2.1). On the basis of material balance one expects $g(NH_2) = g(H) + 2g(H_2) - 2g(NH)$. The best assumption seems to be that $g(NH) \cong g(H_2)$ and this leads to a preferred value of 10.4 for $g(NH_2)$.

More recently Boyd, Willis, and Miller (71–0216) have shown that their product yields from radiolysis of pure ammonia with single pulses of electrons (1.0 – 1.7 MeV) at very high dose rate ($\geqslant 10^{26}$eV·g^{-1}s^{-1}) are constant with g(H) = g(NH_2) =10.4 and g(H_2) = g(NH) = 0.74. At the high dose rates employed, radical–product reactions are not significant and they assume the following mechanism:

(13) $NH_2 + H \rightarrow NH_3$
(13′) $NH_2 + H \rightarrow NH + H_2$
(14) $NH_2 + NH_2 \rightarrow N_2H_4$
(15) $NH_2 + NH_2 \rightarrow NH + NH_3$
(18) $NH + NH \rightarrow N_2H_2{*} \rightarrow N_2 + H_2$
(24) $H + H \rightarrow H_2$

They take $k_{14} + k_{15} \cong 2.3 \times 10^9$ dm^3 mol^{-1}s^{-1} and calculate, using a computer program based on that of Schmidt (66–8024), $G(N_2H_4)$, $G(H_2)$ and $G(N_2)$ for various values of k_{14}/k_{15} and k_{13}, $k_{13'}$, k_{18} and k_{24}. $G(N_2H_4)$ depends mainly upon k_{13} and k_{14} and $G(H_2)$ depends primarily upon k_{13}, for fixed values of k_{13} and k_{14}.

Agreement between calculated and observed product yields is achieved for very reasonable values of the various specific rates ($k_{13} = 1.8 \times 10^{10}$, $k_{13'} = 2.9 \times 10^9$, $k_{14} = 1.8 \times 10^9$, $k_{15} = 5 \times 10^8$, $k_{18} = 5 \times 10^{10}$ and $k_{24} = 1.6 \times 10^8$ dm^{3}mol^{-1}s^{-1}). These results represent a re–examination and extension of an earlier study (69–0272).

2.2.2. Yields of Ionic Species

Johnson and Simic (68–0659, 67–0369) have determined $g(NH_4^+)$ from the reduction by SF_6 of $G(H_2)$ from mixtures of NH_3 and propane. $G(H_2)$ is 8.0 for NH_3 containing 1.5 mole percent propane. Addition of 0.2 mole percent SF_6 reduces $G(H_2)$ to 4.1. SF_6 reacts rapidly with thermal electrons (66–9159) but only very slowly with hydrogen atoms and free radicals generally (67–0093, 66–0249, 64–9016). Therefore, the observed reduction in $G(H_2)$ is attributed to modification of the neutralization process. In NH_3–C_3H_8, neutralization of NH_4^+ is assumed to proceed via (11) and (12) whereas in the presence of SF_6, NH_4^+ is neutralized by SF_6^-. This latter process is assumed not to produce H or H_2 and hence $\Delta G(H_2) = g(NH_4^+)$. The value obtained, 3.9, agrees well with $g(NH_4^+)$ calculated from W =26.5 eV per ion pair (64–0177) assuming essentially all positive ions are converted to NH_4^+ before neutralization.

Nishikawa, Kuroda, and Matsuura (69–0326) also have studied the NH_3–C_3H_8–SF_6 system; but while results are qualitatively similar, they find the decrease in $G(H_2)$, $\Delta G(H_2)$ is only about 2. Their value of $G(H_2)$ for the ternary system is about the same, 3.8, as that reported by Johnson and Simic but $G(H_2)$ for NH_3–C_3H_8 is significantly lower.

Johnson and Simic (68–0659) have investigated the system NH_3–C_3H_8–N_2O which might be expected to be similar to the NH_3–C_3H_8–SF_6 system since both N_2O and SF_6 are good electron scavengers and poor H–atom scavengers. Although addition of N_2O to mixtures of NH_3 and C_3H_8 does reduce $G(H_2)$, the decrease, 3.0, is less than that produced by addition of SF_6, 3.9. Nishikawa, Kuroda, and Matsuura (69–0326) have also studied this system and report similar results.

More recently Eyre and Smithies (70–0479) have carried out similar studies on mixtures of ammonia and isopropanol (0.5%). $G(H_2)$ is 11.4 for this system and introduction of SF_6, N_2O or CCl_4 reduces $G(H_2)$ to limiting values which are respectively 7.9, 8.1 and 7.4. They conclude that $\Delta G(H_2) = g(NH_4^+)$. Using the weighted mean of $\Delta G(H_2)$ they obtain $g(NH_4^+) = 3.4$. Presumably, the yield of H from sources other than ion–neutralization is then 7.0.

3. Product Yields

H_2, N_2 and N_2H_4 are the products observed in radiolysis of gaseous ammonia but yields depend upon a number of parameters such as temperature, pressure and dose rate. Yields at approximately 20°C and one atmosphere pressure are summarized in section 3.1, and the influence of various parameters is discussed in 3.2.

3.1. Product Yields for Radiolysis Under Static Conditions at ~ 20° C and ~ 1 Atmosphere

H_2 and N_2 are the only measurable products at dose rates up to at least $2 \times 10^{18} eV \cdot g^{-1} s^{-1}$ (table 3.1.1); $G(H_2) = 5.0 \pm 1.0$ and $G(N_2) = 1.7 \pm 0.3$. Presumably, the steady–state concentration of hydrazine is kept very low because of radical–hydrazine reactions (see sec. 2.1.2).

At very high dose rates ($\geqslant 10^{26} eV \cdot g^{-1} s^{-1}$) hydrazine is produced in significant yield in static systems (71–0216, 69–0272) because radical–product reactions do not compete effectively with radical–radical reactions. Hydrazine is also a product in flow systems (see sec. 3.2.6).

In all cases the total dose was sufficiently low to preclude variations in product yields associated with high conversion (see sec. 3.2.1). Indeed, the only obvious variables are dose rate and the LET (linear energy transfer), of the radiation. Both of these factors may contribute to the relatively large scatter in yields but it is clear from table 3.1.2 that they alone are not responsible. Other probable contributing factors include the presence of trace impurities and problems in dosimetry. The neutralization process in particular should be quite sensitive to trace impurities, the presence of which would probably lead to low yields (see sec. 2.1.1). Most of the results summarized in this sec. are based on dosimetry with nitrous oxide. Problems associated with gas phase dosimetry in general (71–0062, 67–0546, 71–0179) and the nitrous oxide dosimeter in particluar (71–0062, 68–0318, 67–0027, 66–0434, 61–0103) have been discussed elsewhere.

TABLE 3.1.1. *Product yields from radiolysis of gaseous ammonia with various radiations under static conditions at ~ 20°C and ~ 1 atm*[a]

Radiation	$G(-NH_3)$	$G(H_2)$	$G(N_2)$	$G(N_2H_4)$	Dose Rate ($eV \cdot g^{-1} s^{-1}$)	Comments	Reference
1 MeV e^-	3.0	4.5	1.5	0.0	2×10^{18} [b]	Yields depend upon dose rate. See section 3.2.2	Jones.67–0270
1.0 – 1.7 MeV e^-	—	3.6	1.0	0.58[e]	2×10^{26} and 2×10^{27} [d]	Pulse radiolysis.	Boyd..71–0216 and Willis..69–0272
~ 250 keV e^-	—	2.3[e]	0.68[e]	0.07[c]	~ 10^{26} (4.0×10^{18} eV/pulse).[e]	Pulse radiolysis.	Meaburn.68–0101
$^{60}Co-\gamma$	2.7 – 4.7	4.1 – 7.0	1.4 – 2.3	0.0 – 0.001	—	See table 3.1.2.	—
$^1H^+$ (0.8 MeV)	4.0	6.0	2.0	0.0	$\cong 3 \times 10^{15}$ [f]	Yields depend on dose rate. See section 3.2.2	Horscroft64–0174
$^2H^+$ (2 MeV)	—	—	—	0.5	not reported	No attempt to measure $G(H_2)$ or $G(N_2)$.	Lampe...63–0098
$^4He^{2+}$	3.0 – 4.2[g]	—	—	—	—	See table 3.1.3.	—
Reactor (γ + n)	3.8	5.7	1.9	—	—	—	Dolle58–0051

a. For yields at other temperatures and pressures see section 3.2.

b. N_2O dosimetry; $G(N_2) = 10.0$ (66–0434).

c. N_2H_4 is a significant product in static system only when dose rate is high enough to reduce the importance of radical–N_2H_4 reactions.

d. N_2O dosimetry; $G(N_2) = 12.4$. Value obtained by adiabatic calorimetry (68–0318). Probably applies only to very high dose rates.

e. These values are probably low because they are based upon N_2O dosimetry with $G(N_2) = 9.68$. Generally accepted value is $G(N_2) = 10$ for dose rates less than about $10^{19} eV \cdot g^{-1} s^{-1}$. Value may be higher at higher dose rates (see *d* above). The dose rate is estimated from the dose per pulse on the basis of a cell volume of 0.68 liters and a pulse duration of ~ 40 ns.

f. Dosimetry based on charge collection; value in $eV \cdot g^{-1} s^{-1}$ involves estimate of effective volume. This is lowest dose rate employed.

g. Most yields originally reported as molecules per ion pair (*M*/*N*); these have been converted to *G* assuming *W* = 30.5 eV per ion pair in NH_3 for $^4He^{2+}$ radiation (53–0008).

Jungers (36–0001) has studied the relative rates of decomposition of NH_3 and ND_3 by $^4He^{2+}$ radiation at 525 torr. At 20°C, the ratio $G(-NH_3)$: $G(-ND_3)$ is 1.27. Absolute yields were not reported.

TABLE 3.1.2. *Product yields for gamma radiolysis at ~ 20°C and ~ 1 atm*[a]

$G(-NH_3)$	$G(H_2)$	$G(N_2)$	$G(N_2H_4)$	Dose Rate (eV·g^{-1}s^{-1})	Dosimetry	Reference
4.7	7.0	2.3	0.0005 – 0.001	1.5 x 10^{16}	Not stated.	Sorokin.64–1757
4.2 (4.0)[b]	6.3 (6.0)[b]	—	—	7.0 x 10^{15}	N_2O; $G(N_2)$ = 10.6.	Anderson.67–0546
4.0	6.0	2.0	0.0	6.0 x 10^{16}	N_2O; $G(N_2)$ = 10.0.	Kazanjian.68–0555
3.8	5.7	1.9	0.0	1.4 x 10^{16}	N_2O; $G(N_2)$ = 10.0.	Johnson.68–0659[c]
(3.3)	(4.9)	(1.6)	—	(5 x 10^{14})	Fricke.[d]	Dolle58–0051
3.0	4.5	1.5	—	6.9 x 10^{15}	C_2H_4; $G(H_2)$ = 1.2.	Buchanan.70–0134
2.9	4.3	1.4	0.0	2 x 10^{15}	N_2O; $G(N_2) + G(O_2)$ = 12.0.	Nishikawa.68–0051
2.7	4.1	1.4	0.0	5 x 10^{14}	N_2O; $G(N_2)$ = 10.0.	Carstensen67–0701
2.7	4.1	—	—	Not given.	—	Nishikawa..68–0505
2.7	4.1	1.4	—	9 x 10^{14}	N_2O; $G(N_2)$ = 10.0.	Nishikawa..69–0326
2.9	4.4	1.4	$\leq$ 0.005	3 x 10^{15}	N_2O; $G(N_2)$ = 10.0.	Eyre.70–0479

a. Results from 63–0165 excluded as unreliable.

b. Corrected on the basis that $G(N_2)$ = 10.0 rather than 10.6 (66–0434).

c. See also 67–0369.

d. Without wall corrections; values are of questionable validity.

TABLE 3.1.3. *Yields for radiolysis with alpha particles at ~ 20°C and ~ 1 atm*[a]

Source	$G(-NH_3)$	$G(H_2)$	$G(N_2)$	Dose Rate (eV·g^{-1}s^{-1})[b]	Comments	Reference
Rn	3.0[c]	4.5[c]	1.5[c]	—	Used $^4He^{2+}$ sources of comparable strength to those used by Luyckx (34–0003).	Wourtzel 19–0001
Rn	3.8	—	—	—	See immediately above. Yield depends upon dose rate; value given obtained by extrapolation to zero dose rate.	Jungers32–0002
Rn	4.2	—	—	~ (0.1 – 5) x 10^{16}	Yield depends upon dose rate; value given obtained by extrapolation to zero dose rate.	Luyckx34–0003
Ra	3.6	—	—	~ 5 x 10^{13}	—	Essex.34–0001
Ra	3.6	—	—	~ 6 x 10^{14}	—	Burtt.57–0018
^{210}Po	3.5	5.2	1.7	7.6 x 10^{17}	—	Kazanjian.68–0555

a. In all studies except 68–0555, yields were originally reported as molecules per ion pair (*M*/*N*). These have been converted to *G* assuming *W* = 30.5 eV per ion pair for $^4He^{2+}$ radiation (53–0008).

b. In all studies except 68–0555 dose rates were not reported as such. Values were calculated from data given. In 68–0555 N_2O was used as dosimeter and $G(N_2)$ was assumed to be the same as for $^{60}Co-\gamma$ (10.0). Recent work of Sears (69–0085) supports this assumption. Dose rates for other studies have been estimated from original data and *W* = 30.5 eV per ion pair.

c. Original data leads to $G(-NH_3)$ = 2.6. Values cited here are based on recalculations by Jungers (32–0002).

3.2. Effect of Various Parameters

3.2.1. Dose

At dose rates such that H_2 and N_2 are the only products, $G(H_2)$ and $G(N_2)$ are independent of total dose up to at least 8 x 10^{22}eV/g (table 3.2.1). At very high conversions, yields should decrease because of $NH_2 + H_2 \rightarrow NH_3 + H$ (64–0174, 32–0002). The inhibiting effect of H_2 has been observed in photochemical studies of NH_3 (55–7001, 44–7000).

At dose rates of the order of 10^{26}eV·$g^{-1}s^{-1}$, N_2H_4 is a product and because N_2H_4 reacts with H and NH_2, product yields may be independent of dose over a more limited range. Available data indicate independence of dose extends at least up to 6 x 10^{20}eV/g (at 10^{27}eV·$g^{-1}s^{-1}$) (69–0272). At these high dose rates the total dose is delivered as a series of pulses of very short duration (50–100 ns).

Table 3.2.1. *Effect of dose*

Radiation	Effect of $G(-NH_3)$[a]	Max. Dose (eV/g)	Reference
Fast e^-	none	8 x 10^{22} [b]	Sorokin.65–0523
Fast e^- (1 MeV)	none	4.5 x 10^{21}	Jones.67–0270[c]
$^{60}Co-\gamma$	none	3 x 10^{22}	Kazanjian.68–0555[d]
$^4He^{2+}(^{210}Po)$	none	6 x 10^{22}	Kazanjian.68–0555
$^1H^+$(0.8 MeV)	none	6 x 10^{21} eV totally absorbed in 0.5 cm^3.	Horscroft64–0174

a. At dose rates employed N_2 and H_2 were the only products observed. Relevant dose rates can be found in tables 3.1.1 and 3.1.2.

b. Corresponds to about 5% conversion.

c. See also 69–0272 for results with fast e^- at very high dose rate (10^{27}eV·$g^{-1}s^{-1}$).

d. See also 58–0051, 64–1757, 67–0701, 70–0134.

3.2.2. Dose Rate

At pressures near one atmosphere $G(-NH_3)$ decreases with increasing dose rate (table 3.2.2) and the magnitude of the effect decreases with decreasing pressure (67–0271, 34–0003).

Sorokin and Pshezhetskii (65–0523) report $G(-NH_3)$ independent of intensity; however, their investigation was limited to a relatively small (eight–fold) variation in dose rate. The results of Jones, Sworski and Williams (67–0271) obtained under similar conditions, but for a much wider (100–fold) variation in dose rate, indicate that $G(-NH_3)$ should change only by about 10% over the range employed by Sorokin and Pshezhetskii.

Burtt and Baurer (55–0010) and Burtt and Zahlen (57–0018) have reported $G(-NH_3)$ increases with increasing intensity at 200 torr but the intensities were much lower than are usually encountered (table 3.2.2).

The observed decrease in $G(-NH_3)$ with increasing dose rate has not been satisfactorily explained. No effect is expected on the basis of the simple mechanism discussed in sections 2.1.1 and 2.1.2. That mechanism assumes that ions and excited neutrals produced in the early stages of radiolyisis undergo reactions that lead principally to NH_2, H, NH, and H_2. The radicals in turn react with each other and with other intermediates such as N_2H_4 and N_2H_3 to give the observed products.

If reaction (23) is included in the mechanism, $G(-NH_3)$ would

$$(23)\ H + NH_3 \rightarrow H_2 + NH_2$$

be expected to decrease with increasing intensity. The specific rate of (23) has not been accurately measured but estimates of 5 $dm^3mol^{-1}s^{-1}$ (65–0555) and 200 $dm^3mol^{-1}s^{-1}$ (69–0272) have been reported for temperatures near 20°C. If k_{23} is in fact as high as 200 $dm^3mol^{-1}s^{-1}$, reaction (23)

TABLE 3.2.2. *Effect of dose rates at ~ 23°C*

Radiation[a]	Dose Rate ($eV.cm^{-3}s^{-1}$)	Effect on $G(-NH_3)$	Reference
1 MeV e^-	$6.5 \rightarrow 650 \times 10^{14}$ [b]	Decreases from 3.5 to 2.6 at 700 torr; negligible effect at 200 torr.	Jones..67–0271
Fast e^- [c]	$8 \rightarrow 60 \times 10^{14}$	None.	Sorokin.65–0523
$^1H^+$	$4.0 \times 10^{14} \rightarrow 9.8 \times 10^{19}$ [d]	Decreases from 4.0 to 1.6 at 300 torr (only *P* studied). *G* appears to be leveling off at ~ 1.6.	Horscroft64–0174
$^4He^{2+}$	$10^{12} \rightarrow 5 \times 10^{13}$	Decreases 30% at 450 – 700 torr; effect diminishes below 450 and is negligible below ~ 140 torr.	Luyckx34–0003[e]
$^4He^{2+}$	$1.7 \rightarrow 30 \times 10^{10}$	Increases from 2.4 to 3.4 at 200 torr.	Burtt.55–0010, 57–0018

a. No results from a single laboratory for $^{60}Co-\gamma$ radiation.
b. Originally reported in eV/min. Cell volume was ~ 26 cm^3.
c. Energy not specified; very limited dose rate range.
d. Originally reported in eV/s absorbed in a total volume of 0.5 cm^3.
e. See also 32–0002.

should compete at the dose rates employed and thus could account for the observed dose rate dependence.

At very high dose rates ($\geqslant 10^{26} eV \cdot g^{-1}s^{-1}$), the system is somewhat simpler because radical–product reactions are not significant. At 20°C, yields are unchanged when the dose rate is increased from $2 \times 10^{26} eV \cdot g^{-1}s^{-1}$ to $2 \times 10^{27} eV \cdot g^{-1}s^{-1}$ (1.0 – 1.7 MeV e^-; 71–0216). However, at higher temperatures yields of H_2 and N_2H_4 are lower at the higher dose rate and the effect increases with increasing temperature (see fig. 3.2.3.1). $G(N_2)$ remains insensitive to changes in dose rate up to the highest temperature studied, 460°C. At 20° reaction (23) probably does not compete effectively with radical–radical reactions at these high dose rates and thus dose rate effects would be expected to be negligible. At higher temperatures, reaction (23) will compete more favorably.

3.2.3. Temperature

At dose rates less than about $2 \times 10^{18} eV \cdot g^{-1}s^{-1}$ $G(-NH_3)$ increases markedly with increasing temperature and appears to reach a plateau value, of about 10 near 200°C. Although there is agreement on the plateau value, there is significant variation in data at intermediate temperatures (see fig. 3.2.3.1) which may result at least in part from differences in dose rate and pressure. At all temperatures H_2 and N_2 are the only products.

A number of interpretations of the effect of temperature have been proposed. Anderson and Winter (67–0546) attributed the increase in $G(-NH_3)$ with increasing temperature to changes in solvation of $NH_4{}^+$ and the influence of solvation upon ion–neutralization. At high temperature $NH_4{}^+$ is presumed to be unsolvated and the pertinent reactions are

$$NH_4{}^+ + e^- \rightarrow NH_3* + H$$
$$NH_3* \rightarrow NH_2 + H.$$

At low temperatures $NH_4{}^+$ is fully solvated and the neutralization reaction is more appropriately written

$$NH_4{}^+(NH_3)_n + e^- \rightarrow (NH_3)*_{n+1} + H.$$

The excess energy associated with the excited NH_3 complex is about 80 kcal less than that for NH_3* produced by neutralization of unsolvated $NH_4{}^+$ and as a consequence, further dissociation to NH_2 and H is not energetically possible.

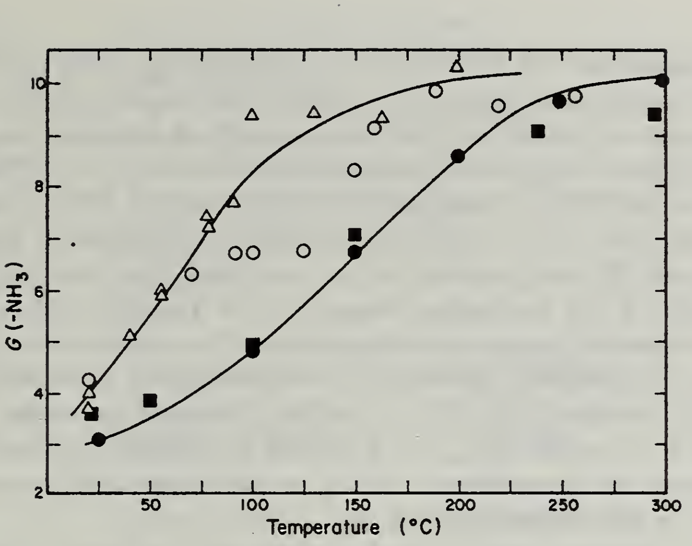

FIGURE 3.2.3.1. *Variations of $G(-NH_3)$ with temperature at dose rates less than* $10^{19}eVg^{-1}s^{-1}$. Original data in terms of $G(H_2)$; $G(-NH_3)$=2/3 GH_2). ○ 67–0546 (7.0 x $10^{15}eV\cdot g^{-1}s^{-1}$); ● 67–0270 (2.0 x $10^{18}eV\cdot g^{-1}s^{-1}$); △ 68–0659 (1.4 x $10^{16}eV\cdot g^{-1}s^{-1}$); ■ 70–0479 (3 x $10^{15}eV\cdot g^{-1}s^{-1}$).

Solvation of NH_4^+ in gaseous ammonia is known to occur (68–0032, 66–9067, 64–9015) and modification of ion–neutralization in the manner suggested is not unreasonable. However, considerably higher temperatures than these are required to produce the necessary changes in solvation (68–0032, 66–9067). For example at 100°C and 1 torr $n = 2$ and neutralization to give more than one H is still endothermic (69–0326, 66–9067). Also, Johnson and Simic (68–0659) have found $G(H_2)$ from mixtures of ammonia and propane and depression of $G(H_2)$ from such mixtures by SF_6 are independent of temperature, and they conclude that the hydrogen yield from neutralization of NH_4^+ by e^- is independent of temperature.

Jones and Sworski (67–0270) have interpreted the effect of temperature in terms of competition between reactions (13), (22), (23) and (24).

$$H + NH_2 + M \rightarrow NH_3 + M \tag{13}$$
$$H + N_2H_4 \rightarrow H_2 + N_2H_3 \tag{22}$$
$$H + NH_3 \rightarrow H_2 + NH_2 \tag{23}$$
$$H + H + M \rightarrow H_2 + M \tag{24}$$

They assume that reaction (23), which has an energy of activation of 10–15 kcal/mol (62–0131) is unimportant at room temperature but becomes significant at higher temperatures. Johnson and Simic (68–0659) reject this interpretation on the basis that the energy of activation for reaction (23) is too high to account for their observed temperature dependence. They suggest that increase in $G(-NH_3)$ with temperature is best explained in terms of competition between reactions (13) and (22). An Arrhenius plot of their data leads to an apparent energy of activation of about 2.1 kcal/mol. (A similar treatment of the data of Jones and Sworski (67–0270) leads to a value of 1.7.) In terms of their mechanism this apparent energy of activation is to be identified with the differences in activation energies of reactions (22) and (13). Reaction (22) has been reported to have an activation energy of 2.0 kcal/mol (62–0131) while (13) would be expected to have an activation energy near zero. Thus, the observed temperature dependence agrees well with their mechanism. An important implication of this mechanism is that reaction (23) is unimportant at least up to 200°C. However available specific rate data indicates that reaction (23) should compete favorably with reaction (22) at temperatures at least as low as 150°C. For example if the reasonable assumption is made that the concentration of NH_3 is at least 10^3 times greater than the steady state concentration of N_2H_4, reaction (23) is about four times faster than reaction (22) at 150°C (specific rates from 62–0131; see also table 2.1).

The temperature dependence of $G(-NH_3)$ at very high dose rates (~ 10^{27}eV·g^{-1}s^{-1}; 69–0272, 71–0216) differs significantly from that described above (see figure 3.2.3.2). $G(-NH_3)$ is constant up to 200°C for a dose rate of 2 x 10^{27}eV·g^{-1}s^{-1}; above 200°C it increases and does not appear to be leveling off at the highest temperature studied (450°C). At 2 x 10^{26}eV·g^{-1}s^{-1} the effect is qualitatively similar but $G(-NH_3)$ is constant only up to about 125°C. Reaction (22) should be unimportant at the high dose rate employed, and hence interpretation based upon competition between reactions (13) and (22) can be ruled out. At very high dose rates the effect of temperature appears to be the result of the increasing importance of reaction (23) at higher temperatures. Kinetic analysis of the observed temperature dependence for a dose rate of 2 x 10^{27} eV·g^{-1}s^{-1} leads to k_{23} = 3.6 x 10^9 exp (−10,500/RT) dm^{3}mol^{-1}s^{-1}. The energy of activation is in agreement with reported values of 10–15 kcal/mol (62–0131, 65–0555). However, a similar analysis of data for a dose rate of 2 x 10^{26}eV·g^{-1}s^{-1} leads to k_{23} = 8 x 10^7 exp (−7,200/RT) dm^{3}mol^{-1}s^{-1}. Boyd, Willis and Miller (71–0216) attribute this inconsistency in k_{23} to variations with temperature of the various rate constants required in their calculations of k_{23}.

Studies with $^4He^{2+}$ radiation lead to results which are at least qualitatively similar. Thus, Jungers (36–0001) reports an increase in $G(-NH_3)$ by a factor of 1.9 (absolute yields not reported), and Wourtzel (19–0001) reports the following values: t(°C), $G(-NH_3)$; 18, 2.8; 108, 5.6; 220, 8.3; 315, 9.0. The values of Jungers and Wourtzel were originally reported as M/N and have been converted to G assuming W = 30.5 eV per ion pair for $^4He^{2+}$ radiation (53–0008).

Eyre and Smithies (70–0479) have suggested that part of the observed increase in $G(-NH_3)$ with increasing temperature may be the result of increased thermal decomposition of N_2H_3 and/or N_2H_2; and they use such an argument to account for the observed discrepancy between g(H) calculated from the limiting values of $G(H_2)$ at high temperatures and g(H) obtained by scavenger methods (see sec. 2.2.1).

Finally, it should be noted that $\Phi(-NH_3)$ for photolysis of gaseous ammonia also increases with temperature over this same range (32–7001, 34–7003, 44–7000), but results are limited and in poor quantitative agreement.

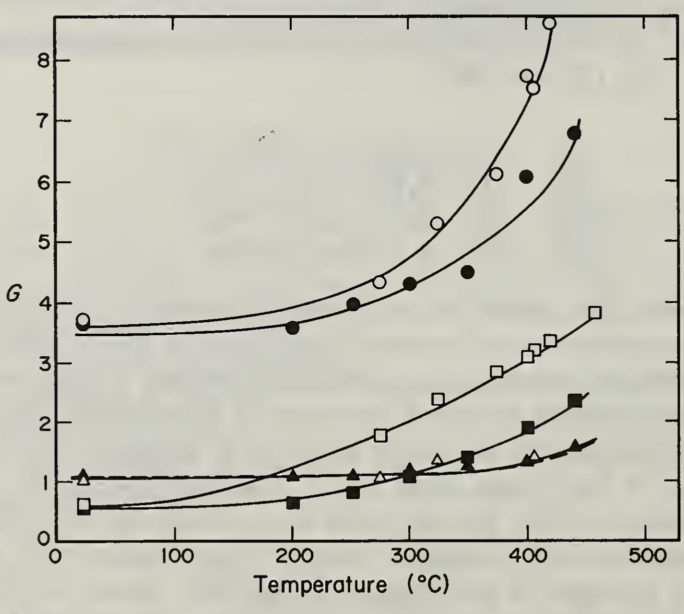

FIGURE 3.2.3.2. *Yields of H_2, N_2H_4 and N_2 from radiolysis of NH_3 vs. temperature (71–0216, 69–0272).* ○$G(H_2)$, □$G(N_2H_4)$, and △$G(N_2)$at 2 x 10^{26}eV·g^{-1}s^{-1}; ●$G(H_2)$, ■$G(N_2H_4)$,and △$G(N_2)$ at 2 x 10^{27}eV·g^{-1}s^{-1}.

3.2.4. Pressure

One atmosphere and below: In a number of the studies summarized in table 3.2.4 $G(-NH_3)$ has been reported to increase with decreasing pressure at pressures below one atmosphere.

Jones, Sworski, and Williams (67–0271) using 1 MeV electrons and Carstensen (67–0701) using ^{60}Co–γ radiation found $G(-NH_3)$ independent of pressure down to 400 torr. Below 400 torr

TABLE 3.2.4. *Effect of pressures*[a]

Radiation	Pressure Range	Effect on $G(-NH_3)$	Reference
1 MeV e^-	47 → 800 torr	See fig. 3.2.4 for results at 23°C; At 200°C. $G(-NH_3)$ is independent of P.	Jones..67–0271
Fast e^- [b]	50 → 500 torr (20°C)	Decreases with increasing P; appears to approach limit at ~ 500 torr. G not given.	Sorokin.65–0523
$^{60}Co-\gamma$	200 → 650 torr (23°C)	See fig. 3.2.4.	Carstensen67–0701
$^{60}Co-\gamma$	100 → 760 torr (23°C)	None.	Buchanan.70–0134
$^{60}Co-\gamma$	400 torr → 3.2 atm (41°C)	None.	Johnson.68–0659
$^{60}Co-\gamma$	100 → 700 torr (20°C)	None.	Eyre.70–0479
$^1H^+$	200 → 600 torr (22°C)	Decrease linearly with increasing P, from 1.93 to 1.73.	Horscroft64–0174
$^4He^{2+}$	80 → 700 torr (20°C)	Decrease with increasing P; total decrease of 23%.[c]	Luyckx34–0003[d]
$^{60}Co-\gamma$	1 → 12 atm (20°C)	None.	Nishikawa.68–0051
$^{60}Co-\gamma$	1 → 60 atm (120°C)	P(atm), $G(-NH_3)$; 1, 10; 7.7, 15; 9, 14.8; 30, 9.0; 60, 6.6.	Sorokin.64–1757
$^{60}Co-\gamma$	1 atm → 0.312 g/cm^3(137°C)	Sharp decrease from 4.1 to 1.4 at density near 0.15 g/cm^3.	Toi..62–0074[e]

a. In all cases incident intensity was constant and therefore variation in pressure is accompanied by a variation in energy absorbed per unit volume per unit time.

b. Energy not specified.

c. Author attributes important but unspecified part of this decrease to changes in absorbed intensity. See *a* above.

d. See also 57–0018.

e. See also 69–0026.

$G(-NH_3)$ increases from about 2.9 to a maximun of about 4 at 100 torr. Buchanan and Hanrahan (70–0134) failed to observe a similar increase in their study of $^{60}Co-\gamma$ radiolysis of NH_3. They found $G(-NH_3)$ independent of pressure from one atmosphere to 100 torr, the lowest pressure studied. Eyre and Smithies (70–0479) also found $G(-NH_3)$ independent of pressure over this same pressure range.

Luyckx (34–0003) observed an increase in $G(-NH_3)$ of about 23% for a decrease in pressure from 700 to 80 torr in a study of $^4He^{2+}$ radiolysis of ammonia. He attributed an important, albeit unspecified, part of this decrease to the accompanying variations in intensity. Under conditions of constant incident intensity a decrease in pressure is accompanied by a decrease in the energy absorbed per unit volume per unit time. All of the studies summarized in table 3.2.4 were carried out under such conditions; however, the decrease in intensity associated with a change in pressure from one atmosphere to about 100 torr should not affect $G(-NH_3)$ by more than about 10% (see sec. 3.2.2).

Burtt and Zahlan (57–0018) tried to determine the effect of pressure in the range 700 – 70 torr under conditions of nearly constant intensity using $^4He^{2+}$ radiation. They conclude that $G(-NH_3)$ increases with decreasing pressure but the experimental data are limited and not especially convincing.

Horscroft (64–0174) has reported an essentially linear increase in $G(-NH_3)$ of about 10% between 600 and 200 torr in radiolysis with 0.8 MeV protons. At the dose rate employed, intensity effects should be very small (section 3.2.2.) and the 10% increase in $G(-NH_3)$ can probably be attributed solely to the decrease in pressure.

Luyckx (34–0003) has pointed out that his results suggest the existence of an "inversion intensity." Near this "inversion intensity", $G(-NH_3)$ is relatively insensitive to changes in pressure. At higher intensities $G(-NH_3)$ decreases with increasing pressure and at lower intensities it increases with increasing pressure. The inversion intensity arises because $G(-NH_3)$ is independent of intensity at pressures below about 140 torr but decreases with increasing intensity at higher pressures. This may account for some of the discrepancies that have been observed.

$G(-NH_3)$ might be expected to vary with pressure because of the pressure dependence of radical combination reactions. Combination of two NH_2 radicals is apparently pseudo–second–order at pressures in excess of about 0.45 torr (63–9010); however, combination of NH_2 with H and of H with H should remain third order up to significantly higher pressures. Jones, Sworski and Williams (67–0271) attribute their observed increase in $G(-NH_3)$ between 450 and 100 torr to the decreased importance of combination of NH_2 with H. A similar explanation has been offered to account for increases in $\Phi(-NH_3)$ with decreasing pressure in photolysis of ammonia (54–7002, 39–7001, 35–7002); however, the decrease in $\Phi(-NH_3)$ begins at lower pressure (~ 100 torr).

The rapid and irreproducible decrease in $G(-NH_3)$ at pressures below 100 torr reported by Jones and Sworski (67–0270) and by Carstensen (67–0701) is similar to the effect observed by Wiig (37–7002, 35–7002) in photolysis of ammonia. Wiig attributed this decrease to combination of NH_2 with H at the walls.

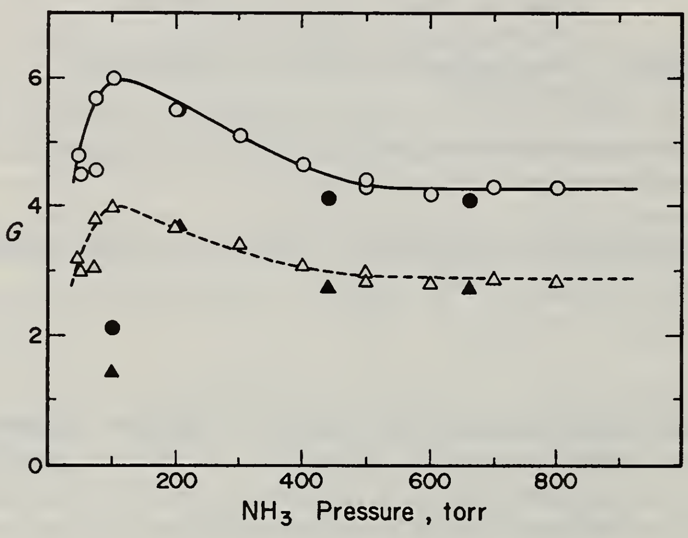

FIGURE 3.2.4. *Variation of* $G(H_2)$ *and* $G(-NH_3)$ *with pressure 23°C.* △$G(-NH_3)$, ○$G(H_2)$, 67–0270 (2 x 10^{18}eV·g^{-1}s^{-1}); ▲$G(-NH_3)$, ●$G(H_2)$, 67–0701 (5 x 10^{14}eV·g^{-1}s^{-1}).

At very high dose rate (2 x 10^{27}eV·g^{-1}s^{-1}), $G(-NH_3)$ increases rapidly with decreasing pressure below about 700 torr (69–0272, 71–0216), but this effect appears to be the result of acceleration of secondary electrons in transient fields created by the pulse.

Pressure above one atmosphere: At higher temperatures, the pressure range can be extended to the point that gas densities approach those of liquid ammonia. Toi, Peterson and Burton (62–0074) studied ^{60}Co–γ radiolysis of gaseous ammonia at 137°C over the density range from 5 x 10^{-4}g/cm^3 to 0.312 g/cm^3. They found $G(-NH_3)$ decreased rather sharply from 4.1 to 1.4 at densities near 0.15 g/cm^3. Further increase in density had little effect upon $G(-NH_3)$. They interpreted this decrease in terms of the effect of ion–clustering upon ion–neutralization. However, this interpretation seems improbable in light of more recent investigation of ion–clustering in ammonia (64–9015, 66–9067, 68–0032). Recent work by Nishikawa, Kuroda, and Matsuura (69–0026) over this same density range is in good agreement with the earlier study of Toi et al. They suggest the decrease in $G(-NH_3)$ is the result of neutralization of NH_4^+ by NH_2^-, i.e.,

$$NH_4^+ + NH_2^- \rightarrow 2NH_3$$

rather than by an electron. They speculate that at high densities NH_2 may compete successfully with NH_4^+ for electrons because of unspecified alteration in the electrostatic field of NH_4^+.

3.2.5. Electric Field

Electric fields have been applied to systems during radiolysis to obtain information about the role of ion–neutralization processes (for a general discussion of this technique see G.G. Meisels, 68–0650, page 364). In the case of ammonia, electric fields less than about 5 $V \cdot cm^{-1}$ $torr^{-1}$ do not significantly affect $G(-NH_3)$.

The earliest investigations (38–0002, 42–0001, 55–0010, 57–0018) were carried out with relatively low–intensity (10^{13} – 10^{14} $eV \cdot g^{-1} s^{-1}$) $^4He^{2+}$ radiation over a pressure range of 200 to 620 torr at 25°C. In the first of these (38–0002), a significant decrease (~ 30%) in $G(-NH_3)$ with increasing field strength was reported at 620 torr, and on the basis of this observed decrease it was concluded that 34% of the overall reaction was attributable to ion–recombination. However, this decrease was not observed in subsequent studies under similar conditions in the same laboratory using more highly purified ammonia (55–0010, 57–0018).

More recently, Jones and Sworski (67–0270) carried out a study of the effect of applied field upon radiolysis with 1 MeV electrons. At 200 torr and 23°C they find $G(-NH_3)$ is independent of field strength up to about 5 $V \cdot cm^{-1}$ $torr^{-1}$; $G(-NH_3)$ increases with increasing field strength above 5 $V \cdot cm^{-1}$ $torr^{-1}$ because of excitation of NH_3 by collision with electrons accelerated in the field. These results suggest that the net chemical effect of ion–neutralization is the same whether the neutralization occurs homogeneously or at a surface.

3.2.6. Flow Rate

Most studies of gaseous ammonia have been made under static conditions. In such cases, hydrazine is not obtained in measurable yields at dose rates below ~ $10^{26} eV \cdot g^{-1} s^{-1}$ (69–0272, 68–0101) presumably because of radical–hydrazine reactions. Jones, Sworski and Williams (67–0271) have studied radiolysis of NH_3 in this low dose rate range with 1 MeV electrons under both static and flow conditions. Hydrazine is not produced in measurable yields under static conditions but it is an important product in flow systems. Yields of N_2H_4 increase with increasing flow rate and decreasing intensity. At constant flow rate and intensity, $G(N_2H_4)$ increases markedly with increasing temperature. At a constant beam current of 5 μA and constant flow rate of 2.5 dm^3/min, $G(N_2H_4)$ increases from 0.62 to 2.97 as the temperature is increased from 25°C to 300°C. The highest yield observed was $G(N_2H_4) = 3.95$ for a beam current of 0.05 μA and a flow rate of 2.5 dm^3/min at 300°C.

In flow systems hydrazine is removed from the reaction zone and rapidly diluted so that radical–hydrazine reactions are considerably less important than in static systems. Increasing temperature and decreasing intensity further reduce the probability of such N_2H_4–consuming reactions. An increase in temperature is assumed to increase the imnortance of reaction (23) relative to the reaction of H with N_2H_4, and decrease

$$(23)\ H + NH_3 \rightarrow H_2 + NH_2$$

in intensity probably favors production of N_2H_4 by reducing the steady–state concentration of H.

Appendix 1. Selected Properties of Species Involved in Radiolysis of Gaseous Ammonia

See tables A.1.1 and A.1,2.

TABLE A.1.1. *Properties of neutral species*[a]

Species	$\Delta H_f°$(298 K) (kcal/mol)	*I.P.* (eV)	*P.A.* (eV)	*E.A.* (eV)	*D*(298 K) (kcal/mol)	Other properties
NH_3	−11.02	10.2	9.2–9.4[b]	c	*D*(NH_2–H) = 104 ± 2	*W* = 30.5 ± 0.4 (^{210}Po–α),[h] 26.5 ± 0.4 (1 MeV e^-).[i] S_A = 0.719[j]. UV spectrum.[k] e^- impact spectrum.[l]
NH_2	41	11.4	—	1.21,1.22[d]	*D*(NH–H) = 90 ± 2	UV spectrum.[m] Fluorescence spectrum[n]. ESR spectrum.[o]
NH	79	13.1	—	—	*D*(N–H) = 85 ± 2	UV spectrum.[p] Fluorescence spectrum.[q]
N_2H_4 (g)	22.80	8.74	—	—	*D*(H_2N–NH_2) = 59 ± 3 *D*(N_2H_3–H) = 76 ± 2	—
N_2H_3	~ 47[e]	7.88	—	—	—	—
N_2H_2	49 ± 5[f]	9.85	—	—	*D*(HN=NH) = 109 ± 5[g]	—
H	52.10	13.6	—	—	—	—
H_2	0	15.4	3.0	-0.72	*D*(H–H) = 104.2	—
N_2	0	15.6	—	—	*D*(N–N) = 225.96	—

a. Unless otherwise indicated values have been taken from the following sources. Standard heats of formation ($\Delta H_f°$), Wagman..... 68–9060; Ionization potentials (*I.P.*), Franklin.....69–9067; proton affinities (*P.A.*) and electron affinities (*E.A.*), Vedeneyev....62–9017; bond dissociation energies (*D*), Darwent 70–9007.

b. See also 55–9002 and 68–7069. Entropy of protonation is −27.55 eV/deg (55–9002).

c. Doesn't form a stable negative ion with thermal electrons. At ~ 3 eV NH^- is detected (34–9002). See also 66–0298.

d. Page 73, 62–9019.

e. Calculated from *D*(N_2H_3–H) and $\Delta H_f°$ of H and N_2H_4.

f. Calculated by combining mass spectrometric and thermal data (Foner and Hudson 58–9004).

g. Calculated from $\Delta H_f°$ of N_2H_2 and NH.

h. Biber..53–0008.

i. Meisels 64–0177.

j. Stopping power relative to air, Meisels 64–0177.

k. 105–165 nm with 0.7 nm resolution, Okabe and Lenzi67–7484 (includes threshold for various photodissociation processes); 140–220 nm, Watanabe 54–9006; 85–230 nm, Duncan 35–9001.

l. Skerbele and Lassettre 65–9040.

m. Herzberg and Ramsay 52–7001; Ramsey 53–7003. Gordon, Mulac and Nangia 71–0169 (pulsed radiolysis).

n. Okabe and Lenzi 67–7484.

o. Adrian..62–5011 (in argon at 4.2 K); Marx.68–5178; Smith.(70–0335) ($^{14}NH_2$, $^{14}ND_2$, $^{15}NH_2$, $^{15}ND_2$).

p. Meaburn and Gordon 68–0101 (pulsed radiolysis); Husain and Norrish 63–7008; Ramsay 53–7003.

q. Okabe and Lenzi 67–7484; Becker and Welge 63–6002.

TABLE A.1.2. *Properties of ionic species*[a]

Ion	ΔH_f° (298.2 K) (kcal/mol)	*A.P.* (eV)	Relative abundance (2×10^{-7} torr)	Comments
NH_4^+	154 (55–9002)	—	0	Accounts for 97% of positive ions at 1 torr (66–0298) because of rapid ion–molecule reactions. Solvated at normal temperatures and pressures (66–9067, 68–0032, 64–9015, 65–0775, 71–9024).
NH_3^+	223	10.2	100	Rapidly converted to NH_4^+ at *P* near 1 torr (66–0298).
NH_2^+	304	16.0	40.92	Rapidly converted to NH_4^+ at *P* near 1 torr (66–0298).
NH^+	382	17.1 (+H_2) 21.6 (+2H)	4.50	See table 2.1 for reactions of NH^+.

a. Unless otherwise indicated values have been taken from the following sources. Standard heats of formation (ΔH_f°) and appearance potentials (*A.P.*), Wagman.....68–9060; relative abundances, Melton 66–0298.

Appendix 2. Additives Used in Studies of Ammonia Radiolysis

Tables A.2.1 and A.2.2 are intended primarily as an index to the additives that have been employed in studies of the radiation chemistry of gaseous ammonia. No attempt has been made to include detailed results; however, a number of these additives have been given rather extensive consideration in section 2. Tables A.2.1 and A.2.2 do not include studies of additives employed exclusively for purposes of synthesis (viz., synthesis of amines).

TABLE A.2.1. *Additives: Binary mixtures*

Additive	Concn. range, mol %	Radiation	Comments	Reference
Argon	0 → 80	^{60}Co–γ and fast e$^-$	Efficient energy transfer from Ar to NH_3.	Sorokin.65–0523
Benzene	0 → 4.3	^{60}Co–γ	Used to determine $g(H_2)$. See table 2.2.3.	Carstensen67–0701
Benzene	3.0	^{60}Co–γ	ditto.	Johnson.68–0659
Benzene	0 → 7.4	^{60}Co–γ	ditto.	Eyre.70–0479
Carbon tetrachloride	2 → 9	^{60}Co–γ	Used to study ion–neutralization. See section 2.1.1.	Nishikawa.68–0051[b]
Carbon tetrachloride	0 → 5	^{60}Co–γ	ditto.	Eyre.70–0479
Cyclohexane	0 → 6.5	^{60}Co–γ	Used to determine g(H). See section 2.2.1.	Eyre.70–0479
Deuterium	0 → 20	1 MeV e$^-$	G(HD) from NH_3–D_2 used to estimate g(H). See section 2.2.1.	Jones.67–0270
Deuterium	0 → 4.7	^{60}Co–γ	Suggest chain reaction involved in production of HD.	Johnson.68–0659
Ethylene	0 → 7	1 MeV e$^-$	Used to determine $g(H_2)$. See table 2.2.3.	Jones.67–0270
Ethylene	2 → 4	^{60}Co–γ	ditto. Also used C_2D_4.	Nishikawa.68–0051
Ethylene	0 → 3	250 keV e$^-$	Pulse radiolysis. Decreases $t_{0.5}$ for decay of NH.	Meaburn.68–0101
Hydrazine	0 → 1.3 at 600 torr 0 → 4 at 200 torr	1 MeV e$^-$	Used to determine g(H). See section 2.2.1.	Jones.67–0270
Hydrazine	0 → 1	^{60}Co–γ	ditto.	Carstensen67–0701
Hydrazine	5.3 and 7.4	^{60}Co–γ	Very limited study.	Nishikawa..69–0326
Hydrazine	0 → 2.2	^{60}Co–γ	Used to determine g(H)	Eyre.70–0479
Hydrogen	9 → 50	0.8 MeV $^1H^+$	Results are not consistent, but some indication that $G(-NH_3)$ decreases at high concn. of H_2.	Horscroft 64–0174
Hydrogen	12 → 90	$^4He^{2+}$ (Rn)	$G(-NH_3)$ decreases but relatively high concn. of H_2 required.	Jungers32–0002
Iso–propanol	0 → 4.3	^{60}Co–γ	Used to determine g(H). See section 2.2.1.	Eyre.70–0479
Krypton	~ 90	2 MeV $^2H^+$	N_2H_4 only product studied.	Lampe...63–0098
Methanol	0 → 10	^{60}Co–γ	Used to determine g(H).	Carstensen67–0701
Methanol	0 → 8.3	^{60}Co–γ	ditto.	Eyre.70–0479
Neon	0 → 60	^{60}Co–γ and fast e$^-$ [a]	Efficient energy transfer from Ne to NH_3.	Sorokin.65–0523
Neon	~ 90	2 MeV $^2H^+$	N_2H_4 only product studied.	Lampe...63–0098
Nitrogen	6 → 50	0.8 MeV $^1H^+$	Energy transfer from N_2 to NH_3 at high N_2 concns.	Horscroft64–0174
Nitrogen	17 → 99	$^4He^{2+}$(Rn)	Energy transfer from N_2 to NH_3 at high N_2 concns.	Jungers32–0002
Nitrous Oxide	0 → 10	^{60}Co–γ	Used to study ion–neutralization. See section 2.1.1.	Nishikawa.68–0051
Nitrous Oxide	0 → 100	^{60}Co–γ	ditto.	Johnson.68–0659

TABLE A.2.1. *Additives: Binary mixtures* – Continued

Additive	Concn. range, mol %	Radiation	Comments	Reference
Nitric Oxide	0 → 13	^{60}Co–γ	Reduced $G(H_2)$ to 0.69. $G(N_2)$ = 11.9 and presumably $G(N_2)$ = g(NH) + $g(NH_2)$.	Eyre.70–0479
	0 → 0.7	2 MeV e$^-$	Pulse radiolysis. Studied effect of NO on decay of NH_2 and NH. Calculate specific rates for NO + NH and NO + NH_2.	Gordon..71–0169
Oxygen	0 → 3 x 10^{-3}	^{60}Co–γ	$G(H_2)$ and $G(N_2)$ reduced.	Carstensen67–0701
Oxygen	0 → 6	250 keV e$^-$	Pulse radiolysis, no yield data. Report reduction in $t_{0.5}$ for decay of NH in presence of O_2.	Meaburn.68–0101
Phosphine	0 → 100	^{60}Co–γ	Yields consistent with $NH_2 + PH_3 \rightarrow NH_3 + PH_2$ $H + PH_3 \rightarrow H_2 + PH_2$ $2PH_2 \rightarrow PH_3 + PH$ $2PH \rightarrow P_2 + H_2$.	Buchanan.70–0653
Propane	0 → 6.6	^{60}Co–γ	Used to estimate g(H). See section 2.2.1 and also table A.2.2.	Johnson.68–0659
Propane	0 → 8.6	^{60}Co–γ	ditto.	Nishikawa..69–0326^c
Propane	0 → 20	^{60}Co–γ	ditto. Find $G(H_2)$ depends upon dose.	Eyre.70–0479
Propylene	1.5	^{60}Co–γ	Used to determine $g(H_2)$. See table 2.2.3.	Johnson.68–0659
Propylene	0 → 3.8	^{60}Co–γ	ditto.	Nishikawa..67–0263
Propylene	0 → 5	^{60}Co–γ	ditto.	Sorokin.64–1757
Propylene	0 → 7.4	^{60}Co–γ	ditto.	Eyre.70–0479
Propylene	0 → 9	fast e$^{-\,a}$	ditto.	Sorokin.65–0523
Propylene	0 → 8	1.0 – 1.7 MeV e$^-$	Pulse radiolysis. Very high intensity.	Willis..69–0272
Propylene	0 → 3.3	250 keV e$^-$	Pulse radiolysis. Results in increases in $G(N_2H_4)$ (0.07 to 0.18).	Meaburn.68–0101
Propylene	0 → 10	2 MeV e$^-$	Pulse radiolysis. Studied effect of C_3H_6 on decay of NH_2.	Gordon..71–0169
Sulfur hexafluoride	0 → 1.1	^{60}Co–γ	Very limited study. See also table A.2.2.	Nishikawa.69–0326
	0 → 10	2 MeV e$^-$	Pulse radiolysis. Studied effect of SF_6 on decay of NH_2. Used to estimate importance of ion–neutralization.	Gordon..71–0169
Xenon	0 → 56	0.8 MeV $^1H^+$	Efficient energy transfer from Xe to NH_3.	Horscroft64–0174
Xenon	0 → 80	^{60}Co–γ	ditto.	Sorokin.65–0523
Xenon	~ 24	X–rays (40 kV)	ditto.	Guenther.37–0001

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a. Energy not specified.

b. See also 67–0263.

c. See also 68–0505 and 69–0326.

Table A.2.2. *Additives: Ternary mixtures*

Additives	Concn. range, mol %	Radiation	Comments	Reference
H_2 and N_2	H_2: 0 → 75 N_2: 0 → 25	$^{4}He^{2+}$(Rn)	—	Jungers32–0002
C_3H_8 and N_2O	C_3H_8: 0 → 12 N_2O; 1.5 and 3.0	^{60}Co–γ	See section 2.2.2.	Johnson.68–0659
C_3H_8 and N_2O	C_3H_8: 1 → 4 N_2O: 5	^{60}Co–γ	See section 2.2.2.	Nishikawa..69–0326
C_3H_8 and SF_6	C_3H_8: 1.5 SF_6: 0.2	^{60}Co–γ	See section 2.2.2.	Johnson.68–0659[a]
C_3H_8 and SF_6	C_3H_8: 3.6 SF_6: 0 → 1.6	^{60}Co–γ	See section 2.2.2.	Nishikawa..69–0326
iso–propanol + N_2O	iso–propanol: 0.5% N_2O: O → 1.7%	^{60}Co–γ	See section 2.2.2.	Eyre.70–0479
iso–propanol + SF_6	iso–propanol: 0.5% SF_6: 0 → 1.3%	^{60}Co–γ	See section 2.2.2.	Eyre.70–0479
iso–propanol + CCl_4	iso–propanol: 0.5% CCl_4: 0 → 1%	^{60}Co–γ	See section 2.2.2.	Eyre.70–0479

a. See also 67–0369.

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H_2 and N_2 are the only significant products of radiolysis of gaseous ammonia under static conditions at dose rates less than about $10^{19} eV \cdot g^{-1} s^{-1}$; and $G(H_2) = 5.0 \pm 1.0$ and $G(N_2) = 1.7 \pm 0.3$ for irradiation at 20°C and pressures near one atmosphere. Yields do not appear to depend significantly upon LET (linear energy transfer); and they are independent of dose up to at least 8×10^{22} eV/g. In static systems at dose rates $\gtrsim 10^{26} eV \cdot g^{-1} s^{-1}$, and in flow systems, N_2H_4 is also a product.

At dose rates less than $10^{19} eV \cdot g^{-1} s^{-1}$, $G(-NH_3)$ increases markedly with temperature and reaches a plateau value of about 10 at temperatures near 150 - 200°C. At very high dose rates ($\gtrsim 10^{26} eV \cdot g^{-1} s^{-1}$) $G(-NH_3)$ increases significantly at higher temperatures (value depends upon dose rate) and $G(-NH_3)$ does not appear to be leveling off at the highest temperature studied (460°C). In both dose rate regions the increase in $G(-NH_3)$ is attributed primarily to the increasing importance of $NH_3 + H \longrightarrow NH_2 + H_2$ with increasing temperature. $G(-NH_3)$ also appears to increase with decreasing dose rate. However, the effect is less pronounced than the effect of temperature, and the experimental evidence is not unequivocal.

NH and NH_2 have been observed spectroscopically in pulse radiolysis of NH_3 and such studies lead to $g(NH) = 0.4$. However, this value of g(NH) is low because of errors in dosimetry. $g(NH_2)$ was not obtained directly because the absorptivity of NH_2 was not available. A number of additives has been employed in attempts to determine primary yields of other species involved in radiolysis; however, results with different additives and from different laboratories are in good agreement only in the case of

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$g(H_2)$ (0.7 - 0.8) and $g(NH_4^+)$ (3.3 - 3.9). The best value of $g(H)$ appears to be 10.4 ± 0.6; and this is the preferred value. $g(NH_2)$ is obtained from the material balance, $g(H) + 2g(H_2) = g(NH_2) + 2g(NH)$. The preferred value of $g(NH)$ is 0.75, i,e, $g(NH)$ $g(H_2)$ and this leads to $g(NH_2) = 10.4$.

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