DEACTIVATION PROCESSES IN ACTIVE NITROGEN

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INTRODUCTION

NATURE OF ACTIVE NITROGEN

Though there has long been uncertainty as to the nature of active nitrogen, the matter was in part settled in the mass-spectrometric studies of Jackson and Schiff (1), and Berkowitz, Chupka, and Kistiakowsky (2), where the only components detectable in a gas mixture at about 1 mm. pressure and containing about one percent active nitrogen were the ground state molecule and the ^4S atom. This observation was, of course, consistent with most of the known properties of active nitrogen, in particular Wrede gauge measurements (e.g. 3), the chemical behaviour (page 12), and the kinetics exhibited in the emission of the afterglow (page 3).

A natural conclusion has therefore been that the ^4S atom is the only constituent of active nitrogen (2). However such a generalization is not at all warranted except for primary discharge products. If additional excited species were formed in the course of atom decay*, they would not necessarily occur in measurable concentrations when the initial atom concentration was low or the time of decay short (see calculation on page 67).

In deciding what excited species other than ^4S atoms might be present, it will be noted that only excited molecular states need be considered since the ^4S atom is already in the lowest atomic level and considerably below

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* The general term "decay" will be used throughout this work to refer to such processes as "recombination" (of atoms), "de-excitation" (of excited molecules), or "loss of chemical activity" (of active nitrogen).

the ionic levels. One possible excited molecule, of course, is the vibrationally excited ground-state, which will be hereafter referred to as the $X^{*1}\Sigma$ or simply X* state. It would be stable in respect of radiation since it is homonuclear, while collisional loss of vibrational energy is in general very slow.* Evans and Winkler (8) have concluded that the X* state might originate by a collision induced cross-over from the $A^3\Sigma$ state (hereafter referred to as the A state), which is in turn formed in the course of afterglow emission but does not decay radiatively. However Lichten (9) has recently determined the lifetime of the A state itself to be $\geq$0.01 sec. in agreement with an early estimate by Vegard (10) of 0.1 sec.**, so that this state might also occur in appreciable concentrations.

While N_3 might be expected as a metastable intermediary in homogeneous decay (cf. O_3 (12) and I_3 (13)), the presently accepted decay scheme involves an N-N intermediary. Furthermore the lifetime, tentatively placed at 0.002 sec. by Thrush (14), is not adequate to permit a significant concentration to build up. At present there are no other known molecular states of nitrogen with sufficient stability to contribute to the activity of active nitrogen, though Lichten (9) indicates that this does not mean that none exist.

* Observed and calculated values of the $N_2(X,v=1) \longrightarrow N_2(X,v=0)$ transition probability in collisions with N_2 at 600 to 800°K. range from 2×10^{-10} to 2×10^{-7} (4,5,6). Though the probability would be considerably increased for higher or anharmonic levels, a value comparable with that of the recently detected oxygen analog might still be expected (7).

** Lichten considered that the 2.3×10^{-4} sec. estimate of Muschlitz and Goodman (11) should actually be assigned to the $a^1\Pi$ state.

DECAY OF ^{4}S N ATOMS

A ground-state atom has available at least four modes of decay: homogeneous, radiative, first-order surface, and second-order surface.

(a) Luminous Homogeneous Decay

One of the most striking characteristics of active nitrogen is the emission of yellow-orange afterglow. It has been shown by Rayleigh (15) and later confirmed by Berkowitz *et al*. (2) that the afterglow intensity is proportional to [active nitrogen]^2[inert gas]. (The work cited did *not* determine whether the inert gas could include the active nitrogen itself.) Furthermore, the afterglow was observed *not* to intensify in the neighborhood of surfaces, whether poisoned or unpoisoned (16). The implication is that one, though not necessarily the only, mode of decay of N atoms is homogeneous recombination in which the molecule formed is stabilized by collision with a gaseous third body and then rapidly radiates:

$$\begin{aligned} N + N + M &\xrightarrow{k_2'} N_2^{**} + M \\ N_2^{**} &\longrightarrow N_2^{*} + h\nu \qquad \text{(rapid)} \end{aligned} \qquad [1]$$

where k_2' *without a factor of two* is the rate of atom destruction, M is a third body, and N_2^{**} and N_2^{*} were early identified as the $B^3\Pi$ and A states, respectively. This mode of decay will be hereafter referred to as luminous homogeneous decay, and it will be noted that its end product is the A state, previously stated to be metastable and to give rise to the X* state. Actually the work of Berkowitz *et al*. (2) and of Kistiakowsky and Warneck (17) indicates that luminous homogeneous decay proceeds by a somewhat more elaborate mechanism:

$$
\begin{aligned}
N + N + M &\underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} N_2(^5\Sigma) + M \\
N_2(^5\Sigma) + M &\xrightarrow{k_b} N_2(B^3\Pi) + M \quad \text{(slow)} \qquad [2] \\
N_2(B^3\Pi) &\longrightarrow N_2(A) + h\nu \quad \text{(rapid)}
\end{aligned}
$$

though the overall rate can still be expressed by a simple constant, $k_2' = k_a k_b (k_{-a} + k_b)$. k_2' has been estimated at 4×10^{-33} cc.^{2} molecule^{-2}sec.$^{-1}$ (2)*.

A somewhat different homogeneous decay mechanism was proposed by Oldenberg (18). However it utilizes excited atoms, in disagreement with the mass-spectrometric studies (1,2), and need not be considered further.

(b) Non-luminous Homogeneous Decay

To good approximation, a ^4S atom can only combine into $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$ molecular states (2). For nitrogen the $^7\Sigma$ state is probably higher than the ^4S dissociation energy, while of the remaining states only the $^5\Sigma$ was considered to result in luminous homogeneous decay. It is therefore possible that the following non-luminous species of homogeneous decay might also occur:

$$N + N + M \xrightarrow{k_2''} N_2(A) + M \qquad [3]$$

and

$$N + N + M \xrightarrow{k_2'''} N_2(X^*) + M \qquad [4]$$

where k_2'' and k_2''' give the rate of atom destruction directly. By analogy with luminous homogeneous decay, it would be expected that the detailed mechanism would involve an equilibrium between two free atoms and high vibrational levels of the A or X* state, together with a slower step in

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* The original value has been doubled to take into account the greater rate of atom destruction than afterglow production.

which the molecule was stabilized.

From the above considerations, three distinguishable species of homogeneous decay should be possible, corresponding to equations [2], [3], and [4]. Any experimental homogeneous decay constant, obtained by measurement of _atom concentrations_ would therefore be a sum, $k_2 = k_2' + k_2'' + k_3'''$. Hence if k_2' were determined from absolute _afterglow intensity_ measurements and were found to equal k_2, a necessary conclusion would be that afterglow accompanies _all_ homogeneous decay, at least with the particular third body. Similarly if with some other third body, $k_2 > k_2'$ (e.g. if there were no afterglow), then either non-luminous homogeneous decay or the related processes, energy transfer or catalytic recombination, would be indicated. The latter processes, which differ from homogeneous decay in that an N-M rather than an N-N complex is involved and considerable energy may be transferred to the third body, will be described later.

(c) _Radiative Decay_

Homogeneous recombination in which the molecule is stabilized by radiation, i.e. radiative decay, is not considered by Herzberg (19) to be intrinsically less probable than that in which there is collisional stabilization. However stabilizing radiation is seldom observed in the recombination of atoms and free radicals. For example, the nitrogen afterglow, which might be identified with such radiation, is neither continuous (19, page 400) nor diffuse (19, page 414), and depends on the concentration of inert gas. Radiative decay will therefore not be further considered.

(d) First-Order Surface Decay

The nature of the walls of the apparatus is well known to affect the duration of the nitrogen afterglow (16, 20). Though the surface decay thus indicated would necessarily be superimposed on the homogeneous decay, Rayleigh (16) apparently succeeded in isolating it by determining the rate of afterglow decay when the surfaces were covered with H_3PO_4 (a good poison) or oil (a poor poison). With the former, the slower homogeneous decay was dominant. However, with the oil poison, an additional much more rapid mode of decay was evident. It was first order and non-luminous, and was concluded to be the surface decay.*

A similar conclusion regarding the surface decay of N atoms was reached by Buben and Schekhter (21) and Schekhter (22). They proposed a mechanism in which the gas phase atoms recombine with a layer of atoms adsorbed on the surface:

$$\begin{aligned} \text{N} + \text{surface} &\longrightarrow \text{N-surface} \\ \text{N} + \text{N-surface} &\xrightarrow{k_1} \text{N}_2 + \text{surface} \end{aligned} \qquad [5]$$

where k_1 gives the rate of atom destruction directly. At temperatures and atom concentrations where the surface layer is nearly complete the kinetics are necessarily first-order, but as the temperature is increased, or the atom concentration decreased, the number of atoms adsorbed per unit area of surface will decrease from its maximum (i.e. monolayer) value and become a function of the partial pressure of the atoms. The order will therefore increase to second so that the relevant processes will be better represented as

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* It will be shown in the course of the present work (page 74) that, while Rayleigh's conclusions regarding surface decay were undoubtedly correct, they do not entirely follow from his data.

$$\begin{gathered} \mathrm{N + surface} \rightleftharpoons \mathrm{N\text{-}surface} \\ \mathrm{N + N\text{-}surface} \xrightarrow{k_3} \mathrm{N_2 + surface} \end{gathered} \qquad [6]$$

or simply

$$\mathrm{N + N + surface} \xrightarrow{k_3} \mathrm{N_2 + surface} \qquad [7]$$

In both cases k_3 gives the rate of atom destruction directly.

The low temperature mechanism, i.e. equations [5], has since been interpreted in terms of absolute reaction rate theory by Laidler (23), and Shuler and Laidler (24), who showed that the rate constant of first-order surface decay should be given either by

$$k_1/2 = \bar{c}S\gamma/4V \qquad [8]$$

or*

$$k_1/2 = C_s(S/V)(kT/h)(f^{\#}/F_g f_s)e^{-E/RT} \text{ sec.}^{-1} \qquad [9]$$

where $\bar{c}$ is the mean kinetic velocity, S the area of the surface on which decay occurs, V the volume of the system, γ the collision efficiency or "recombination coefficient", C_s the number per cm.^{2} of surface species, E the activation energy of surface decay, and $f^{\#}$, f_s, and F_g the partition functions for, respectively, the activated complex, the surface reactant, and unit volume of the reacting gas. Hence*

$$\gamma = \frac{C_s h^2}{2\pi mkTb} e^{-E/RT} \text{ (unitless)}, \qquad [10]$$

where b represents the rotational and vibrational factors in F_g (unity in the case of atoms), and

$$E = -Rd(\ln\gamma T)/d(1/T).$$

In practice γ would be obtained from equation [8], which for a cylindrical system of radius r can be written

$$\gamma = 2r(k_1/2)(1/\bar{c}) \qquad [12]$$

* The units of k_1 and γ are consistent only if the units of C_s are <u>cm.</u>$^{-2}$ rather than <u>molecule</u> <u>cm.</u>$^{-2}$

The use of $k_1/2$ rather than k_1 represents a departure from the original treatment (23, 24) but is likely more correct. Thus, considering a given surface site, each instance of decay will be followed by an instance of adsorption. Since dissociation or bond stretching are not involved in the adsorption of an atom, the activation energy should be zero (23) and the process correspondingly rapid. The result is that the observed rate of decay will be double that due to the activated process described by equations [8] and [9]. Conversely, the use of an uncorrected rate constant in equation [12] would make γ high by a factor of two.

Linnett and Marsden (25, 26) have objected to the adsorption mechanism just described in cases where adsorption is known to be weak yet the kinetics are still first-order, for example, in the recombination of O atoms on glass or certain poisons. To explain the behaviour of O atoms they therefore suggested a slightly different mechanism according to which the gas phase atoms combine directly with the structural oxygen of the glass or poison (if the latter is oxygen-containing). With such poisons as KCl, on the other hand, it was assumed either that small amounts of water of hydration were retained or that a superficial layer of oxide was formed. (The latter would necessarily be accompanied by the expulsion of a component of the poison, e.g. Cl from KCl, if it were to differ from adsorption.) This mechanism would give second-order kinetics only at temperatures sufficiently high to decompose the surface compound. Such temperatures would be expected to exceed the "desorption" temperature.

A separate theoretical treatment of this alternate mechanism will not be necessary since the absolute rate expressions (equations [8] to [12]), which were actually derived on the basis of an immobile surface layer of unspecified origin, should still be applicable.

(e) Second-order Surface Decay

It has been shown that first-order surface decay should shift to second-order at elevated temperatures and very low atom concentrations, such that, in the limit, the mechanism degenerates to one in which the atoms recombine homogeneously with the resulting molecule stabilized by collision with a surface (equation [7]). The rate of such a process differs from the two-body collision rate by a steric factor together with a factor to give the probability that the wall is in the vicinity of the collision, i.e. $2\pi r\sigma/\pi r^2$ (27), where σ is the molecular diameter. Since the rate of homogeneous decay similarly includes a factor to give the probability that a gaseous third body is in the vicinity, i.e. σ/λ (28) where λ is the mean free path, the relative rates of second-order surface decay to homogeneous decay are approximately in the ratio $2\lambda/r$, so that only at pressures below about 10^{-2}mm. would the former become the more important (cf. 29). (Similar steric factors have been assumed.) However second-order surface decay would still not be expected to be competitive with first-order, unless it occurred to the exclusion of the latter as at high temperatures or low atom concentrations. This follows from the alternative expression for the rate of second-order surface decay, which relates it to the rate of surface collision by the factor σ/λ_{N-N} (30). The relative rates of second to first-order surface decay are therefore in the ratio $\sigma/\gamma\lambda_{N-N}$, i.e. much less than one for likely values of γ.

Intermediate orders of surface decay are, of course, also possible with rates ranging from the high first-order value to the very low second-order value. Such surface decay would, however, be roughly equivalent to the simultaneous occurrence of first and second-order surface decay.

DECAY OF EXCITED NITROGEN MOLECULES

(a) The A State

While the most natural mode of decay* for an electronically excited molecule is by radiation, the absence of the Vegard-Kaplan bands in active nitrogen and the lack of success in bringing about the absorptive transition $X^1\Sigma \longrightarrow A^3\Sigma$ (31), led Evans and Winkler (8) to conclude that a collision induced cross-over to the X* state was competitive. De-excitation could also occur by collision with surfaces, so that altogether the following processes might be expected:

$$N_2(A) \longrightarrow N_2(X) + h\nu \qquad [13]$$

$$N_2(A) + \text{surface} \longrightarrow N_2(X) + \text{surface} \qquad [14]$$

$$N_2(A) + M \longrightarrow N_2(X^*) + M \qquad [15]$$

where M is a collision partner and $N_2(X)$ the ground state with insufficient vibrational excitation to be reactive.

(b) The X* State

The modes of decay of the X* state leading to loss of chemical activity will depend on the manner in which this state reacts, i.e. on the manner in which a release of energy can be brought about. For example, Evans and Winkler (8) have concluded that for a significant release of energy, a cross-over to the A state would be necessary. This followed from the normally assumed reluctance of vibrationally excited molecules to lose more than one quantum at a time

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* The use of the term "decay" has been mentioned on page 1.

unless there were a simultaneous electronic change. Such a cross-over would place a minimum value on the permitted energies of the X* state, so that after a series of consecutive collisional deactivations a molecule would become <u>abruptly</u> unreactive. Since radiative decay is highly forbidden, the only other mode of decay would be by collision with surfaces. Hence the possible processes are:

$$N_2(X^*) + mM \longrightarrow N_2(X) + mM \qquad [16]$$

$$N_2(X^*) + \text{surface} \longrightarrow N_2(X) + \text{surface} \qquad [17]$$

where m is a number which is greater than one, though not necessarily integral since "$N_2(X^*)$" may be a mixture of states with various degrees of vibrational excitation. Consecutive collisional deactivation with m = 2 was suggested by Walsh and Porter (32) to explain a second-power pressure term in the decay of excited ethylene (33).

However, there is reason to suspect that, owing to a breakdown of the selection rules for high or anharmonic vibrational levels, a cross-over may not be necessary for energy release (19, page 80 ; 34)*. While this might mean that the X* state is not metastable at all, it would enhance the chemical reactivity by eliminating the small transmission coefficient necessarily associated with a spin-forbidden cross-over. A direct energy release would also make m = 1 and thereby remove any possibility of distinguishing the A and X* states on the basis of the pressure dependence of their homogeneous decay.

* High vibrational levels of the ground state are to be distinguished from low levels of excited states. Thus, although the stability of the vibrational levels of the $N_2(B^3\Pi)$ state was shown by Stanley (35, 36) to be unusually low, deactivation still proceeded stepwise.

CHEMICAL REACTIVITY OF ACTIVE NITROGEN

(a) HCN Formation and Direct Reaction

The principal interest of active nitrogen to chemists has been its reactivity, in particular the formation of HCN from hydrocarbons (e.g. 3). With a fast-flow system such a reaction is generally studied by determining the HCN production as a function of reactant flowrate at a given temperature. As the amount of reactant is increased the amount of HCN rises to a plateau value, which may be termed a flowrate plateau, while if the temperature is increased these flowrate plateaus may increase to a temperature independent maximum. Since the maximum flowrate plateau for a given apparatus has invariably been found to be independent of the reactant (e.g. 37) a not unreasonable conclusion has been that it corresponds to a cleanup of that part of active nitrogen capable of forming HCN, namely, for reasons which will be given in a subsequent section, the ^4S atom.

The mechanisms by which HCN is formed have been reviewed by Evans, Freeman, and Winkler (38), who showed that, except with acetylene, the reactions appeared to occur by a bimolecular process involving a long-lived complex:

$$\left.\begin{array}{l} N + M \rightleftharpoons NM \\ NM \longrightarrow HCN + \text{fragments} \end{array}\right\} \quad [18]$$

where M is a hydrocarbon. HCN formation is therefore a special case of what may be called direct reaction, i.e.

$$\begin{array}{l} N + M \rightleftharpoons NM \\ NM \longrightarrow \text{products} \end{array} \quad [19]$$

where M is any reactant. Direct reaction has also been observed in the reactions of active nitrogen with phosphine (39), nitric oxide (40), and nitrogen dioxide (40).

(b) Energy Transfer

In view of the long life of the complex assumed to occur in direct reaction, a possible alternative reaction of N atoms should be energy transfer, i.e.

$$\left.\begin{array}{r}
N + M \rightleftharpoons NM \\
N + NM \longrightarrow N_2 + M^* \\
M^* \longrightarrow \text{fragments}
\end{array}\right\}[20]$$

where M is any reactant. Such a process is similar to homogeneous decay except that (i) an N–M rather than an N–N complex is involved, (ii) the N_2 is formed in a level considerably below the dissociation energy, and (iii) there can be no accompanying afterglow (cf. (ii)). Energy transfer, like direct reaction, would give temperature dependent flowrate plateaus, though the maximum plateau would necessarily occur at one-half the N atom concentration.

The reaction of active nitrogen with HCl (41) and the formation of unsaturated from saturated hydrocarbons (38) have been attributed to energy transfer, and the latter may also play a role in the low temperature reactions of active nitrogen with ethane, neopentane, and ammonia (to be discussed).

(c) Catalytic Recombination

If a maximum flowrate plateau corresponds to a cleanup of the active species, it follows that the reaction has swamped all modes of decay. However a similar swamping is actually implied by the occurrence of any flowrate plateau *per se*, so that the temperature dependence of the plateaus would appear contradictory. A reasonable explanation was given by Forst, Evans, and Winkler (42) who showed that, while it is permissible to think of the usual modes of decay being swamped, a plateau can nevertheless occur in the presence of any amount of decay catalyzed by reactant or product or both, i.e. catalytic recombination. The reason is that catalytic recombination and the main reaction have the same order in respect of the reactant. Provided the relative rates of catalytic recombination to reaction decrease with temperature, the plateau will be temperature dependent, with only the maximum plateau corresponding to a true cleanup.

The mechanism generally assumed in catalytic recombination is of the type

$$\left.\begin{array}{r}N + M \rightleftharpoons NM \\ N + NM \longrightarrow N_2 + M\end{array}\right\} [21]$$

where the reactant M does not necessarily become excited. Such a process, which will be designated homogeneous catalytic recombination, is very similar to energy transfer in that an N-M complex is involved. In fact, perhaps the only distinction from energy transfer lies in the unspecified level of the N_2 which is formed. If the N_2 were in the $^5\Sigma$ state the process would, of course, be accompanied by afterglow.

By analogy with first-order surface decay of atoms, a surface catalytic recombination may also be possible:

$$\left.\begin{array}{r}N + M \rightleftharpoons NM \\ NM + N\text{-surface} \longrightarrow N_2 + M + \text{surface}\end{array}\right\} [22]$$

It is unlikely that it would be accompanied by afterglow.

Combining the two mechanisms of catalytic recombination with the two mechanisms of N atom reaction previously considered, four combined <u>schemes</u> of reaction plus catalytic recombination are obtained. One such scheme has been shown by Forst <u>et al</u>.(42) to account quantitatively for the flowrate plateaus of certain N atom reactions. Conversely, if a given reaction were not consistent with any of the schemes, reaction with excited molecules would be indicated. A theoretical treatment of the four schemes will be given in a later section (page 37).

(d) Reactivity of Excited Molecules

If the metastable excited molecules which are known or suspected to be the end products of the luminous homogeneous decay of N atoms are present in active nitrogen in small amounts, they may be responsible for some of the reactivity of active nitrogen. In fact, catalytic recombination and reaction with excited molecules are in general alternative explanations for low reactivity*, i.e. reactions which give flowrate plateaus lower than the expected maximum plateau. Similarly reaction with both atoms and excited molecules serves to explain abnormally high reactivity.

In attributing reactivity to excited molecules it must be borne in mind, however, that the formation of HCN from hydrocarbons is not a likely reaction of an excited <u>nitrogen</u> molecule in view of the activation energy barrier to be expected (8). Direct evidence to this effect appears to have been obtained in a study of the reaction of active nitrogen with nitric oxide (40). It will be discussed later. Reaction to form C_2N_2 would, presumably, also involve a major activation energy barrier. Accordingly the only reactions to be expected with excited molecules are those resulting from a transfer of energy to the reactant:

$$\left.\begin{array}{r} N_2^* + M \longrightarrow N_2 + M^* \\ M^* \longrightarrow \text{fragments} \end{array}\right\} \quad [23]$$

* Back-reaction may also occur in specific cases (41).

where N_2^* is an unspecified excited molecule. The possibility must always be borne in mind, of course, that the fragments formed will be able to react further with either the atoms or excited molecules.

Examples of reactions which are perhaps better explained in terms of excited molecules than catalytic recombination, are those of active nitrogen with

(i) ammonia and ammonia-ethylene mixtures (43). The reaction of ammonia with active nitrogen was found to be rapid, yet the maximum amount of ammonia destroyed was only one-sixth the amount of HCN formed from ethylene. This maximum appeared to be independent of temperature and of admixed ethylene. Moreover, the afterglow was only slightly affected even in the presence of large amounts of ammonia. The following mechanism has been given (8) to explain this behaviour:

$$\left.\begin{array}{rcl} N_2^* + NH_3 & \longrightarrow & N_2 + NH_3^* \\ NH_3^* & \longrightarrow & NH_2 + H \\ N + NH_2 & \longrightarrow & N_2 + 2H \\ N + NH_3 & \longrightarrow & N + NH_3 \end{array}\right\} [24]$$

(ii) ethylene and ammonia for different energy expenditures in the discharge tube (44). It was observed that the ratio of the amount of ammonia destroyed to the amount of HCN formed from ethylene increased with increasing atom concentration, suggesting that the ammonia reacted only with excited molecules and that these were formed by a high-order mode of atom decay.

(iii) ethane and neopentane (37, 45). HCN production from these reactants was equal to that from ethylene at elevated temperatures, but was much less at room temperature, being in fact comparable with the amount of ammonia destroyed. Since, however, the activation energies changed in the neighborhood of 125°C., a change in the mechanism (such as could arise if two reactive species were present) rather than catalytic recombination seemed to be indicated. If this explanation is correct then the following mechanism may be applicable (8):

$$\left.\begin{array}{r} N_2^* + C_2H_6 \longrightarrow N_2 + C_2H_6^* \\ C_2H_6^* \longrightarrow C_2H_5 + H \\ N + C_2H_5 \longrightarrow HCN + CH_3 + H \end{array}\right\} \quad [25]$$

and, at elevated temperatures only,

$$N + C_2H_6 \longrightarrow HCN + CH_3 + 2H \qquad [26]$$

(iv) nitric oxide (40). The amount of nitric oxide destroyed exceeded the HCN production from ethylene, at all temperatures, yet a reaction chain did not seem to be involved. This indicated reaction both with N atoms and with excited molecules capable of transferring energy,

$$\left.\begin{array}{r} N_2^* + NO \longrightarrow N_2 + NO^* \\ NO^* \longrightarrow N + O \\ N + NO \longrightarrow N_2 + O \end{array}\right\} \quad [27]$$

but incapable of forming HCN from ethylene.

DECAY OF H AND O ATOMS

Though the present work is concerned only with active nitrogen, the behavior of H and O atoms will be of interest by way of comparison.

(a) Homogeneous Decay

Neither H nor O atoms recombine with emission of light, though they exhibit well defined homogeneous decay. However, there has been considerable disagreement on the relative efficiencies of H_2 and H as third bodies in the recombination of H atoms, while the whole mechanism of the homogeneous decay of O atoms is complicated by the stability of ozone (12), the counterpart of the transition complex in the recombination of other atoms. The homogeneous decay of O atoms will therefore not be further considered. Typical values for the rate constant of the homogeneous decay of H atoms are given in Table I.

(b) Surface Decay

The first really conclusive studies on the surface decay of any atom or free radical were those of Smith (53) on H atoms and Linnett and Marsden (25, 26) on O atoms. In both cases atom concentrations in a side arm attached to a discharge tube were measured by means of a thermocouple probe. Since complications due to flow were eliminated, the mathematical analysis of the results was fairly simple. The main conclusions were that first-order surface decay was the dominant mode of decay at the pressures (< 0.15 mm.) and temperatures ($< 450^{\circ}$C.) used, and that the collision efficiencies (γ) were in the range 10^{-3} to 10^{-5} for H_3PO_4 or clean glass surfaces. The calculated collision efficiencies were, however, high by a factor of two owing to the use of k_1 where $k_1/2$ was required (see page 8). Values of E and C_s for H atoms are available from other studies: $E = 0.9$ kcal.mole^{-1} (54), $C_s = 1.35 \times 10^{15}$cm.$^{-2}$ (55, 56, 24), where E applies only to dry surfaces (24). The corresponding values for O atoms can be calculated from the data of Linnett and Marsden as given in Table I of reference (25) (Fig. 8 of this reference appears to have an error in the ordinate): $\gamma = 1.2 \times 10^{-4}/2$ at 17°C. and $3.56 \times 10^{-4}/2$ at 400°C. Hence $E = 2.0$ kcal.mole^{-1} and $C_s = 2.7 \times 10^{14}$cm.$^{-2}$.

It should be pointed out that the method used by Linnett and Marsden to study the surface decay of O atoms

TABLE I

Homogeneous decay rate constants for H atoms.

Source	Third body	Rate constant cc.^{2}molecule^{-2}sec.$^{-1}$ (x10^{32})
Amdur *et al.* (46)	H_2 + H	3.9
Amdur (47)	H	5.8
Amdur (48)	H	6.1
	H_2	3.0
Farkas *et al.* (49)	H_2	9.4
Smallwood (27)	H	3.8
	H_2	7.8
Smallwood (50)	H	4.7
Steiner *et al.* (51)	H_2	2.5
Steiner (52)	H_2	3.6
		mean = 5.1

was incapable of distinguishing between true first-order surface decay and a process of the type (12, 57)

$$\left.\begin{array}{lll} O + O_2 + M \longrightarrow O_3 + M & & \text{(slow)} \\ O + O_3 \longrightarrow 2O_2 & & \text{(rapid)} \end{array}\right\} [28]$$

PRESENT PROBLEM

Whereas the mechanism of recombination is well understood for H atoms, and understood in its most essential features for O atoms, studies on the decay of active nitrogen, and therefore on the recombination of the N atoms which are its major constituent, have generally been qualitative. In fact the only N atom decay constant that has apparently been published is that for luminous homogeneous decay (2), though the data of Rayleigh (16) and Back (58) enable surface decay constants for H_3PO_4 surfaces to be derived (page 52). The order itself of N atom surface decay has only been determined directly in one instance (16).

The present work was therefore undertaken to confirm the order of the surface decay of N atoms, and to obtain decay constants for both the surface and homogeneous decay. At the same time several reactions characterized by low reactivity were investigated in an attempt to determine whether the low reactivity was more consistent with N atom reaction accompanied by catalytic recombination or with reaction with excited molecules.

EXPERIMENTAL

MEASUREMENT OF THE ACTIVITY

The measurement of N atom concentrations, such as is necessary in a study of the decay of active nitrogen, is complicated by the fact that, though active nitrogen contains the ^4S atom as a major constituent, there is still a possibility that excited molecules are present, if only in low vibrational levels of the ground state (i.e. <u>not</u> the X* state). Virtually any excited form would, of course, be deactivated on a metal surface (9), so that measurements of the activity using a thermocouple probe (53, 25, 26) would be of uncertain significance. On the other hand, the production of HCN from ethylene under conditions of cleanup (high ethylene flowrates and elevated temperatures), a mode of measurement frequently used in past work (e.g. 42, 41), would likely reflect the <u>atom</u> concentration alone owing to the high activation energy to be expected in most reactions involving excited nitrogen molecules (see page 15). HCN production also has the advantages that it is not subject to mechanical failure and, since very little cyanogen and generally no other nitrogen containing compound at all is formed (59, 37), it provides an absolute value of the atom concentration. Production of HCN from ethylene was therefore chosen to measure the N atom concentration and the results were checked using ethane*.

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* Actually excited molecules <u>were</u> shown to be present but formed only by homogeneous atom decay (page 65). Accordingly any HCN production due to them was uncontroversially eliminated by utilizing what was, in effect, extrapolation to zero atom concentration (see page 32).

To determine whether certain active nitrogen reactions occurred to a limited extent because of loss of activity due to catalytic recombination or because the reactions occurred only with excited molecules present in limited concentration, several reactions of this type were also used to measure the activity. The reactions chosen were HCN production from ethylene and ethane, and the destruction of ammonia, all in the neighborhood of room temperature (cf. page 16).

APPARATUS (SERIES 1 to 11)

The use of chemical estimations of the activity in active nitrogen meant, of course, that a fast-flow system rather than the much simpler diffusion system of Smith (53) or static system of Rayleigh (16) had to be used. Two general types of flow system were considered. In the one, used in much of the early H atom work (e.g. 27) and more recently in an N atom study by Back (58), an atom-containing gas stream is analyzed at successive points as it flows through a tube. Atom concentrations as a function of time are thus obtained. In the other, which resembles that used in the greater part of the work of Winkler and co-workers (see in particular 37, 3, 60), the atom-containing gas stream is passed through a tube of fixed dimensions and then analyzed in a reaction vessel. In this case time is less readily varied so that the variation must lie in some other parameter. It was the latter method, using pressure variation, which was chosen for the present work since it is perhaps better able to distinguish between first and second-order processes (cf. page 16).

The apparatus, in the form used in the experiments of series 1 to 11, is shown in Fig. 1. Dry, oxygen-free nitrogen* at atmospheric pressure was introduced at A through a needle reduction valve B and a capillary flowmeter C. The length of the capillary was so chosen that unrestricted passage of the gas through the needle valve gave the highest desired pressure (5 mm.) in the region following the capillary. In the discharge tube D the nitrogen was subjected to a rapid condensed discharge and thereby partially or completely dissociated into atoms depending on the energy expenditure. Internal electrodes were used which were about 60 cm. apart. (The electrodes were machined from solid aluminum to the following dimensions: length = 7.0 cm., outside diameter = 1.8 cm. (less at the end of attachment), depth to which the interior was drilled = 4.0 cm., inside diameter = 7/16 inch. Two set screws were used to affix them to lengths of 0.060 inch diameter tungsten wire which were in turn sealed to the pyrex of the discharge tube by means of nonex. Electrodes of this type had a virtually indefinite life in active nitrogen and were interchangeable.)

The atom-containing mixture was then passed through a tube E which will be called the "decay tube". In most of the work it had a volume of 281 cc., a length of 31.7 cm., and an inside diameter of 3.36 cm. However in series 2 a much smaller decay tube was used (14.0 by 1.55 cm.; volume = 26 cc.) and in series 1 and 11 a long, narrow one (55 by 1.55 cm.; volume = 104 cc.). The 281 cc. decay tube was used in all experiments which were to be treated theoretically. Its large volume served to increase the time of decay and therefore (i) to lower the N atom concentration sufficiently,

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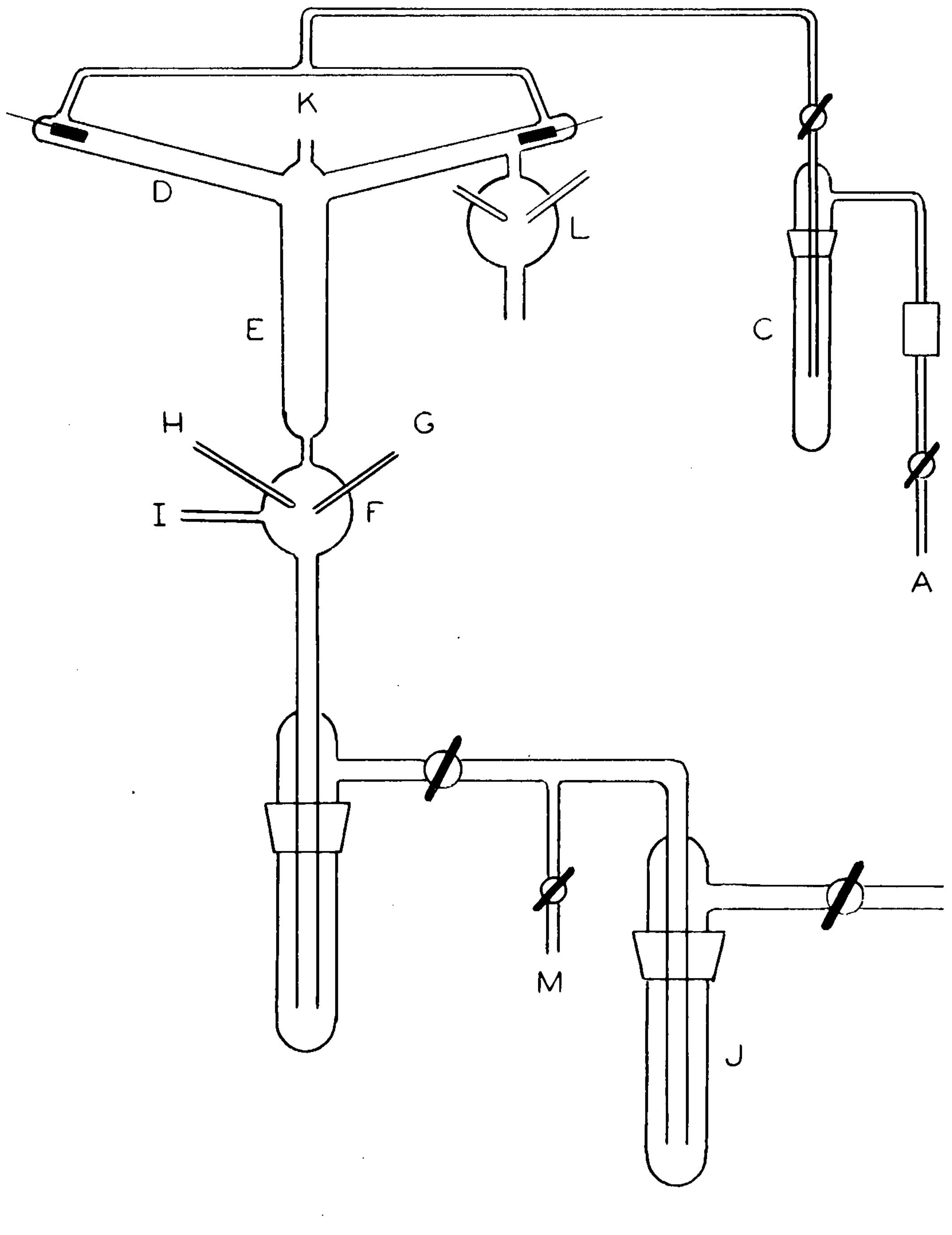
* The method of purification is that described in references (37) and (60) rather than (3), i.e. passing the nitrogen over heated copper and through a liquid air trap.

Figure 1

Diagram of apparatus.


K
D
L
E
C
B
H
G
I
F
A
M
J

even under conditions of complete initial dissociation, for cleanup to be readily achieved and (ii) to make the effect of dissociation on the decay time less marked (Appendix C). Its large diameter served (i) to reduce the pressure gradient in the decay tube (Appendix A) and (ii) to reduce the surface decay rate constant. A cylindrical, electrically heated furnace was built around the decay tube to determine the temperature effects on decay. Its temperature was measured by two thermocouples placed between the furnace and the glass at respectively 8 and 22 cm. from the top. At the lower end of the 281 ml. decay tube only was a constriction 2.0 cm. long and with 0.60 cm. inside diameter which served (i) to terminate the region of decay sharply and independently of pressure, (ii) to enable independently heated furnaces to be built around the decay tube and reaction vessel, (iii) to enable separate poisoning of the decay tube and reaction vessel, (iv) to reduce further the pressure gradient in the decay tube, and (v) to prevent back diffusion of the reactant from the reaction vessel. (Only at much higher reactant flowrates than were needed to consume all the active nitrogen did any back diffusion occur, as indicated by the appearance of the reaction flame (including that of CCl_4) in the decay tube).

The decay tube was followed by a 300 cc. spherical reaction vessel F of radius 4.0 cm. into which the reactant was injected through jet G. It was surrounded by a second furnace, the temperature of which was measured by a thermocouple in the well H. A McLeod gauge was attached at I.

The arrangement for metering in the reactants has been described elsewhere (37). Two separate systems were employed, one for ethylene and ethane, and one for ammonia. The latter had a ballast volume of only 100 cc. and storage volume of only 300 cc., so that pressure changes during an experiment were greatly exaggerated. This facilitated the measurement of the amount of ammonia destroyed. The ethylene, ethane, and ammonia were from the same cylinders as were used in previous work (37, 43) and were all purified by three bulb-to-bulb distillations. (To remove possible traces of water a piece of glass tubing shaped like an inverted funnel was dropped into one of the bulbs and the space above it filled with KOH pellets.)

After reaction, the gas mixture was finally led through a trap surrounded by liquid air in order that the HCN or ammonia could be condensed from the gas stream for analysis. The pumps (one Welch duoseal and one Cenco megavac), which followed the trap, were readily able to give an ultimate vacuum of 5 microns.

The Wrede gauge K was present only during the experiments of series 4 and 12, and the special reaction vessel L only during the experiments of series 12.

In the majority of the experiments the discharge tube, decay tube, and reaction vessel were poisoned by drawing up a 20 % aqueous solution of Na_2HPO_4. This poison was used, rather than the more efficient H_3PO_4, since it did not react with ammonia and was unusually stable and reproducible. (The poison was changed many times during the course of the experiments when the apparatus was modified or suffered breakage.) In a few experiments of series 6 and 10 the poison on the reaction vessel alone was changed to KCl *;

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* This was accomplished by washing the Na_2HPO_4 off the reaction vessel and then drawing up a 10 % aqueous solution of KCl.

however, KCl could not be used in the discharge tube or on any heated surface since the active nitrogen then reacted with it, creating an intense reddish-orange glow. Series 11 involved the use of a number of different poisons applied to the entire reaction system.

To protect the poison the system was left evacuated when not in use and was isolated from trap J during analyses. Similarly, to restore the poison to a reproducible state, each experiment was preceded by a three minute period during which the discharge was operated while nitrogen, but not reactant, was passed through the system.

Power was supplied from a 220 volt A.C. source* transformed first with a 2400 watt, 220 volt variac and then with an 1897 watt, 110—>4820 volt transformer, and finally rectified with two Raytheon 866A tubes in parallel. The weakest element in the circuit was the variac which burned out several times. For most of the work the secondary circuit had a resistance of 1250 ohms and a capacitance of either 4 μfd (for pressures < 1.7 mm.) or 2 μfd (for pressures > 1.7 mm.). If the variac were adjusted to give a flash rate of 60 per second (except in the pressure range 1.2 to 1.7 mm. when 30 to 40 per second was adequate), complete dissociation of the nitrogen could be brought about. (This is treated in detail in a later section). Under these conditions the current through the primary of the variac at 220 volts was in the range 10 to 15 amperes.

APPARATUS (SERIES 12)

A major variation in the reaction system was used in the experiments of series 12. One of the nitrogen leads to

* In series 1, 2, 3, and 11 a 110 volt A.C. source was used.

the discharge tube was sealed off and a glass plug dropped into the constriction at the bottom of the decay tube. (The outlet for the Wrede gauge K served to admit the plug.) A new 300 cc. reaction vessel L (with reactant jet and thermocouple well) was then attached through the usual constriction directly to the discharge tube near an electrode. The remainder of the apparatus was unchanged.

The object was to obtain N atoms which had minimum opportunity to undergo homogeneous decay either before reaching the reaction vessel or within it. Thus, by operating under conditions of complete dissociation, homogeneous decay was minimized in the discharge tube, expecially when the nitrogen was prevented from flowing through the body of the discharge tube by having the nitrogen lead remote from the reaction vessel sealed off. A low atom concentration, obtained by passing the atoms over the metal surface of an electrode rather than through a decay tube, then ensured that homogeneous decay would also be minimized in the reaction vessel. Accordingly, any excited molecules formed directly in the discharge process and any arising from surface atom decay should still have been present, but those arising from homogeneous atom decay should have been virtually eliminated.

ANALYTICAL PROCEDURE AND PRESSURE MEASUREMENTS

The only analyses required in the present work were for the HCN produced from ethylene and ethane, and for destruction of ammonia. HCN production was determined by titrating the recovered HCN with $AgNO_3$ (61) after it had been distilled at -23°C. from trap J (previously coated with solid CCl_4) into a removable unit M containing about 15 cc. of frozen water (cf. 62). The amount of ammonia destroyed, on the other hand, was obtained as the difference between the measured amount drawn from the storage vessel and the amount recovered, the latter being determined simply by a distillation into a 150 cc. calibrated volume. This was possible since unreacted ammonia was the only condensible product of the ammonia reaction.

A sufficient amount of product to enable convenient analysis was generally obtained with reaction times of 100 seconds, though the time was often increased to 200 seconds when ammonia was the reactant.

Besides product analyses, each experiment was also characterized by a pressure as measured in the reaction vessel. Two readings were made, one during the three minute preliminary discharge, and one after the reaction had been in progress for 30 seconds. The two generally agreed well, except that,at higher pressures pressure increases of 0.1 to 0.2 mm. accompanied the reaction. Only those readings made during the reaction will be subsequently recorded.

NITROGEN FLOWRATE

Measurements of the nitrogen flowrate were needed both to derive a general correlation between flowrate and partial pressure, and to calculate the time spent by the nitrogen in the decay tube. A calibrated one liter bulb was therefore attached at A (Fig. 1) and the nitrogen flowrate measured as a function of the pressure preceding the capillary C, i.e. of the flow head.* Further measurements relating the flow head to the pressure in the reaction vessel then provided the

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* The manometers, one preceding and one following the needle valve B, are not shown in Fig. 1.

desired relationship (Table II and Fig. 2). All measurements were made at room temperatures between 25 and 30°C., and are seen to be independent of the capillary and decay tube.

It is evident from Fig. 2 that the molar flowrates varied linearly with pressure above about 0.30 mm., such that a general correlation between flowrate and partial pressure can be written in the form

$$[N_2]_{\mu m/s.} = 59.0(P - 0.15) \qquad [29]$$

where P is the total pressure in mm. and µm/s. is the abbreviation for micromoles per second.

The time spent by the nitrogen in the decay tube follows from equation [29]. The volume flowrate, i.e. $[N_2]_{\mu m/s.} \times 10^{-6} \times RT/P$, has an average value at 25°C. and in the region 1 to 3 mm. of 1006 cc.sec.$^{-1}$. (The volume flowrate is not quite independent of pressure). Therefore the time spent in the 281 cc. decay tube, i.e. the time of decay in the absence of dissociation, is

$$t_o = \frac{281}{1006} \times \frac{298}{T} = 0.279 \times \frac{298}{T} \text{ sec.} \qquad [30]$$

where T is the average temperature of the decay tube.

TABLE II

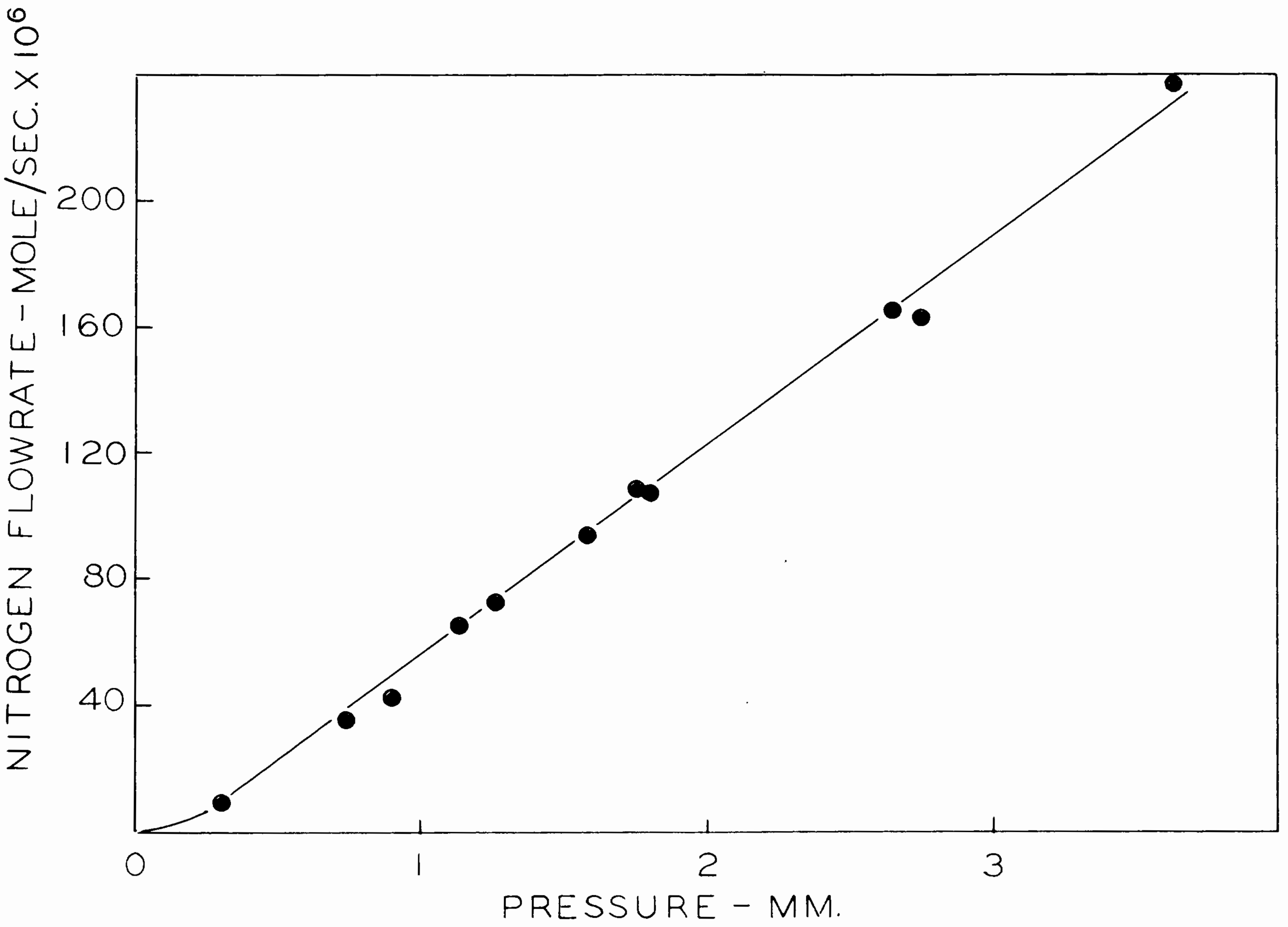
Nitrogen flowrate at various pressures

Pressure in the reaction vessel mm.	Capillary and decay tube*	Nitrogen flowrate µm/s.
0.30	2	10.0
0.74	3	35.6
0.90	1	42.4
1.25	1	65.8
1.38	2	72.5
1.70	1	93.9
1.99	3	109.4
2.01	2	108.3
2.88	2	165
2.98	3	163
3.97	2	242

* 1 = short capillary, 26 cc. decay tube. 2 = long capillary, 26 cc. decay tube. 3 = long capillary, 281 cc. decay tube.

Figure 2

Nitrogen flowrate as a function of pressure.


NITROGEN FLOWRATE - MOLE/SEC. X 10^6
200
160
120
80
40
0
1
2
3
PRESSURE - MM.

THEORY

DECAY EQUATIONS FOR ATOMS

To derive decay equations for atoms, i.e. equations which will relate the atom concentration measured in the reaction vessel to the decay constants, it is necessary to know the rate controlling step in each mode of decay. The modes of decay available for N atoms have been treated in detail in an earlier section and their rate controlling steps may be summarized as follows:

(i) homogeneous decay (cf. equations [1] to [4]),

$$N + N + M \xrightarrow{k_2} N_2^* + M \qquad [31]$$

where M is a third body and N_2^* an unspecified excited molecule. It will be recalled (page 5) that the rate constant k_2 gives the total rate of the luminous and nonluminous varieties of homogeneous decay such as would be obtained when the decay of active nitrogen was followed by measurements of atom concentration.

(ii) first-order surface decay (cf. equation [5]),

$$N + N\text{-surface} \xrightarrow{k_1} N_2 + \text{surface} \qquad [32]$$

(iii) second-order surface decay. Here the rate controlling step is given directly by equation [7], i.e.

$$N + N + \text{surface} \xrightarrow{k_3} N_2 + \text{surface} \qquad [7]$$

Before proceeding further it will be necessary to introduce certain simplifications. Thus the two modes of surface decay will be assumed to have such different efficiencies that only the one or the other will be significant under given conditions. In terms of the various surface decay mechanisms that have been considered this situation should prevail at temperatures or atom concentrations where the number of atoms attached per unit area of surface either approached its maximum value or approached zero, i.e. where intermediate orders did not occur. For homogeneous decay only extreme cases of third body efficiency will be treated. In the one, which in the present work turns out to correspond to a lower limit of k_2, N_2 and N will be considered to be equivalent as third bodies for N atom recombination, so that [M] becomes simply the total observed pressure P. In the other, which corresponds to an upper limit of k_2, the efficiency of N as a third body will be considered to be much less than that of N_2, so that [M] becomes (P - [N]).*

Depending on the order of surface decay and the relative efficiencies of N_2 and N as third bodies, four differential equations of decay are therefore possible:

$$d[N]/dt \begin{cases} = -k_1[N] - k_2[N]^2P & [33] \\ = -k_1[N] - k_2[N]^2(P - [N]) & [34] \\ = -k_3[N]^2 - k_2[N]^2P & [35] \\ = -k_3[N]^2 - k_2[N]^2(P - [N]) & [36] \end{cases}$$

The significance of each is obvious. If $[N]_o$ is the value of [N] at t = 0, the integrated solutions of equations [33] and [35] are, respectively,

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* In the event that evidence were obtained that the efficiency of N were greater than that of N_2, the case where [M] = [N] would have to be considered instead. This case, cannot, of course, be eliminated _a priori_ since according to the luminous homogeneous decay mechanism of Berkowitz _et al._ (equation [2]) the main function of the third body is to induce an electronic transition. The matter could perhaps be settled by comparing the afterglow intensity in the light originating in the discharge tube under conditions of complete dissociation with the more readily visible afterglow in the decay tube.

$$P/[N] = P/[N]_o e^{k_1 t} + (e^{k_1 t} - 1)k_2 P^2/k_1 \qquad [37]$$

and

$$1/[N] - 1/[N]_o = (k_3 + k_2 P)t \qquad [38]$$

Though an exact solution to equation [34] can also be obtained*, it is not readily used for interpreting experimental data unless $[N]_o = P$ and $[N] \ll P$. Then

$$\ln P/[N] - k_1 t \approx k_2 P/\sqrt{q}\ \ln \frac{1 + k_2 P/\sqrt{q}}{1 - k_2 P/\sqrt{q}} \qquad [39]$$

where $q = k_2{}^2 P^2 + 4k_1 k_2$. If, in addition, $k_2 P \ll 2\sqrt{k_1 k_2}$ an even simpler form arises,

$$1\Big/(\ln P/[N] - k_1 t) \approx \frac{1}{2} + 2k_1\Big/k_2 P^2 \qquad [40]$$

Equation [40] is obviously valid only at low pressures and also requires a prior knowledge of $k_1 t$ obtained from equation [37]. Since surface decay will be shown to be first-order (page 49), equation [36] will not be further considered except to note that at not too low pressures its integrated solution reduces to equation [38]. It will be noted that equations [37], [38], and [40] have been written in forms suited for use in studies where the pressure is varied.

* The exact solution is

$$\frac{1}{2}\ln\frac{[N]^2}{[N[_o^2} \times \frac{k_1 + k_2 P[N]_o - k_2[N]_o^2}{k_1 + k_2 P[N] - k_2[N]^2}$$

$$- \frac{k_2 P}{2\sqrt{q}}\ \ln \frac{-2k_2[N] + k_2 P - \sqrt{q}}{-2k_2[N] + k_2 P + \sqrt{q}} \times \frac{-2k_2[N]_o + k_2 P + \sqrt{q}}{-2k_2[N]_o + k_2 P - \sqrt{q}} = -k_1 t$$

where q is as in equation [39].

In interpreting experimental data in terms of equations [37], [38], or [40], the data obtained at low pressures must be weighted more heavily than those at high pressures. For example, in plots of $P/[N]$ versus P^2, the limiting slopes as $P \longrightarrow 0$ would be derived rather than slopes of best fit. (This is equivalent to an extrapolation to zero atom concentration.) The reasons are the following: (i) equations [33] to [40] actually presume a number of conditions respecting diffusion, the pressure gradient in the decay tube, etc., such that the equations are more valid at low pressures (see Appendix A). (ii) Equation [40] is <u>inherently</u> valid only at low pressures. (iii) If excited molecules are present, there is a possibility that their reactivity will be superimposed on that of the atoms; however if they are formed only by homogeneous atom decay, their concentration necessarily falls off rapidly as the pressure is decreased.

Though equations [37], [38], and [40] can in general be applied to studies in which any one of $[N]_o$, time, or pressure is varied, pressure variation alone is used in the present work. However, in this case, it is necessary that the initial dissociation be complete, i.e. $[N]_o = P$, since otherwise $[N]_o$ becomes an unknown function of P. While this necessitates great energy expenditures, it has the advantage that a precise control of the flashrate is not necessary. Moreover, it allows the different orders of surface decay to be unambiguously distinguished simply by comparing the low pressure asymptote of a graph of $[N]_{\mu m/s.}$ versus P with the line corresponding to the maximum possible N atom flowrate, i.e. $2[N_2]_{\mu m/s.}$ versus P. The asymptote would coincide with this line if the surface decay were second-order, but would have a much reduced slope ($Pe^{-k_1 t}$) if it were first-order. These relations hold irrespectively of the relative efficiencies of N_2 and N as third bodies.

DECAY EQUATIONS FOR EXCITED MOLECULES

(a) Equation Applicable in Conjunction with the Apparatus of Series 1 to 11

A decay equation for excited molecules applicable in conjunction with the apparatus of series 1 to 11 can be derived in a manner similar to that used for the atom decay equations. The modes of decay available for excited nitrogen molecules have been treated in detail in an earlier section where it was shown that the rate controlling steps to be expected were as follows:

(i) radiative decay (only for the A state; cf. equation [13]),

$$N_2^* \xrightarrow{k_4} N_2 + hv \qquad [41]$$

where N_2^* is an unspecified excited molecule.

(ii) surface decay (cf. equations [14] and [17]),

$$N_2^* + \text{surface} \xrightarrow{k_5} N_2 + \text{surface} \qquad [42]$$

(iii) homogeneous decay (cf. equations [15] and [16]),

$$N_2^* + mM \xrightarrow{k_6} N_2 + mM \qquad [43]$$

where M is a collision partner and m a number (>1) to take into account the possible necessity of multiple collisions to de-excite a vibrationally excited molecule. The value of m need not be integral.

However, whereas N atoms are formed only in the discharge process, excited molecules may be either primary discharge products or arise from homogeneous or surface atom decay. In the latter two cases an additional term will occur in the differential equation of decay corresponding to the rate controlling step involved in the formation of the excited molecules. For formation from homogeneous atom decay this step is

$$N + N + M \xrightarrow{k_2/2} N_2^* + M \qquad [44]$$

so that the differential equation of decay is

$$d[N_2^*]/dt = \tfrac{1}{2}k_2[M][N]^2 - (k_4 + k_5 + k_6[M]^m)[N_2^*] \qquad [45]$$

Some difficulty is encountered at this point since equation [45] is not capable of solution unless the atom concentration can be approximated by a simple exponential law of the form

$$[N] = [N]_o e^{-bt}$$

where b is an unspecified function of P. The approximation would be strictly valid only if N atoms decayed by first-order modes alone, though is obviously good at low pressures when first-order modes will dominate. Substituting $[N] = [N]_o e^{-bt}$ and making the simplification that N_2, N_2^*, and N are equivalent collision partners, so that [M] becomes simply the total observed pressure P, equation [45] becomes

$$d[N_2^*]/dt = \tfrac{1}{2}k_2 P[N]_o^2 e^{-2bt} - K[N_2^*] \qquad [46]$$

where $K \equiv k_4 + k_5 + k_6P^m$. If $[N_2^*] = 0$ at $t = 0$, the integrated solution of equation [46] follows readily as

$$[N_2^*] \equiv \frac{\frac{1}{2}k_2P[N]_o^2}{K - 2b}(e^{-2bt} - e^{-kt}) \qquad [47]$$

Equation [47] is most conveniently employed when $[N]_o = P$ and b is expressed in terms of P/[N]:

$$\frac{[N_2^*]}{\frac{1}{2}k_2tP^3} = \frac{[N]^2/P^2 - e^{-kt}}{Kt - 2\ln P/[N]} \qquad [48]$$

Given [N] and $[N_2^*]$, Kt and thence K may then be found by trial and error methods, and the individual decay constants $(k_4 + k_5)$ and k_6 finally derived by plotting K against such a power of pressure as gives a linear relation. In such a plot the limiting slope as P —> 0 would be used (i) for the reasons given in connection with equations [33] to [40], (ii) since equations [46] to [48] are inherently valid only at low pressures, and (iii) to correct for the fact that when a reactant does not interfere with N atom decay, e.g. it allows the afterglow to persist unchanged, excited molecules would be produced by the homogeneous atom decay which continues in the reaction vessel.

Decay equations in which the excited molecules are formed other than by homogeneous atom decay were not required in the present work.

(b) Equations Applicable in Conjunction with the Apparatus of Series 12

A decision between the various modes of formation possible for excited molecules is most readily made using an experimental arrangement in which minimum opportunity is provided for the atoms to undergo homogeneous decay either before reaching the reaction vessel or within it. In the present work this was accomplished by sealing a reaction vessel directly to the discharge tube near an electrode and then operating under conditions of complete dissociation. The metal surface of the electrode, of course, served to destroy most of the atoms and thereby minimize homogeneous decay in the reaction vessel. Three cases will be considered:

(i) N_2* formed by homogeneous atom decay. Provided no homogeneous atom decay occurs in the discharge tube, $[N_2^*]$ is given simply by

$$\begin{aligned}[N_2^*] &= \tfrac{1}{2}[N] \times (\text{Fraction of } [N] \text{ decaying homogeneously}) \\ &= \tfrac{1}{2}[N] \times \frac{1}{[N]} \int_0^{[N]} \frac{k_2P[N]d[N]}{k_1 + k_2P[N]} \\ &\approx \tfrac{1}{2} \int_0^{[N]} (k_2/k_1)P[N]d[N] \\ &= k_2P[N]^2/4k_1 \qquad [49]\end{aligned}$$

where [N] is the atom concentration entering the reaction vessel.* It has been assumed (i) that the reactant does not interfere with atom decay, e.g. it allows the afterglow to persist unchanged, (ii) that the decay of N_2* within the reaction vessel can be neglected since it competes with reaction, and (iii) that a spherical reaction vessel followed by a narrow tube can be approximated by a cylinder of the same radius as the reaction vessel. Though this approximation makes k_1 somewhat *small*, and $[N_2^*]$ as given by equation [49] therefore somewhat *large*, it eliminates complications due to k_1 varying with distance.**

(ii) *N_2* formed by surface atom decay*. While an unpredictable amount of destruction of N_2* would accompany its formation by surface decay on an electrode, a lower limit for $[N_2^*]$ is clearly that formed by surface decay *in the reaction vessel*, i.e.

$$[N_2^*] \gg [N]/3 \qquad [50]$$

Here it has been assumed (i) that the reactant does not interfere with atom decay and the decay of N_2* can be

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* Equation [49] can also be derived from equation [47] by letting K and [N] approach zero, and replacing $[N]_0$ by [N].

** Streamlined flow is assumed. Were the flow turbulent, k_1 would, of course, be a constant.

neglected (as before), (ii) that homogeneous atom decay in the reaction vessel can be neglected (cf. calculation on page 52), and (iii) that for every two N atoms forming an N_2*, which then reacts, a third is consumed by reaction with fragments of the reactant. This is true at least in the reaction of active nitrogen with ammonia where the step $NH_2 + N \longrightarrow N_2 + 2H$ (cf. equations [24]) is believed to occur.

The significance of destroying most of the atoms on an electrode can now be seen: when $[N] \ll P$, the amount of N_2* predicted by equation [49] is much less than that predicted by equation [50].

(iii) $\underline{N_2*}$ formed in the discharge process. If N_2* were a primary discharge product it would necessarily occur in large amounts when the reaction vessel was attached directly to the discharge tube. Therefore, in the event that low concentrations of N_2* were observed in accordance with equation [49], it would mean that primary formation could be eliminated as well as formation from surface atom decay.

CATALYTIC RECOMBINATION

Since catalytic recombination is a possible cause of low reactivity, it was necessary to derive equations which could be used to determine if particular cases of low reactivity encountered in the present work were in fact due to catalytic recombination and, if so, to calculate the rate constant of the catalytic recombination. It has been shown with regard to the reactions of N atoms that four combined schemes of reaction plus catalytic recombination are possible, so that there will be four cases to treat:

Scheme 1: direct reaction plus homogeneous catalytic recombination,

$$N + M \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} NM$$

$$NM \xrightarrow{k_7} nHCN + p(\text{reactive fragments}) \qquad [51]$$

$$N + NM \xrightarrow{k_8} N_2 + M$$

Though a detailed treatment of scheme 1 was made by Forst et al. (42) a much simplified version as given in Appendix E will be sufficient for the present purposes. It is shown that the effective N atom concentration $[N]_e$, i.e. the concentration leading to HCN formation from reactant M, is

$$[N]_e = (n + p)k_7/k_8 \ln(1 + k_8[N]/(1 + p)k_7) \qquad [52]$$

The distinction between n and p is best made by considering a specific case. Suppose ethyl cyanide reacted with N atoms as follows:

$$N + C_2H_5CN \rightleftharpoons N\cdot C_2H_5CN$$

$$N\cdot C_2H_5CN \longrightarrow 2HCN + CH_3 \quad (\text{slow})$$

$$N + CH_3 \longrightarrow HCN + 2H \quad (\text{rapid})$$

Then n = 2, p = 1. Therefore n will differ from one only when M is a cyanide, while (1 + p) will be equal to the number of reactive carbon atoms in M.* (The quantity p was not used in the original treatment (42).)

In practice, catalytic recombination by scheme 1 would be identified simply by noting if the observed limits of the ratio $[N]_e/[N]$ were

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* The definitions of $[N]_e$, n, and p would be suitably modified for types of direct reaction in which products other than HCN were formed.

$$\lim_{[N]\to 0} [N]_e/[N] = 1$$

and

$$\lim_{[N]\to \infty} [N]_e/[N] = 0$$

The ratio k_8/k_7 could then be obtained by trial and error solution of equation [52], and the rate constant for homogeneous catalytic recombination, i.e. $k_{2(M)} = k_8k_a/k_{-a}$, found by multiplying k_8/k_7 by the rate constant for HCN production, i.e. k_7k_a/k_{-a}. $k_{2(M)}$ gives the rate of atom destruction directly without a factor of two.

<u>Scheme 2</u>: direct reaction plus surface catalytic recombination,

$$\begin{aligned} N + M &\rightleftharpoons NM \\ NM &\xrightarrow{k_7} nHCN + p(\text{reactive fragments}) \qquad [53] \\ NM + N\text{-surface} &\xrightarrow{k_9} N_2 + M + \text{surface} \end{aligned}$$

Here n, p, and $[N]_e$ would have the same significance as in scheme 1. It will be noted that since the recombination step requires the migration of a <u>short-lived species</u> (the complex) to a surface, k_9 may have a marked pressure dependence besides the normal dependence on the nature of the surface. This is to be contrasted with the surface decay of a long-lived species such as N atoms (see Appendix D). Scheme 2 will not be further considered except to note that since the reaction and recombination steps have similar orders in respect of the complex, the ratio $[N]_e/[N]$ will be independent of [N], at least for similar poisons and surfaces (cf. Appendix E).

Scheme 3: energy transfer plus homogeneous catalytic recombination,

$$\begin{aligned} N + M &\rightleftharpoons NM \\ N + NM &\xrightarrow{k_{10}} N_2 + M^* \\ M^* &\longrightarrow p(\text{reactive fragments}) \\ N + NM &\xrightarrow{k_8} N_2 + M \end{aligned} \qquad [54]$$

Here the effective N atom concentration $[N]_e$ would be defined as that leading to destruction of M, so would have a maximum value of $[N]/(2 + p)$ in the absence of catalytic recombination, while the value of p would be so chosen that it corresponded to the additional N atoms lost by reaction with fragments of M. Scheme 3 will not be further considered except to note that for reasons similar to those given in connection with scheme 2, the ratio $[N]_e/[N]$ will be independent of [N] though in this case for all pressures and poisons (cf. Appendix E).

Scheme 4: energy transfer plus surface catalytic recombination,

$$\begin{aligned} N + M &\rightleftharpoons NM \\ N + NM &\xrightarrow{k_{10}} N_2 + M^* \\ M^* &\longrightarrow p(\text{reactive fragments}) \\ NM + N\text{-surface} &\xrightarrow{k_9} N_2 + M + \text{surface} \end{aligned} \qquad [55]$$

Here p and $[N]_e$ would have the same significance as in scheme 3, while k_9 may be pressure dependent as in scheme 2. Scheme 4 will not be further considered except to note that it would be characterized by the following limits for the ratio $[N]_e/[N]$ (cf. Appendix E):

$$\lim_{[N]\to 0} [N]_e/[N] = 0$$

and

$$\lim_{[N]\to \infty} [N]_e/[N] = 1/(2 + p)$$

To determine the relative effect of temperature on the rates of catalytic recombination and reaction, it is necessary to express the rate constants k_7 to k_{10} as functions of temperature, using absolute rate theory involving the appropriate partition functions:

Constant	Activation energy kcal.mole^{-1}	Temperature dependence	Source
k_7	2 to 7 *	$Te^{-E_7/RT}$	(63)
k_8 or k_{10}	~ 0	$T^{-1/2}$	(63)
k_9	~ 1 **	$T^{-3/2}e^{-E_9/RT}$	(24)

The temperature effects then follow as:

k_8/k_7 and k_9/k_7 ---> 0 as temperature increases
k_8/k_{10} independent of temperature
k_9/k_{10} approximately independent of temperature.

Thus while catalytic recombination by schemes 1 and 2 would be eliminated at elevated temperatures (cf. 42, Table I), that by schemes 3 and 4 would persist. It should be pointed out that schemes 3 and 4 might appear to have a temperature effect by virtue of the additional process NM --> (products) setting in at elevated temperatures.

* Reference (45).
** From Table XI of the present work.

RESULTS

A: DECAY OF N ATOMS

In order that the choice of the experiments described in the sections to follow will be better understood, a brief statement of the method may be made: the N atom concentration reaching the reaction vessel after a period of decay in the decay tube was measured as a function of pressure by HCN production from ethylene and ethane under conditions of cleanup, and using sufficient energy expenditures to bring about complete initial dissociation.

CONDITIONS OF CLEANUP

A cleanup of N atoms was stated in an earlier section to be achieved only at high reactant flowrates and above a certain temperature.* For the reactants used in the present work the minimum temperatures were readily obtained from published data (37, 43): about 300°C. for ethylene and ethane, and room temperature for ammonia. Cleanup temperatures were used in all experiments except those of the first three series and several of series 7.

Since minimum flowrates, on the other hand, depend on the atom concentration, on the reaction temperature, and on factors peculiar to each apparatus, the results of past

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* It should be emphasized, however, that the observation of a flowrate plateau at a single temperature is not sufficient reason to assume cleanup, since such a plateau can occur in the presence of any amount of catalytic recombination.

work could not be used. It was therefore necessary to determine, at a series of atom concentrations, the minimum flowrate applicable with each reactant and reaction temperature. The data obtained in connection with these preliminary experiments will not be given, though it will be understood that in all experiments to be described plateau flowrates of reactant were used.

EXTENT OF INITIAL DISSOCIATION

The first four series of experiments were designed to determine if complete initial dissociation, i.e. $[N]_o = P$, could be brought about without excessive energy expenditures. In series 1 the amount of HCN formed from ethylene at 0.80 mm. pressure and a capacitance of 4 µfd. was determined as a function of primary voltage and thence flashrate. The 104 cc. decay tube was used and both the decay tube and reaction vessel were unheated. Discharge was observed to start at 35 volts, while the HCN production remained constant from 45 to 70 volts (Table III, Fig. 3).

In series 2 the 26 cc. decay tube was used in order that the time of decay would be shortened and the data therefore indicate more directly the variation of $[N]_o$. However a cleanup of N atoms was difficult to achieve, so that the destruction of ammonia (ΔNH_3), which will be shown in a later section to be due to excited molecules formed in small amounts from the atoms, was measured instead. The decay tube and reaction vessel were both unheated. The results, obtained as a function of pressure, primary voltage, and capacitance are given in Table IV and Fig. 4. It is seen that, as the pressure was increased, the ammonia destruction at each primary voltage and capacitance at first followed a

TABLE III

Series 1. HCN production from ethylene as a function of primary voltage.

Exp.	Primary voltage	HCN μm/s.
33	35	0
34	38	1.77
30	45	6.10
35	53	5.96
31	60	6.27
32	70	6.30

Decay tube: 104 cc.

Pressure: 0.80 mm.

Figure 3

Series 1. HCN production from ethylene as a function of primary voltage.

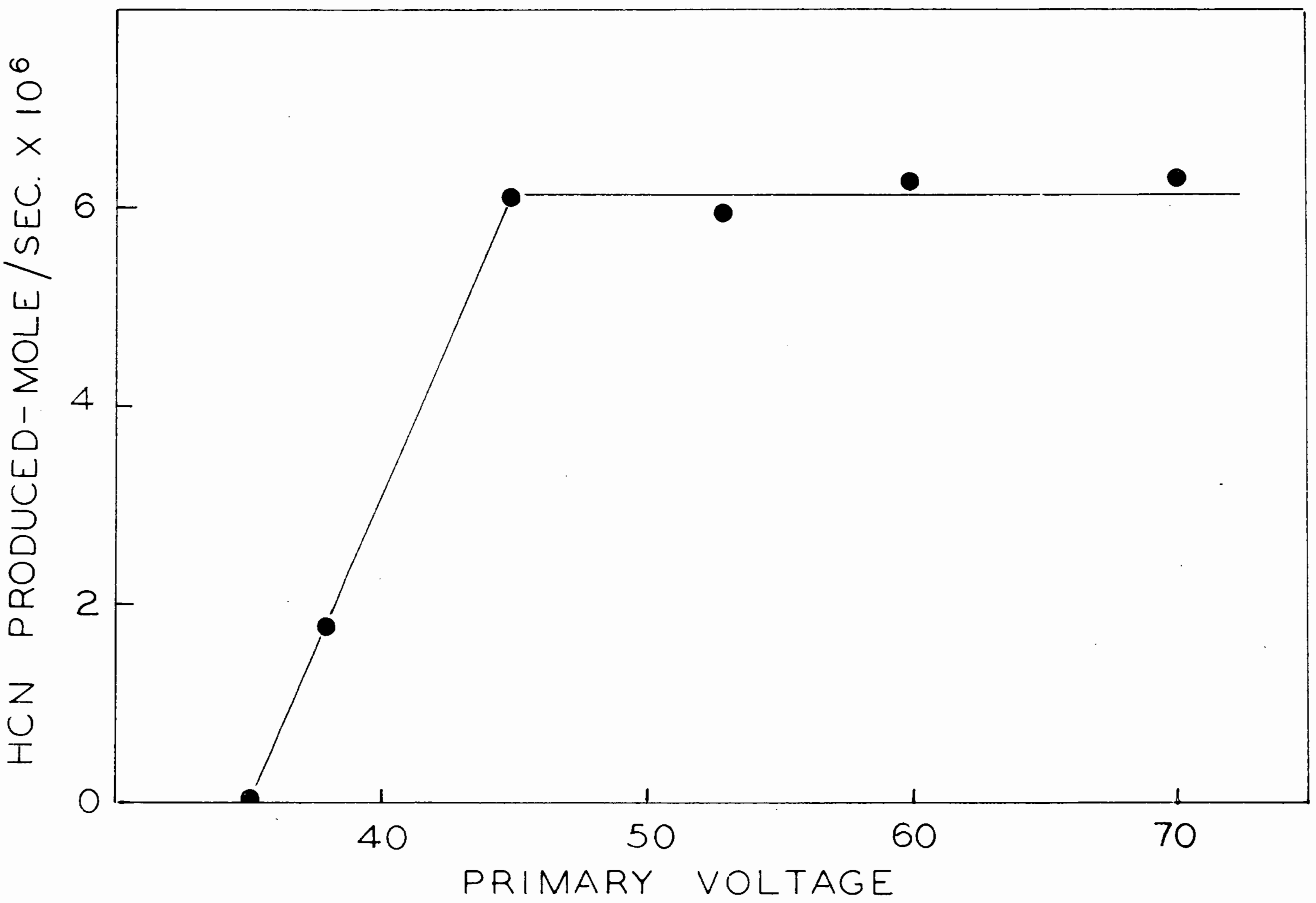

HCN PRODUCED-MOLE/SEC. X 10^6
0
2
4
6
40
50
60
70
PRIMARY VOLTAGE

TABLE IV

Series 2. Ammonia destruction as a function of pressure, primary voltage, and capacitance.

Exp.	Pressure mm.	ΔNH_3 μm/s.	Exp.	Pressure mm.	ΔNH_3 μm/s.
Primary voltage: 45; Capacitance: 4μfd.					
442	0.79	1.52	443	1.22	1.67
449	1.05	2.81	444	1.29	1.90
450	1.19	3.13	447	1.28	0
Primary voltage: 65; Capacitance: 4μfd.					
437	0.27	0.26	317	1.58	3.95
437A	0.61	0.67	439	1.93	4.63
391	0.93	1.99	440	2.21	4.03
311	1.31	4.20	441	2.45	4.00
318	1.42	3.99	446	2.55	0
316	1.51	4.16			
Primary voltage: 75; Capacitance: 4μfd.					
328	1.07	3.31	323	2.22	5.15
327	1.28	4.02	335	2.22	5.21
319	1.42	4.32	338	2.22	5.62
326	1.47	4.40	306	2.26	5.45
310	1.60	4.00	352	2.26	4.81
325	1.62	4.81	336	2.26	5.32
320	1.64	4.71	389	2.32	4.94
313	1.75	4.58	337	2.41	5.64
324	1.77	4.99	333	2.50	5.33
312	1.83	4.95	452	3.08	5.38
307	1.95	5.00	451	3.09	5.42
330	2.18	5.33	453	3.24	5.11
315	2.18	5.32	448	3.50	0
308	2.20	5.46			

Decay tube: 26 cc.

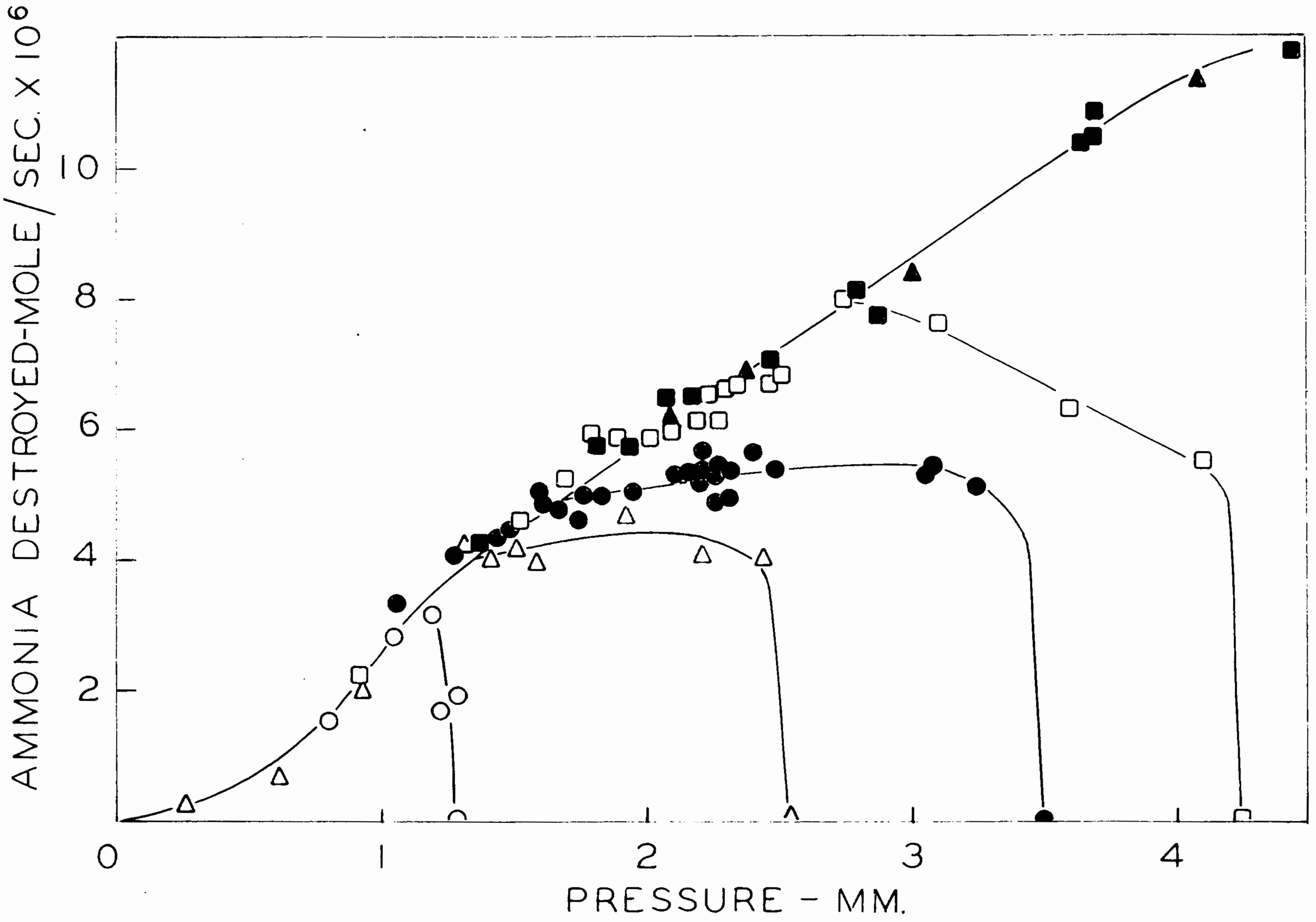
TABLE IV (cont.)

Exp.	Pressure mm.	ΔNH_3 μm/s.	Exp.	Pressure mm.	ΔNH_3 μm/s.
Primary voltage: 85; Capacitance: 2 μfd.					
390	0.92	2.24	339	2.28	6.10
349	1.51	4.67	397	2.29	6.62
348	1.70	5.21	342	2.47	6.67
351	1.81	5.92	341	2.49	6.58
346	1.90	5.89	458	2.75	7.98
347	2.01	5.89	457	3.11	7.66
393	2.09	5.99	454	3.60	6.31
343	2.20	6.11	456	4.09	5.52
331	2.23	6.55	455	4.25	0
345	2.25	6.59			
Primary voltage: 100; Capacitance: 2 μfd.					
394	2.10	6.13	402	3.01	8.36
398	2.39	6.88	459	4.08	11.32
Primary voltage: 110; Capacitance 1 μfd.					
434	1.51	4.43	429	2.77	8.08
432	1.81	5.73	418	2.87	7.74
433	1.94	5.75	425	3.64	10.37
435	2.08	6.44	420	3.68	10.47
431	2.17	6.46	424	3.70	10.85
430	2.48	7.09	436	4.59	11.91

Figure 4

Series 2. Ammonia destruction as a function of pressure, primary voltage, and capacitance.

Primary voltage	
○	45
△	65
●	75
□	85
▲	100
■	110


AMMONIA DESTROYED-MOLE/SEC. X 10^6
10
8
6
4
2
0
1
2
3
4
PRESSURE - MM.

common curve, but finally dropped below as the flashrate decreased to zero. No energy expenditure would bring the reactivity above this common curve.

In <u>series 3</u> a more precise energy variation study was conducted at 1.4 mm. pressure with the flashrate electronically controlled.* The 281 cc. decay tube was used and both the decay tube and reaction vessel were unheated. The exact amount of energy expended in terms of CV^2f, where C is the capacitance, V the primary voltage, and f the flashrate, could thus be determined. The results are given in Table V and Fig. 5. As in series 1 and 2, the reactivities of ethylene and ammonia were readily made independent of energy expenditure, and it will be noted that the values then corresponded to those at 1.4 mm. pressure obtained in series 8 (Fig. 14) and series 9 (Fig. 15). (The conditions in series 8 and 9 corresponded closely to those in series 3.)

The observation in the preceding series that reactivities could be made independent of energy expenditure indicates, of course, either that the desired condition of complete initial dissociation was in fact achieved, or else that an equilibrium condition of partial dissociation occurred. Accordingly, in <u>series 4</u> a Wrede gauge made of sintered glass** was attached to the discharge tube as indicated in Fig. 1 (K), and then connected to a differential

---

* A General Electric FG105 thyratron was incorporated into the high voltage circuit. A 90 volt dry-cell was sufficient to keep it non-conducting, so that the flashrate could be controlled by shorting out the dry-cell with a variable speed, motor-driven, rotary spark gap.

** A Fisher filter stick (catalog number 20-674) of fine porosity was used.

TABLE V

Series 3. HCN production from ethylene and ammonia destruction as functions of CV^2f

Exp.	C μfd.	R * ohms	f $sec.^{-1}$	V' ** volts	V ** volts	CV^2f ∝power	HCN or ΔNH_3 μm/s.
HCN production							
529	1	5000	21.9	75	73.1	.115	2.63
530	2	2500	21.8	75	73.1	.233	3.25
532	4	1000	21.8	60	58.5	.299	3.23
535	2	6500	22.0	115	86.6	.330	3.37
531	2	2500	21.8	90	87.7	.336	3.52
536	2	2500	29.6	85	79.4	.373	3.74
528	4	1250	21.8	75	73.1	.466	3.67
533	4	1250	21.8	75	73.1	.466	3.81
538	2	2500	29.8	100	93.2	.518	3.73
534	4	1250	21.9	85	82.9	.600	4.03
Ammonia destruction (ΔNH_3)							
543	1	5000	22.1	65	63.3	.088	0.39
542	1	5000	29.7	75	69.9	.145	0.38
544	2	2500	22.4	75	72.9	.238	0.51
539	2	2500	29.5	85	79.3	.371	0.81
541	4	1250	29.4	75	70.1	.578	0.81
545	4	1250	22.3	85	82.6	.608	0.99
540	4	1250	29.8	85	79.2	.747	0.61
547	4	1250	29.7	90	83.9	.836	0.72

Decay tube: 281 cc.

Pressure: 1.4 mm.

* R is the resistance in the high voltage circuit.

** V' is the variac setting, whereas V is the "effective" primary voltage taking into account the rate of charge of the condensers, i.e. $V = V'(1 - \exp(-t/RC))$. In calculating V, $t = 0.8 \times 1/2 \times 1/f$ was used, where 0.8 is the fraction of a rotation during which the spark gap was open and 1/2 takes into account the half-wave nature of the rectified high voltage current.

Figure 5

Series 3. HCN production from ethylene and ammonia destruction as functions of CV^2f.

<u>Ethylene</u>

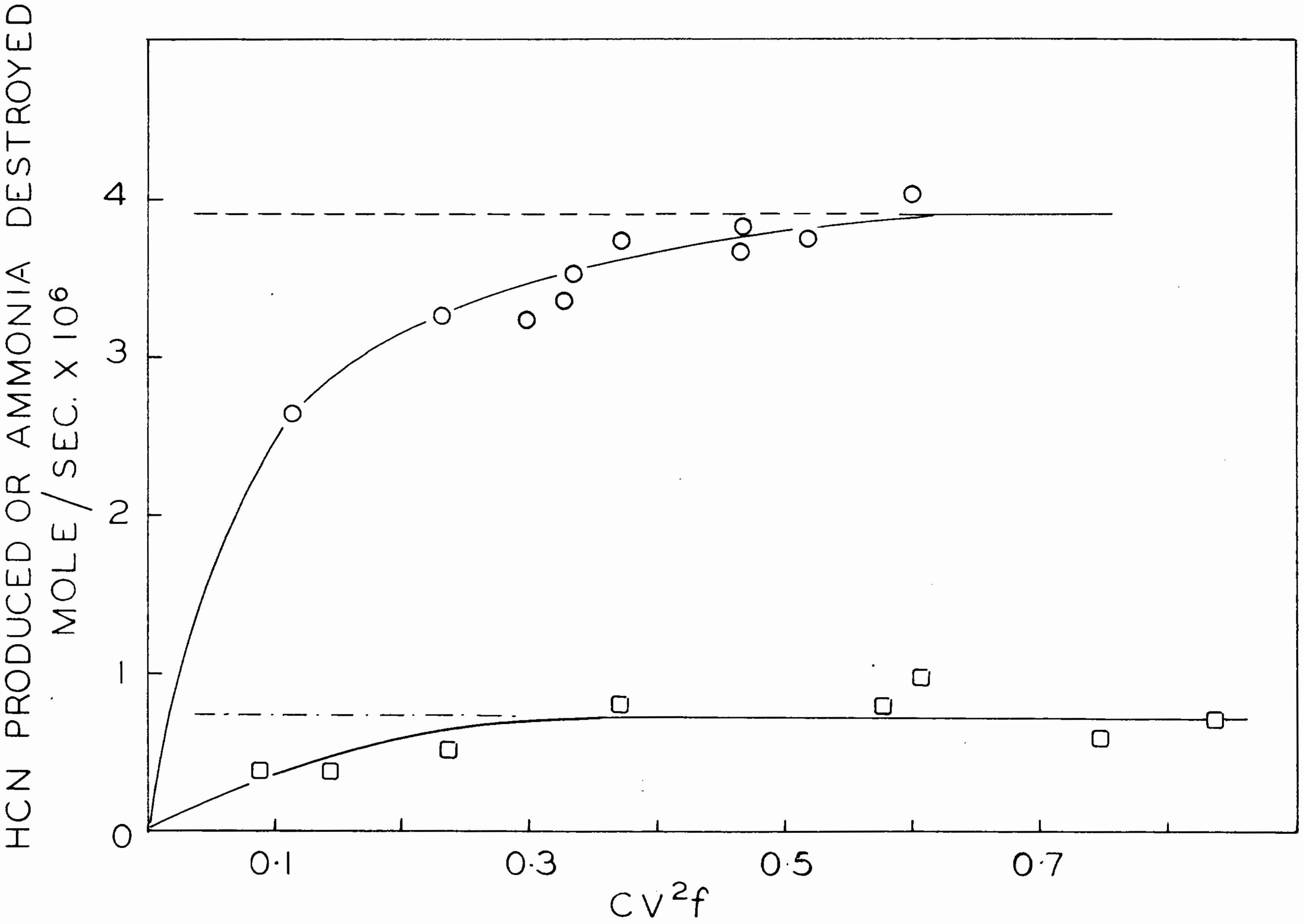
○ Present

- - - - - From series 8

<u>Ammonia</u>

□ Present

—·—·— From series 9


HCN PRODUCED OR AMMONIA DESTROYED
MOLE / SEC. X 10^6
0
1
2
3
4
0·1
0·3
0·5
0·7
CV^2f

manometer consisting of a nearly horizontal U-tube filled with diffusion pump oil. The manometer was calibrated against a McLeod gauge. However, some difficulty was encountered using the Wrede gauge since each reading required at least 20 minutes before the manometer was steady. The result was that as successive readings were made at the high energy expenditures used, the discharge tube became contaminated with material from the electrodes and the poison was thereby made less efficient (Table VI A). (A similar effect has been observed by Linnett and Marsden (25).) In an attempt to counteract this contamination, ethane was therefore injected into the nitrogen stream at a point prior to the discharge tube for a few seconds at the beginning of several experiments. The polymeric material which would be laid down on the walls of the discharge tube was expected to restore the apparatus to a condition more nearly like that during normal experiments, and greatly increased [N]/P values were in fact observed (Table VI B).

In interpreting the gauge measurements, it must be borne in mind that they represent the <u>average</u> atom concentrations in the discharge tube, not those at the instant of discharge. The observed [N]/P values should therefore be compared with the maximum average values obtainable at the flashrates used, i.e. with

$$\overline{[N]/P} = 1/t\int_0^t ([N]/P)dt$$

$$= -k_1/k_2P^2 + (1/k_2tP^2)\ln((1 + k_2P^2/k_1)e^{k_1t} - k_2P^2/k_1), \quad [56]$$

---

* The two leads to the manometer were passed through a liquid air trap to prevent volatile substances, which were found to be present in the diffusion pump oil, from creating false pressure differences.

TABLE VI

Series 4. Wrede gauge measurements.

Exp.	Pressure mm.	Flashrate sec.^{-1}	Capacitance μfd.	ΔP * mm.	[N]/P **
A: Without ethane.					
881	1.63	40	4	.220	.46
882	1.63	20	4	.170	.35
882A	1.63	40	4	.220	.40
883	1.63	29	4	.185	.39
884	1.63	22	4	.115	.30
885	1.30	16	4	.070	.18
886	1.30	60	4	.160	.42
887	1.30	30	4	.095	.25
888	1.30	30	4	.080	.21
889	1.30	60	2	.085	.22
890	1.30	30	4	.065	.17
891	1.30	60	2	.075	.20
892	1.30	30	4	.065	.17
893	1.30	60	2	.070	.18
894	1.30	30	4	.065	.17
895	1.30	20	4	.050	.13
896	1.30	30	2	.050	.13
896A	1.30	60	2	.070	.18
897	2.55	30	2	.100	.13
897A	2.55	60	2	.280	.36
B: Ethane admitted prior to experiments 898-900, 906, 907.					
898	1.37	30	4	.215	.54
899	1.37	20	4	.235	.59
899A	1.37	60	2	.225	.57
900	1.37	60	2	.230	.58
900A	1.37	60	2	.245	.62
901	2.60	60	2	.390	.51
902	2.60	60	2	.390	.51
903	1.37	60	2	.205	.50
904	1.37	60	2	.215	.52
905	2.60	60	2	.360	.47
906	2.60	60	2	.350	.46
907	2.60	60	2	.295	.39

* Pressure difference across differential manometer.

** $[N]/P = \Delta P/(1 - 0.5\sqrt{2})P = \Delta P/0.293P$ (64)

where [N]/P has been expressed in terms of equation [37]. Substituting in equation [56] the value P = 1.4 and values of the decay constants at 400°C. as given in Table XI, namely k_2 = 1.77 and k_1 = 17.2, the following values are obtained:

time = 1/flashrate sec.	$\overline{[N]/P}$
1/60	0.83
1/30	0.73
1/20	0.64
1/10	0.44
1/60 *	0.71
1/30 *	0.58

It is seen that, while the $\overline{[N]/P}$ values calculated for high flashrates and for normal values of k_1 are slightly in excess of the gauge measurements, the effect of a moderate increase in the surface decay constant k_1, such as would result if the discharge tube were contaminated from the electrodes, is sufficient to make the values agree quite closely. Complete initial dissociation therefore appears to have been achieved, a conclusion in agreement with the work of Armstrong and Winkler (44).**

* With k_1 doubled.

** Complete initial dissociation has also been obtained in H atom studies (e.g. 46) so that it should be possible to apply the present method to H atom decay. A suitable reaction for measuring atom concentrations might be that between H atoms and HBr (65).

The $\overline{[N]/P}$ values given above are of incidental interest in that they indicated the upper limits of active nitrogen concentration that can be obtained at a given flashrate by shortening the decay tube or increasing the flowrate.

With the information obtained in series 1 to 3, the minimum energy expenditures which will bring about complete initial dissociation at a given pressure could in principle be determined. However a general statement of conditions which give adequate, but otherwise unspecified, energy expenditures will be sufficient for the present purposes:

Pressure mm.	Resistance ohms	Capacitance μfd.	Flashrate sec.^{-1}
0 to 1.7	1250	4	≥ 30
1.7 to 4	1250	2	60

The desired flashrate is obtained, of course, by adjusting the primary voltage, i.e. the variac setting. All subsequent experiments will be understood to be conducted under these conditions.

ETHYLENE AND ETHANE AT ELEVATED TEMPERATURES

The actual study of the decay of active nitrogen, using reactions which probably involve only N atoms, was now undertaken. With the furnace on the reaction vessel set for about 350°C.* and the decay tube (281 cc.) either unheated

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* When the decay tube was at 400°C. it was not necessary to heat the reaction vessel to achieve maximum reactivity with ethylene (cf. series 7). This was not true, however, with ethane (cf. series 10).

(average temperature = 55°C.; <u>series 5</u>) or at 400°C. (<u>series 6</u>), the HCN production from ethylene and ethane was determined as a function of pressure. The results are given in Tables VII and VIII, and Fig. 6. The maximum possible N atom flowrates, obtained from the observed relation between nitrogen flowrate and pressure (Fig. 2) by doubling the flowrate values to take dissociation into account, are also indicated in Fig. 6. The experimental values for the two series were obtained in random order so that any differences would be real and not due to permanent changes in the glass or poison. In some of the experiments of series 6 the poison on the reaction vessel alone was changed to KCl. The fact that the low pressure asymptotes of the curves for HCN production lead to a pressure slightly greater than zero (0.15 mm.) probably has no great significance since a similar property was observed in the relation between nitrogen flowrate and pressure (Fig. 2).

The main conclusions to be drawn from Fig. 6 are the following:

(i) Since the amounts of HCN formed from ethylene and ethane coincided at all pressures investigated, a complete cleanup of N atoms rather than fortuitously similar reactivities <u>without cleanup</u> is proven.

(ii) Since the use of KCl on the reaction vessel had no effect on the results, surface effects may be assumed absent unless KCl and Na_2HPO_4 happen to have equivalent poisoning qualities. However there is reason to believe (page 66) that KCl is a much <u>better</u> poison than Na_2HPO_4. The absence of surface effects further confirms that cleanup was achieved.

(iii) Heating the decay tube greatly increased the number of N atoms which reached the reaction vessel, though, since the decay constants will be shown to <u>increase</u> with

TABLE VII

Series 5. HCN production from ethylene and ethane as a function of pressure with the decay tube unheated but the reaction vessel at about 350°C.

Exp.	Reactant*	Pressure mm.	HCN µm/s.
1035	2	0.32	1.29
1025	1	0.57	2.67
1027	1	0.65	3.26
1029	1	0.72	4.03
1030	2	0.73	3.96
684	1	0.80	5.19
1028	1	1.00	5.77
1026	1	1.35	7.12
1031	2	1.62	8.11
1023	1	1.62	7.41
1024	1	1.62	8.50
606	1	1.72	8.19
1036	2	2.18	9.50
1036	1	2.29	8.81
1039	1	2.29	9.55
1042	1	2.80	10.5
1041	1	2.81	11.0
685	1	2.93	11.5
1033	2	2.98	11.0
1034	2	2.98	11.0
1040	1	3.67	12.2
1043	1	3.72	12.6
1032	2	3.78	11.3

Decay tube: 281 cc.

* 1 = ethylene. 2 = ethane.

TABLE VIII

Series 6. HCN production from ethylene and ethane as a function of pressure with the decay tube at 400°C.

Exp.	Reactant*	Temperature of reaction vessel**	Pressure mm.	HCN µm/s.
1044	1	2	0.30	1.24
638	1	1	0.33	2.28
1046	2	2	0.50	4.75
1045	1	2	0.53	4.64
1022	1	2	0.57	4.45
762	1	1	0.61	7.29
648	1	2	0.78	8.98
754	1	2	0.87	11.2
654	2	2	0.93	11.7
637	1	1	0.94	10.8
759	1	1	1.27	15.1
758	1	2	1.27	15.2
1020	1	2	1.39	13.5
775	1	1	1.39	15.1
636	1	1	1.41	15.7
773	1	1	1.41	14.0
774	1	1	1.41	14.2
746	1	2	1.42	17.1
786	1	1	1.50	14.2

In experiments numbered between 746 and 786 the poison on the reaction vessel was KCl.

Decay tube: 281 cc.

* 1 = ethylene. 2 = ethane.
** 1 = unheated. 2 = about 350°C.

TABLE VIII (cont.)

Exp.	Reactant*	Temperature of reaction vessel**	Pressure mm.	HCN µm/s.
667	1	1	1.55	17.5
652	2	2	1.57	18.7
653	2	2	1.58	16.5
681	1	2	1.58	16.0
680	1	2	1.58	15.8
678	1	2	1.58	15.6
658	2	2	1.64	15.6
1047	2	2	2.51	21.3
1051	2	2	2.55	20.8
761	1	1	2.60	23.2
760	1	1	2.60	22.0
649	1	2	2.96	23.5
672	1	1	2.98	24.1
669	1	1	2.98	23.3
675	1	2	3.00	23.7
763	1	2	3.01	25.5
674	1	2	3.02	24.8
655	2	2	3.09	25.6
1050	2	2	3.37	27.7
1049	2	2	3.41	27.2
670	1	1	3.94	26.4
671	1	1	3.91	28.5
677	1	2	3.97	27.9
676	1	2	3.97	28.3

* 1 = ethylene. 2 = ethane.

** 1 = unheated. 2 = about 350oC.

Figure 6

Series 5 and 6. HCN production from ethylene and ethane as a function of pressure at elevated temperatures.

<u>Decay tube at 55°C.</u>

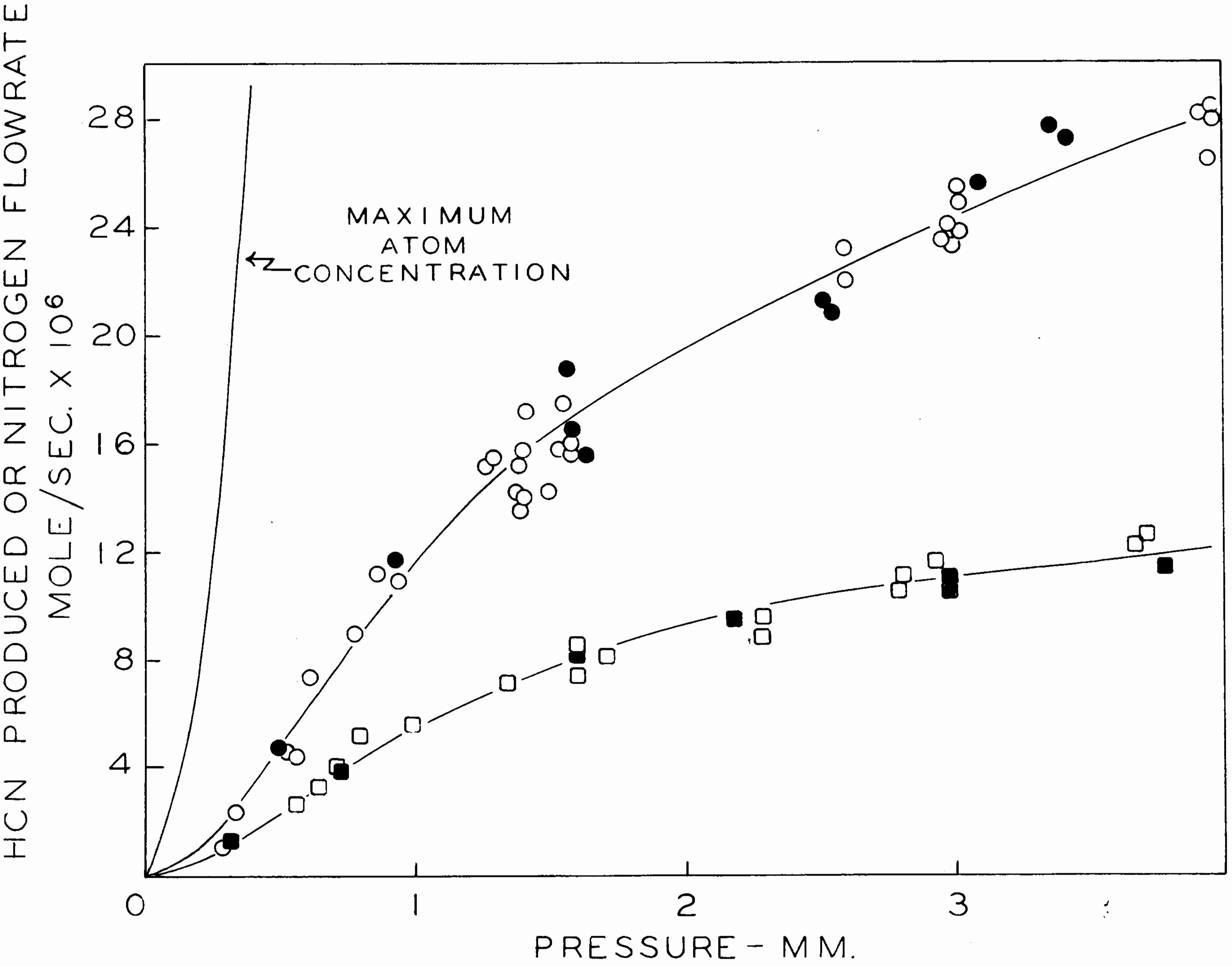
☐ Ethylene

■ Ethane

<u>Decay tube at 400°C.</u>

○ Ethylene

● Ethane


HCN PRODUCED OR NITROGEN FLOWRATE
MOLE/SEC. X 10^6
28
24
20
16
12
8
4
0
1
2
3
PRESSURE - MM.
MAXIMUM
ATOM
CONCENTRATION

temperature, this effect must be due solely to a decreased time of decay.

(iv) The forms of the curves for HCN production are at least superficially consistent with the decay equations. In particular, since the low pressure asymptotes do not coincide with the line giving the maximum atom concentration, the surface decay is shown to be first order and the relevant decay equations are therefore [37] and [40].

(v) The curves for HCN production diverge only slightly from their low pressure asymptotes up to 2 mm. pressure. Surface decay is therefore more important than homogeneous decay in this pressure region, at least with the poison used. (With a more efficient poison the relationship might have been quite different.)

To supplement the data of series 5 and 6, the HCN production from ethylene was also determined with the decay tube (281 cc.) at temperatures between 55°C. and 400°C. The pressure was maintained constant at 1.4 mm., and the reaction vessel was sometimes unheated and sometimes at about 350°C. The results, including mean values from series 5 (Fig. 6), 6 (Fig. 6), and 8 (Fig. 14), are given in Table IX and Fig. 7. (The conditions in series 8 were similar to those in series 5 except that the reaction vessel was unheated.) It is seen that at the lower decay tube temperatures the ethylene reactivity is markedly influenced by the reaction vessel temperature.

The most obvious conclusion to be drawn from Fig. 7 is that, at decay tube temperatures above 200°C., sufficient heat is carried down to the reaction vessel to bring the ethylene reactivity to its maximum value. The observation

TABLE IX

Series 7. HCN production from ethylene as a function of the temperature of the decay tube.

Exp.	Temperature of reaction vessel*	Temperature of decay tube °C.	HCN µm/s.
**	1	55	3.9
**	2	55	7.3
783	1	70	4.27
784	1	120	5.57
779	1	120	5.53
778	1	130	6.18
785	1	145	7.05
781	1	180	8.94
780	2	180	9.19
777	1	260	11.6
776	1	290	12.2
774	1	380	14.2
786	1	380	14.2
773	1	390	14.0
775	1	390	15.1
**	2	400	15.1

Decay tube: 281 cc.

Pressure: 1.4 mm.

* 1 = unheated. 2 = about 350°C.

** Mean values from series 5 (Fig. 6), 6 (Fig. 6), and 8 (Fig. 14).

Figure 7

Series 7. HCN production from ethylene as a function of the temperature of the decay tube.

Reaction vessel unheated

○ Present

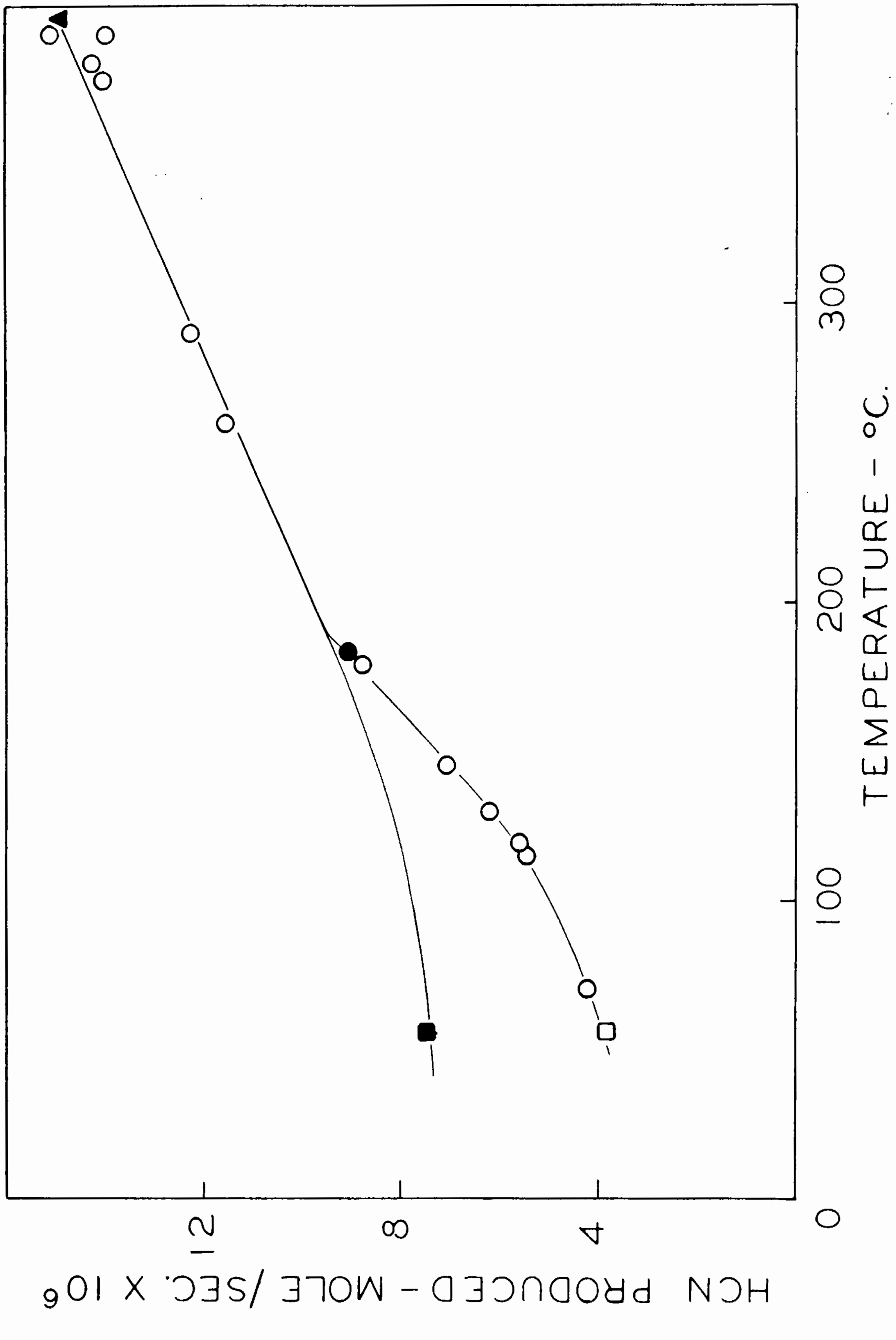
□ From series 8

Reaction vessel at 350°C.

● Present

■ From series 5

▲ From series 6


HCN PRODUCED - MOLE /SEC. X 10^6
4
8
12
0
100
200
300
TEMPERATURE - °C.

that in series 6 the ethylene reactivity was not influenced by the reaction vessel temperature, whereas a very pronounced temperature effect was indicated between series 5 and 8. (Fig. 14), was therefore quantitatively reasonable. Considering the upper curve alone in Fig. 7, it is also evident that the effect of temperature on decay varies continuously without maxima over the range studied. All conclusions on N atom decay may therefore be generalized over this range. Such a generalization would not otherwise follow, since, as seen in the H atom study of Smith (53) and in several instances cited by Shuler and Laidler (24, page 1215), the surface recombination coefficient may maximize under certain conditions.

CALCULATION OF DECAY CONSTANTS AND RELATED QUANTITIES

As a first step in fitting the data of series 5 and 6 to the relevant decay equations [37] and [40], it was necessary to convert the observed HCN flowrates into partial pressures. This was done by means of the empirical relation between nitrogen flowrate and pressure (i.e. equation [29]), with a suitable correction for the fact that dissociation brings about an increased flowrate rather than an increased pressure with the apparatus used. These relations are discussed in Appendix B and lead to the following equation:

$$[N]_{mm.} \approx \frac{[N]_{\mu m/s.}(P - [N]_{\mu m/s.}/118)}{59.0(P - 0.15)} \qquad [73]$$

Values of P/[N] calculated from the data of series 5 and 6 by means of equation [73] are included in Table X.

TABLE X

Data used for the calculation of N atom decay constants.

Pressure mm.	[N] = HCN* μm/s.	Conversion factor μm/s.<—> mm.	P/[N]	$\frac{1}{\ln P/[N] - k_1 t}$
Temperature of decay tube: 55°C.				
0.5	2.3	.0233	9.32	24.
1.0	5.4	.0140	9.74	11.6
1.5	7.7	.0180	10.4	5.26
2.0	9.3	.0176	12.2	3.22
2.5	10.3	.0174	13.95	2.25
3.0	11.0	.0173	15.75	1.76
3.5	11.6	.0172	17.55	1.48
4.0	12.2	.0172	19.1	1.32
Temperature of decay tube: 400°C.				
0.5	4.6	.0223	4.87	23.
1.0	11.6	.0180	4.79	37.
1.5	16.0	.0171	5.48	6.21
2.0	19.4	.0168	6.14	3.64
2.5	22.2	.0167	6.73	2.72
3.0	24.4	.0166	7.40	2.17
3.5	26.4	.0166	7.97	1.87
4.0	28.0	.0166	8.59	1.64

* Mean values from series 5 and 6 (Fig. 6).

To obtain k_1, the lower limits of k_2, and certain related quantities, plots of $P/[N]$ versus P^2 in accordance with equation [37] were now made (Figs. 8 and 9). From the intercepts of the limiting slopes as P —> 0 *, i.e. $e^{k_1 t}$, the quantity $k_1 t$ was obtained, with k_1 following from equation [77], i.e.

$$k_1 \approx \frac{k_1 t + \ln 2 - \frac{1}{2}e^{-k_1 t}}{t_0} .$$

(The derivation of equation [77] is given in Appendix C.) The lower limits of k_2 could then be obtained from the limiting slopes themselves, i.e.

$$\frac{d(P/[N])}{dP^2} = (e^{k_1 t} - 1)k_2/k_1 , \qquad [57]$$

and values for the collision efficiency (γ), the activation energy of surface decay (E), and the number per cm.^{2} of surface species (C_s) from equations [12], [11], and [10], respectively.

Finally, to obtain the upper limits of k_2, plots of $1/(\ln P/[N] - k_1 t)$ versus $1/P^2$ in accordance with equation [40] were made (Fig. 10). (Values of $1/(\ln P/[N] - k_1 t)$ were included in Table X.) The upper limits of k_2 followed from the slopes of the lines joining the point (0, 1/2) with <u>high</u> $1/P^2$ values, i.e.

$$\frac{d(1/(\ln P/[N] - k_1 t))}{d(1/P^2)} = 2k_1/k_2 . \qquad [58]$$

The values for the decay constants and related quantities are given in Table XI.

* It will be recalled (page 32) that the decay equations were more nearly valid at low pressures, so that limiting slopes as P —> 0 are to be preferred to slopes of best fit.

Figure 8

Analysis of the data of series 5 in accordance with equation [37].

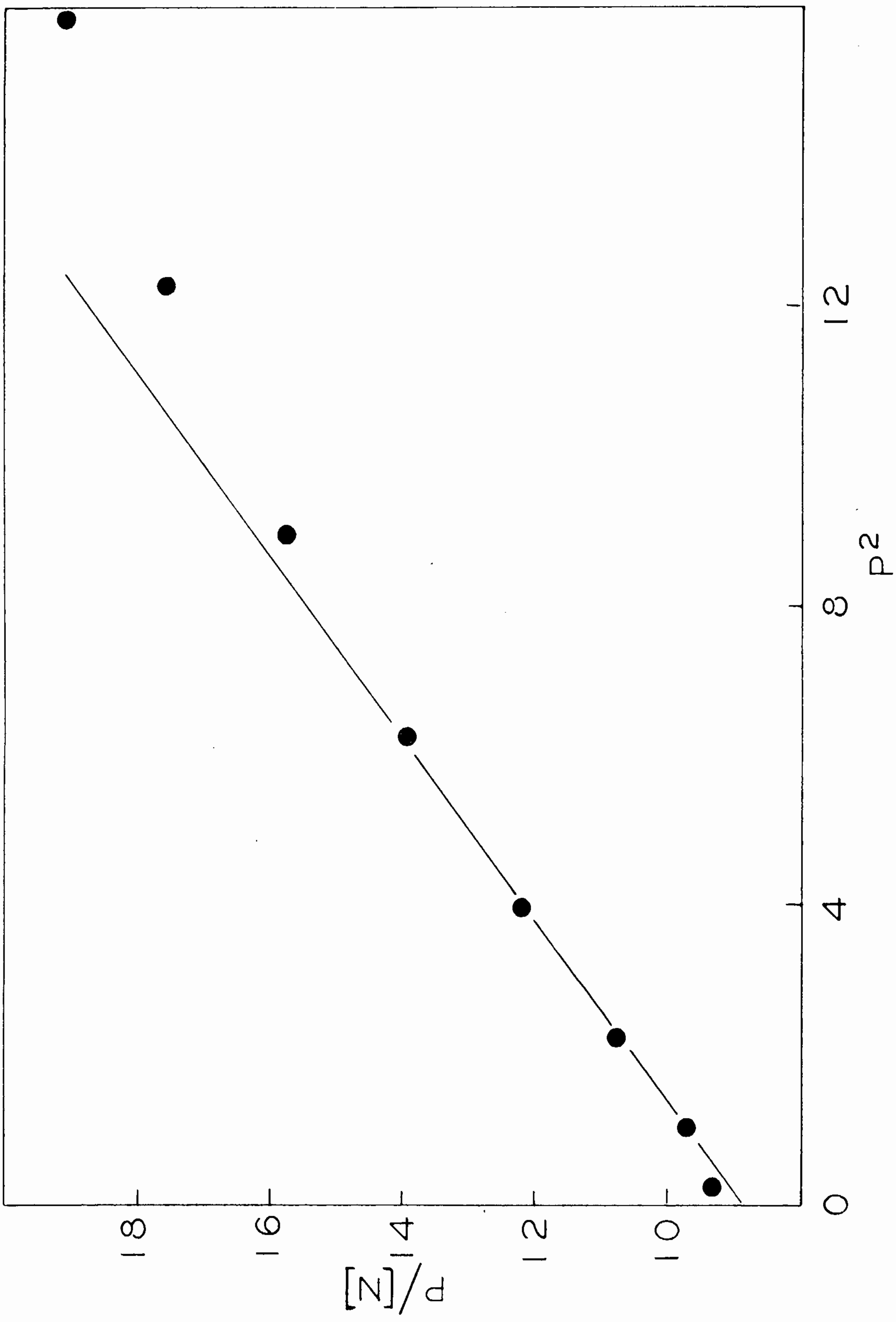

P/[N]
10
12
14
16
18
0
4
8
12
P²

Figure 9

Analysis of the data of series 6 in accordance with equation [37].

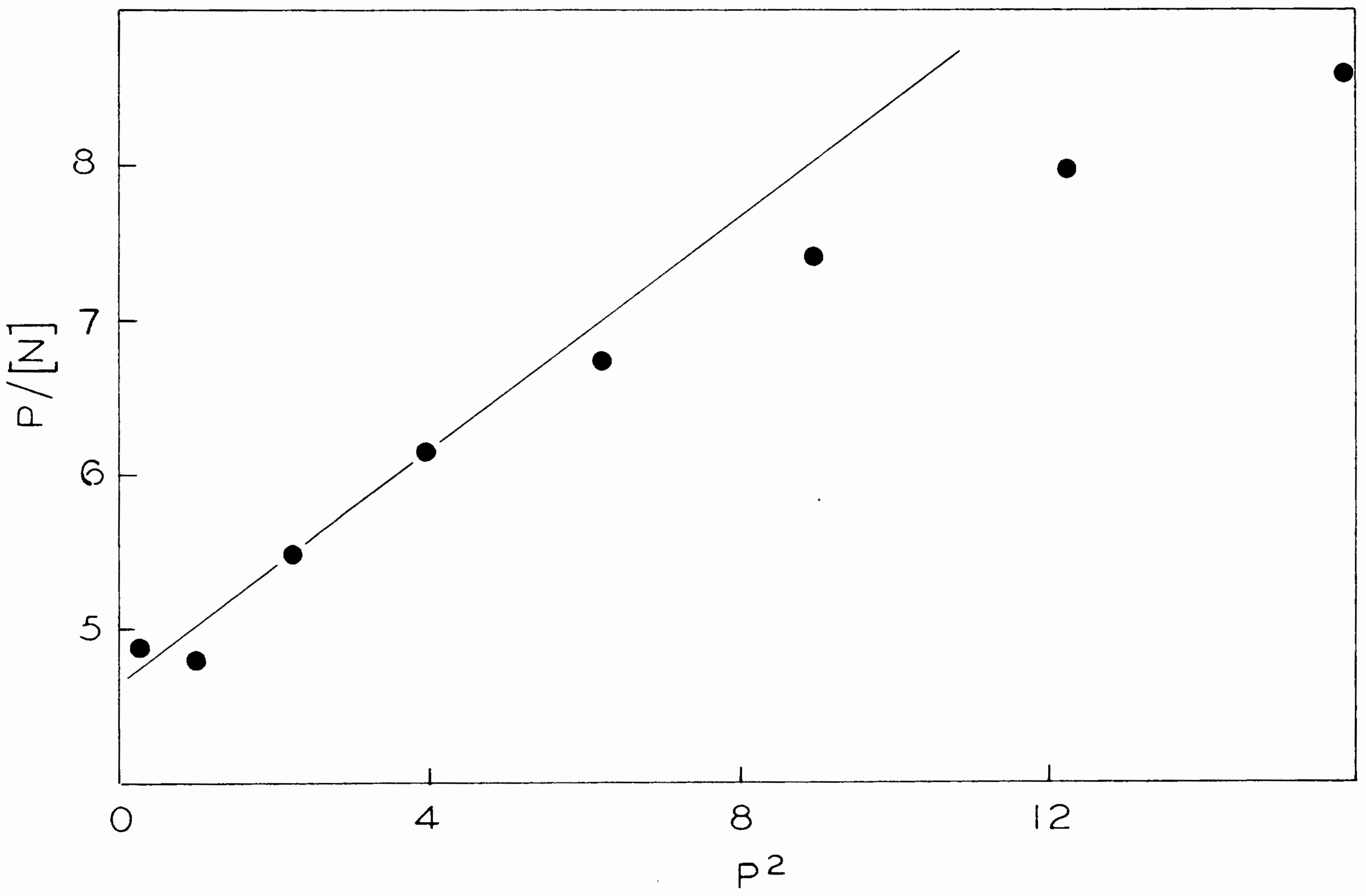
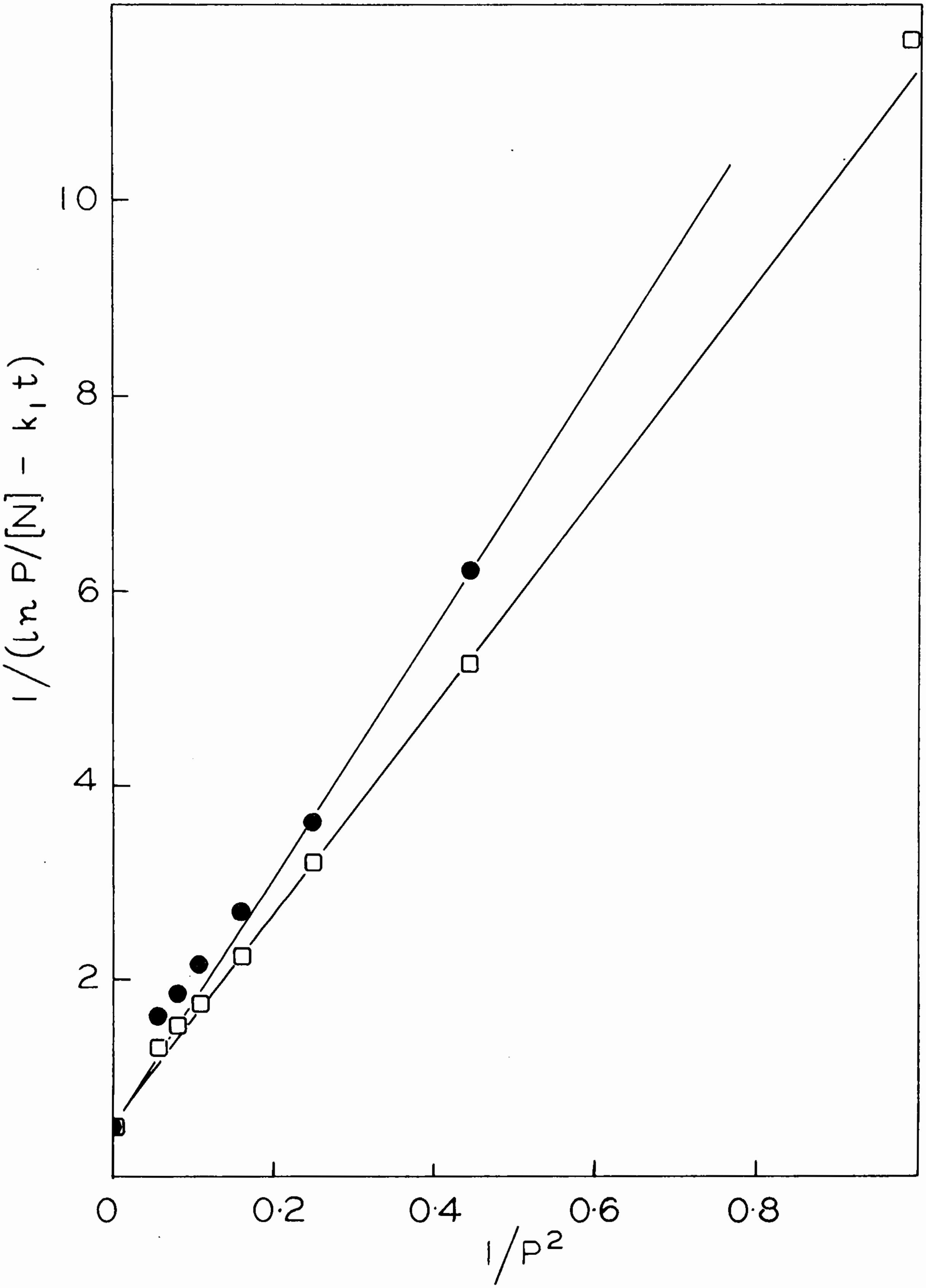

P/[N]
8
7
6
5
0
4
8
12
P²

Figure 10

Analysis of the data of series 5 and 6 in accordance with equation [40].

□ Series 5
● Series 6



1/(ln P/[N] − k₁t)
10
8
6
4
2
0
0·2
0·4
0·6
0·8
1/P²

TABLE XI

The N atom decay constants and related quantities.

Quantity	Value at 55°C.*	Value at 400°C.*
k_1t	2.19	1.54
k_1	11.1 sec.$^{-1}$	17.2 sec.$^{-1}$
γ	2.65×10^{-4}	2.86×10^{-4}
k_2(lower limit)**	1.15 A	1.77 A
	1.32×10^{-33} B	8.6×10^{-33} B
k_2(upper limit)**	2.04 A	2.73 A
	2.35×10^{-33} B	13.2×10^{-33} B
E	1.02 kcal.mole^{-1}	
C_s	1.90×10^{14} cm.$^{-2}$	
γ^+	0.45×10^{-4}	—
γ^{++}	2.7×10^{-8}	—

* A = mm.$^{-2}$sec.$^{-1}$. B = cc.^{2}molecule^{-2}sec.$^{-1}$

** Values for k_2, obtained from those at 55°C, by using 298°K. in the factor to convert mm.$^{-2}$ to cc.^{2}molecule^{-2}, are as follows: $> 1.09\times10^{-33}$, $< 1.94\times10^{-33}$.

\+ For HPO_3 as calculated from the data of Back (58).

++ For HPO_3 as calculated from the data of Rayleigh (16).

To evaluate exactly the relative importance of homogeneous and surface decay under the prevailing conditions, the following relation can be used:

(mean ratio of homogeneous to surface decay)

$$= 1/P \int_0^P (k_2/k_1)P[N]d[N] = k_2P^2/2k_1 \qquad [59]$$

(cf. equation [49].) Using $k_1 = 11.1$ and $k_2 = 1.15$ this expression yields 0.057 at 1 mm. and 0.83 at 4 mm. The previous conclusion is therefore confirmed that homogeneous decay is of secondary importance below about 2 mm. pressure.

SURFACE DECAY CONSTANTS FOR HPO_3

The method used in this study can be extended to investigate the surface decay of N atoms on poisons other than Na_2HPO_4 provided only that the poison does not interfere with the reaction used to measure the atom concentration, and that the discharge tube be poisoned, separately if necessary, with something which does not react with active nitrogen when heated (e.g. not KCl: page 25).

An important poison on which to obtain information would be the one used in the majority of active nitrogen studies, namely HPO_3. While this poison was not used at all in the present work (except incidentally in series 11), tentative estimates of the collision efficiency (γ) for N atoms can be obtained from measurements of afterglow intensity (I) by Rayleigh (16) and Back (58).

In both cases time, rather than pressure, was varied, so that a decay law in differential form must be used. Noting that $I \propto [N]^2$, the derivation of the relevant law is as follows. For atoms decaying by surface and homogeneous decay (cf. equations [33] and [34]),

$$\frac{d[N]}{dt} = -k_1[N] - k_2[N]^2[M] \qquad [60]$$

Hence,

$$d\ln[N]/dt = -k_1 - k_2[N][M]$$

$$= 1/2\ d\ln I/dt \quad ,$$

or, taking the limiting slope as [N] --> 0,

$$\lim_{I \to 0} d\ln I/dt = -2k_1 \qquad [61]$$

(a) Data of Rayleigh (16, Table I).

Since Rayleigh gave the afterglow intensity in units of n, where $I \propto 2^n$, it was necessary to rewrite equation [61] in the form

$$\lim_{n \to 0} dn/dt = -2k_1/\ln 2 \qquad [62]$$

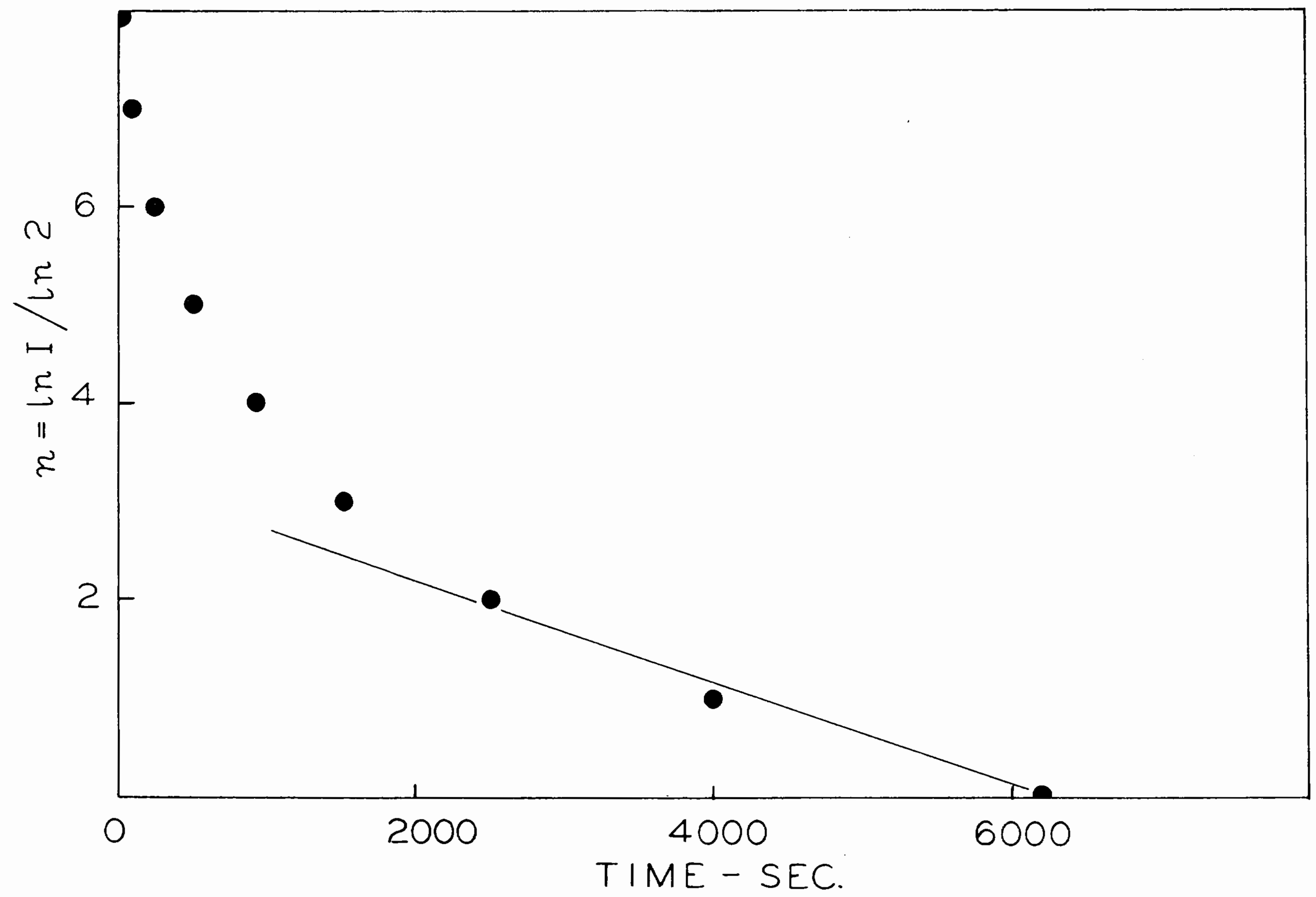
A plot of n versus t is given in Fig. 11, the limiting slope of which is 5.39×10^{-4} sec.$^{-1}$ The value for γ was obtained by means of equation [8] with appropriate substitution for S/V (Rayleigh's system was a sphere of radius 14.5 cm.):

$$\gamma = 4r(k_1/2)(1/3\bar{c})$$

$$= 2.7\times10^{-8} \qquad [63]$$

Figure 11

Data of Rayleigh. Afterglow intensity as a function of time.


$n = \ln I / \ln 2$
6
4
2
0
2000
4000
6000
TIME - SEC.

The validity of this calculation will depend on the size of the term neglected in equation [62], i.e. $-2k_2[N][M]/\ln 2$. Assuming 0.01 % dissociation (Berkowitz et al. (2) estimated the initial dissociation to be 1 %) and a pressure of 0.02 mm. (Rayleigh mentions 0.013 and 0.035 mm. in various sections of reference (16)), and using for k_2 the value 1.15 mm.$^{-2}$sec.$^{-1}$ obtained in the present work (Table XI), this term amounts to 1.3×10^{-7}. Such a value is much less than the limiting slope.

(b) Data of Back (58, Table VI).

Back gave the afterglow intensity in proportional units and time in "distance along the decay tube"(x). Hence equation [61] can be rewritten

$$\lim_{I \to 0} \partial \ln I/\partial x \cdot \partial x/\partial t = -2k_1 \qquad [64]$$

where $\partial x/\partial t$ is the linear flowrate, 64.7 cm. sec.$^{-1}$ (evaluated from the volume flowrate, 1830 cc.sec.$^{-1}$, and the radius of the decay tube, 3 cm.). A plot of lnI versus x is given in Fig. 12, the limiting slope of which is 0.0333 cm.$^{-1}$ The value for γ follows from equation [12]: 0.48×10^{-4}.

(c) Data of Back (58, Table VII).

Here the radius of the decay tube was 1.2 cm., so that $\partial x/\partial t$ = 405 cm.sec.$^{-1}$ A plot of lnI versus x is given in Fig. 13, the limiting slope of which is 0.0117 cm.$^{-1}$ Hence, $\gamma = 0.42\times10^{-4}$. The average value of γ based on Back's data, 0.45×10^{-4}, is thus about 1/6 the value obtained in the present work for an Na_2HPO_4 surface.

Since Back obtained approximate values of the atom concentration by measuring the HCN production from ethylene, though using an unheated reaction vessel, the term neglected in equation [64], i.e. $-2k_2[N][M]$, can be evaluated with

Figure 12

Data of Back (wide decay tube).
Afterglow intensity as a function of distance.

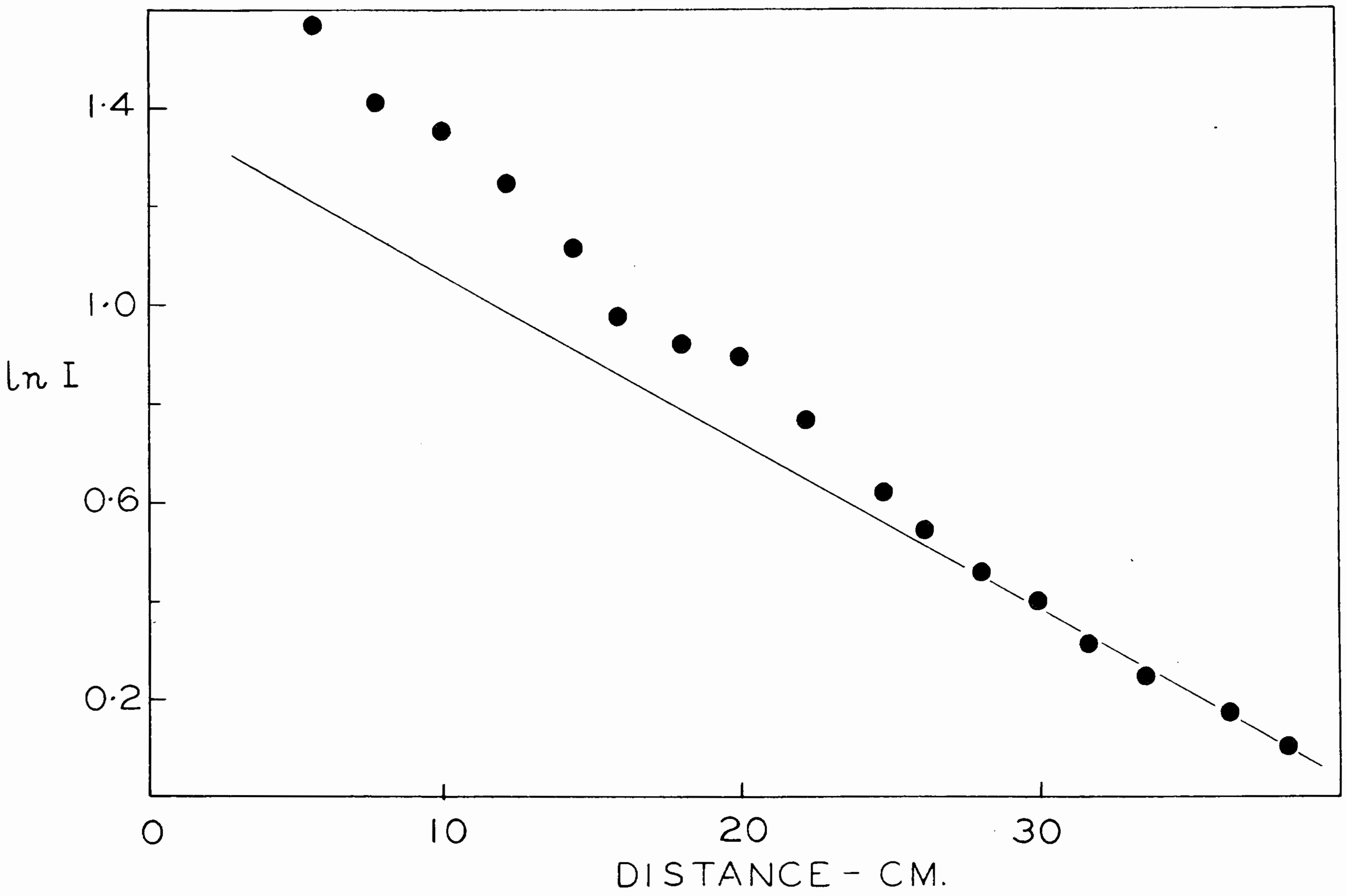
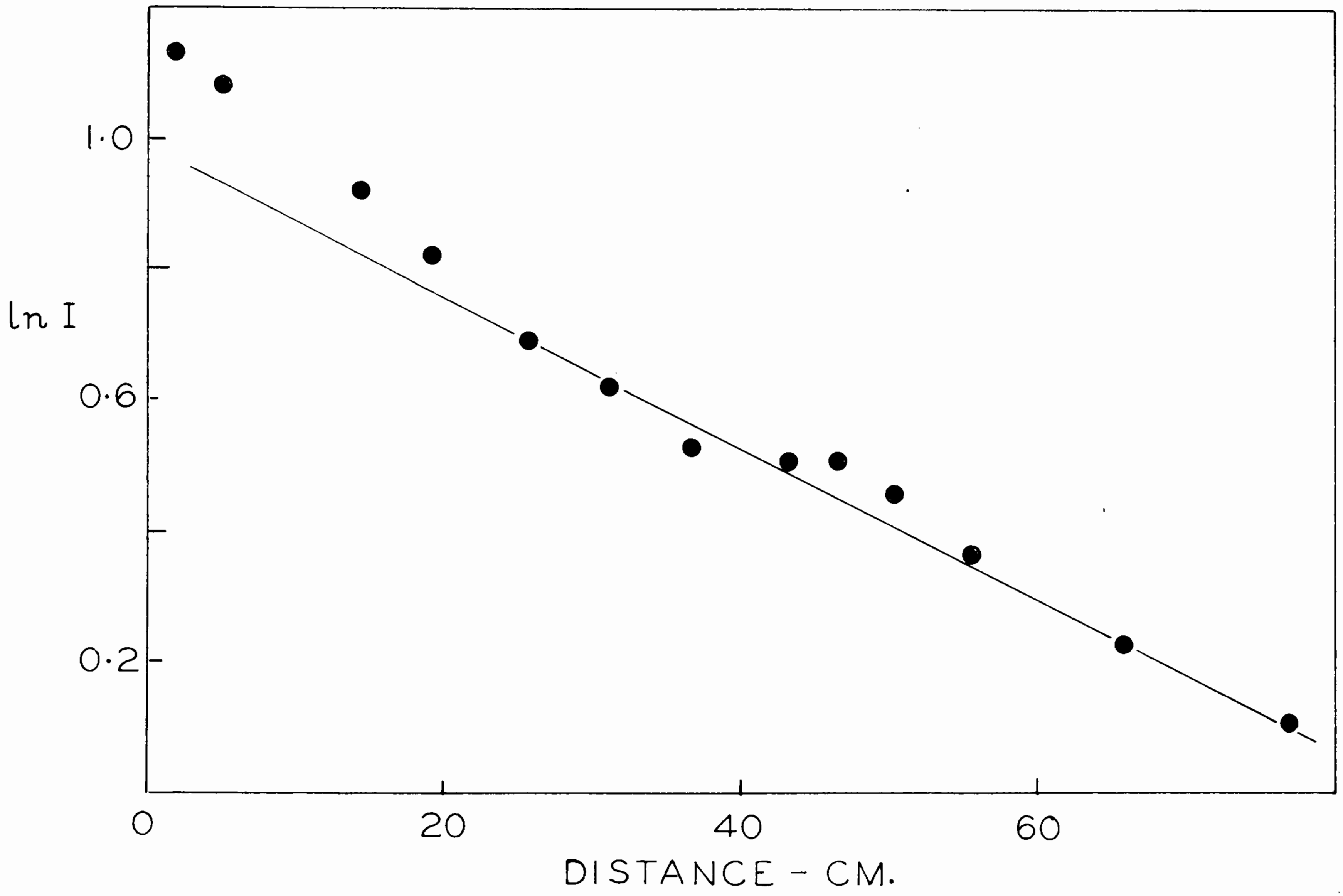

ln I
1·4
1·0
0·6
0·2
0
10
20
30
DISTANCE - CM.

Figure 13

Data of Back (narrow decay tube).
Afterglow intensity as a function of distance.


ln I
1·0
0·6
0·2
0
20
40
60
DISTANCE - CM.

reasonable certainty and shown to be negligible in the regions of Figs. 12 and 13 where the limiting slopes were derived.

The various values of γ for HPO_3 have been included in Table XI, though discussion of the extreme lack of agreement in them will be reserved for a later section.

RESULTS

B: LOW REACTIVITY

As outlined previously, the concentration of active nitrogen reaching the reaction vessel after a period of decay in the decay tube was measured chemically as a function of pressure. However, the reactions used were ones which occurred to only a limited extent (HCN production from ethylene and ethane, and the destruction of ammonia, all in the neighborhood of room temperature), the object being to determine whether these reactions were better explained in terms of catalytic recombination or excited molecules.

It will be understood that all experiments to be described utilized plateau flowrates of reactant and, except in series 11, sufficient energy expenditures to bring about complete initial dissociation.

ETHYLENE AT ROOM TEMPERATURE

In series 8 the production of HCN from ethylene was determined as a function of pressure with both the decay tube (281 cc.) and reaction vessel unheated. The results are shown in Table XII and Fig. 14. The afterglow was completely extinguished in all experiments. The corresponding atom concentrations, previously obtained by reacting ethylene and ethane at 350°C. (Series 5), are also indicated in Fig. 14. It is seen that the HCN production at room temperature ($[N]_e$) is generally substantially lower than the atom concentration ($[N]$), although the two become more nearly equal at low pressures.

TABLE XII

Series 8. HCN production from ethylene as a function of pressure with both the decay tube and reaction vessel unheated.

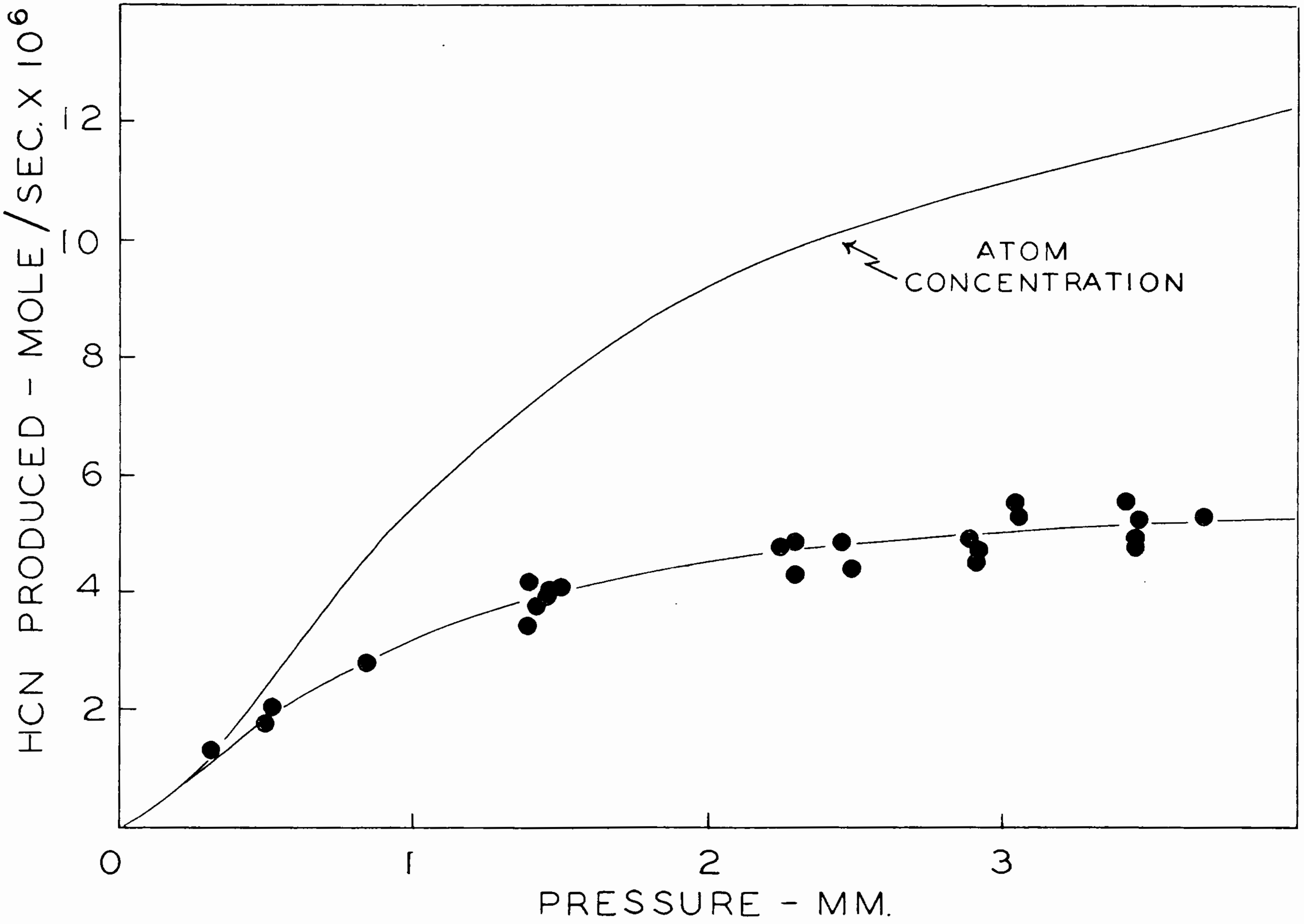
Exp.	Pressure mm.	Reaction temperature °C.	HCN µm/s.
Low reaction temperature.			
517	0.31	40	1.36
600	0.50	45	1.79
521	0.52	55	2.06
518	0.84	60	2.86
798	1.38	50	3.43
800	1.39	65	4.19
597	1.42	65	3.80
590	1.46	70	3.97
509	1.47	75	4.03
510	1.49	70	4.07
601	2.24	75	4.86
599	2.29	75	4.91
603	2.30	70	4.32
520	2.46	85	4.89
519	2.49	75	4.48
516	2.89	75	4.93
512	2.91	75	4.89
514	2.91	75	4.57
591	3.04	90	5.54
595	3.05	75	5.35
618	3.42	85	5.66
619	3.45	75	4.86
617	3.46	80	4.96
616	3.46	80	5.27
522	3.68	90	5.33
High reaction temperature.			
615	3.97	95	7.90
602	3.99	105	8.59
594	4.00	95	7.57
593	4.01	90	7.02
613	4.85	100	9.25
614	5.00	100	8.94

Decay tube: 281 cc.

Mean reaction temperature: 75°C.

Figure 14

Series 8. HCN production from ethylene as a function of of pressure with both the decay tube and reaction vessel unheated.


HCN PRODUCED - MOLE / SEC. X 10^6
0
2
4
6
8
10
12
1
3
PRESSURE - MM.
ATOM CONCENTRATION

Since the ratio $[N]_e/[N]$ varies with $[N]$ in precisely the manner characterizing catalytic recombination by scheme 1, it seems safe to conclude that the low reactivity observed for ethylene was due entirely to catalytic recombination of N atoms. It was therefore possible to obtain a value for the rate constant for homogeneous catalytic recombination of N atoms on ethylene, i.e. $k_{2(C_2H_4)}$, by trial-and-error solution of equation [52]. If $n = 1$ and $p = 1$ this equation assumes the form

$$[N]_e = 2k_7/k_8 \ln(1 + k_8[N]/2k_7) \qquad [65]$$

and it is readily shown (Table XIII) that the data are consistent with

$$k_8/2k_7 = 0.28\ \mu\text{m/s.}^{-1} \approx 0.28/59\ \text{mm.}^{-1}$$

$$= 1.71 \times 10^{-19}\ \text{cc.molecule}^{-1}$$

(In converting mm.$^{-1}$ to cc.molecule^{-1}, the mean reaction temperature of 75°C. was used.) As discussed earlier, k_8/k_7 is equal to the ratio of $k_{2(C_2H_4)}$ to the rate constant for HCN production from ethylene. A rough value for the latter has been obtained by Greenblatt and Winkler (66): 3.69×10^{-14} cc.molecule^{-1}sec.$^{-1}$ at 298°K., so that

$$k_{2(C_2H_4)} = 13 \times 10^{-33}\ \text{cc.}^2\text{molecule}^{-2}\text{sec.}^{-1}$$

Since catalytic recombination by scheme 1 would be markedly temperature dependent (see page 41), the abnormally high HCN production observed at pressures $\gtrsim 4$ mm. is adequately explained on the basis of the somewhat higher

TABLE XIII

Data used for the calculation of k_8/k_7.

Pressure mm.	$[N]_e$ = HCN* µm/s.	$[N]$ = HCN** µm/s.	Predicted values of $[N]_e$ when $k_8/2k_7 = 0.25$	$k_8/2k_7 = 0.30$
0.5	1.8	2.3	1.8	1.7
1.0	3.2	5.4	3.4	3.2
2.0	4.5	9.3	4.8	4.4
3.0	5.1	11.0	5.3	4.9
4.0	5.4	12.2	5.6	5.1

* Mean values from series 8 (Fig. 14).
** Mean values from series 5 (Table X).

reaction temperatures observed (Table XII). In fact, these temperatures were just entering the range demonstrated in series 7 (Fig. 7) to bring about a marked change in the ethylene reactivity. (In series 7 HCN production was measured as a function of the temperature of the decay tube.)

ETHANE AND AMMONIA AT ROOM TEMPERATURE

(a) Series 9 and 10

In series 9 and 10 the production of HCN from ethane and the destruction of ammonia were determined as functions of pressure with the reaction vessel unheated and the decay tube (281 cc.) either unheated (average temperature = 55°C.; series 9) or at 400°C. (series 10). The results, some of which were obtained with KCl as the poison on the reaction vessel, are given in Tables XIV and XV, and Figs. 15 and 16. The afterglow was extinguished only in the presence of ethane. The corresponding atom concentrations, previously obtained by reacting ethylene and ethane at 350°C. (series 5 and 6), are also indicated in Figs. 15 and 16. It is seen that, in marked contrast to the behavior of ethylene, the reactivities at room temperature ($[N]_e$) are substantially lower than the atom concentration ($[N]$) even at the lowest pressure.*

It is apparent from the manner in which the ratio $[N]_e/[N]$ varies with $[N]$ that the low reactivities observed for ethane and ammonia were <u>not</u> due to catalytic recombination by scheme 1. Moreover, since the afterglow

---

* This was also demonstrated in series 2 (Fig. 4), where the destruction of ammonia was measured at various pressures using the 26 cc. decay tube.

TABLE XIV

Series 9. HCN production from ethane and ammonia destruction as functions of pressure with both the decay tube and reaction vessel unheated.

Exp.	Pressure mm.	HCN or ΔNH_3 µm/s.	Exp.	Pressure mm.	HCN or ΔNH_3 µm/s.
HCN production,					
621	0.32	0.09	623	3.02	1.53
624	0.92	0.44	622	3.93	2.10
620	1.45	0.89			
Ammonia destruction.					
494	0.31	0.10	495	1.53	1.08
493	0.34	0.09	496	1.53	1.02
550	0.75	0.27	545	1.53	1.04
549	0.79	0.42	612	1.98	1.07
548	0.81	0.36	485	2.00	1.01
492	0.93	0.72	497	2.00	1.19
558	1.44	0.95	487	2.01	1.30
555	1.45	0.74	483	2.02	1.11
556	1.46	0.79	606	2.05	1.25
541	1.48	0.81	498	3.02	1.46
547	1.49	0.72	503	3.02	1.28
539	1.50	0.81	611	3.03	1.63
553	1.50	0.79	502	3.06	1.28
554	1.50	0.89	605	3.12	1.37
557	1.50	0.90	607	4.01	2.03
559	1.50	0.95	604	4.04	1.45
540	1.51	0.61	608	4.04	2.27

Decay tube: 281 cc.

Figure 15

Series 9. HCN production from ethane and ammonia destruction as functions of pressure with both the decay tube and reaction vessel unheated.

● Ethane
○ Ammonia

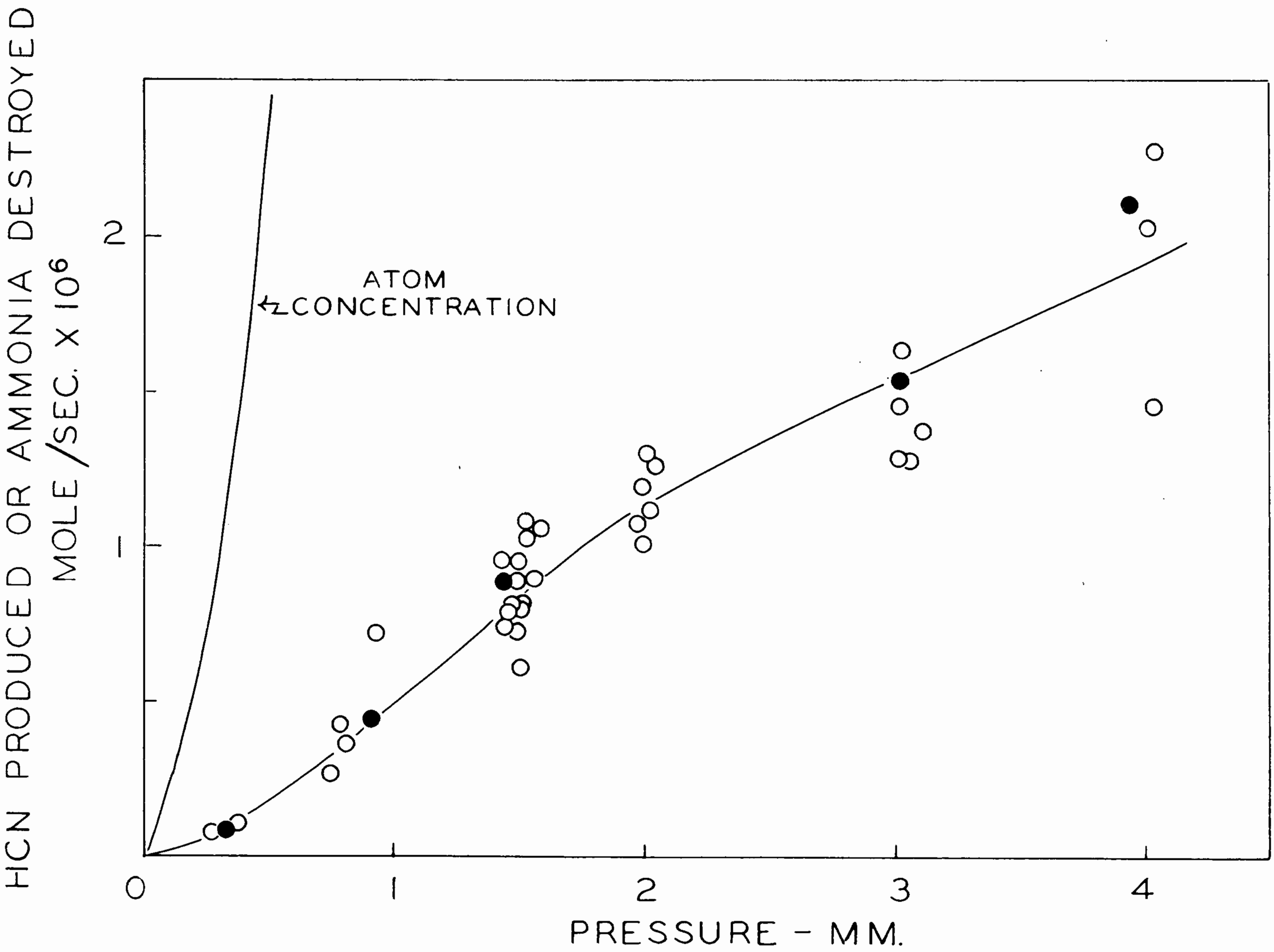

HCN PRODUCED OR AMMONIA DESTROYED
MOLE /SEC. X 10⁶
2
1
0
1
2
3
4
PRESSURE - MM.
ATOM
CONCENTRATION

TABLE XV

Series 10. HCN production from ethane and ammonia destruction as functions of pressure with the decay tube at 400°C. but the reaction vessel unheated.

Exp.	Pressure mm.	Reaction temperature °C.	HCN µm/s.
HCN production; low reaction temperature.			
628	0.33	45	0.55
1065	0.55	35*	1.14
634	0.96	75	2.05
729	0.98	60	2.74
745	1.03	80	3.24
742	1.50	90	4.47
728	1.52	75	4.31
1062	1.61	85*	4.17
1066	2.60	130*	8.34
1064	2.64	115*	6.98
1063	3.82	145*	9.40
HCN production; high reaction temperature.			
659	1.42	105	6.75
804	1.47	115	5.77
803	1.48	110	4.75
802	1.49	120	5.45
625	1.60	110	5.93
626	1.61	110	5.85
744	2.73	135	13.3
743	2.78	140	16.3
660	3.07	165	16.0
730	3.11	115	15.0
633	3.19	160	16.7
805	3.29	195	16.6
643	4.09	190	24.2
663	4.20	190	25.6
664	4.23	185	26.3

Decay tube: 281 cc.

* Constriction sprayed with dry-ice-acetone.

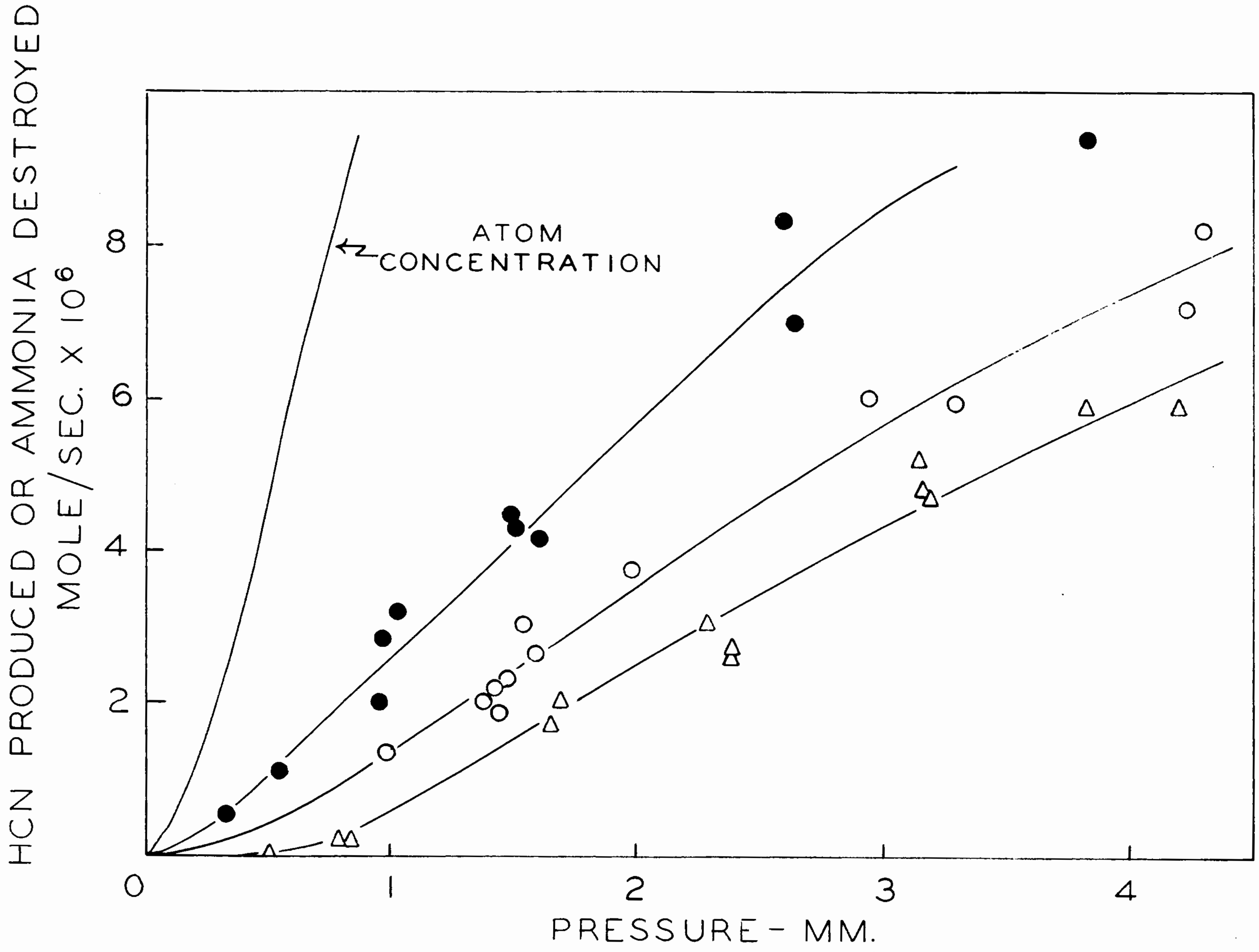
TABLE XV (cont.)

Exp.	Pressure mm.	ΔNH_3 µm/s.
Ammonia destruction; poison on reaction vessel: Na_2HPO_4.		
1061	0.52	0.00
1057	0.80	0.26
1056	0.84	0.26
1058	1.66	1.72
1055	1.70	2.04
691	2.28	3.11
1060	2.39	2.77
1059	2.39	2.67
694	3.15	5.19
1053	3.18	4.69
690	3.22	4.69
1054	3.82	5.52
689	4.20	5.53
Ammonia destruction; poison on reaction vessel: KCl.		
733	1.00	1.35
769	1.38	2.05
767	1.43	2.24
768	1.44	2.30
766	1.45	1.87
734	1.55	3.03
765	1.60	2.67
732	1.98	3.75
739	2.94	6.00
737	3.28	5.94
735	4.23	7.18
736	4.30	8.21

Figure 16

Series 10. HCN production from ethane and ammonia destruction as functions of pressure with the decay tube at 400°C. but the reaction vessel unheated.

- △ Ammonia with Na_2HPO_4 poison
- ○ Ammonia with KCl poison
- ● Ethane


HCN PRODUCED OR AMMONIA DESTROYED
MOLE/SEC. X 10^6
8
6
4
2
0
1
2
3
4
PRESSURE - MM.
ATOM CONCENTRATION

persisted in the presence of ammonia, schemes 2 and 4, which involve surface catalytic recombination, would also appear to be eliminated, at least with ammonia. (The absence of afterglow in the presence of ethane merely indicates that the complex N$\cdot C_2H_6$ is stable, but implies nothing about the reactivity of ethane.) On the other hand, different ammonia reactivities resulted in those experiments of series 10 where KCl was the poison on the reaction vessel. A surface effect of some kind is therefore strongly implied, and, were it not for the fact that an adequate explanation can be made on other grounds (page 66), the results might be interpreted as <u>prima facie</u> evidence for surface catalytic recombination. (It will be recalled that HCN production from ethylene was unaffected by KCl (series 6)).

In series 8 the HCN production from ethylene, with both the decay tube and reaction vessel unheated, was abnormally high at the highest pressures. This difficulty was even more apparent with ethane in series 10, presumably since the heat generated by the reaction was supplemented by that carried down from the decay tube. (Cf. also series 6 where, under conditions similar to those of series 10, the <u>maximum</u> ethylene reactivity was observed at all pressures.)* In an

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* Variability in the amount of heat generated by the reaction, or carried down from the discharge tube and connecting tube, may account in part for the widely divergent temperature affects previously reported for ethylene and substances of similar reactivity. Examples where a large temperature effect was observed are ethylene (41; also series 8 of the present work). Examples where the temperature had little or no effect on the reaction are ethylene (67), ethyl chloride (68), propylene (69), and butene (70).

attempt to lower the reaction temperature, the constriction in the decay tube was therefore wrapped with "Kleenex" and sprayed with dry-ice-acetone during several experiments, and it was only for these, and the few other experiments in which a low reaction temperature was observed, that results were given in Fig. 16. However the reaction temperatures were still somewhat high, so that the results are of less quantitative value than those of series 9 (Fig. 15). Since the apparatus was not designed to thermostat the reaction vessel properly, the ethane reaction was not studied further.

(b) Series 11

While the results of the preceding section indicated that the low reactivities of ammonia, and perhaps also ethane, were not due to catalytic recombination by schemes 1, 2, or 4, the possibility remained that they could be explained in terms of scheme 3. In fact, scheme 3 would be one of the more likely to occur, since it would account for the apparent temperature independence of the ammonia flowrate plateau and for the change in the activation energy of the ethane reaction. (This would arise from the process $N{\cdot}C_2H_6 \longrightarrow$ (products) setting in at elevated temperatures.) Now, it will be recalled (page 41) that scheme 3 is characterized by the constancy of the ratio $[N]_e/[N]$ as $[N]$ is varied. Accordingly, in series 11 the ammonia and ethylene reactivities were compared at a constant pressure of 2.1 mm. but using different poisons. The 104 cc. decay tube was used and both the decay tube and reaction vessel were unheated. The complete results are given in Table XVI and a summary, including calculations of the ratio $[N]_e/[N] = \Delta NH_3/HCN$, in Table XVII. Since the variations in the ratio $[N]_e/[N]$ for different poisons are well beyond the experimental error, even when cognizance is taken of the fact that the HCN

TABLE XVI

Series 11. HCN production from ethylene and ammonia destruc-as functions of the poison with both the decay tube and reaction vessel unheated.

Exp.	Poison	HCN µm/s.	Exp.	Poison	HCN µm/s.
HCN production					
261	KCl	3.75	177	As_2O_5	7.35
263		3.94	179		6.10
268		4.13	181		5.77
			183		6.10
229	$BiCl_3$	5.58			
231		5.25	201	$ZnCl_2$	7.07
233		4.49	202		7.20
237		4.96	207		6.77
275	Na_2HPO_4	4.31	217	$ZnCl_2$*	5.65
278		4.17	219		5.50
281		4.00	222		4.97
256	B_2O_3	4.26	192	85% H_3PO_4	5.70
258		3.90	195		5.79
			200		4.93

Decay tube: 104 cc.

Pressure: 2.1 mm.

* The reaction vessel was packed with a sufficient number of glass rods to double the surface area.

TABLE XVI (cont.)

Exp.	Poison	ΔNH_3 µm/s.	Exp.	Poison	ΔNH_3 µm/s.
Ammonia destruction.					
260	KCl	0.43	132	As_2O_5	3.08
262		0.12	133		2.43
264		0.37	134		3.13
266		0.13	135		2.37
267		0.55	136		2.86
269		0.66	137		3.23
270		0.40	138		3.09
			139		2.96
230	$BiCl_3$	0.64	140		2.97
232		0.73	141		2.97
235		0.74	144		2.65
236		0.36	145		2.26
238		0.63	178		3.39
274	Na_2HPO_4	1.20	205	$ZnCl_2$	3.76
276		0.72	206		3.78
277		1.16	208		3.78
279		1.02	211		3.52
280		1.07	214		3.16
283		1.09	209		3.53
286		1.15	210		3.59
291		1.05			
292		0.98	215	$ZnCl_2$*	3.87
293		1.07	216		3.37
302		1.04	218		3.26
			220		3.14
127	B_2O_3	2.29	221		2.90
128		2.22			
129		1.79	190	85% H_3PO_4	3.77
130		1.79	191		3.54
131		1.78	193		3.66
255		1.97	194		3.17
257		1.31	196		3.76
			197		3.19
			199		3.02

* The reaction vessel was packed with a sufficient number of glass rods to double the surface area.

TABLE XVII

Data used for the calculation of $[N]_e/[N]$ as a function of poison.

Poison	$[N]_e = \Delta NH_3$* µm/s.	$[N]$ = HCN* µm/s.	$[N]_e/[N]$
KCl	0.38	3.94	0.10
$BiCl_3$	0.62	5.07	0.12
Na_2HPO_4	1.05	4.16	0.25
B_2O_3	1.88	4.08	0.46
As_2O_5	2.88	6.33	0.45
$ZnCl_2$	3.59	7.01	0.51
$ZnCl_2$**	3.31	5.37	0.62
85% H_3PO_4	3.44	5.47	0.63

Pressure: 2.1 mm.

* Mean values from series 11 (Table XVI).
** Reaction vessel packed with glass rods.

production from ethylene was determined in an unheated reaction vessel, catalytic recombination by scheme 3 is eliminated. (Nothing is decided about schemes 2 and 4 since they involve a surface dependent process). The data of Table XVII are of incidental interest in showing H_3PO_4, As_2O_5, $ZnCl_2$, and $BiCl_3$ to be comparable for inhibiting the surface decay of N atoms, though the lower efficiency indicated for KCl may have been due in part to the reaction previously indicated to occur between heated KCl and active nitrogen.

(c) Series 12

Although the low reactivity of ammonia appears to be consistent with none of the four schemes of N atom reaction plus catalytic recombination, it is desirable to have confirmatory evidence. In principle, such evidence could have been obtained from measurements of the ammonia reactivity (i.e. $[N]_e$) as a function of pressure, as in series 9 and 10, simply by noting whether the ratio $[N]_e/[N]$ was constant, with the proviso that in making a decision on schemes 1 and 4 similar atom concentrations would be compared, while with schemes 2 and 4, the comparison would be restricted to atom concentrations obtained with similar poisons and pressures. (The possible effect of pressure on surface catalytic recombination was indicated on page 39.) However the variation of the ratio $[N]_e/[N]$ was not sufficient for an unambiguous argument. In series 12 additional data on ammonia were therefore obtained with the usual Na_2HPO_4 poison but using the modified apparatus in which the reaction vessel was attached directly to the discharge tube near an electrode, and one of the nitrogen leads was sealed off. In some of the experiments the polarity of the electrodes was reversed. The results, including the corresponding atom concentrations obtained by reacting ethylene at 350°C., are given in Table XVIII and Fig. 17. The ratio $[N]_e/[N] = \Delta NH_3/HCN$ was now evaluated at various pressures from the three relevant series, 9, 10, and 12 (Table XIX). Since there is great variability in the values, even amongst those corresponding to similar atom concentrations and pressures, the absence of catalytic recombination by all four schemes is confirmed.

Further evidence against schemes 1, 2, and 3 is contained in the data of Armstrong and Winkler (44), where the ratio $\Delta NH_3/HCN$ was found to <u>increase</u> with increasing atom concentration at constant poison and pressure. Such an increase is consistent, of course, only with scheme 4, where

$$\lim_{[N] \longrightarrow 0} [N]_e/[N] = 0.$$

However this scheme has been eliminated on other grounds.

It may therefore be concluded with some certainty that the low reactivity of ammonia is not explained by N atom attack, whether by direct reaction or energy transfer, and whether accompanied by homogeneous or surface catalytic recombination. While the argument has been less completely developed with ethane, the data were adequate to demonstrate that the low reactivity was <u>not</u> due to the type of catalytic recombination (scheme 1) observed to occur with ethylene and perhaps to be expected with hydrocarbons generally. Moreover, since the reactivity of ethane as a function of pressure with the decay tube unheated was identical with that of ammonia under the same conditions (series 9), it appears reaction schemes other than (1) play no part in the ethane reaction either.

TABLE XVIII

Series 12. HCN production from ethylene and ammonia destruction as functions of pressure using the modified apparatus in which the reaction vessel is attached directly to the discharge tube.

Exp.	Pressure mm.	HCN or ΔNH_3 µm/s.	Exp.	Pressure mm.	HCN or ΔNH_3 µm/s.
HCN production; nitrogen lead remote from reaction vessel sealed off.					
974	0.62	1.23	972	2.71	8.75
971	1.30	4.13	970	3.72	10.7
968	1.60	5.49	969	3.81	11.6
973	2.62	8.25			
HCN production; nitrogen lead nearer reaction vessel sealed off.					
985	1.00	4.17	1007	2.63	13.9
1008	0.95	3.80	994	3.79	14.1
984	1.59	9.17	992	3.80	13.1
995	1.63	7.80	1005	3.85	15.7
993	2.51	12.3	1006	3.85	15.7

Decay tube: none.

TABLE XVIII (cont.)

Exp.	Pressure mm.	HCN or ΔNH_3 µm/s.	Exp.	Pressure mm.	HCN or ΔNH_3 µm/s.
Ammonia destruction; nitrogen lead remote from reaction vessel sealed off.					
980*	1.21	0.00	978	2.61	0.97
979	1.54	0.06	1011*	2.63	0.90
962	1.61	0.00	967	3.76	1.29
975	1.62	0.15	966	3.77	1.20
976	1.62	0.00	1014	3.84	1.83
963	1.64	0.00	1012*	3.87	1.67
977	2.60	1.06	1010	3.89	1.98
Ammonia destruction; nitrogen lead nearer reaction vessel sealed off.					
986	0.92	0.00	989	2.69	2.21
990	1.61	0.43	987	3.88	5.26
998	1.61	0.38	988	3.88	5.17
1000	1.62	0.25	1004	4.05	5.02
999	2.65	3.07	1003	4.06	5.64

* With polarity of electrodes reversed.

Figure 17

Series 12. HCN production from ethylene and ammonia destruction as functions of pressure using the modified apparatus in which the reaction vessel is attached directly to the discharge tube.

Remote nitrogen lead sealed off

□ Ethylene
■ Ammonia

Nearer nitrogen lead sealed off

○ Ethylene
● Ammonia

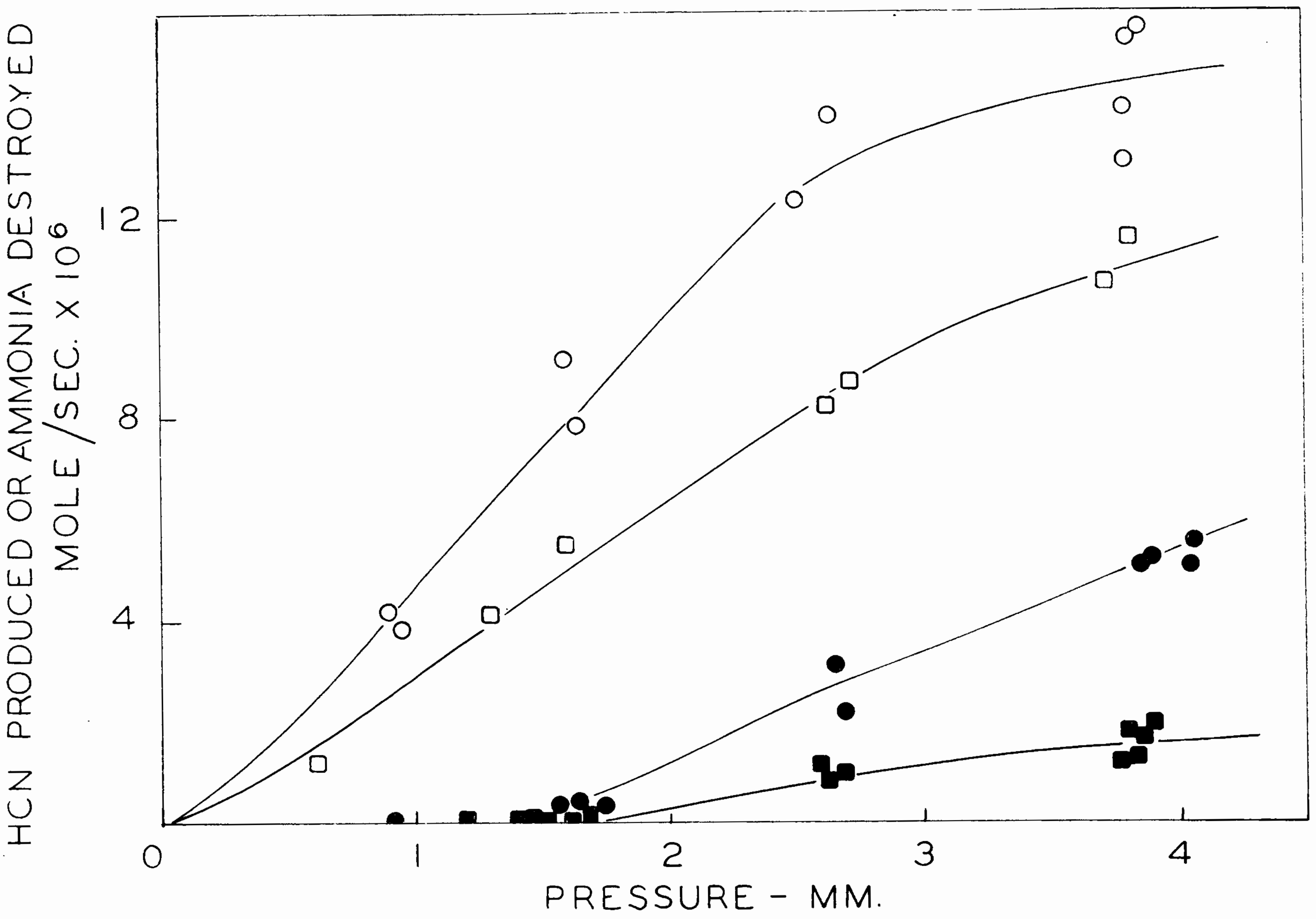
HCN PRODUCED OR AMMONIA DESTROYED
MOLE / SEC. X 10^6
12
8
4
0
1
2
3
4
PRESSURE - MM.

TABLE XIX

Data used for the calculation of $[N]_e/[N]$ as a function of atom concentration and pressure.

Series	Pressure mm.	$[N]_e = \Delta NH_3$* µm/s.	$[N] = HCN$* µm/s.	$[N]_e/[N]$
9	1	0.45	5.4	.08
	2	1.15	9.3	.12
	3	1.55	11.0	.14
	4	1.90	12.2	.16
10	1	0.6	11.6	.05
	2	2.5	19.4	.13
	3	4.35	24.4	.18
	4	5.65	28.0	.20
12**	1	0.0	2.9	.00
	2	0.2	6.3	.03
	3	1.2	9.6	.13
	4	1.5	11.3	.13
12***	1	0.0	4.6	.00
	2	1.2	9.9	.12
	3	3.3	13.8	.24
	4	5.3	14.7	.36

Poison: Na_2HPO_4

* Mean values from Figs. 6, 15, 16, and 17.
** Nitrogen lead remote from reaction vessel sealed off.
*** Nitrogen lead nearer reaction vessel sealed off.

Now, it was pointed out in an earlier section that the elimination of the four schemes in which catalytic recombination can occur is tantamount to elimination of reaction with N atoms. An inescapable conclusion of the present work therefore appears to be that ammonia, and perhaps also ethane, react only with excited molecules at room temperature. The reactivities at elevated temperatures may, of course, be entirely different; in fact, it was concluded from measurements of HCN production from ethylene and ethane at 350°C. (series 5 and 6) that the high temperature ethane reactivity corresponded exactly to the atom concentration.

One difficulty with an interpretation based on excited molecules is that the most likely mechanisms (equations [24] and [25]) require the amount of HCN produced from ethane to be twice the amount of ammonia destroyed. While such a relation is fairly consistent with the ethane and ammonia reactivities obtained with the decay tube at 400°C. (series 10), equal reactivities were observed when the decay tube was unheated (series 9). The implication is either that the excited molecules are subject to a "catalytic de-excitation" on ethane which is favored by lower temperatures, or else that HCN production from N atom attack on the fragments created in the reaction of the excited molecules with ethane must compete with catalytic recombination on the ethane itself.

It might be of interest to treat the reactions of active nitrogen with phosphine, HCl, and ethylene (in the latter case by considering the amount of acetylene formed), by the methods presented here, to determine if any of them were better explained by reaction with excited molecules than by reaction with N atoms as presently suggested (39, 41, 38).

FORMATION OF THE EXCITED MOLECULES

If excited molecules are present it is necessary to determine their mode of formation before any conclusions on their identity and decay can be made, and the modified apparatus used in series 12 was in fact designed for this purpose. It has been shown that with this apparatus the concentration of excited molecules in the reaction vessel should be given by equation [49], i.e.

$$[N_2^*] = k_2P[N]^2/4k_1 \quad ,$$

if the molecules are formed by homogeneous atom decay; or by equation [50], i.e.

$$[N_2^*] \gg [N]/3 \quad ,$$

if formed by surface atom decay. On the other hand, the concentration of excited molecules formed directly in the discharge process would be unpredictable but probably large. The ΔNH_3 values previously obtained using the modified apparatus (Table XIX) were therefore compared with predictions from equations [49] and [50] (Table XX). (The predictions from equation [49] were made by substituting $k_2 = 1.15$ and $k_1 \geq 11.1 \times 1.68/4.0 = 4.66$ (Table XI), where 4.0 is the radius in cm. of the reaction vessel and 1.68 that of the decay tube for which k_1 was derived. The approximate factor 1/59 to convert partial pressures in mm. to flowrates in µm/s. was also introduced, so that the equation assumed the form $[N_2^*]_{\mu m/s.} \approx 0.00105\ P[N]^2$.)

It is seen that at no pressure is there even remote agreement with equation [50], whereas below about 2 mm. the

TABLE XX

Data used for establishing the mode of formation of N_2*.

Pressure mm.	[N] = HCN* μm/s.	[N_2*] = ΔNH_3* μm/s.	Predicted values of [N_2*] **	Predicted values of [N_2*] ***
Nitrogen lead remote from reaction vessel sealed off.				
1	2.9	0.0	0.0	$\gg$ 1.0
2	6.3	0.2	0.1	$\gg$ 2.1
3	9.6	1.2	0.3	$\gg$ 3.2
4	11.3	1.5	0.5	$\gg$ 3.8
Nitrogen lead nearer reaction vessel sealed off.				
1	4.6	0.0	0.0	$\gg$ 1.5
2	9.9	1.2	0.2	$\gg$ 3.3
3	13.8	3.4	0.6	$\gg$ 4.6
4	14.7	5.3	0.9	$\gg$ 4.9

* Mean values from series 12 (Table XIX)

** Assuming that N_2* is formed by homogeneous atom decay, so that $[N_2^*] \approx 0.00105\ P[N]^2$.

*** Assuming that N_2* is formed by surface atom decay, so that $[N_2^*] \gg [N]/3$.

agreement with equation [49] is satisfactory. At higher pressures the observed values of ΔNH_3 are considerably higher than predicted by equation [49], particularly for experiments in which the nitrogen flowed through the body of the discharge tube. However, this is adequately explained by the occurrence of a small amount of homogeneous decay in the discharge tube in spite of operating under conditions of apparently complete initial dissociation. The complete absence of reaction with ammonia at lower pressures is also good evidence that the excited molecules were not primary discharge products. In fact, in series 9 and 10, where a 281 cc. decay tube was used, substantially greater reactivities were observed with ammonia at the lower pressures (Table XIX). It therefore appears safe to conclude that the excited molecules are formed only as a result of homogeneous atom decay*.

This result was, of course, anticipated (i) since a known metastable molecule (the A state) is the end product of luminous homogeneous decay, while a suspected metastable molecule (the X* state) may be formed by a collision-induced cross-over from the A state; (ii) since surface decay probably leads to a highly de-excited molecule (page 73); (iii) since any excited molecules formed in the discharge process would be dissociated at the high energy expenditures

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* The possibility that a fraction of the homogeneous decay by-passes the excited molecules is unlikely, in view of the conclusion reached in a later section (page 73) that all homogeneous decay goes by the same route. However, the possible formation of excited molecules in some instances of surface decay is less readily eliminated.

used*; and (iv) since the ratio $\Delta NH_3/HCN$ was observed to <u>increase</u> as [N] and pressure were simultaneously increased (Table XIX) or as [N] alone was increased (44), suggesting that the excited molecules were formed by a high-order mode of atom decay.

The different reactivities noted for ammonia with different poisons on the reaction vessel (series 10) may now be explained. In general, when a reactant does not interfere with the atom decay, e.g. it allows the afterglow to persist unchanged, the normal decay of the atoms in the reaction vessel would continue to produce excited molecules in accordance with equation [49], i.e.

$$[N_2^*] = k_2P[N]^2/4k_1$$

where k_1 depends on the poison. It therefore remains to show that the concentration of excited molecules would have the correct order of magnitude. Substituting $k_2 = 1.15$, $P = 2$ mm., and $[N] = 19.4$ µm/s. (from Table X), it follows that the amount of N_2^* formed in a reaction vessel poisoned with Na_2HPO_4, for which $k_1 \geq 4.66$, will be ≤ 0.79 µm/s. The value of k_1 for a surface poisoned with KCl may be assumed to be similar to that for HPO_3**, i.e. 1/6 the value for

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* It is possible that under conditions of only partial initial dissociation, or when the nitrogen is dissociated by means other than a condensed discharge, excited molecules may also be formed in the discharge process.

** Smith (53) found that the collision efficiency for H atoms was the same for surfaces poisoned with HPO_3 and KCl, though the assumption that this is true for N atoms as well is obviously open to question.

Na_2HPO_4. Hence, $[N_2{*}] \leq 6 \times 0.79 = 4.74$, and the additional $N_2{*}$ formed in the reaction vessel with KCl as poison will be $\leq$ 4 µm/s. Such an amount is consistent with the observed difference of about 2 µm/s. (Fig. 16) so that, provided the assumed efficiency of KCl is correct, there is no need to seek an effect of KCl on the reaction itself. (It will be noted that a necessary consequence of this conclusion is that ΔNH_3 values obtained with KCl, HPO_3, or any other efficient poison <u>on the reaction vessel</u> will be unsatisfactory for use in a theoretical treatment of the decay of $N_2{*}$ <u>in the decay tube</u> such as is given in a following section.)

The failure of mass-spectrometric studies (1, 2) to detect excited molecules may also be explained by reference to equation [49]. However in this case, the decay of the excited molecules is not justifiably neglected, nor is the time during which the molecules are formed sufficiently long for complete decay of the atoms as assumed in equation [49]. A high upper limit for $[N_2{*}]$ will therefore be obtained by the calculation. Using $k_2 = 1.115$, $P = 1$ mm., $[N] = 0.01$ mm., and $k_1 = 11.1 \times 1.68/0.8 \times 1/6 = 3.9$, where 1.68/0.8 is a correction for the difference in the radii of the decay tubes and 1/6 for the use of HPO_3 as poison, it follows that the amount of $N_2{*}$ formed was $\ll 7.4 \times 10^{-6}$mm., i.e. $\ll 0.00074\ \%$ of the total gas. It is therefore little wonder that excited molecules were not detected.

DECAY OF THE EXCITED MOLECULES

Since it has been established that the excited molecules are formed only by homogeneous atom decay, it should be possible to fit the measurements of ammonia destruction as a function of pressure which were obtained in series 9 and 10 (Figs. 15 and 16) to the relevant decay equation, i.e.

$$\frac{2[N_2^*]}{k_2tP^3} = \frac{[N]^2/P^2 - e^{-Kt}}{Kt - 2\ln P/[N]} \qquad [48]$$

Values of t (from k_1t and k_1) and lower limits of k_2 were obtained from Table XI. The term $2[N_2^*]/k_2tP^3$ was then evaluated, using only those ΔNH_3 values obtained with a reaction vessel poisoned with Na_2HPO_4 and using the factors to convert µm/s. to mm. as given in Table X. The terms $[N]^2/P^2$ and $2\ln P/[N]$ followed directly from the P/[N] values in Table X. Values of Kt and thence K were finally derived by trial-and-error solution of equation [48] (Table XXI), and the individual decay constants $(k_4 + k_5)$ and k_6 from the intercepts and limiting slopes of plots of K versus P^m, where m = 1 (Fig. 18). (A less satisfactory fit was obtained with higher powers of pressure). The decay constants, including the collision efficiency of the homogeneous decay, are as follows:

Quantity	Value at 55°C.*	Value at 400°C.*
$k_4 + k_5$	0.0 $sec.^{-1}$	0.0 $sec.^{-1}$
k_6	7.4 $mm.^{-1}sec.^{-1}$	11.4 $mm.^{-1}sec.^{-1}$
	2.5×10^{-16} A	7.9×10^{-16} A
m	1	1
Collision efficiency**	1.5×10^{-6}	3.4×10^{-6}

* A = $cc.molecule^{-1}sec.^{-1}$
** Using $\sigma = 3.84 \times 10^{-8}$cm.

TABLE XXI

Data used for the calculation of N_2* decay constants.

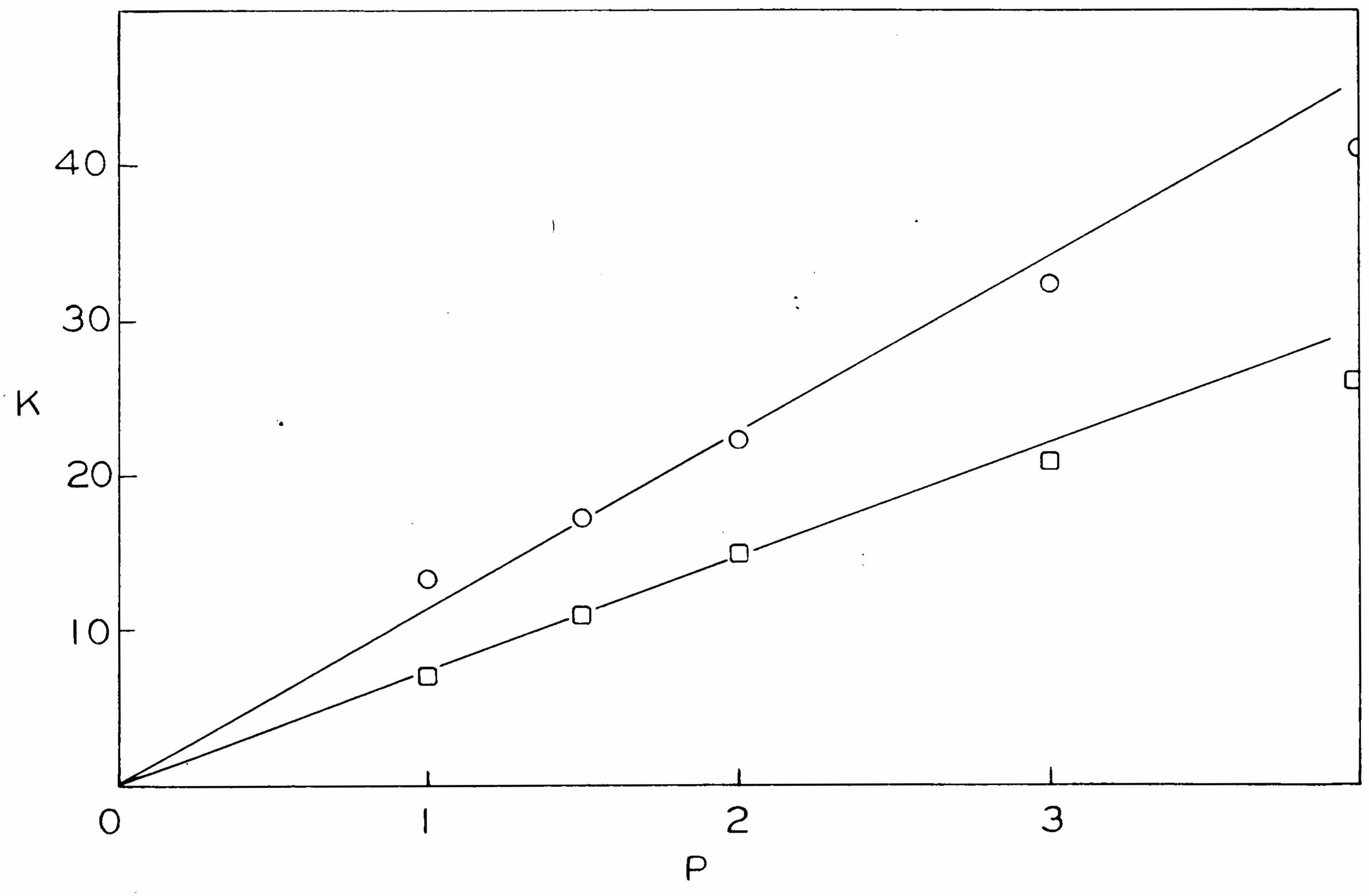
Pressure mm.	$[N_2*] = \Delta NH_3$* µm/s.	$2[N_2*]/k_2tP^3$	$[N]^2/P^2$	$2\ln P/[N]$	Kt	K $sec.^{-1}$
Temperature of decay tube: 55°C.; k_2 = 1.15; t = 0.198 sec.						
1.0	0.45	.0752	.0105	4.552	1.40	7.1
1.5	0.85	.0398	.00857	4.760	2.20	11.1
2.0	1.15	.0222	.00672	5.002	3.00	15.1
3.0	1.55	.00870	.00402	5.514	4.15	21.0
4.0	1.90	.00448	.00274	5.900	5.00	26.2
Temperature of decay tube: 400°C.; k_2 = 1.77; t = 0.0896 sec.						
1.0	0.60	.136	.0436	3.134	1.20	13.4
1.5	1.55	.0956	.0333	3.402	1.55	17.3
2.0	2.50	.0660	.0265	3.630	2.00	22.3
3.0	4.35	.0336	.0182	4.002	2.90	32.4
4.0	5.65	.0184	.0135	4.302	3.70	41.3

* Mean values from series 9 and 10 (Figs. 15 and 16).

Figure 18

Analysis of the data of series 9 and 10 in accordance with equation [48].

□ Series 9
○ Series 10


K
40
30
20
10
0
1
2
3
P

It must be emphasized that the decay constants are highly approximate owing to the necessity of taking limiting slopes and therefore over-weighting the less precise values of ΔNH_3 obtained at low pressures. Also, in view of the undefined form of K, the satisfactory fitting of the data to equation [48] was inevitable and does not constitute further proof of the presence of excited molecules nor of their mode of formation.

DISCUSSION

DECAY OF N ATOMS

The present work has confirmed, in agreement with Rayleigh (16), Buben and Schekhter (21), and Schekhter (22), that the surface decay of N atoms follows first-order kinetics. While this result was anticipated, it is perhaps significant that close similarities exist in the behavior of N, H, and O atoms. All exhibit first rather than second-order surface decay with collision efficiencies (γ) in the range 10^{-3} to 10^{-5}, activation energies (E) in the range 1 to 2 kcal.mole^{-1}, and values of 10^{14} to 10^{15}cm.$^{-2}$ for the number per cm.^{2} of surface species (see Table XI and page 18). It would therefore be expected that the mechanism of the surface decay of N atoms would be the adsorption mechanism which has been so successful in explaining the behavior of H atoms (24). This mechanism, it will be recalled (page 6), proposes that the gas phase atoms combine with a layer of atoms adsorbed on the surface. However Linnett and Marsden (25) have pointed out that at room temperature O atoms are only weakly adsorbed on glass. To explain the first-order decay they therefore suggested a slightly different mechanism according to which the gas phase O atoms combine directly with the structural oxygen of the glass or poison, with water of hydration, or with a surface layer of oxide (page 8).

Since there seems to be no information available on the adsorption of N atoms on Na_2HPO_4 or related solids, it is not possible to decide whether the surface layer responsible for the surface decay consisted of adsorbed atoms or a true surface compound (a nitride or nitrate).* Very indirect evidence in favor of the latter may lie in the observation (page 25) that active nitrogen reacted with heated KCl to create an intense reddish-orange glow such as appears to have been observed in the reaction of active nitrogen with HCl (41). However, whatever the origin of the layer, it evidently remains intact even at 400°C. so that it was valid to assume, in deriving equations [33] to [40], that first and second-order surface decay were not competitive.

The homogeneous decay of N and H atoms is perhaps less comparable than the surface decay, since the rate constants for N atoms (Table XI) appear to be an order of magnitude smaller than those for H atoms (Table I), in spite of the greater diameter of nitrogen. However, the difference is probably adequately explained by the steric factor shown by Berkowitz <u>et al</u>. (2) to be associated with the $N_2(^5\Sigma) \longrightarrow N_2(B^3\Pi)$ transition. It will be recalled that a special case is also presented by O atoms owing to the stability of ozone (equations [28]).

A positive temperature coefficient was observed for the N atom homogeneous decay constant. This was unexpected in view of Rayleigh's (15) observation of a negative coefficient in measurements of afterglow intensity between liquid air temperature and 100°C., and it is therefore possible that the results of the present work were subject to a large, systematic error. Perhaps the most likely source of such an error lies in the assumption of complete initial dissociation, since, had $[N]_o/P$ steadily decreased

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* It was stated on an earlier page that the decision does not affect the validity of equations [8] to [12].

as pressure was increased, the effect would have been indistinguishable from a pressure dependent mode of decay. However, no pressure dependence in $[N]_0/P$ was observed in the Wrede gauge measurements (Table VI B). Even if it did occur, such dependence should presumably have the same magnitude at all decay tube temperatures, so that the temperature coefficient (though not the actual constants) should remain unaltered. The positive temperature coefficient therefore appears to be real. Actually, the disagreement with Rayleigh's work is perhaps not serious, since the present work applies to a completely different temperature range (55 to 400°C.).

If the positive temperature coefficient observed by Robinson and Amdur (54) in the decay of H atoms could be attributed not only to the surface decay, but also to the homogeneous decay, the present results for N atoms could be considered to have good precedent.

DETAILS OF THE DECAY MECHANISMS

It was stated in an earlier section that a ^4S atom can only combine into $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, and $^7\Sigma_u^+$ molecular states, that the $^7\Sigma_u^+$ state of nitrogen is probably higher than the ^4S dissociation energy, and that the $^5\Sigma_g^+$ state of nitrogen is probably the precursor of the afterglow. Therefore, since it has been observed both by Rayleigh and in the present work* that the afterglow intensity remains unchanged in the neighborhood of various surfaces, both the transition complex and the final molecule formed in surface decay must be in the A or ground states. In making a

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* The apparatus used was constructed by Dr. A. Fontijn of this Department. It had a window suitable for observing reaction flames.

further decision between these two states, it will be noted that the excited molecules observed in the present work were apparently formed from homogeneous atom decay. Furthermore, since the surface layer responsible for the surface decay remained intact at 400°C., any molecules formed by surface decay would be expected to exist briefly in close association with the wall, and extensive de-excitation would result whatever the nature of the transition complex. It may therefore be concluded that, while the transition complex might be in the A state, the final molecule formed in surface decay is in the ground state. However, the matter is not proved beyond question.

With homogeneous decay there exists a similar choice of paths and it was, in fact, considered by Berkowitz _et al_. (2) that recombination into the $^5\Sigma$ state with subsequent afterglow emission accounted for only part of the decay. This conclusion was based on a comparison of the rate constant for luminous homogeneous decay ($k_2' = 4 \times 10^{-33}$; see page 4 (note)) with the rate constant for a three-body collision process ($\sim 10^{-32}$). However comparing k_2' with the _total_ homogeneous decay constant at 25°C. as obtained in the present work ($k_2 = 1.09$ to 1.94×10^{-33} (Table XI)), it appears that all homogeneous decay must give rise to afterglow since the constants are essentially equal. Actually a less tentative value of k_2' would be highly desirable.

Provided the various conclusions about surface and homogeneous decay _are_ correct, the mechanisms of N atom decay may be summarized as follows:

Surface decay:

$$\begin{aligned} N(^4S) + \text{surface} &\longrightarrow N(^4S)\text{-surface} \\ N(^4S) + N(^4S)\text{-surface} &\longrightarrow N_2(^x\Sigma)\text{-surface} \\ N_2(^x\Sigma)\text{-surface} &\longrightarrow N_2(^1\Sigma) + \text{surface} \end{aligned} \qquad [66]$$

where x may be 1 or 3 but not 5.

Homogeneous decay:

$$\begin{aligned} 2N(^4S) + N_2 \text{ (or N)} &\rightleftharpoons N_2(^5\Sigma) + N_2 \text{ (or N)} \\ N_2(^5\Sigma) + N_2 \text{ (or N)} &\longrightarrow N_2(B^3\Pi) + N_2 \text{ (or N)} \\ N_2(B^3\Pi) &\longrightarrow N_2(A) + h\nu \\ N_2(A) &\longrightarrow ? \end{aligned} \qquad [67]$$

A tentative elaboration of the last step will be made later.

RAYLEIGH'S PERSISTENT AFTERGLOW

The value of γ for N atom recombination on a surface poisoned with HPO_3 was calculated in the present work from the data of Rayleigh (16) to be about 2.7×10^{-8}. Such a value is several orders of magnitude below the value of 0.45×10^{-4} obtained from the data of Back (58) and the value for H atoms of 2×10^{-5} (53). Moreover the curved portion of Fig. 11 cannot be explained by the homogeneous decay term $-2k_2[N][M]/\ln 2$ neglected in equation [62], since this term was shown to be negligible compared with the surface decay term $-2k_1/\ln 2$. (Actually Rabinowitch (34) concluded that the curvature was consistent with the rate of homogeneous decay; however he assumed that the value of k_2 was 3×10^{-31}*, rather than 2×10^{-33} as found in the present work.) Provided Rayleigh's data are correct, they would therefore appear to indicate that, at the very low atom concentrations that would prevail after he had stored active nitrogen six hours, the surface decay began to shift from first to second order. Such intermediate-order surface decay would, of course, introduce curvature into a ln[N] versus time relation.** Furthermore, its rate could assume values ranging from the high first-order value to the very low second-order value (the latter being even lower than the rate of homogeneous decay (see page 9)), so would have the correct order of magnitude.

By this interpretation, rather than one based on homogeneous decay, the first-order surface decay constant should have been obtained, not from the slope as [N] —> 0, but from that as [N] —> maximum. It would then have been much closer to the value of 0.45×10^{-4} obtained from Back's data. It is possible that a detailed analysis of Fig. 11 would also yield the activation energy of deadsorption*** of N atoms from HPO_3, a quantity of great

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* This value is for 1 % initial dissociation (cf. 2) and is ten times that derived by Rabinowitch on the assumption of 10 % initial dissociation. However, whether the dissociation was 1 % or 10 % does not affect the argument.

** Rayleigh's data for an oil surface would also apply to intermediate-order surface decay, and the linearity of the ln[N] versus time relation (Fig. 4 of reference (16)) must therefore be only approximate.

*** Or "decomposition" in terms of the surface decay mechanism of Linnett and Marsden.

importance to an understanding of the behavior of N atoms. For example, its value would determine at what temperature or atom concentration second-order surface decay should appear and therefore under what conditions active nitrogen could best be stored.

CATALYTIC RECOMBINATION

Since homogeneous decay with N_2 or N as third bodies is closely related to homogeneous catalytic recombination, a comparison of the rate constants is of interest. The available constants, including the three-body collision rate ($2Z_3/n^3$, where n is the number of particles per cc.), are as follows:

Constant	Value $cc.^2 molecule^{-2} sec.^{-1} (\times 10^{33})$	Temperature °C.	Source
k_2	1.32 to 2.35	55	Table XI
$k_{2(C_2H_4)}$	13	75	page 57
$k_{2(CH_3CN)}$	186	160	(42)
$2Z_3/n^3$	73	75	(28)*

It is seen that homogeneous catalytic recombination is one or more orders of magnitude more rapid than homogeneous decay, and, in the presence of CH_3CN, even occurs at a slightly greater rate than three-body collisions.

* Glasstone states that to a first approximation $Z_3 = Z_2\sigma/\lambda$, where Z_2 is the number of two-body collisions per cc. per sec. In calculating Z_2 the values M = 14 and $\sigma = 3.0\times10^{-8}$ cm. (3) were used, though the slightly larger value $\sigma = 3.84\times10^{-8}$ cm. was used for σ/λ.

If steric factors were known it might be possible to estimate the relative stabilities of the N–M complexes formed in catalytic recombination and the N–N complex of homogeneous decay, i.e. the $^5\Sigma$ state. (The only steric factor available is a very tentative one for homogeneous decay (2)). However, considering the catalytic recombination processes alone, it seems permissible to conclude that, since the value of $k_{2(CH_3CN)}$ is greater than $k_{2(C_2H_4)}$, the stability of $N \cdot CH_3CN$ is greater than that of $N \cdot C_2H_4$. This is consistent with the observed low rate of HCN formation from CH_3CN *, and it is likely that an empirical correlation would enable a general prediction of catalytic recombination rates from reaction rates or vice versa.

Three types of N atom recombination have been observed to involve no afterglow and therefore to bypass the $^5\Sigma$ state: surface decay, the energy transfer assumed in the reaction of N atoms with HCl**, and homogeneous catalytic recombination. It is significant that, in contrast to homogeneous decay, where two free atoms form an N–N complex (the $^5\Sigma$ state), these processes all involve an N–M complex as in the homogeneous decay of O and I atoms (12, 13). In other words, it appears that, just as decay initiated by two free atoms <u>always</u> leads to the $^5\Sigma$ state (page 73), that in which one atom is initially complexed, whether to the wall or another molecule, <u>always</u> leads to the $^1\Sigma$ or $^3\Sigma$ states. With surface decay, a further restriction to the $^1\Sigma$ state has already (though only tentatively) been made.

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* The rate of HCN formation from CH_3CN is 3.60×10^{-16} cc.molecule^{-1}sec.$^{-1}$ (42) and from C_2H_4 is 3.69×10^{-14} (66).

** This reaction might be due to excited molecules (cf. page 63).

Such a restriction is obligatory for the HCl reaction from energy considerations.*

EXCITED MOLECULES

Reasonably satisfactory evidence that excited molecules are present in active nitrogen appears to have been obtained in the present work. In particular, it was shown that the molecules were formed only from homogeneous atom decay. However Back (58) has concluded from experiments in which it was attempted to reduce the decay time of active nitrogen that the excited molecules are a primary, rather than secondary, discharge product. (She found that the amount of ammonia destroyed continued to increase as the decay time was decreased). It is suggested that the apparent contradiction is due to the fact that Back sampled the active nitrogen from the _middle_ of the discharge tube _at low flashrates_ (14 $sec.^{-1}$). Accordingly there was ample opportunity for homogeneous decay to occur within the discharge tube. The fact that she observed the HCN formation from ethylene to fall off with decreasing decay time in a sigmoidal manner also means very little since (i) the reaction zone was unheated, (ii) there was extensive back diffusion, and (iii) flowrate plateaus were not obtained.

A further conclusion of the present work was that the only mode of decay exhibited by the excited molecules was homogeneous decay with first-power pressure dependence. This observation seems to be in general agreement with

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* The mechanism of the HCl reaction is believed to be $N + N \cdot HCl \longrightarrow N_2 + HCl^*$, $HCl^* \longrightarrow H + Cl$. If HCl* is to be identified with an electronically excited state, then it must lie at at least 4.43 eV. (i.e. $^1\Pi$), so that the N_2 formed would lie at, or below, 9.76 - 4.43 = 5.33 eV. This is lower than the level of the A state (6.2 eV.).

the expected behavior of the known (or suspected) metastable nitrogen molecules, i.e. the A and X* states.* In particular, parallels can be drawn between (i) the absence of radiative decay, the long life of the A state, and the inability of a harmonic, homonuclear vibrator to radiate; (ii) the non-zero homogeneous decay constant, the collision-induced cross-over suggested by Evans and Winkler (8) as being a mode of decay of the A state, the collisional deactivation which is necessarily important with homonuclear vibrators, and the mode of reaction to be expected with excited nitrogen molecules in general (energy transfer in collisions of the second kind); (iii) the very low collision efficiencies and the forbidden nature of the transitions involved with both the A and X* states; and (iv) the observed first-power pressure dependence, and the expected dependence for either an electronic cross-over or for the deactivation of an anharmonic vibrator. (Anharmonic vibrators might deactivate in one step due to a breakdown of the selection rules. See page 11.)

While this agreement lends considerable weight to the results that have been obtained, it appears to eliminate any possibility of identifying the excited molecules with one or the other of the A and X* states, at least with the data available. However it is likely that the decision could be made by a careful spectroscopic or mass-spectrometric study of active nitrogen at high concentrations. (The impossibility of detecting excited molecules at low active nitrogen concentrations was indicated earlier.)

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* Here the X* state is to be distinguished from low lying vibrational levels of the ground state. The latter would be comparatively inert.

In the meantime the final step in the homogeneous decay scheme begun on page 74 must remain ambiguous:

$$N_2(A) + M \xrightarrow{k_6} N_2(X^*) + M \qquad [68]$$

or

$$N_2(A) + M \longrightarrow N_2(X^*) + M \quad \text{(rapid)}$$
$$N_2(X^*) + M \xrightarrow{k_6} N_2(X) + M \qquad [69]$$

APPENDIX

A: ASSUMPTIONS IN THE DECAY EQUATIONS

The decay equations assume a number of simplifying conditions beyond the basic ones given on page 29. The use of a time-independent pressure, P, requires that there be no significant pressure gradient in the decay tube whether due to flow, heating, or dissociation. This is known to be true, especially when a constriction is present.* Axial diffusion, i.e. diffusion in the direction of flow, must transport an insignificant amount of mass compared with the flow. This is borne out by the following calculation: the maximum contribution by diffusion to the flow occurs initially when, at a pressure of 2 mm., it amounts to

$$- D\partial[N]/\partial t \cdot \partial t/\partial x \cdot A = 3.7\ \mu m/s. \qquad [70]$$

where $D = \bar{c}\lambda/3$; $\partial[N]/\partial t = (k_1P + k_2P^3)(n_\mu/P)$, n_μ = number of micromoles per cc. at a pressure P; $\partial t/\partial x = t_0/2\times 31.7$, t_0 is given by equation [30], 2 = factor to take dissociation into account, 31.7 = length of the decay tube; and A = cross-sectional area of the decay tube. Since the flow under the same conditions is 220 μm/s., diffusion can be neglected.** This would not necessarily be true at higher pressures owing to the greater value of $\partial[N]/\partial t$.

* With the discharge off and using the 26 cc. decay tube, the gradient was 0.5 % at 2.1 mm. and 2 % at 0.3 mm. With the discharge on (complete dissociation) the gradients increased to only 5 %. The gradients would be less with the 281 cc. decay tube as a result of both the greater diameter and the presence of the constriction.

** Steiner (52) has made a similar calculation to determine if diffusion could be neglected.

Radial diffusion, on the other hand, must eliminate any radial concentration gradient. A detailed treatment as given in Appendix D shows that this condition is realized at low pressures. The decay tube must be of uniform diameter so that k_1 will be constant. The use of plots extending over a pressure range requires that the flowrate of nitrogen vary directly with pressure, for only then will the linear velocity of the gas and thence the decay time be pressure independent. That this assumption is valid follows from the approximate linearity of Fig. 2, though, in contrast to the other effects, the validity <u>increases</u> with pressure. The effect of dissociation on the time of decay must also be pressure independent. This is shown in Appendix C to be true only at low pressures or large decay times. The use of an average decay tube temperature in calculating the time of decay (Appendix C) assumes that the temperature of the decay tube is uniform, a condition perhaps better realized at higher temperatures.

It may therefore be concluded that while the decay equations are not exact, they should be reasonably valid at lower pressures.

B: CONVERSION OF FLOWRATES TO PARTIAL PRESSURES

It has been shown that above about 0.30 mm. the relation between nitrogen flowrate and pressure is linear (Fig. 2) and can therefore be represented simply by

$$[N_2]_{\mu m/s.} = 59.0(P - 0.15). \qquad [29]$$

Neglecting the effect of dissociation, a relation applicable to N atoms <u>formed in the N_2 stream</u> follows as

$$[N]_{\mu m/s.} = 59.0([N]_{mm.}/P)(P - 0.15). \qquad [71]$$

However equation [71] must be corrected for the fact that with the apparatus used, dissociation brought about an increased flowrate rather than an increased pressure such that

$$\text{flowrate} \propto \frac{P}{P - [N]_{mm.}/2} \qquad [72]$$

This relation follows from the continuity equation given by Steiner (52). Substituting for $[N]_{mm.}$ in equation [72] the approximate value $[N]_{\mu m/s.}/59.0$ obtained from equation [71], and then using the result as a correction factor for equation [71], one obtains the desired relation:

$$[N]_{mm.} \approx \frac{[N]_{\mu m/s.}(P - [N]_{\mu m/s.}/118)}{59.0(P - 0.15)} \qquad [73]$$

APPENDIX

C: THE TIME OF DECAY

It has been shown that the average time of flow through the 281 cc. decay tube in the region 1 to 3 mm. is

$$t_o = 0.271 \times 298/T \text{ sec.} \qquad [30]$$

provided the nitrogen is undissociated. The increased flowrates arising from dissociation will reduce the time, so that it is necessary to find a relation between t_o and the true time t. Let x be distance measured along the decay tube, x_o the length of the decay tube, and v the linear flowrate in the absence of dissociation. Then, if there is no dissociation,

$$x_o/v = t_o \qquad [74]$$

while if there _is_ dissociation,

$$dx/dt = v/(1 - [N]/2P) \qquad [75]$$

While an expression for [N]/P as a function of t could be obtained from equation [37], and equation [75] then integrated, the result is too complex to be useful and is also pressure dependent. However, by neglecting homogeneous decay, [N] is given simply by $[N] = Pe^{-k_1 t}$, so that equation [75] integrates to

$$x_o/v = t + \ln 2/k_1 - e^{-k_1 t}/2k_1 \qquad [76]$$

Hence, on equating the two expressions for x_o/v given by equations [74] and [76], and rearranging, the desired relation is obtained:

$$k_1 = \frac{k_1 t + \ln 2 - \frac{1}{2}e^{-k_1 t}}{t_o} \qquad [77]$$

Equation [77] is necessarily valid only at low pressures (when homogeneous decay is of secondary importance) or at large decay times (when the entire effect of dissociation becomes less marked).

APPENDIX

D: RADIAL DIFFUSION

As a result of surface decay it is inevitable that a radial concentration gradient of some kind will exist, and that the surface decay will therefore be self-inhibiting. However such an effect has in the past been generally treated with such a rigid application of Fick's laws that a simple method of correcting for radial diffusion has apparently not been obtained. This was the case, for example, in the work of Steiner (71) on H atom decay.

Now, as the formal approach involves assigning variability to the "shape" of the gradient, it was natural to try an approach in which a constant "shape" was used.

It will therefore be necessary to determine the best constant shape. Consider a cylindrical system containing a gaseous mixture which includes atoms subject to surface decay. The effect of the surface decay will, of course, be to lower the atom concentration at the immediate surface. This effect will be counteracted by diffusion from the interior, the relevant law being (72)

$$u(R,t) = \frac{2u(R,0)}{r} \sum_{m=1}^{\infty} \frac{J_o(a_m R)}{a_m J_1(a_m r)} e^{-Da_m^2 t} \qquad [78]$$

where u(R,t) is the atom concentration, r is the radius of the system, R is the variable corresponding to r, J_o and J_1 are Bessel functions, $a_m r$ is the mth zero of J_o, and $D = \bar{c}\lambda/3$. However provided Dt is sufficiently large, the law simplifies to

$$u(R,t) = \frac{2u(R,0)}{a_1 r} \frac{J_o(a_1 R)}{J_1(a_1 r)} e^{-Da_1^2 t} \qquad [79]$$

so that the gradient it describes is essentially conical. That is, as seen along a diameter, it appears as an inverted "V". Such a gradient has a constant shape and it is evident that it will correspond fairly closely to the true gradient in cases where diffusion is rapid or decay is slow. More specifically the time required for a small amount (e.g. 1 %) of decay must be comparable to or greater than

$$t' = r^2/8.2\bar{c}\lambda.* \qquad [80]$$

This condition can be shown to hold in the present work, where the average time for 1 % decay during the initial 75 % of decay at 55°C. and 2 mm. is 0.0012 sec., compared with t' = 0.0020 sec.

A simple expression for the effect of radial diffusion when the surface decay is first-order can now be readily obtained by assuming a conical gradient. Equating the rate of decay to the rate of diffusion in the manner indicated by Steiner (71), one obtains

$$2 \times \bar{c}[N]'\gamma/4 = -D\partial u(R,t)/\partial R = (\bar{c}\lambda/3r)([N]'' - [N]') \qquad [81]$$

where [N]' is the atom concentration at the surface of the decay tube and [N]" that at the center. The necessity of

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* This relation was derived by putting $\exp(-Da_1^2 t)$ equal to a suitable multiple of $\exp(-Da_2^2 t)$, in particular $e \times \exp(-Da_2^2 t)$.

the factor of two on the left side was indicated in an earlier section. It is readily shown that the average atom concentration in a cylindrical system, [N], is related to [N]' and [N]" by

$$[N] = \frac{1}{3}[N]'' + \frac{2}{3}[N]' \qquad [82]$$

Combining equations [81] and [82],

$$[N]' = [N]/(1 + \gamma r/2\lambda) \qquad [83]$$

where the term $(1 + \gamma r/2\lambda)$ is the desired correction for radial diffusion. The rate constant of surface decay is therefore more correctly given by

$$k_1' = k_1/(1 + \gamma r/2\lambda) = k_1/(1 + \alpha P) \qquad [84]$$

where k_1 is given by equation [8] and $\alpha = 3.16 \times 10^4 \gamma r/T$ mm.$^{-1}$ if $\sigma = 3.84 \times 10^{-8}$ cm.

If similar arguments are applied to a spherical system, where

$$[N] = \frac{1}{4}[N]'' + \frac{3}{4}[N]' \qquad [85]$$

then $\alpha = 3\gamma r/8\lambda = 2.37 \times 10^4 \gamma r/T$ mm.$^{-1}$. It can be proven that, provided $\alpha P \ll 1$, no correction is necessary to the rate constant of homogeneous decay in either a cylindrical or spherical system.

The treatment given is general and can be applied to experimental situations other than the present one, e.g. static systems. However it would not be valid for a short-lived species formed some distance from a surface. In such a case a very marked pressure effect would be expected (cf. page 39). As far as the present work is concerned, since α would only amount to 0.043 mm.$^{-1}$ (for r = 1.68 cm., γ = 2.65x10^{-4}, T = 328°K.), the correction for radial diffusion can be neglected, at least at the lower pressures. However the correction could become quite important at low temperatures or high pressures.

APPENDIX

E: CATALYTIC RECOMBINATION

Since the majority of the experiments described in the present work were conducted at high reactant flowrates, it is sufficient in deriving equations for catalytic recombination to treat the case of complete consumption of the N atoms. In so doing it will be assumed, as proven by Forst *et al.* (42), that $[N]_e$ is independent of the lifetime of NM.

Scheme 1 (cf. equations [51]). The basic differential equations are

$$d[N]/dt = -(1+p)k_7[NM] - k_8[N][NM]$$

and

$$d[N]_e/dt = +(n+p)k_7[NM].$$

Hence

$$d[N]/d[N]_e = -\frac{1+p}{n+p} - k_8[N]/(n+p)k_7 \qquad [86]$$

Equation [52] now follows by integrating equation [86] from $[N] = [N]$, $[N]_e = 0$ to $[N] = 0$, $[N]_e = [N]_e$.

Scheme 2 (cf. equations [53],

$$d[N]/dt = -(1+p)k_7[NM] - k_9[NM]$$

$$d[N]_e/dt = +(n+p)k_7[NM]$$

$$d[N]/d[N]_e = -\frac{1 + p}{n + p} - k_9/(n + p)k_7$$

$$[N]_e = \frac{(n + p)[N]}{1 + p + k_9/k_7} \qquad [87]$$

<u>Scheme 3</u> (cf. equations [54]),

$$d[N]/dt = -(2 + p)k_{10}[N][NM] - k_8[N][NM]$$

$$d[N]_e/dt = + k_{10}[N][NM]$$

$$d[N]/d[N]_e = -(2 + p) - k_8/k_{10}$$

$$[N]_e = \frac{[N]}{2 + p + k_8/k_{10}} \qquad [88]$$

<u>Scheme 4</u> (cf. equations [55]),

$$d[N]/dt = -(2 + p)k_{10}[N][NM] - k_9[NM]$$

$$d[N]_e/dt = + k_{10}[N][NM]$$

$$d[N]/d[N]_e = -(2 + p) - k_9/k_{10}[N]$$

$$[N]_e = \frac{[N]}{2 + p} - \frac{k_9}{(2 + p)^2 k_{10}} \times \ln(1 + k_{10}(2 + p)[N]/k_9) \qquad [89]$$

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

(1) A method is described for investigating both the surface and homogeneous decay of N atoms, in which the atom concentration reaching a reaction vessel after a period of decay in a decay tube is measured as a function of pressure by the HCN produced from ethylene or ethane at high reactant flowrates and elevated temperatures. It was necessary to operate under conditions of complete initial dissociation to enable a theoretical interpretation of the results. The apparatus was essentially a modification of the fast-flow system used by Winkler and co-workers.

(2) The theory relating to atom decay has been developed in detail, including a treatment of the factors which might affect its validity. Particular attention has been given to an estimate of the effect of a diffusion-limited radial concentration gradient on the rate of surface decay.

(3) The results indicated that the surface decay of N atoms proceeded by a first-order mechanism between 55^{o}C. and 400^{o}C., with the collision efficiency for an Na_2HPO_4 surface essentially constant at 2.7×10^{-4}. The value of the activation energy of the surface decay was 1.02 kcal.mole^{-1} and the number per cm.^{2} of surface species was 1.90×10^{14}. Depending on the temperature and whether or not N_2 and N were considered equivalent as third bodies, the homogeneous decay rate constant varied from 1.3×10^{-33} to 13×10^{-33} cc.^{2}molecule^{-2}sec.$^{-1}$ Homogeneous decay was therefore concluded to be of secondary importance below about 2 mm. pressure under the prevailing conditions.

(4) Similarities in the surface decay of N, H, and O atoms were pointed out, although it was not possible to decide whether N atom surface decay involved an adsorption mechanism (as with H atoms) or one in which a layer of nitride or nitrate is formed on the surface (by analogy with the O atom mechanism). The homogeneous decay of N atoms, on the other hand, appeared to be an order of magnitude slower than that of H atoms, and an unexplained positive temperature coefficient was observed.

(5) From a comparison of the rate constant for homogeneous decay at 25°C. (1.09 to 1.94×10^{-33}) with the rate constant for the production of afterglow obtained by Berkowitz et al. (2) (4×10^{-33}), it was concluded that all homogeneous decay gives rise to afterglow. Evidence was also presented that the molecules formed in the surface decay of N atoms were in a highly de-excited state.

(6) Calculations made from the data of Rayleigh (16) and Back (58) concerning the surface decay of N atoms on HPO_3 indicated that at the low atom concentrations prevailing in Rayleigh's experiment the surface decay began to shift from first to second-order.

(7) As an extension of the study on the decay of N atoms, general treatments have been made of the theory relating to the formation and decay of excited molecules, and that relating to catalytic recombination of atoms under conditions of complete consumption of the atoms.

(8) Evidence was presented that the low reactivity observed for ethylene at room temperature was entirely due to homogeneous catalytic recombination of the N atoms with a rate constant of 13×10^{-33} at 75°C. Such a rate is an order of magnitude greater than that of homogeneous decay at a similar temperature.

(9) On the other hand it was concluded that N atom attack, whether or not accompanied by catalytic recombination, did <u>not</u> account for the low reactivity of ammonia and ethane, both at room temperature. This was considered good evidence that excited molecules were present.

(10) To determine the mode of formation of the excited molecules a modified apparatus was designed in which the reaction vessel was attached directly to the discharge tube near an electrode. The results indicated that the excited molecules were formed only by homogeneous atom decay. It was therefore possible to show that the two mass-spectrometric studies of active nitrogen that have been made (1,2) could not have detected excited molecules even if the molecules did not decay at all.

(11) Tentative values of the rate constants for the decay of the excited molecules indicated that the only mode was homogeneous decay with a first-power pressure dependence. However it was not considered possible, on the basis of the information available, to identify the excited molecules with one or the other of the two known (or suspected) metastable nitrogen states, i.e. the vibrationally-excited ground state and the $A^3\Sigma$ state. For example, it was pointed out that homogeneous decay

with a first-power pressure dependence could equally well characterize an anharmonic vibrator or an electronic state decaying by a collision induced crossover.

(12) Several points of general interest in active nitrogen work were brought out. In the construction of the apparatus it was shown advantageous to precede the reaction vessel by a constriction, to use Na_2HPO_4 as the poison, and to use electrodes machined from solid aluminum. The method of measuring reactivities as a function of pressure under conditions of complete initial dissociation was shown capable of identifying or disproving both catalytic recombination and N atom reaction, and should therefore be of use in the study of reactions of uncertain mechanism such as that of active nitrogen with HCl. The variability in the amount of heat generated by the reaction, or carried down from the discharge tube and connecting tube, was shown to be sufficient to eliminate catalytic recombination under some conditions but not under others.

(13) Since complete dissociation of hydrogen is readily brought about, the present method would be particularly suited to the study of H atom decay.

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