
QUARTERLY REVIEWS

THE PRODUCTION, DETECTION, AND ESTIMATION OF ATOMS IN THE GASEOUS PHASE

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WITH the exception of the atoms of the inert gases and of certain metallic vapours, free atoms possess high chemical reactivity. Atomic reactions have been of interest to chemists since the early part of the present century, and progress in this field has been determined largely by the development of experimental methods both to produce atoms and to follow the course of their reactions. It is the purpose of this Review to consider the scope and limitations of the different techniques now in use for the study of such reactions.

In 1911, Strutt¹ gave an extensive description of the properties of atomic oxygen and atomic nitrogen produced by a high-frequency electrical discharge and, in 1920, Wood² produced high concentrations of hydrogen atoms by using a low-frequency electrode discharge. About the same time, Langmuir³ showed that hydrogen could be dissociated on a hot tungsten filament and, a few years later, photochemical methods of producing atoms were in use.⁴ In recent years, the microwave discharge, flash photolysis, and shock tubes have been added to the methods available for the production of atoms, and these developments are responsible to some extent for an increased interest in atomic reactions.

Whereas there is a number of methods which may be used to demonstrate the presence of atoms in a reaction system, relatively few yield reliable quantitative information. Of these, even fewer measure absolute atom concentrations which are necessary for the evaluation of absolute rate constants of atomic reactions.

A comprehensive review of studies of atomic reactions up to 1953 has been given by Steacie.⁵ References to much of the more recent work, with particular reference to the stabilisation of energetic species at low temperatures, have been given by Bass and Broida.⁶

In addition to their intrinsic interest, atomic reactions are important

¹ Strutt, *Proc. Roy. Soc.*, 1911, *A*, **85**, 219.

² Wood, *Proc. Roy. Soc.*, 1920, *A*, **97**, 455.

³ Langmuir, *J. Amer. Chem. Soc.*, 1912, **34**, 1310; 1915, **37**, 417.

⁴ Noyes and Leighton, "The Photochemistry of Gases", Reinhold Publ. Corp., New York, 1941.

⁵ Steacie, "Atomic and Free Radical Reactions", Reinhold Publ. Corp., New York, 1954.

⁶ Bass and Broida, "Formation and Trapping of Free Radicals", Academic Press, London, 1960.

in many branches of chemistry. Atoms are known to be reactive intermediates in many complex reactions, *e.g.*, flames and explosions, and a knowledge of their reactions is valuable in elucidating the overall reaction mechanisms. With the advent of high-altitude, high-speed rockets, the physics and chemistry of the free atoms present in the upper atmosphere have assumed greater importance and, at lower altitudes, atomic reactions are thought to play a significant role in the formation of "smog".

The Production of Atoms

Atoms are produced from stable molecules by supplying sufficient energy to the molecules to cause them to dissociate. The energy may be supplied in a number of different ways, *e.g.*, heat (hot filament), light (resonance lamp), collision with high-speed electrons (discharges), etc. Ideally, it would be desirable to produce a given concentration of atoms in a single, known, electronic state, in the absence of reactive by-products. As will be seen in the following sections, this ideal is very rarely achieved. Reactive by-products may be formed along with the atoms or may arise from reactions of the atoms. For example, hydrogen atoms may be produced by the photosensitised decomposition of an alkane, but for each atom produced an alkyl radical is also produced.

Details of the different methods of producing atoms are given in the appropriate sections below, but the following generalisations may be made at this stage:

(a) With the exception of the shock-tube technique, thermal methods are used to produce low concentrations of atoms from weakly bound diatomic molecules at low pressures in static or flow systems.

(b) Photolysis is the most readily controlled method and may be used in static or circulating systems at any pressure to produce low concentrations of atoms in either the ground state or an electronically excited state.

(c) Radiolysis is rarely used since it produces very low yields of atoms together with other reactive ionic and radical species.

(d) Electrical discharges have been used to obtain relatively high concentrations of hydrogen, oxygen, and nitrogen atoms in fast flow systems at low pressures.

(e) So-called "hot" atoms can be produced by bombardment of a gas with a beam of neutrons. These atoms are quite different from normal atoms in their reactions since they possess a very considerable excess of energy.

All the above methods produce a more or less steady supply of atoms. The use of flash-photolysis and shock-tube techniques enables one to obtain very high, transient concentrations of atoms in static systems.

Thermal Methods.—When thermal methods are employed, it is usual to use the elements as sources of atoms. In the laboratory, temperatures in

excess of 2000°K are difficult to attain, and consequently it is necessary for a molecule to have a fairly low dissociation energy if appreciable yields are to be obtained. The method has therefore been limited very largely to the production of atoms from H₂, Cl₂, Br₂, I₂, and metallic sodium, the corresponding dissociation energies being 103, 57, 45, 35, and 17 kcal./mole respectively. Three methods of supplying the heat have been used: (i) The reaction vessel is enclosed in a furnace; (ii) an electrically heated filament maintained at a high temperature is present in the gas; (iii) the gas is subjected to a shock wave.

Although the fast flow of a substance through a tube surrounded by a furnace has been used to produce free radicals, it has found little application in the production of atoms. Hydrogen and deuterium atoms have been obtained in a static system at about 1000°K in the study of the conversion of para-hydrogen into ortho-hydrogen and of ortho-deuterium into para-deuterium, and of the exchange reactions between hydrogen and deuterium.⁷ In general, other reactants cannot be mixed with hydrogen in such a system since they would decompose at the high temperatures which are necessary. More recently, Scheer,⁸ working at very low pressures, has produced a beam of iodine atoms by pumping them from a quartz tube containing iodine at 1100°K. An attempt to stabilise the atoms at very low temperatures in a solid matrix was unsuccessful.

Owing to the low dissociation energy of the Na₂ molecule, sodium vapour in equilibrium with the molten metal is very largely monatomic. A stream of sodium atoms can, therefore, be obtained by passing an inert carrier gas over the molten metal. If this is then passed into an atmosphere of a substance such as an alkyl halide, the sodium atoms will abstract the halogen atoms to form a sodium salt and an alkyl radical. Work in this field up to 1951 has been reviewed by Warhurst.⁹

Langmuir³ was the first to show that hydrogen is dissociated on a heated tungsten filament at very high temperatures. At low pressures, the atoms diffused to the walls and reduced metallic oxides. More recently, Tollefson and LeRoy¹⁰ produced a stream of hydrogen atoms at low pressures by passing the gas very rapidly over a heated tungsten filament electrically maintained at about 1700°K. The atom concentration measured by an isothermal calorimeter was in the region of 0.1%. Klein and Scheer¹¹ have also used this method to produce hydrogen atoms in a static system at very low pressures. The atoms are allowed to diffuse to the walls where they react with a thin layer of solid olefin at 77°K. Other atoms have not been obtained by the filament method, probably because many of them would attack the filament.

⁷ Farkas, "Ortho-hydrogen, Para-hydrogen and Heavy Hydrogen", Cambridge Univ. Press, 1935.

⁸ Scheer, unpublished work, quoted on page 22 of reference 6.

⁹ Warhurst, *Quart. Rev.*, 1951, 5, 44.

¹⁰ Tollefson and LeRoy, *J. Chem. Phys.*, 1948, 16, 1057.

¹¹ Klein and Scheer, *J. Phys. Chem.*, 1958, 62, 1011.

During the last fifteen years, the shock-tube technique has been increasingly applied to the study of chemical problems. When a shock wave passes through a gas, the gas is compressed adiabatically and a rapid rise in temperature results. With monatomic gases, temperatures as high as $18,000^{\circ}\text{K}$ may be obtained, but the higher heat capacities of diatomic and polyatomic gases, together with the heat absorbed in dissociation, will lead to a much smaller rise in temperature. The temperature attained is controlled in practice by the strength of the shock, and for a given gas the stronger the shock, the higher the temperature. Such a shock wave may be generated in the laboratory by the sudden bursting of a diaphragm in a brass tube. On the high-pressure side of the diaphragm is an inert driver gas at a pressure of a few atmospheres. When the diaphragm bursts, the driver gas expands rapidly into the region of low pressure in which is the gas to be studied. The main application of this technique to the production of atoms has been in the study of the recombination of bromine and iodine atoms in the presence of various third bodies. A number of other simple systems involving atoms has been investigated, and references to this work are to be found in a recent review of this technique by Pritchard.¹²

Photochemical Methods.—The use of light as a source of energy is the basis of some of the most widely used methods of producing atoms. The two most important reasons for the popularity of photochemical methods are that (1) the amount of energy per photon and hence the amount of energy absorbed per molecule can be controlled by varying the wavelength of the incident radiation, and (2) the rate of input of energy can be controlled by adjusting the intensity of the source. For radiation of constant intensity over long periods of time, the most stable source is a resonance lamp, such as a medium-pressure mercury lamp, which emits radiation at several wavelengths. Light of the required wavelength is obtained by interposing a filter between the source and the reaction cell. The cell contains the absorbing molecule which is the source of atoms, together with the other reactant which should not absorb the incident radiation. Since the output of even the most powerful resonance lamp is relatively low, the rate of production of atoms is also low, and consequently photochemical reactions are usually studied in static or circulating systems. Although the steady-state concentration of atoms is too low to be measured, it is usually unnecessary to know this value. By making use of competing reactions, relative values of rate constants, pre-exponential factors, and energies of activation may be determined from product analyses.

Since photochemistry is concerned with the study of atomic and free-radical reactions, only a few representative methods of producing atoms can be mentioned in a review of this nature. For a fuller discussion, the reader is referred to standard text-books.^{4,5}

Photochemical methods of producing atoms can be conveniently clas-

¹² Pritchard, *Quart. Rev.*, 1960, **14**, 46.

sified under three main headings: (a) direct photolysis, (b) photosensitised decomposition, and (c) flash photolysis. These will be considered in turn.

(a) When a diatomic molecule absorbs a quantum of radiation in the visible or ultraviolet region of the spectrum, it is excited to a higher electronic state. According to the Franck–Condon principle, the most probable transitions are those in which the internuclear distance remains constant. The absorption spectrum of the molecule is determined by this principle, together with the relative positions of the potential-energy curves and the requirements of spectroscopic selection rules. If the minimum of the potential-energy curve of the upper state is at a slightly greater internuclear distance than that of the ground state, the absorption spectrum consists of bands at the longer-wavelength end converging to a continuum at a well-defined wavelength at shorter wavelengths. The onset of the continuum occurs at the maximum wavelength (minimum energy) necessary to dissociate the molecule into atoms, one of which is usually in an excited state. The spectra of oxygen, chlorine, bromine, and iodine all correspond to this description, and in each case, one normal and one excited atom are produced on dissociation. If the upper state is purely repulsive, as in the case of hydrogen, no bands are observed at the long-wavelength end of the continuum.

For direct photolysis to be a useful source of atoms, it is necessary that the region of continuous absorption should occur in an easily accessible part of the spectrum. Continuous absorption by hydrogen and nitrogen occurs only in the extreme vacuum-ultraviolet region, where experimental difficulties are too great for the method to be of use. The oxygen continuum begins at 1759 Å, however, and by using a combined lamp and reaction-cell unit, separated by a thin quartz window, the direct photolysis of oxygen could be used as a source of atoms. Chlorine, bromine, and iodine, on the other hand, are all dissociated by light of wavelength shorter than about 4800 Å, a much more readily accessible region of the spectrum. Consequently, direct photolysis is by far the most important source of halogen atoms. The excess of energy of the excited atom is 2.5, 10.5, and 22.7 kcal./mole. for Cl, Br, and I atoms, respectively, so that whereas the method is excellent for the production of chlorine atoms, it is somewhat less than ideal for iodine atoms.

Although the direct photolysis of hydrogen and oxygen is unsuitable as a source of atoms, both H and O atoms have been obtained by photolysis of other molecules. The primary step in the photolysis of formaldehyde is the formation of a hydrogen atom and a CHO radical.¹³ The photolysis of dideuteroformaldehyde has recently been used as a source of D atoms to study their reactions with hydrogen, methane, and deuterated formaldehyde.¹⁴ Darwent and Roberts¹⁵ have produced deuterium atoms

¹³ Calvert and Steacie, *J. Chem. Phys.*, 1951, **19**, 176.

¹⁴ Klein, McNesby, Scheer, and Schoen, *J. Chem. Phys.*, 1959, **30**, 58.

¹⁵ Darwent and Roberts, *Discuss. Faraday Soc.*, 1953, **14**, 55.

by the photolysis of deuterium sulphide, D_2S , in order to study their reactions with several hydrocarbons.

Oxygen atoms may be obtained by the photolysis of NO_2 at different wavelengths. Photolysis, in which radiation in the region of 3360 Å is used, results in the formation of ground state (3P) atoms, whereas the use of the cadmium resonance line at 2288 Å almost certainly produces atoms in the 1D state.¹⁶ The reactions of oxygen atoms in different electronic states can therefore be studied, although the reactivity of NO_2 itself limits the usefulness of the method.

(b) The dissociation energy of hydrogen is about 103 kcal./mole, which corresponds to the energy available from radiation of about 2750 Å. However, since hydrogen does not absorb in this region no dissociation occurs under these conditions. This difficulty may be overcome by addition of a sensitiser, the function of which is to absorb the radiation and to transfer the energy to the hydrogen by collision. It is clearly desirable that the sensitiser should absorb the incident radiation very strongly, and that it should not interfere with subsequent reaction of the atoms. Since the mercury resonance lamp is the most widely used source of radiation, mercury vapour is an obvious choice as a sensitiser. It will absorb mercury resonance radiation very strongly and is relatively inert. In order that reversal of the resonance radiation should not occur in the lamp, low-pressure lamps are used.

If a mixture of hydrogen and mercury vapour is irradiated with the 2537 Å mercury resonance radiation, the mercury atoms will be excited to the 6^3P_1 state, 112 kcal./mole above the 6^1S_0 ground state. In the absence of the hydrogen, the radiation would be re-emitted, but this is quenched by collision with the hydrogen. Since the hydrogen acquires energy in excess of its dissociation energy, the molecule dissociates and the excess energy appears as kinetic energy of the atoms. The presence of hydrogen atoms in such a system was first demonstrated by the fact that they would reduce metallic oxides present in the reaction cell.¹⁷ Gaseous-phase reactions of the atoms may be studied by the addition of a second gas, but a large excess of hydrogen is necessary to minimise quenching of the excited mercury atoms by the other reactant.

Hydrogen atoms have also been obtained by the mercury-photosensitised decomposition of paraffin hydrocarbons in which the initial reaction is $RH \rightarrow R + H$, followed by $H + RH \rightarrow R + H_2$. If a small amount of an olefin is added to the system, the rate of addition to the olefin relative to the rate of abstraction from the paraffin may be determined by measuring the yield of hydrogen under different conditions.¹⁸

Mercury-photosensitised decomposition of nitrous oxide has proved to be a very convenient source of oxygen atoms.¹⁹ If no other reactant is

¹⁶ Sato and Cvetanovic, *Canad. J. Chem.*, 1958, **36**, 1668.

¹⁷ Cario and Franck, *Z. Phys.*, 1922, **11**, 161.

¹⁸ Jennings and Cvetanovic, unpublished work.

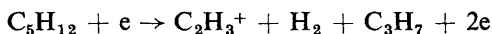
¹⁹ Cvetanovic, *J. Chem. Phys.*, 1955, **23**, 1203; *Canad. J. Chem.*, 1960, **38**, 1678.

present, oxides of nitrogen and mercuric oxide are formed. In the presence of a very small concentration of a substance such as an olefin, which will rapidly remove the oxygen atoms, the reaction is very clean and the rate of production of oxygen atoms can be found by measuring the rate of production of nitrogen. This technique has been used to study the reactions of oxygen atoms with a large number of olefins.

In order to vary the energy input, vapours of other metals have also been used as sensitizers, the most useful being zinc and cadmium. The rare gases, krypton and xenon, can also be used as sensitizers in the vacuum-ultraviolet region of the spectrum, and Groth²⁰ has recently obtained evidence which suggests that nitrogen atoms can be obtained by the krypton-photosensitized decomposition of nitrogen.

(c) In normal photochemical studies, a very low steady-state concentration of atoms is maintained by continuous irradiation. In flash photolysis, however, very high concentrations are produced momentarily by subjecting the reaction mixture to a single intense flash obtained by the discharge of a bank of condensers.²¹ The appearance and decay of reactive intermediates can be observed by following the intensity of their absorption spectra over a period of several hundred milliseconds. Since atoms do not absorb in the accessible region of the spectrum, their reactions can only be inferred from changes in the intensity of other absorption spectra. To avoid the complication of a sharp rise in temperature, the reactants are diluted with a large excess of an inert substance such as nitrogen or argon. Flash photolysis has been widely used in the study of the recombination of halogen atoms in the presence of various third bodies and in the study of combustion processes.²² In the latter studies, it is frequently necessary to introduce a sensitizer such as nitrogen dioxide in order to initiate the reaction, the presence of which may in certain cases interfere with subsequent reactions.

Radiolysis.—This technique has been very little used for the gaseous-phase production of atoms for two main reasons. First, the transfer of energy from a beam of γ -rays to the gas is very inefficient, resulting in extremely low conversions even when a reaction time of several hours is used. Secondly, the very high energy radiation produces many reactive species in addition to atoms. Whereas in the mercury-photosensitized decomposition of pentane, a hydrogen atom and a pentyl radical are the initial products in the radiolysis of pentane, γ -rays cause the emission of secondary electrons from the surface of the reaction vessel, leading to additional reactions²³ such as:



It is therefore very difficult to follow the reactions of the atoms alone and a

²⁰ Groth, *Z. phys. Chem. (Frankfurt)*, 1954, **1**, 300.

²¹ Porter, *Proc. Roy. Soc.*, 1950, *A*, **200**, 284.

²² Norrish and Thrush, *Quart. Rev.*, 1956, **10**, 149.

²³ Futrell, *J. Phys. Chem.*, 1960, **64**, 1634.

large variety of products is found. The addition of a scavenger such as an olefin suppresses the formation of hydrogen by a radical mechanism, and indicates that as much as one-third of the total hydrogen is produced by a molecular mechanism.²⁴

Electrical Discharges.—Electrical discharges have been used for many years to produce a stream of atoms in fast flow systems at low pressures. They have the advantage that high concentrations of atoms are produced, so that a flow system may be used and the atoms may be generated before being mixed with the other reactant.

There are three main types of discharge which are useful to the chemist in the study of atomic reactions: (a) the low-frequency electrode discharge or Wood's tube, (b) the radiofrequency or electrodeless discharge, operating on a frequency of a few Mc./sec., and (c) the microwave discharge, which operates on a frequency of 2500–3000 Mc./sec. A review of electrical discharge techniques has recently been given by Shaw in chapter 3 of reference 6.

In each case, energy is supplied by accelerating electrons under the influence of an applied electric field. The high-velocity electrons collide with molecules, leading to dissociation either by excitation to an unstable electronic state or by a mechanism involving ions. For the discharge to be maintained, the rate of production of electrons in ionising collisions must equal the rate of removal of electrons at the walls or by ion-electron recombination. Consequently, optimum working conditions vary both with the gas to be dissociated and with the type of discharge employed.

The low-frequency discharge was first described by Wood² and was later used extensively by Bonhoeffer for the production of hydrogen atoms.²⁵ It consists of a U-tube, 1–2 metres long with an internal diameter of 2–3 cm., normally of Pyrex glass. The gas is admitted close to the aluminium electrodes at the end of each arm and is withdrawn from the middle of the tube. A mains-frequency voltage of about 2 kv is applied to the electrodes; a steady discharge is normally used, but a pulsed discharge appears to give better results with nitrogen.²⁶ The main disadvantage of the low-frequency of discharge is the risk of contamination with electrode materials. For oxygen, Linnett and Marsden found evidence to suggest that aluminium oxide was carried along in the gas stream.²⁷ The yield of atoms varies widely with different experimental conditions, but for hydrogen atoms Poole²⁸ recommends the use of high flow rates at a pressure of 0.6 mm. Hg. The presence of traces of impurities such as water vapour, and the poisoning of the walls, greatly increase the yield, and these effects are discussed in a later section. This type of discharge tube may be used in the pressure range 0.5–5 mm. Hg, and the addition

²⁴ Back, *J. Phys. Chem.*, 1960, **64**, 124.

²⁵ Bonhoeffer, *Z. phys. Chem.*, 1924, **113**, 199.

²⁶ Evans, Freeman, and Winkler, *Canad. J. Chem.*, 1956, **34**, 1271.

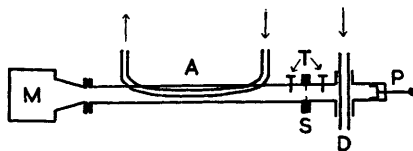
²⁷ Linnett and Marsden, *Proc. Roy. Soc.*, 1956, *A*, **234**, 489.

²⁸ Poole, *Proc. Roy. Soc.*, 1937, *A*, **163**, 404.

of an inert carrier gas such as neon or helium extends the upper limit to about 20 mm. Hg.

The radio-frequency discharge has the advantage that no special discharge tube is necessary and that no electrodes come into contact with the flowing gas. The power is supplied by a radio-frequency oscillator with an output of a few hundred watts in the region 1—20 Mc./sec. The most common form of coupling is a coil of several turns of copper wire wound round a quartz discharge tube with a clearance of about 5 mm. A variable air-condenser across the coil enables one to tune the load to the frequency of the oscillator. In order to avoid the spread of the discharge, an earthed metal screen may be placed between the discharge tube and the coil.²⁹ All leads and electrical instruments must be carefully screened from stray radio-frequency fields. Since this discharge can be maintained at much lower pressures than are possible for electrode or microwave discharges, it is particularly useful in the study of surface reactions of atoms.³⁰

In recent years, the use of the microwave discharge has become increasingly widespread for the production of hydrogen, oxygen, and nitrogen atoms. The usual source of power is a magnetron operating in the frequency range 2500—3000 Mc./sec. with an output of several hundred watts. The output is fed into a standard 3" × 1" waveguide which is in turn coupled to a tunable resonant cavity through which the quartz discharge tube passes (see Figure). It is usually necessary to trigger the



Apparatus for microwave discharge.

M Magnetron. A Water attenuator. T Tuning screws. S Slotted diaphragm. D Discharge tube. P Movable plunger for tuning.

discharge with a Tesla coil. An attenuator is necessary to absorb the power before the discharge is struck, and may take the form of a glass or Polythene tube through which water is passed. The tube is partly lowered into a longitudinal slit in the broad face of the waveguide and is removed after the discharge has been struck. Impedance matching between the magnetron and the discharge is accomplished by means of a movable plunger and a screw tuner. The Figure shows one of many possible arrangements.

The main advantages of the microwave discharge over the radio-frequency discharge are that it is a very intense localised discharge with no tendency to spread, and stray electrical fields are eliminated by the use of the waveguide. It is also possible to maintain a microwave discharge at pressures of several cm. Hg, but the radio-frequency discharge is to be preferred at very low pressures.

²⁹ Jennings and Linnett, *Nature*, 1958, **182**, 597.

³⁰ Greaves and Linnett, *Trans. Faraday Soc.*, 1959, **55**, 1338.

It has long been known that the presence of very low concentrations of impurities greatly increases the percentage dissociation of hydrogen, oxygen, and nitrogen in electric discharges. The presence of as little as 0.05% of water vapour may increase the yield of atoms by a factor of ten or more. Hydrogen which has been purified by passage through a Deoxo unit and silica gel was appreciably dissociated by a microwave discharge, but when it was further dried in a liquid-nitrogen trap, the yield dropped to less than one-tenth of the former value.³¹

Wood² explained the effect of water vapour in terms of poisoning of the walls of the discharge tube, *i.e.*, prevention of recombination of atoms on the walls. However, the insertion of a liquid-nitrogen trap in the hydrogen line results in a rapid drop in hydrogen atom concentration, suggesting a gaseous-phase rather than a surface effect. Kaufman and Kelso³² find rapid and reversible catalytic effects when 0.01% of nitrogen, nitrous oxide, or nitric oxide is added to oxygen which is dissociated in a microwave discharge. Although a surface effect may also be present, it seems that the traces of impurities may facilitate dissociation of the gas in the discharge, perhaps by the initiation of chain reactions.

Surface removal of atoms can be minimised by pre-treating the surface of the discharge tube and reaction vessel with acids such as orthophosphoric acid, but a trace of water vapour is still necessary if high yields of atoms are required. More recently, a mixture of methyltrichlorosilane and dimethyldichlorosilane, known as "Drifilm", has been used,³¹ but water vapour was again necessary to obtain high yields.

The presence of traces of impurities in the gases passing through the discharge is not normally a serious drawback. A more troublesome feature is the production of other potentially reactive products in addition to ground-state atoms. There is no evidence of other reactive species in the products from a hydrogen discharge, but in the cases of oxygen and nitrogen there is considerable evidence of the presence of excited molecules. This evidence is discussed in later sections.

It is difficult to compare the efficiency of the different types of discharge since the yield of atoms depends on the power input as well as the presence of traces of impurities. The products obtained on passing hydrogen or oxygen through a discharge do not appear to depend on the type of discharge, but, as will be seen below, there is evidence to suggest that a powerful condensed electrode discharge through nitrogen produces a second reactive species which is possibly not formed in a micro-wave discharge.

The electrical discharge is seen to be a convenient source of atoms at low pressures and so is well suited to the study of surface reactions and very simple homogeneous reactions such as $O + NO$, $N + NO$, etc., but the necessity of working at low pressures makes the method less suitable for the study of more complex reactions.

³¹ Shaw, *J. Chem. Phys.*, 1959, **31**, 1142.

³² Kaufman and Kelso, *J. Chem. Phys.*, 1960, **32**, 301.

“Hot Atoms.”—A “hot” atom is one which is produced with a great excess of energy and is therefore not in thermal equilibrium with its surroundings. If the atom reacts before attaining thermal equilibrium, the reaction is termed a “hot” reaction. Such reactions normally bear little relation to the reactions of normal atoms and may be distinguished from the latter on addition of a scavenger which will not suppress the reactions of the hot atoms. Hot atoms rapidly lose their excess energy by collision, so that unless they are produced with a vast excess of energy (several hundred kcal./mole), or the “steric factor” is high, hot reactions are not observed.

Hot atoms are usually produced by irradiation of the gas with a beam of neutrons. When chlorine gas is irradiated in this way, atoms of the radioactive isotope, ^{38}Cl , are produced with very high energy and their reactions can be followed by tracer techniques. Hot bromine and iodine atoms may be produced in a similar manner, and recently, hot tritium atoms have been produced from ^3He .³³ A review of hot-atom chemistry up to 1955 has been given by Willard.³⁴

The Detection and Estimation of Atoms

With few exceptions, atoms are always found in systems which contain other species in addition to the atoms, and consequently, the method chosen to detect or estimate the atoms is to some extent governed by the nature of these other species. Although it is possible to demonstrate the presence of atoms in complicated reacting systems (such as flames), quantitative measurements in such systems are difficult to make and have therefore been confined very largely to simple systems in which fairly high concentrations of atoms were present.

Almost any property in which the atom differs from the other species present may be used as a basis for detection. Methods based on such differences as mass, spectra, and chemical reactivity have been widely used, and although some of these methods are of qualitative or semi-quantitative value only, several techniques are now available for the measurement of *relative* atom concentrations with reasonable accuracy. Unfortunately, reliable values of *absolute* atom concentrations are more difficult to obtain. Several different methods were used to measure the absolute atom concentration in the effluent gas from an oxygen discharge, and the values obtained differed by as much as 25%.³⁵ Possible errors involved in the use of the different methods are considered in the appropriate sections below.

For quantitative work it is desirable that the act of measuring the atom concentration should interfere as little as possible with the system under investigation. Alternatively, the atom concentration may be measured in

³³ Henchman, Urch, and Wolfgang, *Canad. J. Chem.*, 1960, **38**, 1722.

³⁴ Willard, *Ann. Rev. Phys. Chem.*, 1955, **6**, 141.

³⁵ Elias, Ogrzylo, and Schiff, *Canad. J. Chem.*, 1959, **37**, 1680.

the absence of the second reactant, after which the reaction is carried out under as nearly identical conditions as possible. In addition, the method employed should be specific for the atoms concerned and should not be affected by the presence of other species in the system. In certain cases, it is desirable to measure the atom concentration at a point or at a given position along a tube rather than to obtain an average over a fairly large volume. The following generalisations may be made concerning the more common methods in use.

(a) The mass spectrometer and the Wrede gauge are the two methods in general use that are dependent on mass difference. Both affect the system to a negligible extent, the Wrede gauge giving absolute values in simple systems at very low pressures, the mass spectrometer being more specific.

(b) Calorimetric methods are based on the heat liberated by the recombination of the atoms. They have a greater effect on the system than the above methods and are unreliable in the presence of other excited species.

(c) Emission spectra give information about excited species only and, since most atoms do not absorb in readily accessible regions of the spectrum, indirect methods are necessary. Spectroscopic methods usually yield values over an extended zone rather than at a point.

(d) Electron spin resonance is just beginning to be used for the gaseous phase. It is very sensitive, has no effect on the system, and has been used both to detect atoms and to obtain relative concentrations.

(e) Chemical reactions of atoms may be used to measure atom concentrations if the reaction is simple and very fast and has a known mechanism. Chemical methods are probably the most reliable methods of estimating oxygen and nitrogen atoms generated by discharges.

Methods Dependent upon Mass Difference.—(a) *The Mass Spectrometer.* Since the application of the mass spectrometer to the study of free radicals has recently been reviewed,³⁶ the reader is referred to that article for an account of the experimental procedure. Since the mass spectrometer can distinguish between atoms of different mass, it may be used for detection of more than one type of atom in a complex reaction. In addition, it is possible to distinguish between different electronic states of an atom, since these have different appearance potentials. Although absolute atom concentrations cannot be measured, because of recombination on the walls of the instrument, reliable relative concentrations can be obtained.

Mass-spectrometric analyses have been carried out on the products obtained when oxygen³⁷ and nitrogen³⁸ are subjected to an electrical discharge. In the case of oxygen, ground-state atoms were found to be the most abundant reactive species, but electronically excited oxygen

³⁶ Cuthbert, *Quart. Rev.*, 1959, **13**, 215.

³⁷ (a) Foner and Hudson, *J. Chem. Phys.*, 1956, **25**, 602; (b) Herron and Schiff, *Canad. J. Chem.*, 1958, **36**, 1159.

³⁸ (a) Jackson and Schiff, *J. Chem. Phys.*, 1955, **23**, 2333; (b) Berkowitz, Chupka, and Kistiakowsky, *J. Chem. Phys.*, 1956, **25**, 457.

molecules in the $^1\Delta_g$ state were present in concentrations in the region of 10–20%. In the case of nitrogen, ground-state atoms were the only reactive species found when a microwave discharge was used.^{38a} When an electrode discharge tube was used, however, a second excited species was found, with an appearance potential of 16.1 eV^{38b} and suggests the presence of metastable nitrogen molecules in an unknown state of excitation. The absence of this appearance potential when a microwave discharge was used may have been caused by unfavourable sampling conditions or may imply that the second species is not formed in a microwave discharge.

(b) *The Wrede Gauge*. This was first described by Wrede³⁹ and has been used to measure absolute atom concentrations in simple systems at low pressures. A detailed account of its construction and use has recently been given.³⁰ The gauge consists of a hole in the wall of the tube along which the gas is flowing. Behind the hole, a catalytic surface is enclosed in a small volume, together with a pressure gauge. Providing that the mean free path in the gas, λ , is at least ten times the diameter, d , of the hole, the flow through the hole is purely molecular. Under these conditions, the recombination of atoms on the catalytic surface behind the hole causes a pressure differential to be set up across the hole. If p is the pressure in the tube, Δp the pressure differential, and α the volume percentage of atoms (no. of atoms/total no. of particles) then, at equilibrium, $\alpha = 3.41 \Delta p/p$, and α may be determined by measuring p and Δp . Since Δp must be known very accurately, it is best measured directly by means of a differential pressure gauge. The time necessary to attain equilibrium is inversely proportional to the area of the hole and directly proportional to the volume behind the hole.

Because of the λ/d requirement, a hole of diameter 0.1 mm. cannot be used in hydrogen at pressures exceeding 0.1 mm. Hg, and in oxygen and nitrogen the maximum pressure would be about 0.07 mm. Hg, at room temperature. The use of sintered discs to decrease the equilibration time at higher pressures may lead to unreliable results, since the large number of small holes in close proximity may be little better than the use of a single larger hole, and will also cause more atoms to be abstracted from the system.³⁰ Care must also be taken to avoid temperature differentials across the hole, which would give rise to spurious readings because of thermal molecular-pressure effects. Similar effects complicate its use at elevated temperatures.

Since Δp is usually measured by means of a thermal-conductivity gauge, the Wrede gauge is suitable for use with a pure gas only. In a reacting system, changes in conductivity may arise from variations in pressure or in composition. If the use of the gauge is confined to very low pressures in pure gases at room temperature, measurements of absolute concentrations should be quite reliable since the readings are not affected by the presence of excited species.

³⁹ Wrede, *Z. Phys.*, 1929, 54, 53

Calorimetric Methods.—Since the dissociation energies of hydrogen, oxygen, and nitrogen are 103, 117, and 225 kcal./mole, respectively, considerable heat is liberated when atoms of these elements recombine, as may be seen from the “hot spots” which are occasionally observed on the walls of fast-flow systems. Bonhoeffer²⁵ coated the bulbs of thermometers with catalytic surfaces and observed appreciable rises in temperature when the thermometers were exposed to a stream of hydrogen atoms. The rise in temperature is only very approximately proportional to the atom concentration, for several reasons. The catalytic activity of the surface is usually temperature-dependent, and may decrease slowly owing to “poisoning” by traces of impurities.⁴⁰ In addition, any excited atoms or molecules present in the system will also liberate heat on striking the catalytic surface, and heat losses will be difficult to estimate. Furthermore, considerable numbers of atoms will be removed from the system in order to produce an appreciable temperature rise. Two modifications of Bonhoeffer’s original method have been developed in an attempt to overcome some of these objections.

(a) *The Catalytic Probe.* This usually consists of a very small piece of metal such as platinum or silver, attached to a thermocouple, the leads of which are encased in silica. The area of the metal is in the region of 1 mm.² so that comparatively few atoms are removed from the system. Since small increases in temperature can be measured accurately, cooling corrections and variations of the catalytic activity with temperature are minimised. Providing that surface poisons as well as excited atoms and molecules are absent, the catalytic probe may be used to obtain relative atom concentrations. Greaves and Linnett were able to correlate the temperature rise of a catalytic probe with the absolute concentrations obtained from a Wrede gauge, suggesting that these assumptions were justified under their experimental conditions.³⁰

(b) *The Isothermal Calorimeter.* Whereas the catalytic probe is designed to abstract as few atoms as possible from the system, the isothermal calorimeter aims to abstract all atoms from a stream of gas, thereby allowing absolute concentrations to be determined. The calorimeter is electrically maintained at a given temperature, and the fall in the input of electrical energy recorded when the discharge is in operation is a measure of the heat supplied to the calorimeter from the gaseous phase. If the flow-rate of the gas and the heat of recombination of the atoms are known, and on the assumption that this is the only source of heat, absolute concentrations may be calculated. Since the process is isothermal, heat losses are constant and the catalytic activity of the surface remains much more nearly constant.

This method was used by Tollefson and LeRoy to measure hydrogen atom concentrations,¹⁰ the detector being a coil of platinum wire. Since

⁴⁰ Fox, Smith, and Smith, *Proc. Phys. Soc.*, 1959, 73, 533.

there is no evidence of the presence of excited atoms or molecules in the effluent gas from a discharge through hydrogen, this method is likely to be very reliable, generally, for the measurement of absolute concentrations of hydrogen atoms in flow systems. Concentrations of deuterium atoms determined in this way agree very closely with values obtained by chemical methods.³⁵

In the case of oxygen, its use is complicated by the presence of excited oxygen molecules.³⁵ The platinum coil was silver-plated. On exposure to the atoms, the silver was rapidly converted into silver oxide which is an excellent catalyst for the recombination of oxygen atoms. When a little nitric oxide was added to the gas stream, the green air-afterglow was completely quenched by the coil, indicating the complete removal of atoms. This was, however, no longer true at temperatures above 100°C, presumably owing to a decrease in the activity of the silver oxide surface.

It was found that chemical methods and Wrede-gauge measurements gave consistently lower readings than those obtained from the isothermal calorimeter, and the discrepancy increased when the detector was coated with cobalt oxide. When all the atoms were removed by a mercury mirror, a considerable amount of heat was still liberated at the cobalt oxide detector, presumably owing to deactivation of excited molecules. It was found that a freshly prepared silver oxide surface removed all the atoms but deactivated very few excited molecules, and this was used to measure atom concentrations. After several runs, however, increasing numbers of excited molecules were also recorded, and a fresh detector was then necessary.

Little is known about the catalytic activity of different surfaces in effecting recombination of nitrogen atoms and, in view of the presence of other reactive species in "active nitrogen", calorimetric methods are of little use in the estimation of nitrogen atoms.

Spectroscopic Methods.—Since the ground-state atoms of most non-metallic elements do not absorb in easily accessible regions of the spectrum, absorption spectroscopy has not been widely used to detect the presence of atoms. However, Tanaka *et al.*⁴¹ were able to show that the concentration of excited atoms in active nitrogen is very low, but they observed strong absorption at 1200 Å, which indicated a much higher concentration of ground-state atoms.

Absorption spectroscopy is widely used in the technique of flash photolysis to detect unstable radicals, but the presence of atoms has to be inferred by indirect methods. In the study of the recombination of iodine atoms, the decay of the atoms is followed by observing the increase in the intensity of the absorption spectrum of molecular iodine, and the appearance of the hydroxyl radical spectrum in a system is usually due to hydrogen-abstraction by oxygen atoms.

⁴¹ Tanaka, Jursa, and LeBlanc, "The Threshold of Space", Pergamon, London, 1957 p. 89.

A quantitative estimate of oxygen and nitrogen atom concentrations has recently been made by using the absorption spectrum of nitric oxide.⁴² When just enough NO_2 is added to quench the faint oxygen afterglow, a molecule of nitric oxide is produced for every oxygen atom present (see below under chemical methods), and the concentration of nitric oxide is then measured spectroscopically. In the case of nitrogen, the afterglow is just quenched by the addition of nitric oxide, and the discharge is then switched off and the nitric acid concentration is again found spectroscopically. In each case, the atomic concentration is equivalent to the nitric oxide concentration.

Emission spectra have been little used in quantitative work, since it is necessary for the species to be present in an excited state for such spectra to be observed. As is to be expected, atomic lines are often observed in discharges, and the emission of radiation by metal atoms is the basis of the familiar flame tests of inorganic qualitative analysis.

Hartel and Polanyi⁴³ measured the concentration of ground-state sodium atoms in a diffusion flame by illuminating the flame with the radiation of a sodium resonance lamp and measuring the intensity of the resonance radiation emitted. Other methods of measuring the concentration of ground-state atoms based on emission spectra have been indirect. When a little nitric oxide is introduced into a flame containing oxygen atoms, a yellow-green continuum is observed due to the occurrence of the reaction $\text{O} + \text{NO} \rightarrow \text{NO}_2 + h\nu$, and this has been used in a qualitative⁴⁴ and semiquantitative⁴⁵ manner to demonstrate the presence of oxygen atoms in hydrogen flames. Further use of this reaction is described in the section below on chemical methods.

Sugden and his collaborators⁴⁶ have recently described a method of measuring the concentration of hydrogen atoms in flames. Small, equal amounts of sodium and lithium are introduced into the burner gases as salt sprays, and the intensities of the resonance lines of each metal are compared, the relative transition probabilities being known. Since sodium atoms do not form compounds, the sodium resonance line is used as a reference. Some lithium is removed as the very stable lithium hydroxide by the reversible reaction, $\text{Li} + \text{H}_2\text{O} \rightleftharpoons \text{LiOH} + \text{H}$. The weakness of the lithium resonance line readily shows up, and from its intensity, and from the calculated equilibrium constant of the above reaction, the concentration of hydrogen atoms may be determined. The concentrations of lithium and sodium are kept very low so as to avoid self-reversal. The temperature of the flame is measured by the sodium-line reversal method. It is estimated that absolute values can be measured to within $\pm 20\%$ and relative values to within $\pm 5\%$.

⁴² Broida, Schiff, and Sugden, *Nature*, 1960, **185**, 760.

⁴³ Hartel and Polanyi, *Z. phys. Chem.*, 1930, **B**, **11**, 97.

⁴⁴ Gaydon, *Trans. Faraday Soc.*, 1946, **42**, 292.

⁴⁵ James and Sugden, *Nature*, 1955, **175**, 252.

⁴⁶ Bulewicz, James, and Sugden, *Proc. Roy. Soc.*, 1956, **A**, **235**, 89.

Electron-spin Resonance.—One of the intrinsic properties of atoms, with the exception of the rare gases, is that they all possess one or more unpaired electrons. If a strong magnetic field is applied to such atoms, the normal system of energy levels is disturbed and splitting of the levels occurs. Since the electron has a magnetic moment associated with it, it will align its spin and moment either parallel or antiparallel to the field if placed in a d.c. magnetic field. The energy splitting between the two levels is given by $g\beta H$, where g is the splitting factor of 2.0023, β is the Bohr magneton, and H is the strength of the magnetic field.

By choosing a suitable value for H , the atom can be made to absorb in the microwave region, the frequency being given by $h\nu = g\beta H$. The sensitivity is much greater at microwave frequencies than at radio-frequencies, and a field of about 3000 gauss is usually used in conjunction with radiation of a frequency in the region of 9000 Mc./sec.

When this method is used to detect atoms in the gaseous phase, the stream of atoms is passed through a quartz tube between the poles of the magnet and at right angles to the broad face of the waveguide. The power is provided by a magnetron or klystron, and a crystal detector may be used to measure the absorption of radiation. Details of practical systems are given by Ingram.⁴⁷

Since the intensity of the absorption will depend on the number of atoms present, the method is ideally suited to the measuring of relative atom concentrations. Shaw used this technique to determine the effect of water vapour on the dissociation of hydrogen in a microwave discharge,³¹ and it has also been used to demonstrate the presence of ground-state atoms in active nitrogen.⁴⁸ The relative concentrations of oxygen atoms have been determined by electron-spin resonance spectroscopy in a study of the recombination of the atoms at surfaces.⁴⁹

The method can be made very sensitive, detecting less than 10^{12} atoms per c.c. (less than 0.1% atoms at 0.1 mm. Hg), but absolute measurements can only be made with the help of a suitable reference measurement. In addition to its high sensitivity, the method has the advantages that it may be used in complex systems to follow relative concentrations of different species simultaneously without in any way affecting the chemical processes, and it also gives an instantaneous reading over a small region of the tube.

Application of electron-spin resonance to the gaseous phase is a very recent development and it is probable that its use will be extended in the near future. Its high inherent sensitivity opens up a prospect that one may be able to measure steady-state concentrations of reactive intermediates during the course of a reaction under favourable conditions.

Chemical Methods.—The high chemical reactivity of atoms has fre-

⁴⁷ Ingram, "Free Radicals as studied by Electron Spin Resonance", Butterworths, London, 1958.

⁴⁸ Heald and Beringer, *Phys. Rev.*, 1954, **96**, 645.

⁴⁹ Strandberg and Krongelb, *J. Chem. Phys.*, 1959, **31**, 1196.

quently served as a basis for a method of detecting their presence. It is the only method which can be used in photochemical systems since the steady-state concentrations of the atoms are too low to be measured by physical methods. In complex systems, however, unless the mechanism is well understood, product analysis may not provide unequivocal evidence for the presence of atoms.

One of the earliest examples of the use of chemical reactivity to demonstrate the presence of atoms in a photochemical system was the reduction of metallic oxides by hydrogen atoms produced by the mercury-photo-sensitised decomposition of hydrogen.¹⁷ Melville and Robb recently used molybdenum trioxide for quantitative work;⁵⁰ this oxide is a yellow powder which becomes blue on exposure to hydrogen atoms. By measuring the rate at which the oxide becomes blue in the presence and the absence of an olefin, and by calibrating the apparatus by using the rate of conversion of para-hydrogen into ortho-hydrogen, absolute rate constants were obtained for the reaction of hydrogen atoms with a number of olefins.

Pearson, Robinson, and Stoddart⁵¹ used the Paneth mirror technique to detect the presence of hydrogen atoms. An antimony mirror on the walls of the tube is slowly removed by the formation of a volatile hydride. A lead mirror, which is not affected by the atoms, is used to remove alkyl radicals before they reach the antimony mirror. This method has not been used for oxygen or nitrogen atoms since the mirrors would rapidly be coated with a non-volatile oxide or nitride. Even when it is used with hydrogen atoms, the results are not very reproducible because of poisoning by traces of impurities, and gaseous-phase reactions are preferable for quantitative work.

For such a reaction to be of use, two general requirements must be fulfilled: (1) the reaction must be simple and the mechanism known, and (2) the reaction must be much faster than any other reaction which removes atoms. A reliable method of following the extent of the reaction is also necessary, and this may be accomplished photometrically if the reaction is chemiluminescent, or alternatively by product analysis.

Iodine has been used as a scavenger for hydrogen atoms and free radicals in the photolysis of a number of compounds.^{4,5} Iodine reacts rapidly with the species formed in the primary photochemical act, forming compounds such as hydrogen iodide and alkyl iodides. This allows one to infer the nature of the species without the complications of secondary processes.

Although the concentration of hydrogen atoms produced in a discharge may be estimated by physical methods, it has been seen that reliable values for oxygen and nitrogen atom concentrations are more difficult to obtain, and gaseous-phase titration of these atoms has become increasingly popular. The various methods used will be dealt with under types of atom.

⁵⁰ Melville and Robb, *Proc. Roy. Soc.*, 1949, *A*, 196, 445.

⁵¹ Pearson, Robinson, and Stoddart, *Proc. Roy. Soc.*, 1933, *A*, 142, 275.

(a) *Deuterium*. If deuterium atoms are produced in a fast-flow system by an electrical discharge or by a heated filament, and are then mixed with an excess of ethylene, the reaction $D + C_2H_4 \rightarrow$ Products is very rapid, and effectively all the deuterium atoms are removed in this way. The products of the reaction are deuterated methanes, ethanes, and ethylenes, and if it is assumed that all atoms present initially are to be found in these products, an analysis of the products for deuterium will enable one to calculate the deuterium atom flow rate. Results obtained in this way agree to within 0.5% with those obtained by means of an isothermal calorimeter.⁵⁵

(b) *Oxygen*. Atomic oxygen reacts very rapidly with nitrogen dioxide according to the equation



the rate constant for this reaction being⁵² in the region of 3×10^{-12} cm.³ molecules⁻¹ sec.⁻¹. Spealman and Rodebush⁵³ added an excess of nitrogen dioxide to a stream of atomic oxygen and froze out the products at liquid-nitrogen temperature. The amount of nitric oxide formed in a given time was then determined, enabling them to calculate the flow-rate of atomic oxygen.

More recently, Kaufman⁵⁴ has used the above reaction in conjunction with the reaction



If a little NO_2 is added to the stream of atomic oxygen, nitric oxide is formed by reaction (1). This, in turn, reacts as in reaction (2) to produce the yellow-green air afterglow. If the flow rate of nitrogen dioxide is slowly increased, more nitric oxide is formed, but fewer atoms remain to react with the nitric oxide until finally a point is reached where the glow is just extinguished. At this point, the flow-rate of the nitrogen dioxide is equal to that of the oxygen atoms. The results obtained by this method agree within experimental error with those obtained by using the method of Spealman and Rodebush, and since the gaseous-phase titration is simpler it has generally been preferred. At pressures in the region of 1 mm. Hg, this is probably the most reliable method of determining absolute concentrations of oxygen atoms, since excited molecules interfere with calorimetric methods and, unless a sintered disc is used, the pressure is too high for the use of a Wrede gauge.

Relative atom concentrations down a tube can be determined photometrically by making use of the green glow emitted in reaction (2). If a little nitric oxide is added to a stream of atomic oxygen, nitrogen dioxide is formed, but since reaction (1) is faster than reaction (2) or the corresponding three-body reaction $O + NO + M \rightarrow NO_2 + M$, the nitric oxide is

⁵² Ford and Endow, *J. Chem. Phys.*, 1957, **27**, 1156.

⁵³ Spealman and Rodebush, *J. Amer. Chem. Soc.*, 1935, **57**, 1474.

⁵⁴ Kaufman, *Proc. Roy. Soc.*, 1958, *A*, **247**, 123.

immediately regenerated and its concentration remains constant down the tube. Hence the intensity of the glow is proportional to the concentration of oxygen atoms at any point, and relative concentrations are readily found. These can be converted into absolute readings by calibrating the system by the nitrogen dioxide titration method or by means of the isothermal calorimeter.

(c) *Nitrogen*. Two quite different chemical methods have been used to determine absolute concentrations of nitrogen atoms. The first of these makes use of the reaction



in a way which is entirely analogous to Kaufman's use of reaction (1) for oxygen atoms. If a little nitric oxide is added, it is all destroyed by reaction (3) so that the system contains both oxygen and nitrogen atoms. Excited nitric oxide molecules may then be formed by slow combination of these atoms in the presence of a third body. Emission from these molecules accounts for the range of colours yellow-pink-blue as the nitric oxide content increases. If sufficient nitric oxide is added, all the nitrogen atoms will be consumed, and there will be no afterglow. At this point, the flow-rate of nitric oxide gas is equal to that of nitrogen atoms, and the stream of gas consists only of nitrogen molecules and oxygen atoms.⁵⁵ If an excess of nitric oxide is added, the green $\text{O} + \text{NO}$ afterglow is produced (reaction 2). Nitrogen atoms were estimated in this manner in a recent study of the rate of recombination of nitrogen atoms by three-body collisions.⁵⁶ In an earlier investigation, the effluent gas was continuously sampled mass-spectrometrically as the nitric oxide flow-rate was increased.⁵⁷ At the "equivalence point", no nitrogen atoms or nitric oxide molecules could be detected, and the flow-rate of nitric oxide was equal to that of the nitrogen atoms. The addition of nitric oxide to a stream of active nitrogen is a useful way of producing a stream of oxygen atoms in the absence of oxygen molecules and has recently been used for this purpose.⁵⁸

The above method of estimating nitrogen atom concentrations assumes that nitric oxide is destroyed only by the atoms and not by any other excited species. This has been disputed by Verbeke and Winkler who determined the atom concentration by measuring the rate of production of hydrogen cyanide in the reaction with ethylene at 400°C. Although the mechanism of this reaction is not well-established, the reaction is fast, and products containing nitrogen, other than hydrogen cyanide, are formed in very small amounts, and it is assumed that all nitrogen atoms produce hydrogen cyanide in the presence of an excess of ethylene.⁵⁹ Concentra-

⁵⁵ Kaufman and Kelso, *J. Chem. Phys.*, 1957, 27, 1209; 1958, 28, 992.

⁵⁶ Harteck, Reeves, and Manella, *J. Chem. Phys.*, 1958, 29, 608.

⁵⁷ Kistiakowsky and Volpi, *J. Chem. Phys.*, 1957, 27, 1141.

⁵⁸ Morgan, Elias, and Schiff, *J. Chem. Phys.*, 1960, 33, 930.

⁵⁹ Verbeke and Winkler, *J. Phys. Chem.*, 1960, 64, 319.

tions determined in this way were compared with results obtained by the nitric oxide titration method at pressures of 1–16 mm. Hg. At all pressures, it was found that the latter method gave much higher values, ranging from 40% higher at 1 mm. Hg to 140% higher at 16 mm. Hg. Verbeke and Winkler suggest that the nitric oxide may be destroyed either by excited nitrogen molecules in the A state, or perhaps by some sort of chain reaction.

Since the reaction of nitrogen atoms with ethylene is not simple, it seems possible that not all the nitrogen atoms react to form hydrogen cyanide, thereby leading to a low result. However, a number of different hydrocarbons differing widely in structure gave the same maximum rate of hydrogen cyanide production. This suggests either that all the hydrocarbons were equally efficient catalysts in causing nitrogen atoms to recombine, which is most unlikely, or that the rate of production of hydrogen cyanide is a true measure of the concentration of the atoms.

It is possible that the different types of discharge used may explain the discrepancy. Verbeke and Winkler used a condensed electrode discharge, which is known to produce a reactive species in addition to ground state atoms.^{38b,60} The microwave discharge, which is more generally employed, does not appear to produce such molecules.^{38a} Ammonia is thought to react with the second excited species,⁶⁰ but the concentration measured by the nitric oxide titration technique was unaffected when ammonia was injected between the microwave discharge and the nitric oxide jet,⁶¹ again suggesting that the microwave discharge does not produce appreciable concentrations of the second excited species. In addition, although ammonia is decomposed to some extent by the products of a condensed discharge through nitrogen,⁶⁰ no reaction was found with the products from a microwave discharge.⁶² Until a little more is known about the second excited species, it seems reasonable to suppose that the nitric oxide titration method is probably quite reliable when used with a microwave discharge, but that the $N + C_2H_4$ reaction at 400°C is the more reliable method when a condensed discharge is used.

Conclusion

Although considerable progress has been made in our understanding of atomic reactions, there is as yet no substantial body of quantitative results. The energies of activation of many reactions can be estimated only by assuming a steric factor of 0.1, and experience has shown that this is often in error by several factors of ten. Reliable rate constants have been obtained for many reactions at room temperature, but much still remains to be done on the effect of temperature and surfaces and the presence of

⁶⁰ Freeman and Winkler, *J. Phys. Chem.*, 1955, **59**, 371.

⁶¹ Herron, Franklin, Bradt, and Dibeler, *J. Chem. Phys.*, 1959, **30**, 879.

⁶² Kistiakowsky and Volpi, *J. Chem. Phys.*, 1958, **28**, 665.

different third bodies in many cases. In addition, little is known about the reactions of excited atoms which are certainly present in some of the more energetic reactions.

The author thanks Dr. J. W. Linnett for reading the manuscript of this Review.