

THE REACTIONS OF ACTIVE NITROGEN
WITH HYDROGEN SULPHIDE AND CARBON DISULPHIDE

by

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INTRODUCTION

The brilliant yellow afterglow shown by nitrogen activated in a discharge tube was first reported by Lewis (1) who studied its behaviour in 1900. He observed that the yellow emission persisted for several seconds after the discharge was stopped, and was able to show that this afterglow produced a banded spectrum identical with part of the N_2 spectrum.

In 1911, R. J. Strutt (2) referred to the yellow, glowing gas from the discharge through nitrogen as "active nitrogen", in the first of a series of papers in which he discussed its physical and chemical properties. He demonstrated that active nitrogen was very reactive chemically; metallic and non-metallic vapours were converted to nitrides, and various hydrocarbons and substituted hydrocarbons yielded hydrogen cyanide as the main product. The reactions with organic compounds showed the emission spectrum of the cyanogen radical within the reaction flame.

Strutt's pioneer work aroused considerable interest, and was followed by contributions from many workers, particularly physicists. This interest has continued actively from Strutt's time up to the present, with increasing emphasis on the chemistry of active nitrogen. The existence of nitrogen atoms and various molecular nitrogen species in the

upper atmosphere, the knowledge that hypersonic high-altitude vehicles will encounter and indeed even produce these entities, and the possibility that atomic nitrogen, along with other free radicals in general, might some day serve as a useful rocket fuel, have prompted widespread and intensive study of active nitrogen.

In line with the two disciplines involved, the introduction to this thesis has been arbitrarily divided into two parts to discuss the physical and the chemical aspects of active nitrogen. For a brief, generalized treatment of the physical aspects of active nitrogen, the reader is referred to a recently published review article by Jennings and Linnett (3).

THE PHYSICAL ASPECTS OF ACTIVE NITROGEN

Nature of the Active Species

Perhaps no product of an electrical discharge has been the subject of more controversy than active nitrogen. Its properties have been variously ascribed to normal (2) and excited atoms (4, 5), to N_2^+ ions (6), to electronically excited N_2 molecules (7, 8), and to the nitrogen analogue of ozone, N_3 (9, 10).

In the last fifteen years, new and more refined experimental methods have helped considerably to elucidate

the nature of active nitrogen, and the reliable evidence available at present indicates strongly that the main chemically reactive species in active nitrogen is the nitrogen atom, predominantly in the 4S ground state. The evidence for this conclusion has been discussed by Evans (11) and Jennings and Linnett (3), and need only be summarized here.

The oldest theory of active nitrogen is that the active substance in the afterglow is nitrogen atoms. This hypothesis was put forward by Strutt in 1911 (2), and by Wrede (12), who used the gauge that bears his name to demonstrate that the afterglow did in fact contain an appreciable concentration of atoms. A Wrede gauge, however, cannot distinguish between ground state and excited atoms.

The first positive evidence of the presence of ground state atoms in the afterglow was obtained by Heald and Beringer (13), who examined the electron paramagnetic resonance spectrum of active nitrogen. Their results indicated the presence of 4S ground state atoms only, but the authors stated that concentrations of excited atoms (2D and 2P) up to 1% of the total atom flux would not be detected by this method. The main conclusion from this work, that active nitrogen consists predominantly of 4S ground state atoms, has quite recently been confirmed by Foner et al. (14), and by Cole and McConnell (15), using the same experimental method.

Mass spectrometric investigations on the afterglow have recently been reported by Jackson and Schiff (16), and by Kistiakowsky and co-workers (17). These authors agree that active nitrogen contains ^4S ground state nitrogen atoms.

In neither of these investigations was there any evidence for excited atoms. However, Tanaka (18) has recently found evidence for ^2D and ^2P atoms in active nitrogen from absorption spectra in the vacuum ultraviolet, and Broida (19) has obtained similar evidence from a spectral analysis of the glow emitted by solid active nitrogen at a temperature slightly above that of liquid helium ($28\text{--}35^\circ\text{K}$). In each case, however, the flow rate of excited atoms was estimated to be about 1% of the total atom concentration; this value would be below the limit of detection by the mass-spectrometric technique.

In their study, Jackson and Schiff (16) obtained some indication that a second species might co-exist with the ^4S ground state atoms in active nitrogen, and they postulated that this second species might be either an excited nitrogen molecule, or N_3 . A second chemically active species has also been inferred by Evans and Winkler (20), from chemical studies, and these authors suggested that it might be a vibrationally excited ground state nitrogen molecule. This idea has received support from the work of Kaufman and Kelso (21).

The idea of a second active species in the nitrogen afterglow has generally been accepted. But its presence cannot be said to be as firmly established as that of the ^4S ground state nitrogen atom, and its exact nature is still a matter of some doubt. A possible origin is quite readily visualized, and the subject will be considered in greater detail in a later section.

At a very recent symposium on free radical stabilization (22), Wall, Brown and Florin, and Jen, have suggested that, although nitrogen atoms are present in active nitrogen, the N_3 molecule might be the main constituent under some conditions. While a full account of this work has yet to be published, it presumably refers to the $\text{N}_2\text{-N}$ complex, which is believed to exist on a surface cooled to 4.2°K (23).

The Decay of Active Nitrogen

According to the Wigner-Witmer Correlation Rules (24) two ^4S atoms, interacting by virtue of their exchange forces, can form only $^1\Sigma_g^+$, $^3\Sigma_\mu^+$, $^5\Sigma_g^+$, and $^7\Sigma_\mu^+$ molecular states. Kelly (25) has suggested that all ^4S nitrogen atoms stabilize into the $^5\Sigma_g^+$ state, but Jennings and Linnett (3) have pointed out that these states, for nitrogen, will be formed in the ratio 1:3:5:7. Any ^2D and ^2P atoms present will recombine into states other than these four. However,

because of the small concentrations involved, their role is quite minor, and may be neglected.

Of these molecular states, the $1\Sigma_g^+$ is the normal ground state molecule, and can suffer no further energy decrease; the $3\Sigma_u^+$ and the $5\Sigma_g^+$ (if stable) states are excited, and the $7\Sigma_u^+$ state is totally repulsive. Ultimately, the $3\Sigma_u^+$ and $5\Sigma_g^+$ states will revert to the normal $1\Sigma_g^+$ state, and this reversion can be by one of several paths, involving energy loss by homogeneous or heterogeneous collision and by radiation, all of which are probably followed in an active nitrogen afterglow.

Because of this complexity, it is convenient to discuss the decay of active nitrogen in relation to the following:

- a) Homogeneous decay with emission of afterglow
- b) The complete spectrum of the afterglow
- c) Heterogeneous decay of active nitrogen.

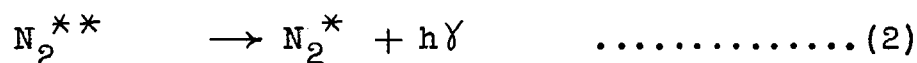
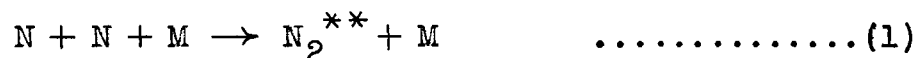
a) Homogeneous Decay with Emission of Afterglow

Each new theory, in attempting to explain the properties of active nitrogen, has generally included within its framework a decay scheme for the afterglow, based on experimental evidence accumulated by Rayleigh and others (26, 27). This evidence is as follows:

- 1) The process giving rise to the afterglow is second order in nitrogen atoms, and first order in molecular nitrogen.

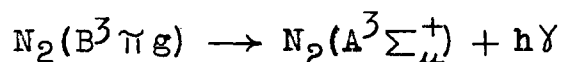
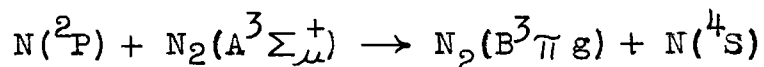
ii) The process has a negative temperature coefficient.

On the assumption that active nitrogen contained atoms, as had been postulated by Strutt in 1911, Miss Sponer (28) suggested that the decay mechanism was

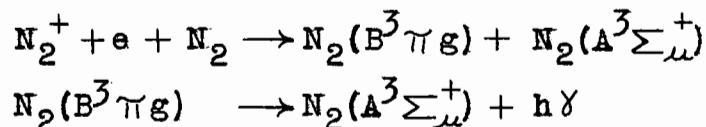


Here, (1) is rate-controlling, (2) is the actual afterglow emitter, N_2^{**} and N_2^* represent electronically-excited nitrogen molecules, (N_2^* being in a state from which no visible afterglow is emitted) and M denotes a third body in the gas phase.

However, the idea that the union of normal atoms accounted for the afterglow was discarded when later and, as it turned out, erroneous evidence led to a lower value for $D(N_2)$. In an attempt to explain their experimental results, Cario and Kaplan (4) proposed an alternative mechanism:



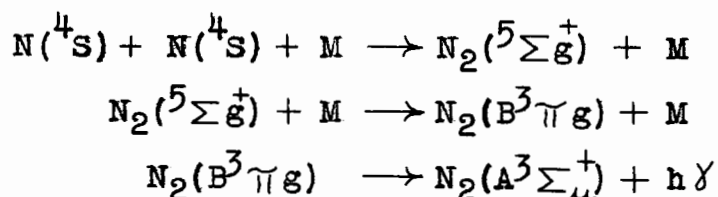
Later, Mitra (6) proposed the mechanism:



However, Mitra later abandoned this theory (29), and the Cario-Kaplan mechanism also fell into disfavour when, contrary to expectation from the theory, Herzberg et al (30) and Worley (31) obtained experimental evidence which showed the absence from the afterglow of an appreciable steady-state concentration of the A state molecules.

For quite some time it was felt that Miss Sponer's simple two-step mechanism of atomic recombination explained quite adequately the decay of active nitrogen with emission of the afterglow. However, the ultimate realization within the past decade that $D(\text{N}_2)$ is almost certainly 9.76 ev. (32) and that active nitrogen contains ^4S ground state atoms, has prompted a further examination of nitrogen atom decay kinetics.

Following an earlier postulate by Gaydon (33), Cario and Reinecke (34) suggested a new mechanism to explain afterglow emission. These authors suggested that two ^4S nitrogen atoms could be stabilized by collision into the $5\Sigma_g^+$ molecular state, which, by an inverse predissociation, may transfer to the $\text{B}^3\pi\text{g}$ state with subsequent emission of the afterglow. The complete mechanism would then be:

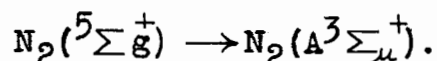


This suggestion has been analyzed quite fully by Gaydon (24) and by Kistiakowsky et al. (17). Gaydon finds the crucial first step to be fully in accord with the Wigner-Witmer Correlation Rules. Kistiakowsky concludes that the mechanism is more logical than that of Miss Spomer, and points out that Reinecke's suggestion has within it the implication that the $^5\Sigma_g^+$ state of nitrogen is slightly stable. In support of this implication, Kistiakowsky cites the work of Herzberg (35) and Broida (19).

Herzberg in 1951 pointed out that if $D(\text{N}_2) = 9.76 \text{ ev.}$, then experimental evidence shows that the $^5\Sigma_g^+$ state is not purely repulsive. Since it is now generally agreed that $D(\text{N}_2)$ is 9.76 ev. , it is presumably safe to assume, on the basis of Herzberg's reasoning, that the potential energy curve for this state has a slight minimum in it. Lippincott et al. have calculated (36) that while the potential energy curve for the $^5\Sigma_g^+$ state might not have an appreciable well in it, it is at least not completely repulsive.

Broida's evidence was derived from a spectroscopic study of active nitrogen condensed on a surface at 4.2°K .

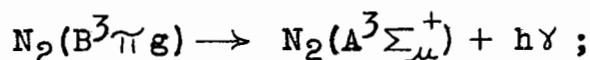
A series of ten bands in the spectral range $\lambda 3572\text{\AA} - \lambda 6390\text{\AA}$ was attributed by him to the transition



It was pointed out at the time that this assignment was quite tentative; and in fact it has just recently been withdrawn (37). It is still too early to assess the effect of this withdrawal upon the Cario-Reinecke mechanism, but the mechanism does appear to be based on sound theoretical conclusions. Presumably spectroscopists will now attempt to find a band system, the head of which can be attributed unequivocally to the $5\Sigma_g^+$ state.

b) The Complete Spectrum of the Afterglow:

An analysis shows that the afterglow contains bands of at least two (and possibly three) separate transitions. The most important of these - and the one known for the longest time - is the band corresponding to the transition,



which is strongest in the orange, the red, and the yellow-green regions of the visible spectrum. This band is actually the afterglow emission characteristic of active nitrogen, and

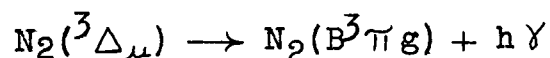
consists of almost all the visible bands of the first positive system of nitrogen, with certain ones selectively enhanced (38). These enhanced bands originate mainly in the 10th, 11th, and 12th vibrational levels of the B state; to a smaller extent, bands also originate from the 2nd, 3rd, 4th and 6th vibrational levels. These latter bands lie predominantly in the photographic infrared region, and the accurate measurement of their wavelengths has been difficult.

In 1957 Kistiakowsky and Warneck (39) suggested that these latter bands should not be considered to arise from B state vibrational levels, but should be regarded as a new band, related to neither the B nor the A state. In the wording of the paper,

the new band probably originates via the $5\Sigma_g^+$ state, through a collision-induced radiationless transition to a state Y, in competition with the transitions to $B^3\Pi_g$.

Following Linnett (3), these Y state molecules presumably radiate to a further state Z.

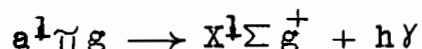
Following publication of this postulate, LeBlanc et al. (40) confirmed the existence of these bands (found also by Kaplan (41)), but thought, contrary to Kistiakowsky, that the lowest state was probably $B^3\Pi_g$. From theoretical reasoning, they suggested as the origin of the bands the transition



but pointed out that an unequivocal assignment of the upper state could not be made on the basis of their experimental results. Quite recently, Bayes and Kistiakowsky (42) have re-measured some band intensities using both N_2^{14} and N_2^{15} .

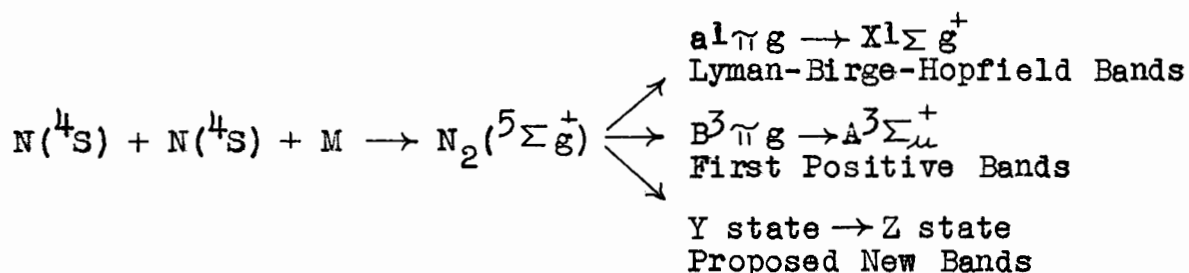
At the moment, the situation is quite indefinite, and relatively little is known about this new band system. Presumably further experiments are in progress, in an attempt to characterize this particular emission.

In addition to the above bands, Tanaka has found in the afterglow a weak system of bands in the vacuum ultra-violet region (18). This particular emission has been attributed to the Lyman-Birge-Hopfield System, corresponding to the transition



Bands due to the NO molecule are occasionally present in the blue and ultra-violet regions of the spectrum, owing to the presence of small quantities of oxygen as an impurity in the nitrogen.

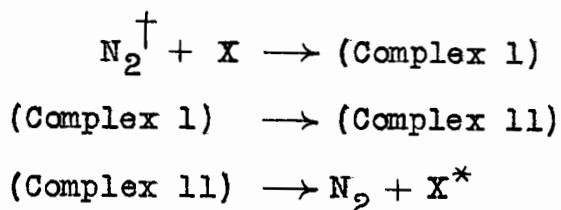
Jennings and Linnett (3) have depicted a complete emission scheme for pure nitrogen, using the Cario-Reinecke proposal for the decay:



Fortuitous two and three body collisions will produce excited molecular nitrogen species distributed among a large number of electronic configurations. With the exception of the transitions mentioned, all excited molecules must revert to the X state in the only way possible, i.e. by collision.

To explain some experimental results obtained from a study of the active nitrogen-ammonia reaction (see later), Evans and Winkler (20) pointed out that electronic de-excitation of these nitrogen molecules did not necessarily demand a concomitant loss of vibrational excitation. They therefore postulated vibrationally excited ground-state molecules as a second species in co-existence with ^4S nitrogen atoms in active nitrogen. These will be designated hereafter as N_2^\dagger . It was suggested that these N_2^\dagger molecules might possess excitation energies greater than 8 ev.

Evans and Winkler developed a scheme by which, for many molecules, collision with N_2^\dagger , followed by resonance transfer of much of this vibrational energy, could lead to dissociation of the collision partner. This suggestion might be pictured schematically as:



In normal circumstances, X^* would contain enough energy to cause dissociation of at least one bond within the molecule, and evidence to be presented later will show that as much as 6.5 ev. energy might be transferred by such a process.

Evans and Winkler were led almost inexorably to the idea of a vibrationally-excited molecule when they assumed the correctness of the experimental evidence then available that no electronically excited molecule had a lifetime sufficient for it to reach the reaction vessel in appreciable quantities. It is now believed, however, that this assumption is not valid and recent work has tended to show that an electronically-excited molecule might live sufficiently long to act as a second species, under the usual conditions of chemical reactions with active nitrogen. Thus for the lifetime of the $\text{A}^3\Sigma_u^+$ state, Lichtin (43) has set a lower limit of 0.01 seconds, in agreement with estimates derived from the experimental results of other workers (44). Muschlitz and Goodman (45) in 1953 suggested a lifetime of the order of 2×10^{-4} seconds for the A state, but their work has been criticized by Lichtin,

who identifies the lifetime assigned by them to the A state with that of the higher lying $a^1\pi_g$ state. Kenty (46) has found some evidence for two long-lived species in active nitrogen, and Lofthus and Mulliken (47) have theorized that these might be the $^3\Delta_\mu$ and $^3\Sigma_\mu^-$ states. This last is only conjecture, and more experimental data are needed before the lifetime of even the A state can be settled.

c) Heterogeneous Decay of Active Nitrogen:

Strutt first suggested that active nitrogen is destroyed at the wall of the containing vessel, as well as in the gas phase (48), and several studies have since shown that this heterogeneous reaction is strongly dependent upon the surface condition of the wall. In particular, it has been found that while an exceptionally clean glass wall will quickly destroy the afterglow, the effect of the wall can be minimized if it is coated with a suitable substance. This "suitable substance" is generally referred to as a poison.

Rayleigh (49) found sulphuric or metaphosphoric acid to be very efficient poisons, while Willey (50) showed paraffin to be rather less efficient. Kelly (25) has recently shown that the efficiencies, as poisons, of ZnCl_2 , As_2O_3 , H_3PO_4 (85%), BiCl_3 , Na_2HPO_4 , B_2O_3 , and KCl , decrease in the order named. There was some indication that the low efficiency

of KCl might have been due in part to a reaction between heated KCl and active nitrogen.

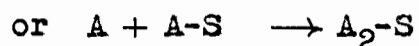
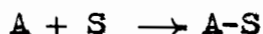
In addition to actual pretreatment of the walls of the containing vessel, the early history of active nitrogen is replete with evidence that certain chemicals, introduced in small amounts as impurities into the nitrogen before it was discharged, can affect the duration and intensity of the afterglow. In a review of his early work, Strutt (51) in 1915 lists the efficiencies of different substances for this purpose in order of decreasing efficiency: H_2S , H_2O , CO_2 , CO , C_2H_2 , C_2H_4 , CH_4 , O_2 , Hg , Cl_2 , H_2 , Ar , He , N_2 . He found H_2S to be so effective that the entire vessel had to be cleaned with aqua regia before its effect could be eliminated completely. Strutt also found that these impurities showed their maximum effect at a concentration corresponding to 0.1% of the nitrogen. Bonhoeffer and Kaminsky (52) confirmed this latter result, and in a later paper, with H_2S as one of the impurities, concluded that the spectrum of the afterglow was independent of the nature of the impurity (53).

According to Willey (50), the relative efficiencies of CO_2 , N_2O , CO and N_2 , for intensifying the afterglow, decrease in the order named.

For quite some time controversy existed as to the exact effect of these additives on active nitrogen. In particular, considerable debate revolved about the effect of oxygen.

However, it is now accepted that these impurities exert their influence on the walls of the containing vessel; in some cases by a simple absorption onto the walls, in other cases by reaction with active nitrogen to produce a substance which, when deposited onto the wall, can act as a poison.

Sufficient evidence is now available to show that nitrogen atoms decay on the surface by a first-order process (49, 54), in conformity with the results obtained for hydrogen atoms (55) and oxygen atoms (56). This result (which does not depend on the wall being poisoned) means, according to Shuler and Laidler (57) that the rate-controlling step must be either



depending on whether the available active centers (S) are sparsely or almost completely saturated respectively with the atomic species (A). Shuler & Laidler suggest that, as regards hydrogen atom recombination, the poisoning effect of water on a glass surface might be attributed simply to a reduction in the number of active sites available, this decrease resulting from a physical adsorption of water vapour

on the glass. But this can serve as only a partial explanation for only one poison.

At the present time, no definite conclusions can be reached concerning the nature of the A-S complex. Linnett and Marsden (58) have suggested, tentatively, that chemical interaction between a gaseous oxygen atom and an oxygen atom incorporated in the glass might play some part in the surface decay of oxygen atoms.

THE CHEMICAL ASPECTS OF ACTIVE NITROGEN

The Reactions with Organic Molecules

Since 1949 a number of papers have appeared from this laboratory discussing the reactions of active nitrogen with a varied group of organic molecules. This work was begun, and is being continued, in the hope that the nature of the reactive component(s) in active nitrogen might be elucidated from the products and kinetic behaviour of such reactions. The initial paper of the series (59) described the reaction of active nitrogen with ethylene, and discussed a reaction mechanism in which nitrogen atoms was assumed to be the sole reactive species. A number of compounds have since been studied; these have included saturated and unsaturated straight-chain hydrocarbons, up to and including some C_{14}

compounds; cycloparaffins, up to and including cyclopentane; partially and totally chlorinated alkanes, up to and including propyl chloride, and carbon tetrachloride, respectively; methyl cyanide; and methyl amine.

For many of these compounds a number of similarities in their reactions with active nitrogen can be listed:

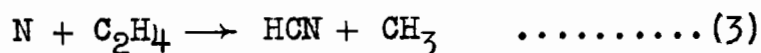
- a) Excepting some of the chlorinated compounds, by far the major product for each reactant is hydrogen cyanide.
- b) This HCN yield varies with temperature up to a limit, generally about $250^{\circ}\text{C}.$, above which a further temperature increase has no appreciable effect.
- c) No organic compound thus far studied has produced HCN in an amount greater than that obtained from the reaction with ethylene at high temperature.
- d) Depending upon the reactant involved, and excluding methane, smaller amounts (relative to the HCN yield) of other hydrocarbons, e.g., CH_4 , C_2H_4 , C_2H_2 , C_4H_{10} , etc. have been found, together with minor amounts of $(\text{CN})_2$ and sometimes small quantities of NH_3 .
- e) Wrede gauge (12) estimates of nitrogen atom concentrations are comparable with those derived chemically by determining the yield of HCN from the ethylene reaction at high temperatures.
- f) The yields of $(\text{CN})_2$ and NH_3 , when these are present

in the products, generally pass through a maximum.

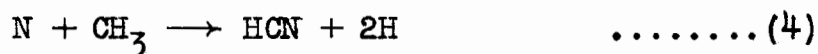
g) All results obtained to date, with organic molecules, can be satisfactorily explained on the basis that the reactive species in active nitrogen is atoms, at a concentration equal to the yield of HCN from the ethylene reaction above the limiting temperature, as defined by (b) above.

A comprehensive review of these reactions has recently been published by Evans, Freeman and Winkler (60). In this paper is postulated a unified mechanism to explain the results obtained in the various studies, on the assumption that the attack is by nitrogen atoms only. This unified mechanism is discussed in terms of some C_3 hydrocarbons; but since ethylene is the only organic reactant used in the present study, the probable mechanism of its reaction with active nitrogen will be described.

Versteeg and Winkler (61) have shown the products of the ethylene-active nitrogen reaction to be: hydrogen cyanide (75%), ethane (10%), methane (9%), acetylene (3%) and cyanogen (2%). Very little polymer is formed. These results are explained on the basis that the initial reaction is

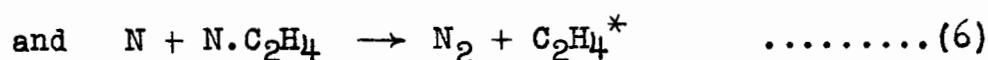


The methyl radical so formed is then considered to react rapidly with a further nitrogen atom

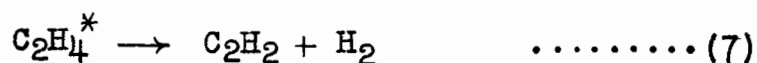


Many of the H atoms formed in (4) will recombine, but some must play a part in the formation of ethane, by hydrogenation of ethylene, while the methane probably occurs by hydrogenation of methyl radicals.

The unified mechanism suggests further that cyanogen and acetylene are formed as by-products of nitrogen atom recombination. The sequence is suggested to be



followed subsequently by



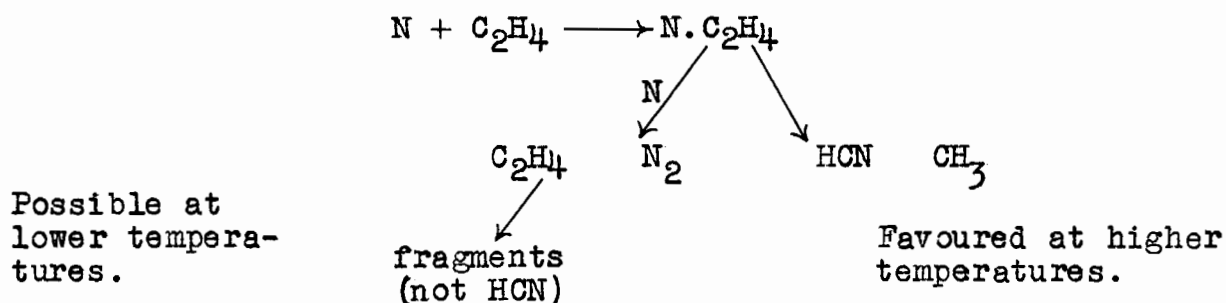
or alternatively by





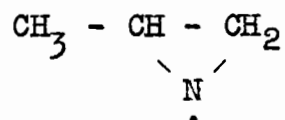
Since reaction (3) involves both a change of spin and the migration of a hydrogen atom, Evans et al. suggest that an activation energy will be associated with it. This implies that the $\text{N.C}_2\text{H}_4$ complex initially formed will have an appreciable lifetime, and Forst, Evans and Winkler (62) have reasoned that this lifetime might be long enough for reaction (6) to occur. If this were to happen the excited ethylene molecule so produced could not decompose to yield HCN, and hence the yield of HCN would not be a measure of the available nitrogen atoms. A rise in temperature, however, would favour decomposition of the complex, to yield HCN until, at a sufficiently high temperature, no complexes would survive long enough for reaction (6) to proceed.

A complete schematic for the initial step would then be

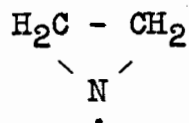


The process depicted by (5) and (6) is generally referred to as "catalytic recombination", and it implies that the concentration of nitrogen atoms can only be determined accurately (by reaction with ethylene) in a region where catalytic recombination is negligible, i.e., above the limiting temperature, as defined previously.

It is natural to speculate on the structure of the $N.C_2H_4$ complex. Trick and Winkler (63) quite early suggested that in the reactions of active nitrogen with unsaturated hydrocarbons the complex might have a cyclic structure. These authors suggested, in fact, that the complex involved in the reaction of active nitrogen with propylene might be



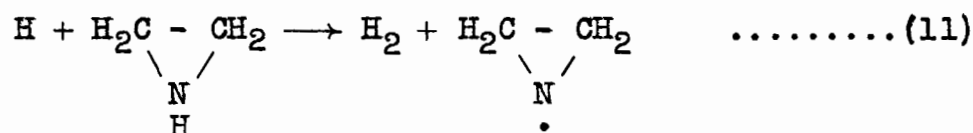
and this structure has been accepted as seemingly reasonable by Evans et al. (60). By inference, then, it might be assumed, without support evidence, that the $N.C_2H_4$ complex has the structure



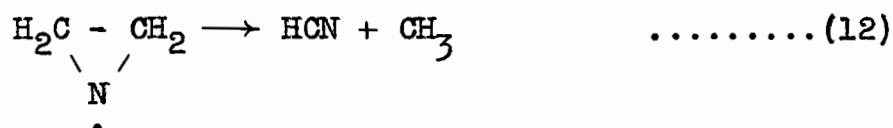
In fact, supporting evidence is not lacking, because Jamieson and Winkler (64) in 1956 showed that the ethylene-

active nitrogen complex might be simulated by hydrogen atom attack on ethylenimine. In this work, the reaction of atomic hydrogen with ethylenimine produced considerable amounts of HCN as the main product, with smaller amounts of methane and some C₂ hydrocarbons, assumed to be ethylene and ethane.

The formation of HCN was explained on the basis of a two-step mechanism:



followed by



The formation of methane and the C₂ hydrocarbons were explained on the basis of secondary reactions involving the methyl radical.

The similarity of reaction (12) to reaction (3) is at once obvious, and this paper by Jamieson and Winkler has considerably strengthened the suggestion that the N.C₂H₄ complex is cyclic.

The Reactions with Inorganic Molecules

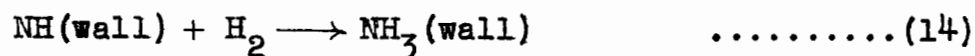
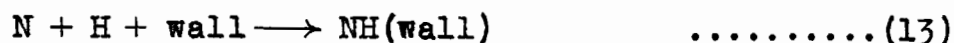
Much of the early work in the chemistry of active nitrogen was concerned with its reactivity towards inorganic compounds, and a number of papers were published in which the

flames of various reactions were analyzed spectroscopically, e.g. (65) and (66). Many of these studies were quite qualitative, and need not be discussed here unless sulphur-containing compounds are involved. In a few of the earlier investigations, however, attempts were made to obtain quantitative information, and these will be described, together with the results of more recent investigations.

Hydrogen

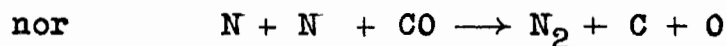
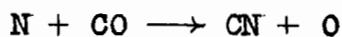
Willey and Rideal (67), Lewis (68) and more recently Kistiakowsky and Volpi (69) have reported that hydrogen does not react with active nitrogen. The last named authors report that ammonia was not formed at either room temperature, or 300°C. Steiner reports that in this reaction a small amount of hydrazine is produced (70). In 1955 Varney (71) reported that the reaction did produce a small amount of ammonia. However, Kistiakowsky and Volpi have pointed out that Varney's results could very well be due to back-diffusion of hydrogen into the discharge tube. This appears to be a reasonable suggestion since Varney reports that the reaction between active nitrogen and methane produced amines, and some oily polymers, whereas studies in this laboratory have shown HCN to be by far the major product (72). Quite possibly Steiner's result might also be explained in this manner.

On the other hand it has been amply verified that active nitrogen, reacting with atomic hydrogen, does produce ammonia (67, 73, 68). The results of Dixon and Steiner (74) suggested that part of the ammonia was formed heterogeneously, and the authors postulated that the yield of NH_3 might serve as an index of the available surface area. The most satisfactory mechanism appears to be



Oxides of Carbon

Carbon Monoxide: Contrary to the conclusion of Willey and Rideal (67), Reinecke (75) and more recently Broida and Heath (76) have claimed that red and violet bands of the CN radical are emitted by mixtures of active nitrogen and carbon monoxide. On the other hand, Kistiakowsky and Volpi (69) obtained no such emission in their work, and found no mass spectrometric evidence for a chemical reaction. They concluded that the positive results of other investigators were caused by some organic impurities in the carbon monoxide used. This is quite probable, since neither:



is thermodynamically favourable.

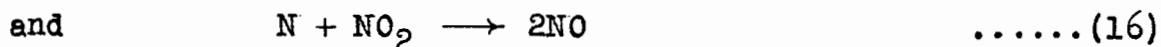
Carbon Dioxide: Willey and Rideal (67) have reported that carbon dioxide does not react with active nitrogen. The only effect observed was dilution of the afterglow, thus confirming the initial observation of Strutt (2).

The failure of carbon dioxide to react has recently been demonstrated also in this laboratory (77). At neither room temperature, nor at 400°C. was a reaction flame observed, nor did the afterglow disappear, except for a momentary disturbance when the carbon dioxide first entered the reaction vessel. At high carbon dioxide flow rates the afterglow was somewhat diminished, but the opposite effect seemed to occur at low flow rates.

Oxides of Nitrogen

Nitric Oxide and Nitrogen Dioxide: Following the pioneering work of Spealman and Rodebush (78), the reactions of active nitrogen with nitric oxide and nitrogen dioxide have been investigated by Kistiakowsky and Volpi (69), Harteck

and Dondes (79) and Verbeke (80). All these authors are agreed that nitrogen atoms react initially by



followed by reactions involving the primary products.

In the work by Verbeke (80), however, 50% more nitric oxide was destroyed than could be accounted for stoichiometrically on the basis of available nitrogen atoms, as estimated by the yield of hydrogen cyanide from the active nitrogen-ethylene reaction at high temperature. Since a chain can scarcely be responsible for this effect, Verbeke concluded that nitric oxide reacts not only with nitrogen atoms, but also with metastable nitrogen molecules. On the basis of the available experimental evidence, however, he was unable to determine the mode of excitation of these molecules, i.e., vibrationally or electronically excited.

Verbeke's suggested mechanism included, in addition to (15), the reaction



followed immediately by



and reaction (18) has inherent in it the suggestion that these excited nitrogen molecules could transfer 6.49 ev. of energy to the nitric oxide molecule.

Nitrous Oxide: Verbeke (80) and Kistiakowsky and Volpi (81) are agreed that nitrous oxide reacts with active nitrogen to less than 5%, in the temperature range 25°C. - 280°C.

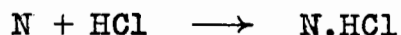
The reactivity of the oxides of nitrogen towards active nitrogen is important from the viewpoint of upper atmosphere research studies, and a good deal more work has still to be done to allow unequivocal mechanisms to be established.

Hydrogen Halides

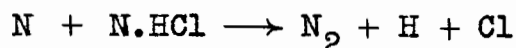
Willey and Rideal (67) in 1927 reported hydrogen iodide and hydrogen bromide to be attacked by active nitrogen, but hydrogen chloride to suffer no decomposition whatever. Ewart and Rodebush (82) found that the iodide and the bromide gave flames with active nitrogen, but the chloride merely destroyed the afterglow below the point of entry.

Wiles and Winkler (83) have recently studied the reaction between active nitrogen and hydrogen chloride. These authors found this compound to be destroyed during the

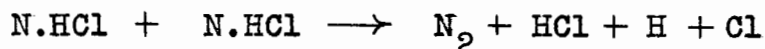
catalytic recombination of nitrogen atoms. This decomposition was pictured schematically as



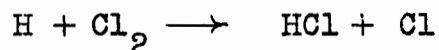
followed either by



or, at high HCl flow rates, by



Secondary processes followed these initial steps, and the decomposition was somewhat complicated by several back reactions, the most important one being



Ammonia

Following upon the earlier work of Dixon and Steiner (84), Freeman and Winkler (85) have studied the reaction of active nitrogen with ammonia. The reaction produced only nitrogen and hydrogen, but ammonia was destroyed to the extent of only one-sixth the concentration of nitrogen atoms, as estimated by the yield from the high temperature ethylene reaction. In addition, the destruction appeared to be

independent of temperature, when the simultaneous destruction of NH_3 by hydrogen atoms, formed during the reaction, was taken into account.

These results could only be explained on the basis that active nitrogen contains two reactive species, one of which is capable of reacting with ammonia, but not with ethylene. Freeman concluded that this second species must be a metastable nitrogen molecule. As mentioned previously, Evans and Winkler later suggested (20) that this second species might be a vibrationally excited ground state molecule, but this is open to question.

Freeman's conclusions have been fully substantiated in a more recent study by Kistiakowsky and Volpi (69), who used a mass spectrometer to identify and estimate the reaction products. They found that, although the nitrogen atom concentration remained unchanged, the afterglow process was quenched, though not completely, by ammonia. In accord with the hypothesis of Freeman and Winkler (85), this quenching was suggested to be due to a reaction between ammonia and excited nitrogen molecules, probably in the $\text{B}^3\Pi_g$ state. Even more recent work by Kelly (25) has shown that the species responsible for the destruction of ammonia is probably formed by

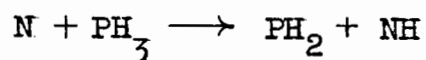
decay of nitrogen atoms. However, the exact mode of excitation of these metastable molecules could not be determined.

It would be reasonable to suppose that ammonia and nitric oxide are destroyed by the same metastable molecule, and in this respect it is worth noting that a $A^3\Sigma_u^+$ molecule need only be in its fourth vibrational level to possess sufficient energy to decompose nitric oxide. At the same time, more than enough energy would be available to initiate decomposition of ammonia. This, however, does not explain the partial quenching of the afterglow by ammonia.

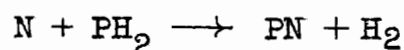
The exact mode of decomposition of NH_3 by active nitrogen is still uncertain, for which reason it is proposed to re-examine the reaction as a function of N_2 pressure in the near future.

Phosphine

On the basis of the results for ammonia, it might be suggested that phosphine should also react only with the second species in active nitrogen. Accordingly, the active nitrogen-phosphine reaction was recently studied in this laboratory by Wiles and Winkler (86). However, the experimental results did not give evidence of a second species. Rather it appeared that the initial step was the thermodynamically favourable hydrogen abstraction reaction:



followed by attack on the PH_2 radical by a second nitrogen atom to yield phosphorous paranitride and hydrogen.



Ammonia was not a product of this reaction, and Wiles and Winkler attributed this to the occurrence of



to the exclusion of



Reactions with Sulphur-containing Compounds

Sulphur:

In the first of a series of papers on active nitrogen, Strutt (2) reports that sulphur, sublimed into a stream of active nitrogen, extinguished the yellow afterglow and produced a blue glow. A green deposit was formed on the wall. In a later paper (87), he found that if the sublimate was recovered and boiled in potash, ammonia was produced, thus indicating that a nitride had been formed. He suggested that this nitride was nitrogen sulphide.

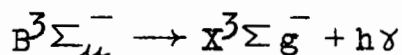
Moldenhauer and Zimmermann have found (88) that nitrogen activated in a discharge tube in the presence of sulphur deposited a black (in thin layers, blue-black) substance on the wall. Exposed to the air, this substance was at first somewhat sticky, but soon became hard. By fractional crystallization and analysis, this black deposit was found to consist of: a yellow compound, N_4S_4 : a red substance, N_2S_5 : and a deep black amorphous powder, NS_2 , or possibly $(NS_2)_x$. The authors were unable to decide on a mechanism to explain the formation of these compounds.

Strutt and Fowler (65) in 1912 investigated the blue glow of the active nitrogen-sulphur flame, and this investigation was continued much later by Fowler and his students (89, 90). These workers have found that the spectrum of this blue glow was banded, consisting of a succession of some thirty principal bands, degraded to the red, and very evenly distributed between $\lambda 4700A$ and $\lambda 2829A$. Little or no continuum was present, and the bands ended abruptly at the lower wave-length limit. Chhabra and Luthra (91) also observed a blue flame when sulphur reacted with active nitrogen, but few details of the spectrum were published.

The blue glow has also been observed by Strutt when "ozone" (in actual fact, oxygen atoms) reacted with sulphur (92),

and in a mixture of hydrogen and hydrogen sulphide under rather extreme experimental conditions (93). In this latter case the spectrum of the glow was exactly equivalent to that obtained in the reaction of active nitrogen with sulphur vapour, and Strutt concluded from this that the colour was due, essentially, to the presence of sulphur. He suggested that the sulphur was in a "peculiar" state.

This conclusion has been verified by Christy and Naudé (94), who have shown that the spectrum is derived from an allowed transition of the S_2 molecule



corresponding to the Schumann-Runge bands of oxygen. In this transition, the B state is excited by 4.04 ev. relative to the X(ground) state (95), and, as with oxygen, dissociation of sulphur in the B state would promote one of the sulphur atoms to an excited state.

In their discharge tube, Christy and Naudé used either pure sulphur, or hydrogen sulphide, but the spectra, from either emission or absorption, were identical.

Hydrogen Sulphide:

Strutt and Fowler have reported (65) that the spectrum obtained when H_2S was introduced into active nitrogen was

identical with that given by sulphur in the same medium. In a later paper, Strutt reports (87) that the hydrogen sulphide-active nitrogen reaction yields a light yellow deposit "which consists, at all events in part, of ordinary sulphide of nitrogen."

Strutt also found (92) the "ozone"-hydrogen sulphide reaction to give a flame identical with that observed in the "ozone"-sulphur reaction.

Sulphur Dichloride:

Strutt reports (87) that the behaviour of SCl_2 in active nitrogen is similar to that of H_2S .

Carbon Disulphide:

Strutt has studied (87) the behaviour of CS_2 in a stream of active nitrogen. A blue deposit was observed to form on the wall of the reaction vessel, and this he attributed to polymeric nitrogen sulphide, $(\text{NS})_x$. A brown-coloured deposit appeared on the chilled surface of a pump trap cooled with liquid air, and he suggested that this was the polymeric carbon monosulphide, $(\text{CS})_x$, obtained previously by Dewar and Jones (96). Strutt postulated the initial reaction to be



In his paper, Strutt made no mention of the explosive properties of $(CS)_x$, as reported by Dewar and Jones.

Spectroscopically, the active nitrogen-carbon disulphide reaction has been studied by Strutt and Fowler (65), and Fowler and Vaidya (89). Strutt and Fowler observed two groups of bands in the spectrum. The first consisted of the same bands as observed with sulphur or H_2S in active nitrogen, although they were only well developed on the red side of $\lambda 3700A$. The second group consisted of bands in the region $\lambda 2920A - \lambda 2550A$, but Fowler and Vaidya ascribed these to the presence of some sulphur monoxide. The only spectroscopic evidence for the presence of carbon was that afforded by a weak band of the CN radical at $\lambda 3883A$.

From the published work, it appears that no continuum was present in the active nitrogen-carbon disulphide reaction, and that the colour of the reaction flame was exactly the same as that observed in the reaction of sulphur or H_2S . It is possible, however, that a continuum was present but submerged in the background, and hence ignored by Fowler and Vaidya, who were interested mainly in the S_2 bands.

THE PRESENT PROBLEM

The only active nitrogen reaction studied to date that seems unequivocally to proceed by hydrogen atom abstraction is the reaction with PH_3 (86).

The present problem was conceived in the possibility that hydrogen abstraction might also occur in the active nitrogen- H_2S reaction, although this reaction should presumably be slightly endothermic.

The results obtained from the H_2S reaction suggested that the study of another sulphur-containing compound might prove profitable. The logical choice for this second study was carbon disulphide, especially so in view of the unreactivity of its sister compound, carbon dioxide, and a study of the CS_2 - active nitrogen reaction forms a second part of the thesis.

EXPERIMENTAL

MATERIALS

Nitrogen, of 99.9% purity, (Dominion Oxygen Co. Ltd.) was passed through copper turnings maintained within the temperature range $390^{\circ}\text{C}.$ - $425^{\circ}\text{C}.$, to remove residual oxygen, and thence through a liquid-air trap to remove possible traces of water, carbon dioxide, etc.

Hydrogen sulphide (98.5% pure, from Matheson Chemical Co.) was subjected to two bulb-to-bulb distillations, the first and last fractions being rejected in each case. This was followed by three complete cycles of thawing, freezing and pumping, which was followed in turn by distillation from an acetone-dry ice slurry. The gas finally obtained was sufficiently dry that it gave no indication of reaction with a clean mercury surface.

Analysis of a sample of hydrogen sulphide purified in this manner showed that, within experimental error, the gas was free of ammonia.

In the later stages of the work with hydrogen sulphide, a sample of higher initial purity (99.5%) became available. After treatment by the purification scheme outlined above, this sample gave results identical with those obtained using the initially 98.5% pure gas.

Ethylene (99% pure, Ohio Chemical Co.) was also treated with two bulb-to-bulb fractionations, followed by a distillation from an acetone-dry ice slurry.

Carbon disulphide (Merck and Co., reagent grade, conforming to A.C.S. specifications) was cycled four times through a treatment which consisted of cooling it to $-78.5^{\circ}\text{C}.$, followed by partial evacuation (10 minutes) and warming (to room temperature) to remove air and volatile hydrocarbons. The liquid was dried by passage as a vapour through granules of activated alumina.

In the temperature range $-23^{\circ}\text{C}.$ $-+6^{\circ}\text{C}.$, the vapour pressure of carbon disulphide purified in this manner agreed within experimental error with published vapour pressures (97,98).

To prevent its attack upon stopcock grease when experiments were not in progress, the purified carbon disulphide was stored at liquid-air temperature. The liquid was never cooled directly from room to storage temperature, experience having shown that any attempt to do so, with any practical amount of liquid, usually caused the storage vessel to break. Consequently a vacuum distillation procedure was used so that carbon disulphide froze directly from the vapour into the solid state.

Apiezon L was used as stopcock lubricant during the work with hydrogen sulphide, while Dow Corning Silicone Grease

was found to be satisfactory for the studies with carbon disulphide.

APPARATUS

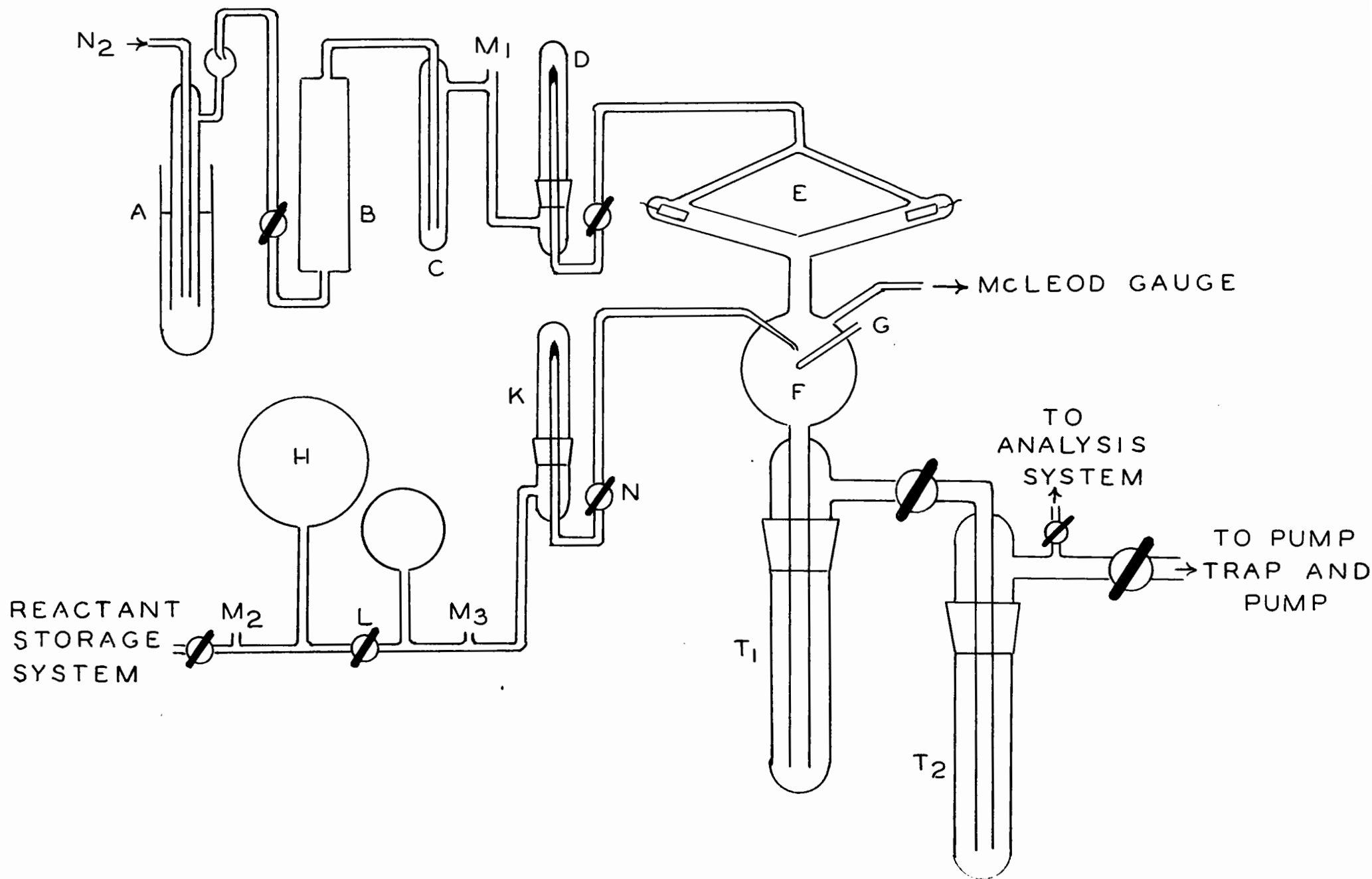
The apparatus, depicted diagrammatically in Fig. 1, was a fast-flow system of the Wood-Bonhoeffer type, constructed of Pyrex glass.

Tank nitrogen, after passage through a manostat A, copper furnace B, and cold trap C, was drawn through a capillary flowmeter D, into the discharge tube E, where much of it was dissociated by a condensed discharge. Under the action of the pump, and emitting the golden-yellow colour commonly associated with active nitrogen, a mixture of molecular nitrogen and its discharge products streamed down into the reaction vessel F, a 500 ml. bulb fitted with a thermocouple well G, and a reactant inlet. The second reactant entered the flow system at this point.

The second reactant passed from a calibrated volume, H, to the reaction flask through flowmeter K, the rate of flow through this latter being dependent upon the pressure behind it, measured with manometer, M₃. This backing pressure was freely variable and the capillary jet within the flowmeter could be replaced, if necessary, with the result that a wide

FIGURE 1

Diagram of Apparatus



range of reactant flow rates was available. By bleeding gas into the system through a scratched stopcock L, the backing pressure could be maintained reasonably constant during the course of an experiment. From the duration of the experiment and the pressure change within the calibrated volume, determined by measurements made before and after an experiment, an average reactant flow rate could be estimated.

The gas mixture from the reaction vessel passed into two traps, T_1 and T_2 , which could be cooled with liquid air or other refrigerant.

The discharge tube, constructed from 28 mm. O.D. tubing, and with each of its arms approximately 310 mm. long, was bent so that it could be poisoned without wetting the electrodes. These latter were machined from solid aluminium stock 70 mm. long, with an outside diameter of 18 mm. (less at the end of attachment), and drilled to a depth of 40 mm., with a hole 11 mm. in diameter. Two set screws were used to affix the electrodes to lengths of B. & S. 54 gauge tungsten wire, which were in turn sealed into the discharge tube.

The discharge tube and reaction vessel were poisoned with an aqueous 2% phosphoric acid solution. This solution was drawn into the discharge tube and allowed to drain slowly, after which the discharge tube and reaction vessel were evacuated. The reaction vessel was then heated to approximately

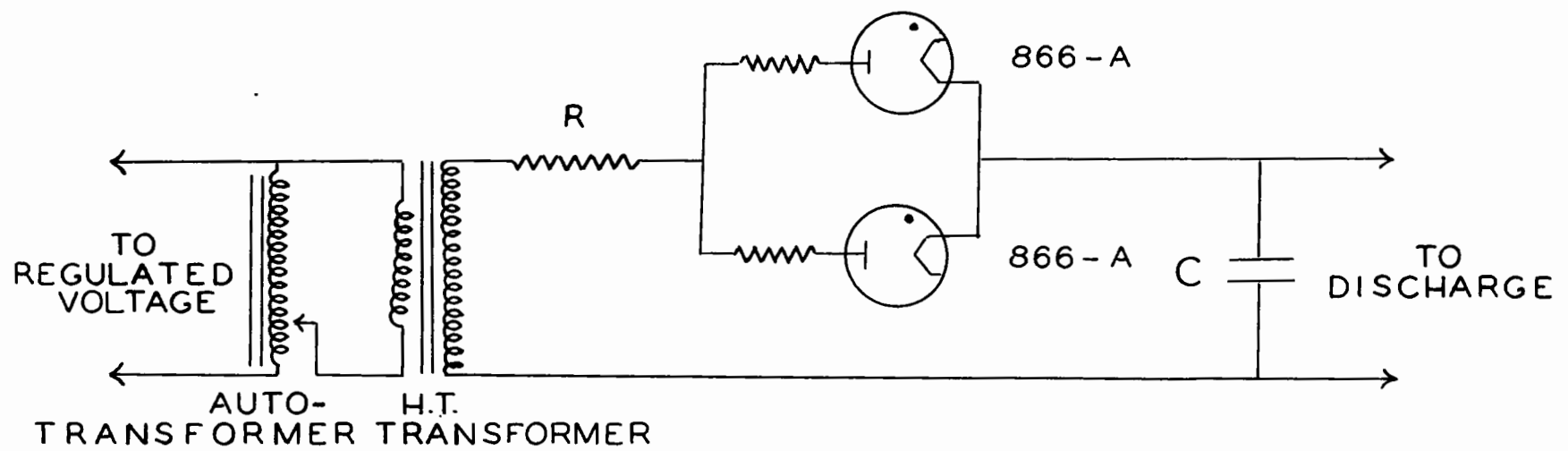
350°C., and held at this temperature for about one hour. This procedure was adopted since it has been reported (55) that metaphosphoric acid is a stable poison only after it has been thoroughly dried.

A Cenco Hypervac "23" pump, capable of an ultimate vacuum of 2×10^{-3} mm., was used throughout the investigation. With a pressure of 770 mm. behind the nitrogen flowmeter, this pump produced a nitrogen pressure within the system of 1.15 mm., corresponding to a molecular nitrogen flow rate of 110×10^{-6} moles/sec. at 25.5°C.

The electrical circuit used to produce a condensed discharge across the discharge tube is shown schematically in Fig. 2. It was comprised of two half-wave rectifiers, which served to charge a $2\mu\text{f}$ capacitor, C, to a voltage sufficient to cause rapid ionization within the discharge tube. At this point the charge was dissipated in a quick flash between the electrodes, to be followed immediately by a new charging cycle. The charging rate was limited by two 5000Ω resistors, and could be varied by an autotransformer in the primary of the plate transformer. In this work the flash rate was about 8 per second.

FIGURE 2

Diagram of Electrical Circuit



PROCEDURE FOR A TYPICAL EXPERIMENT (with reference to Fig. 1)

Several hours previous to a group of experiments, furnace B, and when necessary a similar furnace surrounding the reaction vessel, were turned on, and allowed to reach a steady-state temperature; both these temperatures were recorded. Ordinarily the reactant flow system, nitrogen flow system, and reaction vessel were evacuated until the entire system was at the pump's ultimate vacuum. Cold trap C was immersed in liquid air.

These preliminaries dispensed with, tank nitrogen, and a volume of the second reactant sufficient for several experiments, were admitted to their respective flow systems. The pressure backing the nitrogen flowmeter was adjusted to 770 mm. by the dibutyl phthalate manostat, A. The discharge was twice activated, each time for 4-5 minutes, to clear the electrodes of any possible contamination. Then, regardless of the reactant in use, two experiments to "condition" the walls of the reactant vessel followed, each lasting 100 seconds, and at an approximate average flow rate of 10×10^{-6} moles/sec. No attempt was made to use these experiments to advantage; they were regarded solely as part of the

preliminary work each day.

The pressure backing the reactant flowmeter K was adjusted to provide the desired flow rate. Product trap T_2 was cooled with liquid air, the nitrogen flow was started, and the discharge activated. The temperature within the reaction vessel, measured by the thermocouple, quickly began to rise, but reactant was not admitted until this temperature had reached a certain (arbitrary) value depending upon the wall temperature of the vessel. This temperature rise normally took from 3-5 minutes, and served as a check on the behaviour of the occasionally contrary electrical circuit. If the rise was in any way abnormal, the experiment was not continued.

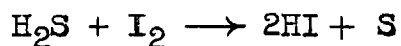
The actual experiment was started by opening stopcock N, and was allowed to proceed for an accurately measured length of time, usually 100 seconds. For flow rates below 3×10^{-6} moles/sec., however, the experiment lasted for 300 seconds. The temperature within the reaction vessel during the experiment was measured at the 50 second mark, regardless of the duration of the experiment.

The reaction was stopped by shutting off the reactant flowmeter, the discharge, and the nitrogen flowmeter, in that order. Pumping was continued until an ultimate vacuum was

achieved, usually about 5 minutes, and then product trap T₂ was isolated from the system, to permit distillation and subsequent analysis of the reaction products.

ANALYSIS

Hydrogen sulphide was analyzed by a method described in Scott (99). Unconsumed reactant was distilled from the product trap into a removable absorber containing frozen out-gassed aqueous 15% sodium hydroxide, in which solution hydrogen sulphide is, of course, completely soluble. The absorber was then removed from the system, warmed to room temperature, and opened to the atmosphere. The solution was acidified, and immediately a measured (excess) volume of standard iodine solution was added. The reaction



went quickly to completion, and the excess iodine was then back-titrated with standard thiosulphate solution, using starch as indicator.

This scheme of analysis was checked by doing "blank" experiments, these being experiments under actual operating conditions, except that the nitrogen discharge was not activated.

The hydrogen sulphide trapped in these blank experiments was analyzed as described above, and by direct weighing; results showed that the analysis by titration was quite satisfactory.

Using the data of Reamer, et al. (100), it was shown that H_2S obeys the Ideal Gas Law to better than 1% at the pressures used in this work. This correction was well within experimental error, and was therefore ignored in estimating flow rates by "PV" calculations.

Any ammonia produced in the active nitrogen-hydrogen sulphide reaction would of course be condensed in the product trap with the H_2S , and this was analyzed in separate experiments in which the recovered H_2S was discarded. For these experiments the removable absorber contained a measured amount of 0.1N acid. After the contents of the absorber had been warmed to room temperature, they were heated on a hot-plate to about $90^{\circ}C.$, to drive off the H_2S , then cooled under running water to room temperature, and the excess acid back-titrated with base to a phenolphthalein end-point.

To ensure a good measure of reproducibility, careful attention to detail was necessary in this analysis, because

ammonia production was estimated by the small difference between two relatively large quantities.

Hydrogen cyanide, produced in the active nitrogen-ethylene reaction as a measure of nitrogen atom concentration, was determined by titration according to the Leibig-Déniges method (101), the gas again being absorbed into 15% NaOH solution. The trapped gas was distilled under rather special conditions. A layer of carbon tetrachloride was quickly frozen onto the product trap after the dewar of liquid air had been removed, with the result that the solid HCN slowly sublimed into the removable absorber. The absorber was then removed from the system, and rapidly warmed to room temperature by plunging its bottom end into hot water. These precautions are customary in this laboratory to minimize analytical error due to polymerization of HCN.

Unreacted carbon disulphide was estimated by distillation into a small, thin glass bulb, which could then be weighed on an analytical balance. "Blank" experiments showed that the vapour did not obey the Ideal Gas Law at room temperature, and it was necessary to construct a correction curve, in order that reactant flow rates might be calculated. This correction curve took the form:

$$\text{Flow Rate CS}_2 \text{ (True)} = 1.21 \text{ Flow Rate CS}_2 \text{ (PV Calculation)}.$$

RESULTS

REACTION OF ACTIVE NITROGEN WITH HYDROGEN SULPHIDE

In the active nitrogen-hydrogen sulphide reaction, the only reaction flame observed was a deep-blue glow that appeared to fill the entire upper half of the reaction vessel. This flame was almost invisible under normal artificial illumination but could be seen clearly in a darkened room. The glow appeared to be somewhat more intense at elevated temperatures, but no quantitative measurements were made to check this point. Unfortunately, the glow was too faint to be examined with a pocket spectroscope.

Rather naively, perhaps, it was thought at one stage of the investigation that this blue glow might be due to traces of oxygen still present in the hydrogen sulphide, because the β system of NO is known to be developed in an active nitrogen afterglow contaminated with oxygen (102). Consequently one sample of gas was subjected to a number of successive low temperature distillations to remove possible traces of dissolved oxygen, but without noticeable effect on the intensity of the glow.

Preliminary work showed that the reaction produced a dark-brown-coloured polymer, much of which was deposited on the wall of the reaction vessel when it was not heated externally. A small amount of this material was carried

along in the gas stream, and deposited on the connecting tubing to the cold trap. This polymer markedly affected the decay of the active nitrogen. It appeared to act as a more efficient poison than the 2% metaphosphoric acid normally used, since the afterglow was perceptibly brighter after some polymer had been deposited on the wall, and it persisted for a greater distance towards the pump. However, this poisoning effect was not permanent, for reasons which will be discussed later.

When the reaction vessel was heated externally, no polymer was deposited on the wall; rather, it was all deposited on the cooler connecting tubing, which gradually acquired a deep-black colour. At the end of a series of experiments at high temperatures, the wall of the reaction vessel was as clean and clear as if it had just been washed and re-poisoned. It was found, too, that a reaction vessel in which polymer had been deposited at lower temperatures could be cleaned by heating it for 2 to 3 hours at 300°C . Although the reaction vessel was evacuated while it was being heated, a small amount of a pale-yellow substance back-diffused into the discharge tube, where it deposited on the wall. This pale-yellow substance changed, once the discharge had been activated, until it resembled in appearance the polymer that was in the reaction vessel before it was heated. This substance also appeared to act as a good poison, and it seemed possible that the

experimental data might become meaningless by significantly different nitrogen atom concentrations before and after diffusion of the material into the discharge tube had occurred. A procedure was finally evolved which enabled a reproducible active nitrogen concentration to be maintained.

After any occasion when the discharge tube and reaction vessel had been cleaned and poisoned (with 2% H_3PO_4) the reaction between active nitrogen and H_2S was allowed to proceed for about twenty minutes in the clean vessel to put a mass of polymer on the wall. (The flow rate of H_2S during this procedure was approximately 10×10^{-6} moles/sec., but no serious attempt was made to keep it constant.) The reaction vessel was then heated to 350°C ., with evacuation, for about three hours, after which nitrogen was admitted and the discharge activated three or four times. When the vessel was heated, sufficient of the light-yellow substance diffused into the discharge tube that the concentration of active nitrogen was not altered when the entire process was repeated.

A discharge tube treated in this way will be referred to in subsequent discussion as "conditioned".

As indicated in the experimental section, the temperature within the reaction vessel was determined after the reaction had proceeded for fifty seconds. The temperatures so recorded can represent only rough relative values since,

except at very low flow rates, the tip of the thermocouple was seldom within the reaction flame. Almost invariably experiments at low H_2S flow rates gave apparent reaction temperatures considerably higher than those recorded at higher reactant flow rates. The only temperatures recorded in the figures and tables are those for moderate and higher hydrogen sulphide flow rates.

The reaction between active nitrogen and hydrogen sulphide was studied in two sets of experiments. In Series I, the only analysis made was for unreacted H_2S ; the results obtained are recorded in Table 1 (p. 53) and Figure 3 (p. 54). Experiments were made under conditions such that the recorded reaction temperatures, in the order in which they were used, were $147 \pm 15^\circ\text{C}$, $330 \pm 5^\circ\text{C}$., $210 \pm 5^\circ\text{C}$., $438 \pm 5^\circ\text{C}$., and $85 \pm 5^\circ\text{C}$. To obtain an apparent reaction temperature of 85°C ., the reaction vessel was surrounded by a flexible plastic dish, into which crushed dry ice was packed before each experiment.

Blank experiments showed that, up to 380°C ., thermal decomposition of the H_2S occurred to less than 3% of the reactant flow rate. Hence, no corrections were necessary for thermal decomposition during the active nitrogen-hydrogen sulphide experiments.

TABLE 1

Reaction of Active Nitrogen with Hydrogen Sulphide

Series I

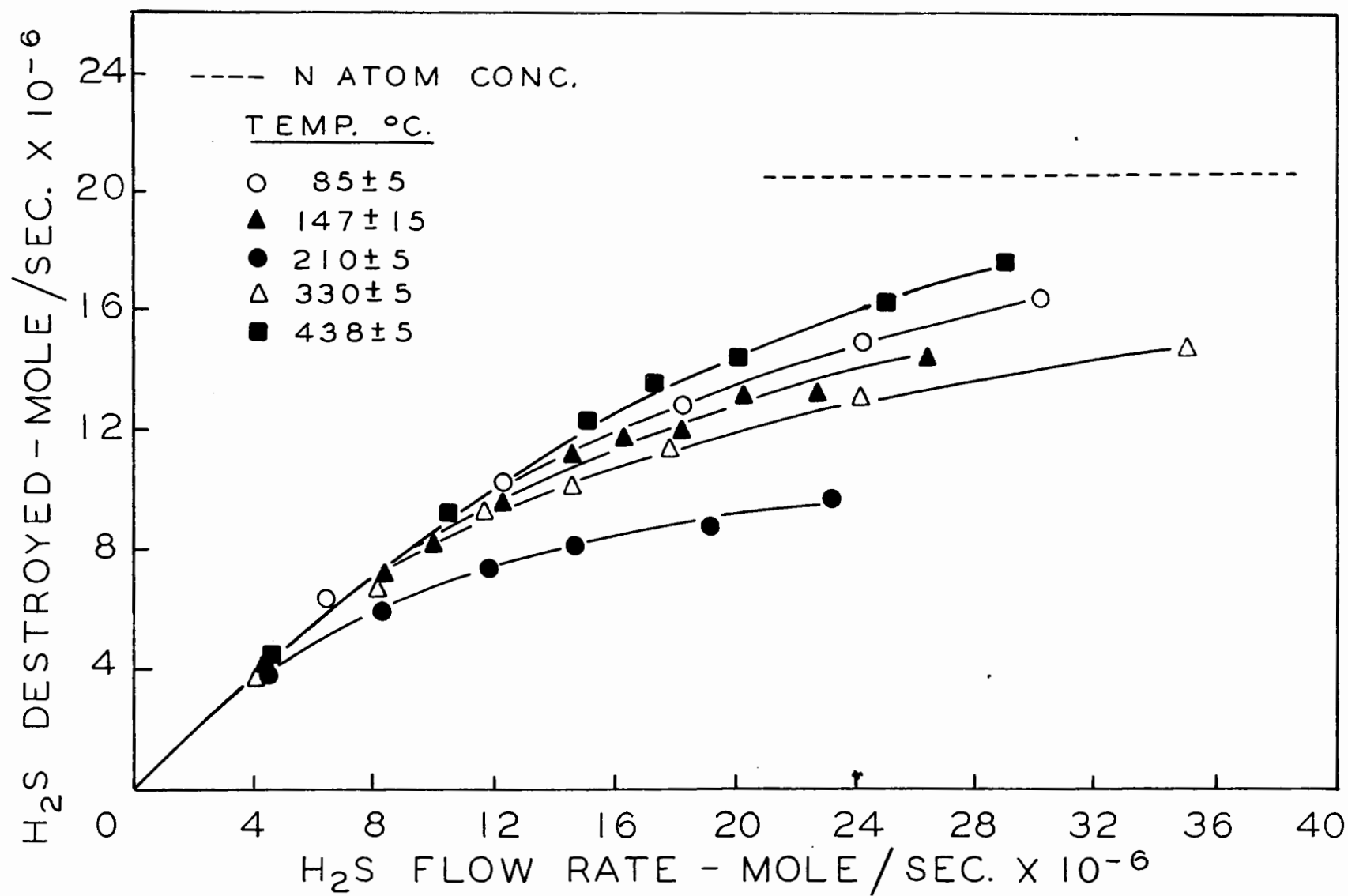
Apparent Reaction Temperature	H ₂ S Flow Rate #	H ₂ S Destroyed #
85 ± 5°C.	6.4	6.4
	12.3	10.3
	18.3	12.9
	24.3	15.0
	30.2	16.4
147 ± 15°C.	4.4	4.3
	8.4	7.2
	10.0	8.3
	12.3	9.6
	14.6	11.2
	16.3	11.8
	18.3	12.1
	20.3	13.2
	22.8	13.3
	26.5	14.5
210 ± 5°C.	4.5	3.9
	8.3	6.0
	11.8	7.5
	14.7	8.2
	19.2	8.8
	23.2	9.8
330 ± 5°C.	4.2	3.8
	8.1	6.8
	11.7	9.3
	14.6	10.2
	17.8	11.5
	24.2	13.1
	29.5	13.6
	35.1	14.7
438 ± 5°C	4.6	4.5
	10.5	9.3
	15.1	12.4
	17.3	13.6
	20.1	14.5
	25.1	16.3
	29.1	17.6

#The units are moles/sec. x 10⁻⁶

FIGURE 3

The Reaction of Active Nitrogen
with Hydrogen Sulphide

Series I.



In the course of Series I, the flow rate of nitrogen atoms was measured on two separate occasions, by determining the maximum amount of HCN that could be obtained from the reaction with ethylene at high temperatures. Averaged over a total of eight experiments, the nitrogen atom concentration was $20.5 \pm 1.0 \times 10^{-6}$ moles/sec.

Although reproducible, the data obtained in Series I appeared rather surprising in their behaviour with change of temperature, and it was thought that they might have reflected some experimental artefact, such as an undetected disturbance in the discharge tube. Also, a qualitative test with Nessler's reagent (103) indicated that small but definite traces of ammonia were formed during the reaction, and it seemed worth while to obtain additional information about its production. Accordingly when Series I was completed, a new discharge tube was introduced into the apparatus, the system was thoroughly cleaned, and the reaction vessel and discharge tube re-poisoned and conditioned, all as outlined previously. A second series of experiments was then made, in which both unreacted hydrogen sulphide and ammonia production were estimated. This entailed two experiments at each flow rate, since, as outlined in the experimental section, the analysis for ammonia required that any residual hydrogen sulphide be removed by

heating the solution.

Experiments were made for measured reaction temperatures of $150 \pm 10^\circ\text{C}$., $202 \pm 5^\circ\text{C}$., and $398 \pm 5^\circ\text{C}$. in that order. In this series the active nitrogen flow rate of $18.7 \pm 0.1 \times 10^{-6}$ moles/sec. was some 9% lower than that in Series I. The results obtained for H_2S destroyed, given in Table 2 and Figure 4, substantiated those of Series I, in that the destruction of H_2S by active nitrogen appears to be minimal at an apparent reaction temperature of about 200°C .

The production of ammonia is recorded as a function of H_2S flow rate in Table 3 and Figure 5A. Using a more cautious experimental technique, and with a slightly higher primary voltage on the transformer, ammonia production was re-examined at $185 \pm 20^\circ\text{C}$. ("room temperature experiments"). The results obtained are recorded in Table 4 and Figure 5B. With these more precise data for ammonia production in the unheated vessel, the maximum in ammonia formation at the low temperature, and the absence of a maximum at higher temperatures is readily apparent. It might be noted also, that the low temperature curve appears to be somewhat sigmoidal at low reactant flow rates.

TABLE 2

Reaction of Active Nitrogen with Hydrogen Sulphide

Series II.

Apparent Reaction Temperature	H ₂ S Flow Rate [#]	H ₂ S Reacted [#]
150 ± 10°C.	4.5	4.4
	7.9	6.8
	12.1	8.6
	16.2	10.1
	20.0	10.9
	22.7	11.2
202 ± 5°C.	4.1	2.8
	8.1	4.6
	12.2	5.5
	16.2	6.0
	20.0	6.3
	23.8	6.5
398 ± 5°C.	9.6	6.6
	16.1	8.6
	23.2	9.4

[#]The units are moles/sec. x 10⁻⁶.

FIGURE 4

The Reaction of Active Nitrogen
with Hydrogen Sulphide

Series II.

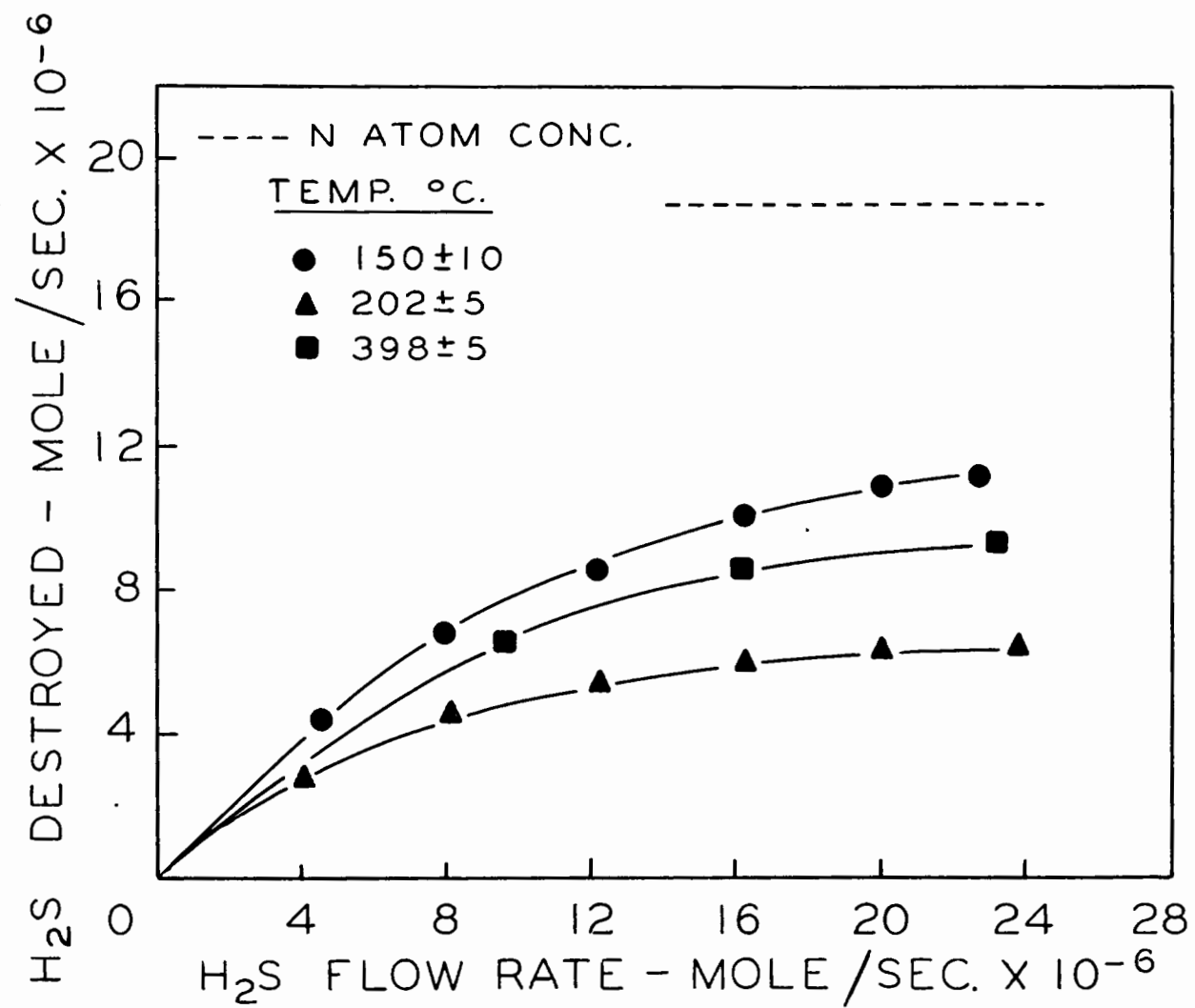


TABLE 3

Recovery of Ammonia in the Reaction of Active
Nitrogen with Hydrogen Sulphide

Series II.

Apparent Reaction Temperature	H ₂ S Flow Rate [#]	NH ₃ Recovered [#]
150 ± 10°C.	2.2	0.29
	4.4	0.44
	8.1	0.33
	12.1	0.28
	16.0	0.33
	24.8	0.24
202 ± 5°C.	2.2	0.25
	4.1	0.26
	8.0	0.32
	12.2	0.39
	16.1	0.43
	19.5	0.45
398 ± 5°C.	2.0	0.14
	4.2	0.20
	7.8	0.24
	12.4	0.42
	16.0	0.33
	20.3	0.43

[#]The units are moles/sec. x 10⁻⁶.

TABLE 4

More Accurate Results of Recovery of Ammonia
in the Reaction of Active Nitrogen with
Hydrogen Sulphide in an Unheated Vessel

Series II.

Apparent Reaction Temperature	H ₂ S Flow Rate [#]	NH ₃ Recovered [#]
185 ± 20°C.	1.7	0.099
	1.8	0.11
	2.1	0.20
	2.4	0.29
	3.4	0.41
	4.2	0.50
	5.6	0.53
	6.9	0.48
	8.9	0.45
	11.0	0.39
	15.3	0.34

[#]The units are moles/sec. x 10⁻⁶.

FIGURE 5

- A. Recovery of Ammonia in the Reaction
of Active Nitrogen with Hydrogen
Sulphide.

Series II.

- B. More Accurate Results of Recovery of
Ammonia in the Reaction of Active
Nitrogen with Hydrogen Sulphide in an
Unheated Vessel.

Series II.

The Polymer

The freshly deposited polymer, which was laid down more thickly on the upper, than on the lower part of the reaction vessel, appeared as a dark brown layer from which a non-condensable gas was slowly evolved. From the relatively large amount of this gas, and its non-condensable character, it was assumed to be nitrogen. The possibility that the gas was hydrogen may be excluded, since, as will be seen later, similar behaviour was observed with a polymer formed in the active nitrogen-CS₂ reaction. Since it was conceivable that the gas was liberated as atomic nitrogen, ethylene was passed over the freshly deposited polymer for one hour while the temperature was increased to 275°C., but no HCN was formed. Hence, the gas was probably liberated in the molecular form.

Comparative experiments in a clean vessel, and in one on which polymer was freshly deposited, showed that the polymer had no effect on the concentration of nitrogen atoms, as reflected in the production of HCN from the active nitrogen-ethylene reaction in an unheated vessel. However, the polymer layer was not stable. About 24 to 36 hours after deposition, a maze of tiny cracks began to appear in it, originally in the regions of thickest deposit, and a significant increase in gas production occurred. Over a period of about 10 hours, the amount of gas produced was sufficient to cause a pressure

increase in the reaction vessel and discharge tube of about 0.08 mm.

As gas evolution increased, small bubbles began to appear, and over a period of 2 to 3 days many of these bubbles expanded to about 1 to 2 cm. in diameter. This was quite variable; one sample of polymer developed a bubble about 3 cm. in diameter. During the period when these bubbles were growing, the rate of out-gassing of the polymer gradually increased until the pressure change was about 0.15 mm., in a 10-hour interval.

Seven to ten days after its deposition, the polymer apparently lost its inertness to active nitrogen, since the production of HCN from ethylene in the vessel then decreased. To restore the activity it was necessary to clean the reaction vessel, either chemically or by strongly heating it.

Qualitative experiments showed that the polymer in a conditioned discharge tube could be stripped from the wall by atomic hydrogen. In one experiment, hydrogen atoms were made in a discharge tube that had been conditioned while the adjacent reaction vessel was perfectly clear. Soon after the discharge tube was turned on, a layer of a white substance appeared on the wall of the reaction vessel, causing it to resemble frosted glass. This white substance, presumably

sulphur, disappeared with a sharp boundary after about 5 minutes attack by hydrogen atoms, with the production of hydrogen sulphide.

A dilute NH_3 solution (5 - 10%), agitated by an air stream, was used to separate the polymer from the wall of the reaction vessel in large flakes. The aqueous solution became a deep violet colour, while the dirty brown flakes and shreds of polymer, filtered from the solution and washed with water, quickly turned to the yellow colour characteristic of bulk sulphur. A sample of this yellow substance was finely ground, dried in vacuo for 36 hours at room temperature, and analyzed.[#] The analysis showed this sample to be at least 92% sulphur, and this result, coupled with the observation that the colour change occurred when the polymer came into contact with a dilute NH_3 solution, rather implies that the polymer deposited onto the wall of the unheated reaction vessel was hydrolyzed by this solution to free sulphur.

Several attempts to remove the polymer layer from the reaction vessel by organic solvents, of which CS_2 proved to be the best, gave rather unsatisfactory results. Only a small amount of material was ever recovered, much less than by using aqueous NH_3 solution. The product recovered by

[#]This analysis was done by the W. Manser, Inc. laboratory, Herrliberg, Switzerland, through the kindness of Dr. A. Taurins of this department.

evaporation of the CS_2 was usually a reddish-brown sticky substance which dried to a hard mass, in the manner described by Moldenhauer and Zimmermann (see page 34 of this thesis). Attempts to fractionate this substance yielded only oils. However, it did contain nitrogen, as indicated by the evolution of ammonia upon alkaline hydrolysis.

On more than one occasion, a small aliquot of the CS_2 solution was shaken in a test-tube with a drop of mercury, as a qualitative test for free sulphur. The test was always positive.

REACTION OF ACTIVE NITROGEN WITH CARBON DISULPHIDE

In the active nitrogen-carbon disulphide reaction a bright pale-blue ("robin's egg blue") reaction flame was observed. This flame, clearly visible in a semi-darkened room, filled the entire reaction flask at high CS_2 flow rates, and continued some distance along the connecting tubing to the pump. At low CS_2 flow rates ($< 3 \times 10^{-6}$ moles/sec.) the active nitrogen was not completely quenched, and under these circumstances the blue reaction flame extended almost to the trap immediately ahead of the pump. Examination with a pocket spectroscope showed the spectrum of the pale-blue flame to be a continuum, which did not extend as far as sunlight into the

red. Comparison with the emission from the reactions of C_2N_2 and CH_2Cl_2 with active nitrogen demonstrated that the spectro-scope used had sufficient resolution to show the banded structure of the CN flame. The CS_2 spectrum was therefore not due to the violet band system of the CN radical.

Preliminary work with carbon disulphide showed the reaction to resemble closely the behaviour observed in the active nitrogen-hydrogen sulphide reaction.

1) In an unheated reaction vessel, the reaction of active nitrogen with CS_2 deposited a good deal of brown polymer on the wall. This polymer was rather similar in appearance to that produced in the active nitrogen- H_2S reaction, and it too slowly evolved gas upon standing.

2) When a heated reaction vessel was used, the polymer deposited on the cooler parts of the apparatus, and the tubing and traps between the reaction vessel and the pump became much more heavily coated with polymer than in the reaction with H_2S .

3) Most of the polymer could be removed from the wall of the reaction vessel by heating it strongly, and as a consequence the polymer was again used to condition the discharge tube. All the experiments with CS_2 were made with a thoroughly conditioned discharge tube. The reaction vessel could not be

completely cleaned by this strong heating, however, and there was always a small amount of black polymer left in patches on the wall.

4) During an experiment a large amount of brownish-black polymer deposited on the wall of the first trap cooled with liquid air. This second polymer appeared rather unstable, and its deposition, if continued long enough (50-100 seconds, depending upon the flow rate of CS_2) usually resulted in an explosion within the trap at liquid air temperature.

This last point will be discussed in more detail in a later section, and it will only be mentioned at this point that these explosions could be avoided if frozen iso-pentane ($-160^\circ\text{C}.$), rather than liquid air, was used as refrigerant for the first trap, T_1 (Fig. 1).

5) As in the active nitrogen- H_2S reaction, the apparent reaction temperatures for low flow rates of CS_2 were significantly higher than those for higher reactant flow rates. As before, the only temperatures reported are those recorded during experiments at moderate and higher flow rates of carbon disulphide.

Two series of experiments were made in the study of the active nitrogen- CS_2 reaction. In series I, experiments were made at 170 ± 5 and $243 \pm 6^\circ\text{C}.$, in that order, and the

results are detailed in Table 5 and Figure 6. It might be noted that two of the experiments at 170°C . (flow rates of CS_2 , 23.0 and 25.6×10^{-6} moles/sec.) were made after the experiments at 243°C . had been completed, with results that were quite in accord with the other data of the lower temperature.

However, series I had to be discontinued before experiments with CS_2 at 400°C . could be made, because, for some unknown reason, the discharge tube began to behave in an erratic manner, as indicated by a significant drop in flash rate. Unfortunately, this occurred also before the concentration of nitrogen atoms could be determined for the system.

A second series of experiments was made after the reaction vessel and discharge tube had been thoroughly cleaned, re-poisoned, and conditioned, as described previously. The experiments were made at 394 ± 10 , 241 ± 6 , and $174 \pm 6^{\circ}\text{C}$., in that order, and the results are recorded in Table 6 and plotted in Figure 7. The concentration of nitrogen atoms in this series, as determined by the HCN produced in the high temperature active nitrogen-ethylene reaction, was $21.0 \pm 0.9 \times 10^{-6}$ moles/sec.

TABLE 5

Reaction of Active Nitrogen with Carbon Disulphide

Series I.

Apparent Reaction Temperature	CS ₂ Flow Rate [#]	CS ₂ Destroyed [#]
170 ± 5°C.	2.5	2.2
	4.0	3.4
	7.3	5.5
	12.0	6.9
	18.5	7.7
	21.9	8.2
	22.2	8.4
	23.0	8.1
	23.2	8.1
	24.9	8.0
	25.6	8.4
	29.3	9.2
243 ± 6°C.	4.1	1.1
	8.0	1.5
	12.1	1.7
	12.5	2.2
	12.6	2.2
	15.9	1.6
	16.3	2.2
	16.7	2.4
	17.5	2.6
	18.7	3.5
	19.2	4.2
	22.3	3.9
	25.5	3.7

[#]The units are moles/sec. x 10⁻⁶.

FIGURE 6

Reaction of Active Nitrogen
with Carbon Disulphide

Series I.

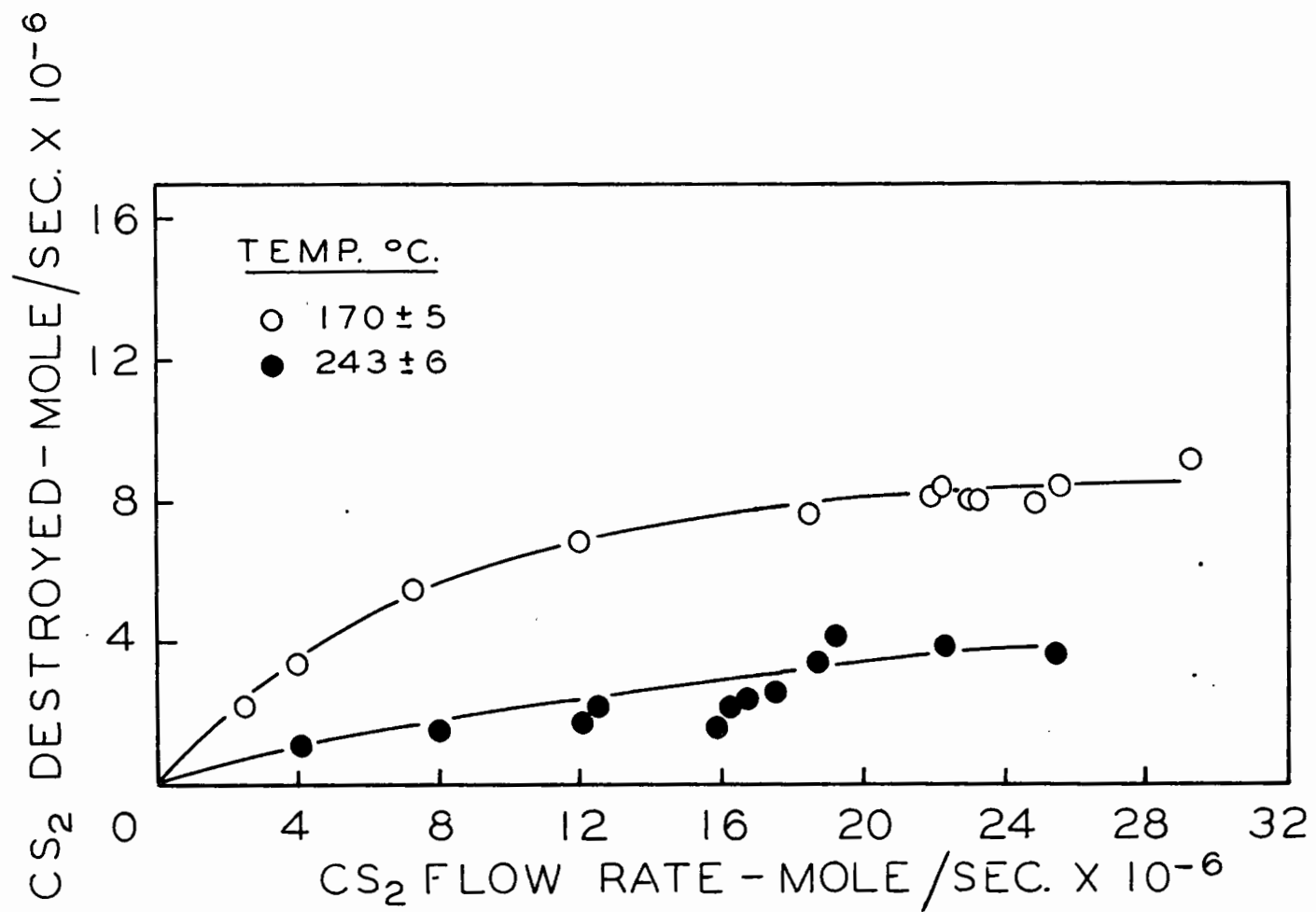


TABLE 6

Reaction of Active Nitrogen with Carbon Disulphide

Series II.

Apparent Reaction Temperature	CS ₂ Flow Rate [#]	CS ₂ Destroyed [#]
174 ± 6°C.	6.4	5.3
	13.1	7.7
	16.9	8.1
	20.9	8.5
	23.1	8.6
	25.6	9.3
	26.8	10.5
	28.0	9.7
	32.1	10.4
241 ± 6°C.	6.1	1.8
	12.2	2.5
	16.5	2.5
	20.1	3.5
	22.2	4.1
	24.0	3.4
	26.0	4.8
394 ± 10°C.	6.2	2.3
	12.0	3.0
	16.5	3.8
	20.2	4.6 ##
	22.0	4.8
	23.0	5.0 ##
	25.5	4.9
	26.3	5.6
	31.1	4.6

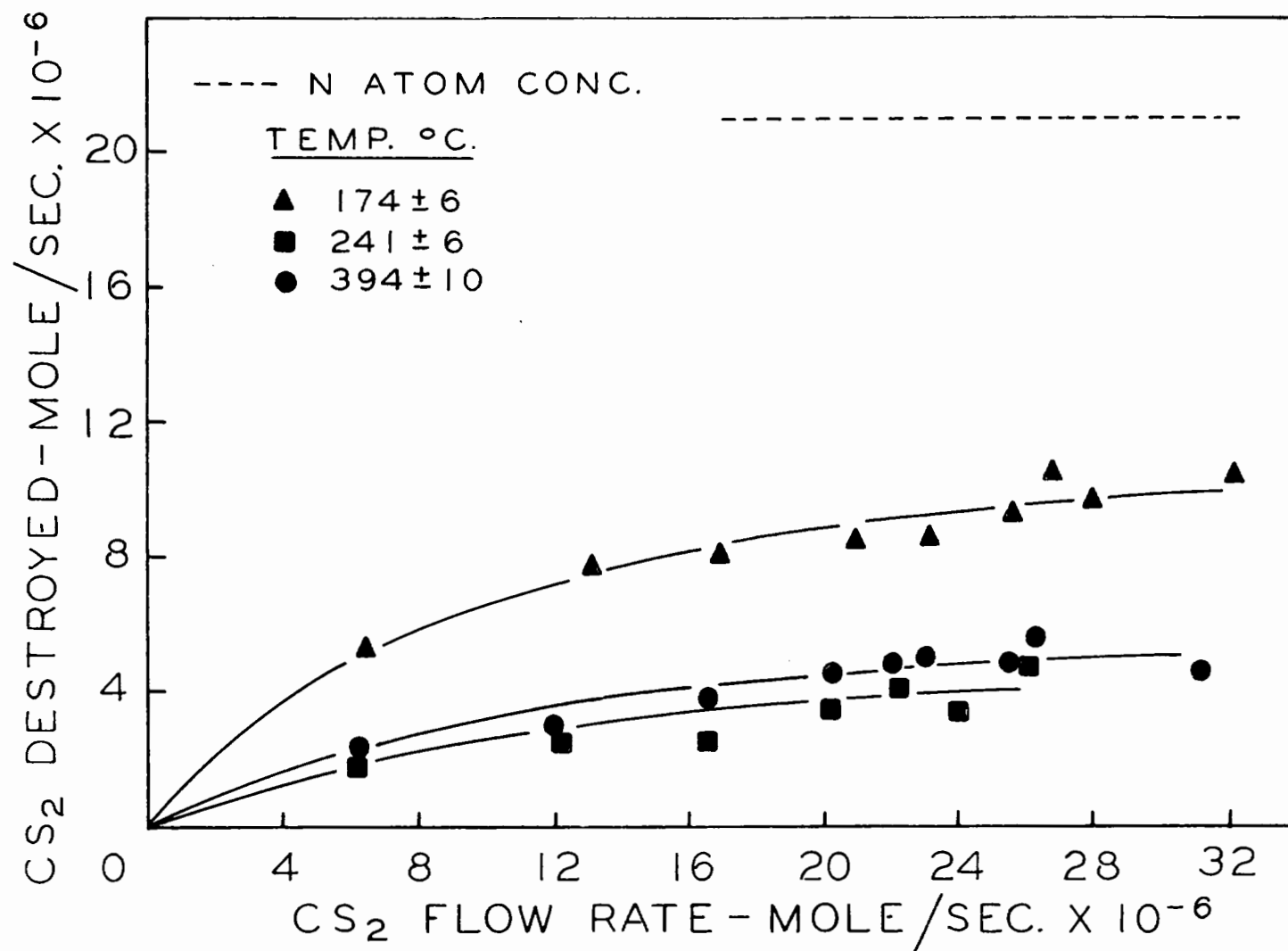
[#] The units are moles/sec. x 10⁻⁶.

Explosion in trap.

FIGURE 7

Reaction of Active Nitrogen
with Carbon Disulphide

Series II.



Three points are of particular interest in this second series:

i) The results appeared to be quite reproducible, as shown by a group of experiments made on the same day, but at different temperatures, in which all the results were in accord with the data obtained previously in the series. Furthermore the high temperature active nitrogen-ethylene reaction gave concordant results for the nitrogen atom concentration, when such experiments were interspersed with those involving CS_2 .

ii) Qualitative tests were made for cyanogen in the condensible reaction products, at all three temperatures, and at approximate CS_2 flow rates of 4, 8, 12, 16, and 25×10^{-6} moles/sec., using the procedure known colloquially as the "Prussian Blue Test" (104). No trace of cyanogen was found in the reaction products, but it is conceivable that some non-volatile paracyanogen was formed.

iii) In two of the experiments recorded in Table 6, a notation is made to the effect that an explosion occurred in the trap. In these experiments liquid air, rather than frozen iso-pentane, was used to trap the unreacted CS_2 from the flowing gas stream. In both experiments there was an explosion in the trap a few seconds after the liquid air had been removed, but fortunately neither was violent enough to damage the apparatus, and analytical data were obtained.

The significance of the results obtained in these two experiments, which were in satisfactory agreement with the data obtained using frozen iso-pentane, will be examined later.

It will be noted that the results of series I, though not as extensive as desired at the time, were fully confirmed by the data for series II.

It is apparent from Figures 6 and 7 that the results obtained from the active nitrogen- CS_2 reaction showed some scatter. The exact cause of this scatter is not known, but it might well be due to absorption of CS_2 vapour by the silicone stopcock grease used. The results of a number of experiments had to be discarded for this reason. Towards the end of series II it was discovered that the influence of the stopcock grease could be minimized if, after every experiment, the reactant flow system was evacuated for 15-20 minutes. This was unfortunately rather wasteful of purified CS_2 , but it had the advantage that any CS_2 absorbed by the grease was removed before the grease became thoroughly saturated.

The Polymers

No work whatever was done on the brown polymer deposited on the wall of the unheated reaction vessel in the active nitrogen-carbon disulphide reaction. It was assumed to be similar to that obtained in the study of the active nitrogen- H_2S reaction, with some contamination by a small amount of the unstable black polymer that deposited so copiously in the low temperature trap ($-190^\circ\text{C}.$).

It was quickly realized in preliminary work that the active nitrogen- CS_2 reaction could be studied successfully only if the explosions observed at $-190^\circ\text{C}.$ were stopped. This was a necessary condition since the reaction was followed by recovery and estimation of the unreacted CS_2 at various reactant flow rates, and it was obvious that the explosions might vitiate the results, apart from possible damage to the apparatus. (On several occasions, at the conclusion of experiments, a vacuum could not be attained prior to distillation of the trapped CS_2 , because the explosion had cracked the wall of the trap).

As mentioned in the Introduction, Dewar and Jones (96) first reported the explosive properties of the CS radical. It is reasonable to infer that the explosions in the present experiments were also due to condensation of CS radicals, formed by the attack of active nitrogen on CS_2 . Since no information was available on possible methods

of moderating or eliminating these explosions, many experiments were made in seeking a way to destroy the explosive properties of the CS radical. In the course of these experiments, several points of interest were observed:

1) The violence of the explosions seemed to be the same when the CS radical was condensed in a clean trap as when it was condensed in a trap coated with polymer from a previous experiment.

2) The violence of the explosion seemed to depend upon the shape of the cooled trap, and it appeared that the more dense the CS deposit, the more violent the explosion.

3) A household copper sponge ("Chore Girl"), at either room temperature or -78.5°C ., inserted ahead of a trap immersed in liquid air, did not prevent the explosions in the trap.

4) A slurry of frozen ethanol (-112°C .) did seem to moderate the explosions that occurred in a subsequent trap cooled with liquid air. A slurry of pentane (-130°C .) was found to be more effective than the ethanol slurry, but did not prevent the explosions entirely.

5) A slurry of iso-pentane (-160°C .) was completely successful in allowing the reaction products to be condensed without subsequent explosion. On a glass surface cooled to -160°C ., the CS radicals condensed over a distance of about

10-15 cm., in a manner similar to that observed when a condensible gas, eg. C_2H_4 , flowed through the same trap cooled in liquid air.

As a consequence of these results, a slurry of isopentane was usually used to trap excess CS_2 from the flowing gas stream. No explosion was ever observed with such trapping conditions, and blank experiments showed that CS_2 vapour was trapped quantitatively.

The actual character of the explosions is difficult to describe. During an experiment, there would be a sudden sharp "click", a flash of light from the trap, and the liquid air coolant would bubble vigorously for several seconds, indicative of a quite exothermic reaction. On several occasions the discharge faltered for a few-tenths of a second, as if there had been a sudden rise of pressure within the reaction system. Examination of a piece of glass cracked by the explosion showed that numerous tiny particles of glass had been gouged from the wall, to form a thin, clearly visible ring of "frosted" glass. Occasionally, the expected explosion did not occur during deposition of CS, but did take place one to two minutes after an experiment had been completed, with the discharge shut off, and no gas flowing through the system.

A sample of the black polymer deposited at -160°C . was removed from the wall of the trap for analysis, with the following results: Hydrogen 0.8%, Carbon 25.1%, Nitrogen 9.1%, Sulphur 55.6%. These results are probably only approximate because of unavoidable absorption of water vapour, as shown by the small amount of hydrogen obtained on analysis. It seems likely that the sample consisted mainly of a mixture of paracyanogen and $(\text{CS})_x$. Since, as will be recalled, no $(\text{CN})_2$ was obtained by distillation from the trap, it is quite possible that its polymerization to paracyanogen is promoted by the polymerized carbon monosulphide.

On the assumption that the CS radical was present, one attempt was made to produce thioformaldehyde in the reaction vessel, and recover it from the gas stream by a trap cooled in liquid air (without first passing the gas stream through a trap at -160°C .). The procedure employed was to mix CS_2 (at about 5×10^{-6} moles/sec.) with molecular hydrogen (at about 35×10^{-6} moles/sec.) in a suitable mixing bulb, and then inject the mixture into a stream of active nitrogen. The molecular hydrogen was drawn from an auxiliary flow system not shown in Figure 1.

A small amount of brownish polymer was trapped, but more significant, perhaps, was the absence of an explosion in the trap.

The analysis of the polymer was: Hydrogen 1.3%, Carbon 27.3%, Nitrogen 8.9%, Sulphur 52.5%; the theoretical analysis for H_2CS is: Hydrogen 4.4%, Carbon 26.0%, Sulphur 69.6%. This indicates that the attempt to produce H_2CS was not successful; rather the polymer, as before, seems to have been composed of a mixture of paracyanogen and polymerized carbon monosulphide.

DISCUSSION

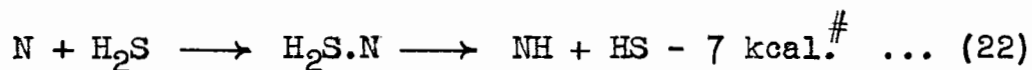
GENERAL OBSERVATIONS

It is readily apparent from Figures 3, 4, 6, and 7, that the reactions of active nitrogen with hydrogen sulphide and carbon disulphide are similar in their behaviour with temperature; in both reactions the amount of reactant destroyed passes through a minimum as the temperature is increased. It is tempting to explain this behaviour in a similar manner for the two substances, and it will be seen that the kinetic mechanisms to be proposed for the separate reactants have a good deal in common.

REACTION OF ACTIVE NITROGEN WITH HYDROGEN SULPHIDE

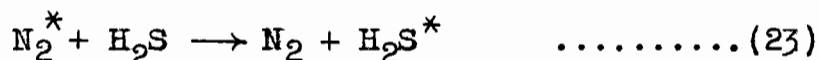
Mechanism of the Reaction

As pointed out in the Introduction, the active nitrogen-hydrogen sulphide reaction was studied in the possibility that, by analogy with the active nitrogen-phosphine reaction (86), hydrogen abstraction might conceivably be the first step in the scheme by which H_2S is destroyed by active nitrogen, the reaction being

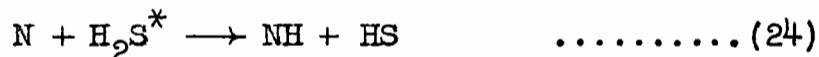


[#]Heats of reaction have been calculated using the bond dissociation energies tabulated in the Appendix.

However, the high rate of reaction, apparent from the almost complete destruction of H_2S at low flow rates, coupled with its observed exothermicity, rather militates against a reaction mechanism that is about 7 kcal. endothermic and would therefore require an activation energy of at least 7 kcal. To counter this it might be suggested that hydrogen abstraction may occur by a two-step process from H_2S molecules that have first acquired energy by collision with excited nitrogen molecules, the second active species that might possibly be present in active nitrogen. The overall process would then be



followed by



However, this suggestion is open to at least two serious objections:

a) The main reason for assuming that excited nitrogen molecules may be present in active nitrogen is to explain the behaviour of the active nitrogen reactions with ammonia and nitric oxide. The explanation requires, however, that the excited molecules can transfer enough energy to these reactants to cause their decomposition, i.e. at least 4.4 ev. to the NH_3 molecule, and at least 6.5 ev. to the NO molecule. Since rupture of the H-SH bond in H_2S would require not more than 4.0 ev., it seems reasonable to assume that enough energy

would be transferred in reaction (23) to cause dissociation of at least one bond within the H_2S molecule. Darwent and Roberts (105) concluded that if highly energetic H_2S molecules are formed as an intermediate in the photochemical decomposition of H_2S , they presumably decompose so rapidly that they are never subject to deactivation by other molecules, so that their presence has no kinetic significance. This statement referred to a wave-length of $\lambda 2288\text{\AA}$., corresponding to 5.4 ev., but should be applicable for comparable amounts of energy transferred to H_2S from excited nitrogen molecules. Obviously, if practically every excited H_2S molecule immediately decomposes, reaction (23) cannot be a precursor to hydrogen-atom abstraction by reaction (24).

b) A further objection to hydrogen-atom abstraction by reaction (23) followed by reaction (24) lies in the experimental fact that an amount of NH_3 corresponding to only about 3% of the available nitrogen atoms was recovered. If the premise of Darwent and Roberts be disregarded, and it is assumed that the lifetime of the excited H_2S molecule is sufficiently long for reaction (24) to occur, a good deal more ammonia than was actually obtained might have been expected, by reactions of the NH radical with excited H_2S molecules at any temperature, or with normal H_2S molecules at higher temperatures. It would be expected, also, that

the yield of ammonia should rise quickly (as a function of H_2S flow rate) to a constant value, and this was not observed.

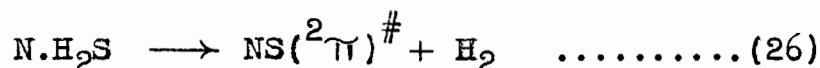
If, for the above reasons, hydrogen-atom abstraction is not kinetically significant in the mechanism of the reaction, an alternative interpretation of the experimental results must be sought, and does seem to be possible on the assumption that atomic nitrogen is the main reactive species in active nitrogen.

The initial step involved in the destruction of H_2S by nitrogen atoms must obviously be the formation of a transition complex



The formation of this complex must occur rapidly to account for the high rate of reaction.

It is reasonable that the complex should then decompose in the reaction



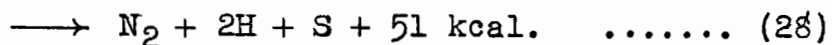
since the over-all reaction is exothermic to the extent of 44 kcal. If reaction (26) were the only reaction responsible for destroying H_2S , it is apparent from Figure 3 that the

[#]The ground state of the NS radical is $^2\pi(106)$.

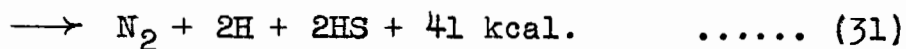
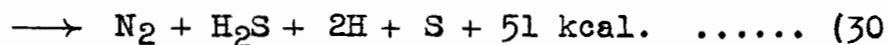
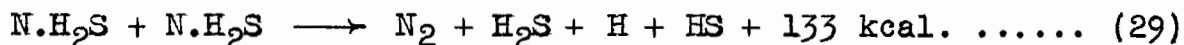
available nitrogen atom flow rate of approximately 20×10^{-6} moles/sec. should cause the decomposition of about 20×10^{-6} moles/sec. of H_2S . This would correspond well with the observation at 85°C . that, at the highest flow rate used, about 15×10^{-6} moles/sec. of H_2S were destroyed, with good indication that a constant rate of destruction ("plateau") would be reached at something in excess of 17×10^{-6} moles/sec. of H_2S destroyed. However, it seems quite impossible to account for the observed decrease, followed by an increase, in the amount of H_2S destroyed as the temperature is increased, without introducing additional reactions into the mechanism.

More detailed examination of reaction (26) shows that it involves both a change of spin and the splitting of two S-H bonds and, as such, is likely to require a significant activation energy. It is suggested, therefore, that at lower temperatures the complex formed in (25) will have a significant life-time such that it might suffer a collision with a second nitrogen atom at low flow rates, or with a second $\text{N.H}_2\text{S}$ complex, at higher flow rates of H_2S , to induce catalytic recombination of nitrogen atoms, with concomitant dissociation of the H_2S molecule(s). This may

be represented by

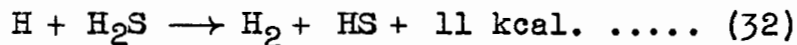


at low flow rates, or by

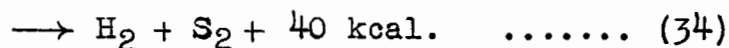
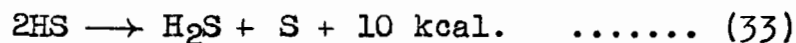


at higher flow rates. All of these reactions are exothermic and may be assumed to be possible.

The hydrogen atoms formed in reactions (27) to (31) should destroy H_2S by the fast reaction



while the HS radicals probably interact by



Darwent and Roberts (105) have found, by a steady-state approximation, that 87% of the effective collisions of two HS radicals results in reaction (33), and the remaining 13%

is accounted for by reaction (34). These authors concluded that reactions (33) and (34) occurred rapidly, and probably without appreciable activation energy. Some, though probably slight, regeneration of H_2S at 85°C . might also result from hydrogen atom reaction with sulphur since, as indicated earlier, hydrogen atoms removed sulphur from the wall of the reaction vessel at room temperature.

It is apparent that the total destruction of H_2S observed at 85°C . may be readily explained by reactions (27-34 incl.), or by a combination of these with reaction (26), although this latter reaction probably makes only a minor contribution at this temperature.

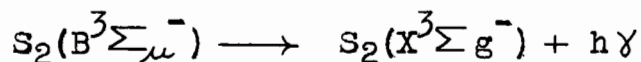
The decrease in destruction of H_2S as the temperature is increased to 210°C . may now be attributed to the increased recombination of hydrogen atoms at the higher temperature, together with increased regeneration of H_2S by accentuated attack of hydrogen atoms on sulphur, perhaps in the gas phase, or as a wall reaction. Furthermore, the observation that the apparent destruction of H_2S increases at still higher temperatures may be explained quite simply if it is assumed that, at the higher temperatures, decomposition of the $\text{N.H}_2\text{S}$ complex by reaction (26) becomes predominant. This would be in accord with the earlier suggestion that this reaction probably has an appreciable activation energy. Decomposition

of the $N.H_2S$ complex by reaction (26) would immediately result in a decrease in the production of H atoms and HS radicals in the system, and this, in turn, should accentuate the decrease in the back reaction (33), since this reaction is second order in HS radicals.

The small amount of NH_3 recovered may be assumed to have no real significance in relation to the main reactions that occurred. This is suggested by the roughly comparable amounts formed over the wide range of temperatures used. It is probable that the small amounts formed had their origin in the known reaction of nitrogen atoms with hydrogen atoms (see page 26 of this thesis), followed by hydrogenation of the NH radical. The observed optimum in NH_3 recovery as a function of H_2S flow rate at $150^\circ C.$, when no optimum was found at higher temperatures, is most baffling. The only suggestion that can be offered at present is that the NH or NH_2 radicals, or perhaps NH_3 itself, in the presence of higher concentrations of H_2S , are incorporated into the polymer that is laid down in the reaction vessel at the lower, but not at the higher, temperatures.

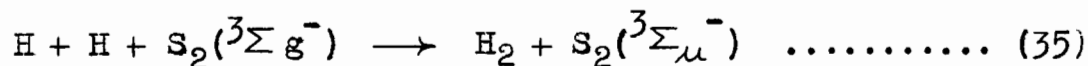
The Reaction Flame

It may be recalled that Strutt and Fowler (65) observed the transition



in the active nitrogen-H₂S reaction flame, but they did not suggest a scheme by which the B state S₂ molecules are produced. It might be possible however, to arrive at a tentative mechanism by consideration of the fact reported by these authors that the S₂ bands extended only to $\lambda 2829\text{\AA}$, at which point they stopped abruptly. This lower-wavelength limit corresponds to 4.38 ev. and this value is too close to D(S₂) to be sheer coincidence. On the basis that D(S₂) = 4.4 ev. it could be argued that this sharp cut-off represents a pre-dissociation of the B state sulphur molecule into two normal ³P atoms. Consequently it is necessary to postulate a mechanism that is sufficiently exothermic to transfer 4.4 ev. energy to the S₂ molecule.

In the flame, such excitation could conceivably be by the reaction

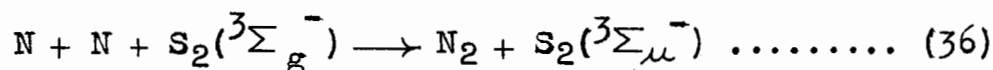


as has been put forth by Gaydon and Whittingham (107) to explain the S₂ bands produced upon the introduction of a small percentage of sulphur dioxide to a jet of hydrogen

burning in air. But the work of Strutt and Fowler (65) implies that if reaction (35) were operative in the active nitrogen-H₂S reaction flame, almost 98% of the liberated energy would leave the complex formed in (35) by way of the S₂ molecule, and this is rather difficult to accept.

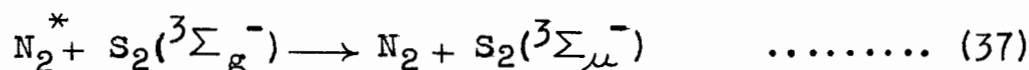
It could be argued that reaction (34) might excite the S₂ molecule, and this is granted, but the exothermicity of the reaction is not nearly enough to excite the S₂ molecule into the B state.

By analogy with reaction (35), it is quite possible that this excitation might be by

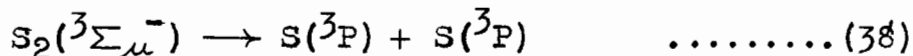


and this reaction cannot be completely excluded from consideration. It rather implies, however, that the observed colour should fade appreciably at high flow rates of H₂S, and this did not appear to be true, although it must be admitted that no quantitative work was done to check this point.

It is suggested that the sulphur bands present in the active nitrogen-H₂S reaction flame result, at least in part, from



followed in some of the cases, if circumstances are favourable, by

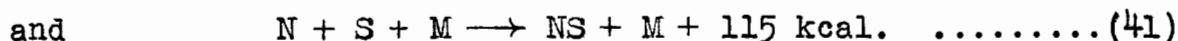
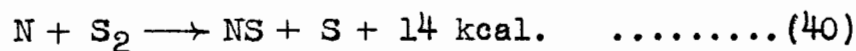
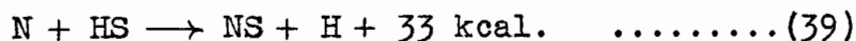


In reaction (37) the symbol N_2^* represents any excited nitrogen molecule present in the system.

This suggestion means essentially that the active nitrogen- H_2S reaction flame is due, not to excitation in a particular chemical reaction, but to energy transfer by collision within the reaction system. An explanation of the brighter reaction flame at higher temperatures, if real, follows logically from this statement.

The Polymer

The appearance of polymer is quite readily understood. Reaction (26) will of course produce the NS radical, which might then be expected to polymerize by a series of steps. The monomer might also be produced, particularly at low flow rates of H_2S , by the additional reactions:



all three of which, however, require a change of spin.

In addition to a number of nitrogen sulphides present within the system in various degrees of polymerization, there will also be free sulphur that might be expected to deposit on the wall of the reaction vessel. It is at once obvious from the suggested kinetic mechanism for the active nitrogen- H_2S reaction that sulphur deposition would be favoured at low temperatures and at higher reactant flow rates.

Thus, it is probably safe to assume that the polymer deposited on the wall of the reaction vessel and its connecting tubing was a mixture of several polymeric substances. It will be recalled that Moldenhauer and Zimmerman (88) found a mixture of polymers to be formed in the active nitrogen-sulphur reaction (although under conditions where the S_2 molecule was probably excited). It is worth noting, too, that N_2S_5 reacts with alkali in alcoholic solution to produce a transient but quite characteristic violet-red colour (108), in a manner similar to that observed in the present study when an aqueous ammonia solution came into contact with the polymer on the wall of the reaction vessel.

It is possible that the observed unstable, rather variable, characteristics of the polymer might be ascribed

to some changes in it under the influence of light, since at least one nitrogen-sulphur compound, N_2S_5 , appears to be stable only in the dark (109).

REACTION OF ACTIVE NITROGEN WITH CARBON DISULPHIDE

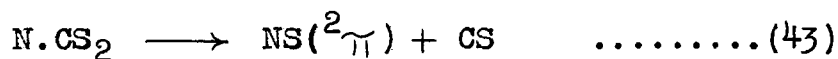
Mechanism of the Reaction

While the study of the active nitrogen-carbon disulphide reaction was more difficult experimentally than the active nitrogen-hydrogen sulphide reaction, it would appear to be a much simpler reaction, since there can be no possibility of hydrogen atom reactions to complicate the mechanism.

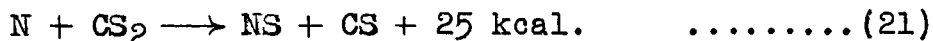
As for the H_2S reaction, it is suggested that the initial step by which CS_2 is destroyed by active nitrogen is formation of a complex with a nitrogen atom



which might be expected to decompose according to



Reactions (42) and (43), taken together, are equivalent to reaction (21)



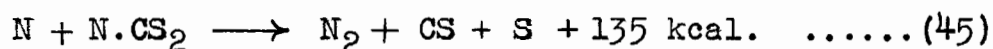
which reaction was first suggested by Strutt as the mode by which the active nitrogen-CS₂ reaction proceeds.

However reaction (21) involves a change of spin if, as seems probable from the relatively long life-time of the CS radical, it is formed in the singlet state. The long life-time is clearly indicated since about 0.3 seconds was required for the CS radical to pass from the reaction vessel to the trap where explosions occurred, to give clear evidence of its presence. Moreover, Porter has found (110), by the flash photolysis of CS₂, that the CS radical was able to exist without appreciable change in concentration for several seconds, and that the half-life of the reaction

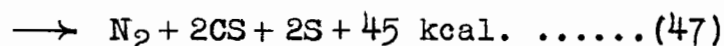
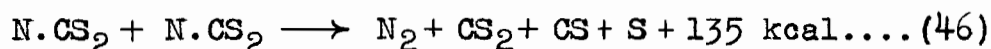


was sixty seconds. He concluded that a half-life of this magnitude implied that the CS radical was in the singlet state. Also, Dyne and Ramsay (111) have produced the CS radical by a high frequency discharge through CS₂ and by photolysis of CS₂, and have concluded that, in the gas phase, CS shows the chemical stability of a normal molecule. This, again, is consistent only with the singlet state of the radical, and further supports the assumption that the CS radical probably emerges from the N-CS₂ complex in the singlet state.

By analogy, then, with H_2S , it is assumed that the destruction of the $\text{N}.\text{CS}_2$ complex by reaction (43) requires an activation energy, so that, at lower temperatures, the complex may have sufficient life-time to suffer collision with a further nitrogen atom, at low flow rates of CS_2 , or with another complex, at higher reactant flow rates. In either case the energy involved in the catalyzed recombination of the nitrogen atoms is sufficient to break the first $\text{C}=\text{S}$ bond in CS_2 . At low reactant flow rates, the reaction would be



while at higher flow rates it would be

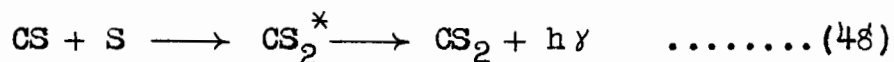


It will be noted that the similarity to the mechanism proposed to explain the active nitrogen- H_2S reaction is not complete, because there is not enough energy available to break both bonds in the CS_2 molecule. Also, if both (46) and (47) proceed at higher reactant flow rates, two nitrogen atoms will destroy between one and two CS_2 molecules.

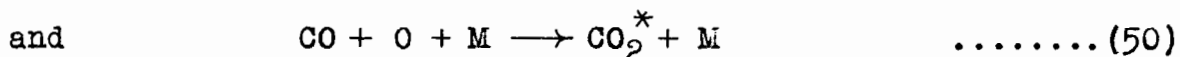
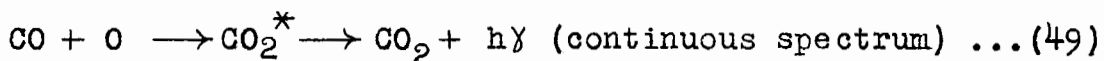
The results obtained indicate again, however, that a reaction to regenerate the parent sulphur compound is an

important factor in the mechanism. It might also be inferred from the experimental results that, with CS_2 , the regeneration reaction requires some activation energy, since otherwise more regeneration of CS_2 , hence less apparent destruction of it, might have been expected than was actually found at 174°C . (Figure 7).

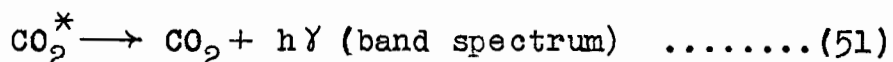
It is suggested that the regeneration step is



in which the collision complex is probably in a triplet state to conserve spin. This is by analogy with the reactions



followed by



by which the CO flame spectrum may be interpreted (112).

Broida and Gaydon (113) have recently concluded from studies of the oxygen atom-CO reaction that reaction (49) has an appreciable activation energy, while (50) followed by (51), which occurred readily at room temperature, was suggested to require little or no activation energy. It is quite possible that reaction (48) might require rather

less activation energy than (49) since the CS radical is less stable and more reactive than CO.

The analogue of reaction (50) is also possible as a regenerative process, i.e.



followed of course by



and by reasoning similar to the above, reaction (52) should have virtually no activation energy.

Because of the activation energy probably associated with reaction (48), in contrast to reaction (52), it might reasonably be suggested that the reaction by which CS_2 is regenerated is (48) rather than (52). However, reaction (52) cannot be completely disregarded because of the abundance of possible third bodies present in the system. Still adhering to the analogy of the reaction of CO with oxygen atoms, it is probable that a final choice between (48) and (52) can only be made on the basis of spectroscopic data, and a spectroscope of sufficient resolution was not available during this study. It will be remembered that examination of the active nitrogen- CS_2 reaction flame with a pocket

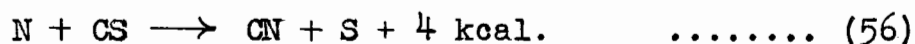
spectroscope revealed the spectrum to be a continuum; but this is scarcely an adequate basis on which to distinguish between reactions (48) and (52).

It is apparent that reactions (45), (46), (47), and (48), the latter with a small but significant activation energy, readily explain both the high rate of destruction of CS_2 by active nitrogen at 174°C . and the decrease in the amount of CS_2 destroyed as the temperature is raised. There remains to be explained the increased destruction of CS_2 at 394°C . relative to that at 241°C ., and this can easily be done by assuming that, at the higher temperatures, the rate of destruction of CS_2 by reaction (43) becomes important relative to its disappearance by reactions (45), (46) and (47), and its regeneration by reaction (48). This explanation is similar to that suggested for the corresponding behaviour of the active nitrogen- H_2S reaction at high temperatures.

The suggestion that reaction (48) has an activation energy raises the important question as to what happens to the sulphur atoms and CS radicals produced at 174°C . that do not react further by (48). The eventual fate of these entities is to deposit on the wall, although they may also react with any excess nitrogen atoms, or with themselves, by:



and, more important, by



followed by



Such reactions would, of course, account for the presence of the small amount of paracyanogen that apparently was present in the polymer found in the trap at -160°C .

As mentioned earlier, emission bands of the S_2 molecule in the B state have been observed in the active nitrogen- CS_2 reaction flame, where possible mechanisms by which they might arise are severely limited. It is suggested that, as in the active nitrogen- H_2S reaction, they originate by a simple transfer of energy by collision.

The Polymers

The polymer that deposited on the wall of the unheated reaction vessel in the active nitrogen- CS_2 reaction is probably the result of active nitrogen reactions with sulphur,

analogous to those suggested for the active nitrogen- H_2S reaction, and these need not be discussed again in detail.

The explosions observed during the polymerization of CS radicals might tentatively be attributed to exothermic polymerization of this radical under conditions that were conducive to excessive rise of temperature in a highly localized region. When the radicals were condensed at the temperature of liquid air, the rate of condensation was probably so rapid that a high concentration of CS radicals was formed in a small region near the surface of the refrigerant. The rapid evolution of heat by polymerization of the radicals might then have caused acceleration of the polymerization to a point where a thermal explosion resulted. On the other hand, at higher trapping temperatures, where the accumulation of CS radicals was not as highly localized in the trap, and the rate of polymerization therefore somewhat slower, the heat of polymerization might have been removed sufficiently well to prevent the acceleration of the polymerization into an explosive rate.

It will be recalled that experiments in which CS_2 was distilled from a trap in which explosion had occurred gave results consistent with those obtained under more normal conditions. This rather implies that the endothermic reaction:



did not proceed to any great extent even at the high temperatures that must have occurred in the explosion.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The reaction between active nitrogen and hydrogen sulphide has been investigated at apparent reaction temperatures of $85^{\circ}\text{C}.$, $147^{\circ}\text{C}.$, $210^{\circ}\text{C}.$, $330^{\circ}\text{C}.$, and $438^{\circ}\text{C}.$

2. The destruction of hydrogen sulphide was a maximum at $85^{\circ}\text{C}.$ and at $438^{\circ}\text{C}.$, when the amounts destroyed approximated the nitrogen atom concentration, as evaluated by the high temperature active nitrogen-ethylene reaction.

At $210^{\circ}\text{C}.$, the active nitrogen appeared to destroy a minimum amount of reactant, since hydrogen sulphide equivalent to only about 45% of the nitrogen atom flow rate was not recovered.

3. At all temperatures the reaction produced a good deal of polymer. At $85^{\circ}\text{C}.$ and $147^{\circ}\text{C}.$, this polymer deposited on the unheated wall of the reaction vessel, while at higher temperatures the reaction vessel remained clean and the polymer formed on the connecting tubing and traps.

4. Minor amounts of ammonia were recovered from the hydrogen sulphide reaction at $150^{\circ}\text{C}.$, $202^{\circ}\text{C}.$, and $398^{\circ}\text{C}.$ The amounts of ammonia recovered at these three temperatures were roughly comparable, and amounted to approximately

2½% of the nitrogen atom flow rate.

A maximum in ammonia production with flow rate of hydrogen sulphide was found at 150°C., but not at the higher temperatures.

5. In the lower part of the temperature range studied, it is suggested that hydrogen sulphide is destroyed while acting as a third body for the recombination of nitrogen atoms. The energy transferred during this process is sufficient to initiate decomposition of the hydrogen sulphide, and further attack upon the reactant is promoted by the hydrogen atoms so formed. It is also suggested that hydrogen sulphide is regenerated to some extent by the interactions of hydrosulphide (HS) radicals.

The apparent minimum in hydrogen sulphide destruction at 210°C. is explained by the greater extent of hydrogen atom recombination at higher temperatures, and by increased regeneration of hydrogen sulphide by hydrogen atom attack upon sulphur, either in the gas phase or at the wall.

At the higher temperatures used, direct attack on hydrogen sulphide by a nitrogen atom is suggested to occur, to yield, by an exothermic reaction, molecular hydrogen and the monomeric nitrogen sulphide (NS) radical.

The recovery of ammonia from the reaction is suggested to be due mainly to reactions between nitrogen atoms and hydrogen atoms, with subsequent hydrogenation of the resulting imino radical.

6. The reaction between active nitrogen and carbon disulphide has been studied at apparent reaction temperatures of 174°C ., 241°C . and 394°C . A maximum amount of carbon disulphide appeared to have reacted at 174°C ., where, at high reactant flow rates, an amount approximating 40% of the nitrogen atom concentration was not recovered.

A minimum amount of apparent destruction of carbon disulphide was found at 241°C ., amounting to only about 20% of the nitrogen atom flow rate. A slight but significant increase in reactant destruction at 394°C . relative to 241°C . was noted, but even at this temperature only half as much of the sulphur compound appeared to be destroyed as was apparently destroyed at 174°C .

7. At all temperatures the reaction produced two polymers. One was quite similar in behaviour to that obtained in the active nitrogen-hydrogen sulphide reaction, in that, at 174°C ., the polymer deposited on the wall of the unheated reaction vessel, but on the connecting tubing and traps at the higher temperatures.

The second polymer produced in the carbon disulphide reaction was carried along in the gas stream, apparently as monomer, until a cold trap was reached, in which it condensed. If this condensation took place at the temperature of liquid air, the monomer, during polymerization, became unstable, probably because of localized heating, and a thermal explosion resulted. There is good reason to suppose that the monomer is the carbon monosulphide (CS) radical.

8. Experiments showed that these explosions could be completely eliminated if the monomer was condensed at $-160^{\circ}\text{C}.$, rather than at $-190^{\circ}\text{C}.$
9. No cyanogen was recovered from the carbon disulphide reaction, but paracyanogen appeared to be present in the polymer that deposited at $-160^{\circ}\text{C}.$
10. It is suggested that, throughout the entire temperature range studied, carbon disulphide acted as a third body for the recombination of nitrogen atoms, acquiring enough energy in this process to be broken up into a sulphur atom and a carbon monosulphide radical.

The apparent minimum in reactant destruction at $241^{\circ}\text{C}.$ is thought to be due to the regeneration of carbon disulphide by a bimolecular reaction involving the sulphur

atom and the carbon monosulphide radical.

Some destruction of carbon disulphide is thought to occur at 394°C . by direct attack of a nitrogen atom, to yield the monomeric nitrogen sulphide and carbon monosulphide radicals.

APPENDIX

Bond Dissociation Energies and Atomic
Heats of Formation used in this Thesis.

Bond	Dissociation Energy Kcal./mole	Source
D(N \equiv N)	225.0	Cottrell (32)
D(H-H)	103.2	Cottrell (32)
D(N-H)	85	Cottrell (32)
D(HN-H)	88	Altshuller (114)
D(H ₂ N-H)	102	Cottrell (32)
D(N-S)	115	Cottrell (32) Note I
D(OC=O)	127	Cottrell (32)
D(C=O)	256	Cottrell (32)
D(HS-H)	92	Stevenson (115) Note II
D(S-H)	82	Calculated, Note III
D(S=S)	101.5	Gaydon (24) Note IV
D(SC=S)	90	Blanchard and LeGoff (116) Note V
D(C=S)	184	Calculated, Note VI
Atomic Heat Formation of H ₂ S	174	Calculated, Note VII
Atomic Heat Formation of CS ₂	274	Calculated, Note VIII

Note I - Cottrell credits the value for $D(N-S)$ to Gaydon(24), who calculated it by an undisclosed method from results of Fowler and Bakker (90). Gaydon ascribed to this calculation an error of ± 23 kcal./mole. Herzberg (95) calculated the value of $D(N-S)$ to be 136 kcal./mole.

Note II - Stevenson calculated the value of 92 kcal./mole for $D(HS-H)$ from appearance potentials, and estimated the error to be ± 2 kcal./mole. Franklin and Lumpkin (117), by a similar experimental approach, derived a value of 95 ± 5 kcal./mole, while the results of Schon and Darwent (118, 119) yield a value for this bond of 89 ± 4 kcal./mole. Cottrell (32) suggests 90 kcal./mole, but questions its accuracy.

Note III - The value of 82 kcal./mole for $D(S-H)$ has been calculated as the difference between the atomic heat of formation of H_2S and $D(HS-H)$. Porter (120) estimated $D(S-H)$ to be $84.9 \pm 5\%$ kcal./mole, from a study of the SH spectrum, using a linear Birge-Sponer extrapolation. Cottrell points out (32) that considering all the assumptions involved, Porter's estimate of his error may be rather optimistic. Ramsay (121), in a similar study, was

able only to bracket the value at $92.7 > D(S-H) > 66.3$ kcal./mole. By an approximate Birge-Sponer extrapolation, he obtained a value of 82.8 kcal./mole for this bond. Gaydon (24) suggests 89 kcal./mole, on the basis of Porter's data.

Note IV - The dissociation energy of the S_2 molecule is not known accurately. Values of 76.1, 83.0, and 101.5 kcal./mole are possibilities. The value used is in conflict with Cottrell (32), who bases his choice of 83.0 kcal./mole on some experimental results at 1550°K. by St. Pierre and Chipman (122).

While the bond dissociation energies quoted in this thesis are consistent within themselves, the choice of $D(S_2)$, upon which several other values depend, is entirely arbitrary.

Note V - The value of 90 kcal./mole for $D(SC=S)$ is based on appearance potentials as measured by Blanchard and LeGoff, with an error estimated at ± 7 kcal./mole. This value of $D(SC=S)$ agrees well with that estimated earlier by Smyth and Blewett (123) (95 ± 11 and 89 ± 11 kcal./mole), although Blanchard and LeGoff point out that the measured appearance potentials differ somewhat. Myerson, et. al.

(124) quote a value of 101 kcal./mole, which was obtained ultimately from the Landolt-Bornstein Tabellen.

Note VI - The value of $D(C \equiv S)$ has been calculated as the difference between the atomic heat of formation of CS_2 and $D(SC \equiv S)$. Cottrell (32) quotes the value put forward by Gaydon (24), which is 166 ± 23 kcal./mole, while Herzberg (95) doubtfully suggests 180 kcal./mole.

Without evidence to the contrary, it might be expected that, to a first approximation, $D(C \equiv S)$ would bear the same relation to $D(SC \equiv S)$ as $D(C \equiv O)$ bears to $D(OC \equiv O)$. The bond energies quoted herein are consistent with this assumption, because $\frac{D(C \equiv S)}{D(SC \equiv S)} = 2.04$ and $\frac{D(C \equiv O)}{D(OC \equiv O)} = 2.01$.

Note VII - The atomic heat of formation of H_2S has been evaluated from calculations published by Evans and Wagman (125). The value actually obtained was 173.6 kcal./mole, but this has been rounded off to the nearest whole number. Gaydon (24) quotes a value of 173.3 kcal./mole.

Note VIII - The atomic heat of formation of CS_2 has been calculated on the basis that the heat of formation of CS_2 from the elements at 298.2 °K. is 27.55 kcal./mole (126).

By analogy with CO_2 , the correction to 0°K. should be quite small (for CO_2 the correction is 0.08 kcal./mole (126)) and this has been ignored, mainly because it has no effect on the calculated value (274.3 kcal./mole) when it rounded off to the nearest whole number. The heat of formation of gaseous S_2 was obtained from Sehon (119).

Gaydon (24) quotes a value of 274.9 kcal./mole for the atomic heat of formation of CS_2 , while Cottrell (32) has estimated a value of 256 kcal./mole , on the basis that $D(\text{S}_2) = 83.0 \text{ kcal./mole}$. For $D(\text{S}_2) = 101.5 \text{ kcal./mole}$, as used in this thesis, the atomic heat of formation of CS_2 becomes 274.5 kcal./mole .

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