THE APPLICATION OF MASS SPECTROMETRY TO CHEMICAL PROBLEMS

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Introduction

Historical.—Positive rays were discovered by Goldstein [1] in 1886. In experiments on the discharge of electricity through gases at low pressure, he used a perforated cathode and noticed that a luminous discharge streamed through the holes in the cathode into the space behind. Wien [2] showed that these rays could be deflected by a magnetic field, and J. J. Thomson [3] subsequently investigated them in great detail by use of the well-known " parabola method ". In this the rays pass through a narrow tube in the cathode and, under the influence of electric and magnetic fields, the narrow beam of ions is drawn out to record a series of parabolic arcs on a photographic plate, each arc corresponding to ions of a definite mass to charge (m/e) ratio.

The intensity of the lines on a photographic plate varies not only with the number of ions striking it, but also with their nature. Thomson replaced the photographic plate by a metal plate in which there was a parabolic slit. By increasing the magnetic field, he could drive one parabola after another into the slit and on to a highly insulated cup or Faraday cage connected to a Wilson electroscope; in this way the ion currents for each value of m/e could be measured electrically and compared. The subject has since developed along two main lines: the accurate comparison of isotopic masses characterised mainly by photographic recording, and the accurate comparison of ion abundances characterised by electrical recording; the former is referred to as mass spectrography (or mass spectroscopy) and the latter as mass spectrometry. The development of mass spectrography is associated with the names of Aston,[4] Bainbridge, Dempster, Jordan, and Mattauch and lies outside the scope of this Review.[5] Mass spectrometry, apart from the experiments of Thomson indicated above, began in 1916 with the construction by Dempster [6] of an instrument for measuring ion abundances. Since then many improvements have been made, especially by Bleakney [7] and by Nier.[8]

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[1] Goldstein, *Sitzungsber. Akad. Wiss., Berlin*, 1886, **39**, 691; *Wied. Ann.*, 1898, **64**, 38; *Phil. Mag.*, 1908, **16**, 372.

[2] Wien, *Wied. Ann.*, 1898, **65**, 440; *Verh. phys. Ges., Berlin*, 1898, **17**, 10.

[3] J. J. Thomson, *Phil. Mag.*, 1907, **13**, 561; " Rays of Positive Electricity and their Application to Chemical Analysis ", Longmans, Green and Co., London, 1913.

[4] Aston, *Phil. Mag.*, 1919, **38**, 707.

[5] See Aston, " Mass Spectra and Isotopes ", Arnold, London, 1942, and Jordan and Young, *J. Appl. Phys.*, 1942, **13**, 526, for reviews of this subject.

[6] Dempster, *Phys. Rev.*, 1918, **11**, 316.

[7] Bleakney, *ibid.*, 1929, **34**, 157; 1930, **35**, 139; 1932, **40**, 496.

[8] Nier, *ibid.*, 1936, **50**, 1041; 1937, **52**, 933; *Rev. Sci. Instr.*, 1940, **11**, 212; 1947, **18**, 398.

Principle of the Mass Spectrometer.—If an ion of mass m and charge e initially at rest is accelerated through a potential difference V, it will attain a velocity v given by

$$\tfrac{1}{2}mv^2 = Ve \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

If the ion now enters a uniform magnetic field of strength H, the lines of force of which are perpendicular to the direction of motion, the ion will be subject to a force depending in magnitude upon H, e, and v, and acting at right angles to both the direction of motion and the direction of the magnetic field. The path of the ion in the field will be a circle of such a radius r that the centrifugal force mv^2/r balances the force Hev due to the field. Thus:

$$mv^2/r = Hev \quad \text{or} \quad r = mv/He \quad \text{or} \quad mv = rHe$$

The radius of the path thus depends upon the momentum mv of the ion. Substituting from (1) for v,

$$m/e = r^2H^2/2V \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

When a number of ions differing in mass are accelerated through the same potential difference V into the magnetic field, the ions of each mass will follow a different path. Thus an ion beam initially consisting of ions of various masses (strictly, ratios of mass to charge) separates into a number of beams each homogeneous with respect to the mass of the constituent ions.

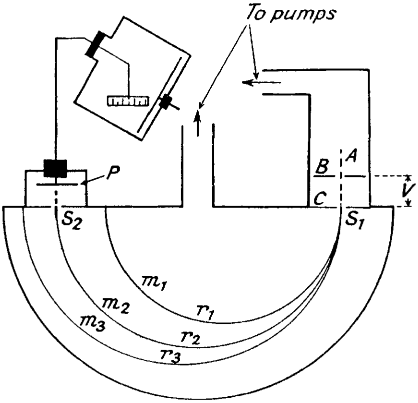

FIG. 1

Schematic diagram of Dempster's mass spectrometer.

In Dempster's[9] apparatus (Fig. 1), ions are formed in the region A, pass through the slit in B, and are accelerated by the potential difference V applied between B and C. A slit in C selects out a thin ribbon of ions which on entering the magnetic field (directed perpendicular to and out of the paper) is bent into semicircles of radii r_1, r_2, r_3, etc., depending on the masses m_1, m_2, m_3, etc., of the constituent ions. By altering V, the paths of these ions can be made to coincide one at a time with the semicircle whose

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[9] Dempster, *Phys. Rev.*, 1922, **20**, 631.

diameter is S_1S_2 ; the ions in question then pass through the slit S_2 and fall upon the collector plate P, and their intensity is registered as the current arriving at P.

Refocusing.—A simple geometrical construction will show that if the beam of ions leaving S_1 is divergent, the semicircular paths of the same radius intersect again on the line S_1S_2 (Fig. 2*a*). This property of refocusing is found for other shapes of magnetic fields.[10] Consider, for example, a sector-shaped field (Fig. 2*b*) which is uniform within and bounded by the angle BOC. If the points AOD lie on a straight line, an ion beam diverging from A will converge at D if the central ray AR is normal to OB and if OR is the radius of curvature of the path of the ion in the field. Such sector fields act both as deflecting prisms and as lenses. The angle BOC is usually chosen to be either 60° (Nier [11]), 90° (Hipple [12]), or 180° (Dempster). The value of the mass resolution $m/\delta m$ signifies that a beam of ions of mass $m + \delta m$ can just be distinguished from a beam of mass m. If perfect refocusing were obtained, the mass resolution would be given by $m/\delta m = OR/(S_1 + S_2)$ where S_1 and S_2 are the widths of the two slits ; it will be noticed that the angle BOC does not enter. In practice, many unavoidable aberrations reduce the resolution below this limit.[13]

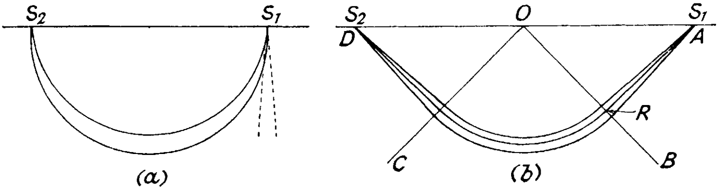

FIG. 2

Refocusing of ions in a magnetic field.

The Ion Source.—Ions produced in a discharge tube have widely different energies, so that ions even of the same mass have different momenta. Since the magnetic prism is a momentum analyser for ions of a given charge, discharge tubes are unsuitable as ion sources for mass spectrometers : the essential features of a suitable source are shown in Fig. 3. Electrons are drawn from the heated filament F, by means of a potential difference between F and the ionisation chamber Ch. A ribbon of electrons enters the chamber Ch through the slit S_3 and, collimated by a local magnetic field between the poles M_1 and M_2, leaves through another slit S_4 to fall upon the electron catcher C which is maintained at a potential positive with respect to the chamber. Molecules of the gas to be studied are led into the chamber through the tube D and there, under the impact of the

[10] Barber, *Proc. Leeds Phil. Lit. Soc.*, 1933, **2,** 427 ; Hughes and Stephens, *Phys. Rev.*, 1934, **45,** 123 ; Stephens, *ibid.*, p. 513 ; 1946, **69,** 691.

[11] Nier, *Rev. Sci. Instr.*, 1940, **11,** 212 ; 1947, **18,** 398.

[12] Hipple, *J. Appl. Phys.*, 1942, **13,** 551 ; Hipple, Grove, and Hickman, *Rev. Sci. Instr.*, 1945, **16,** 69 ; Graham, Harkness, and Thode, *J. Sci. Instr.*, 1947, **24,** 119.

[13] Barnard, " Modern Mass Spectrometry ", Institute of Physics, London, 1953.

electron beam, become ionised. The resulting ions are urged towards the slit S_5 in the plate P_5 by a small potential difference between P_5 and the repeller electrode R. Ions which pass through S_5 are subject to the main accelerating voltage V applied between P_5 and P_1 and pass out of the ion source *via* S_1 in P_1. The two slits S_5 and S_1 serve to select a narrow ribbon of ions. More recent designs have multiple slit systems which function as ion lenses in concentrating and focusing the beam.

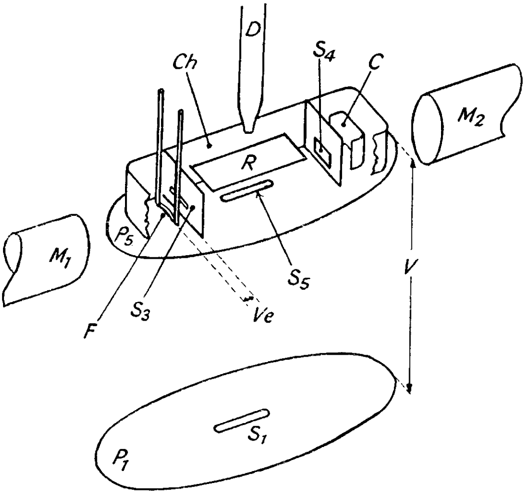

FIG. 3
Essential details of an ion source.

Principal Features of a Mass Spectrometer.—A complete mass spectrometer is a complex instrument. The basic components consisting of the ion source, magnetic analyser, and ion collector require a large amount of auxiliary equipment for their operation. For this Review, only the principal features of a simple instrument will be described.

The analyser tube A (Fig. 4) is made from copper tube of 5 cm. diameter bent through 90° on a radius of about 15 cm. and is flattened to 2 cm. over the section AA in order to fit between the poles of the magnet M, which may be a permanent or an electromagnet. The tube is evacuated through the side arm B to a pressure of about 10^{-7} mm., and can be heated for degassing purposes when necessary. The ion source and collector system are mounted at the ends of the tube. Two pairs of vacuum-tight flanges G_1 and G_2 permit the covers C_1 and C_2 to be removed, giving access to the ion source and collector system. The alignment of the various ion slits in a mass spectrometer and their location with respect to the magnetic field are critical; the flanges G_1 and G_2 are therefore accurately machined, and the ion source slit S_1 and the collector slit S_2 are mounted directly on them.

All electrical leads, except those for the filament, are brought into the tube by insulated connections through the flanges. The filament is heated by current from a source such as the storage batteries E_f. The potential difference V_e between the filament and the ionisation chamber is established

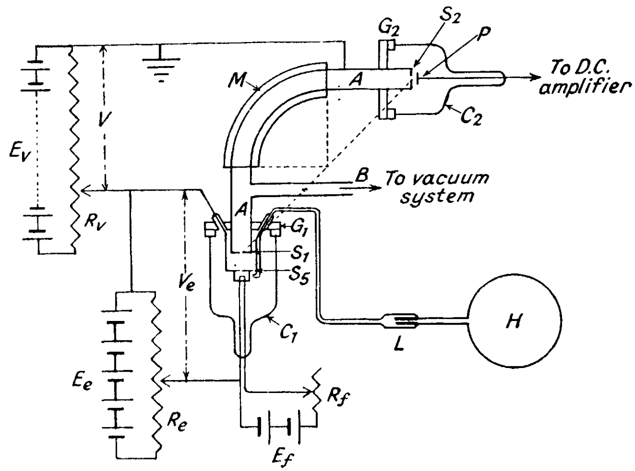

FIG. 4

Schematic diagram of a simple mass spectrometer.

by the battery E_e and can be adjusted by the potentiometer R_e. It is this potential difference which draws off the electrons from the filament and imparts kinetic energy to them. The main ion-accelerating voltage V is

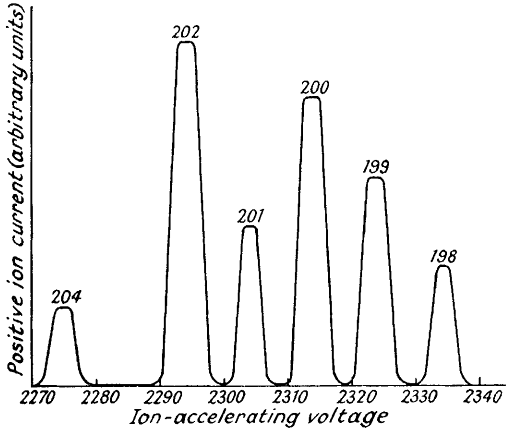

FIG. 5

Mass spectrum of mercury.

applied between the ionisation chamber (*i.e.*, S_5) and the analyser tube (*i.e.*, S_1) and is tapped from the battery E_v by means of the potentiometer R_v. The batteries indicated in Fig. 4 are usually replaced by electronically regulated power supplies. The ion source magnet which collimates the electron beam is not shown in Fig. 4. The gas to be studied flows from a bulb H, which represents a gas-handling system, *via* a suitable leak L into the ionisation chamber.

The ion beams corresponding to different masses can be brought successively through S_2 and on to P by changing the magnetic field (magnetic scanning) or by varying V (voltage scanning). Thus, as V is progressively reduced by means of R_v, the current arriving at P will show a series of peaks, the mass spectrum, when plotted against V (Fig. 5). The height at the top of each peak is a measure of the intensity at the slit S_2 of the ion beam whose m/e corresponds to that value of V (see equation 2). The relative intensities of the beams recorded at S_2 may not reflect exactly the relative intensities of the ions in the ionisation chamber. One cause of such discrimination is that, when each is being recorded, ions of different masses may have slightly different trajectories in the instrument. Unless the discrimination is severe, it will only be important when absolute relative intensities are required. In the majority of applications the mass spectrometer is used as a comparator; for example, in determining changes in isotopic abundances rather than absolute abundances.

Ionisation and Appearance Potentials [14]

Experimental.—Molecules led into the mass spectrometer ion source are there bombarded with electrons, whose kinetic energy is controlled by the voltage applied between the filament and the ionisation chamber (V_e in Fig. 4). If the electron energy is increased from zero, no ions are recorded until the energy reaches a certain critical value, the appearance potential. In the case of hydrogen, this value is 15·4 ev (1 electron volt = 23,050 cal. per mole), when the molecule ion H_2^+ first appears.[15] At 18·0 ev a current of protons is just detectable. The ionisation efficiency curves of ion currents against electron energy are shown in Fig. 6.

The electrons coming from the hot filament are not all of the same energy owing to the Maxwellian distribution of velocities and the voltage drop along the filament. The processes by which energy is transferred from the moving electron to the molecule are governed by wave-mechanical considerations. As a result, the ionisation efficiency curve in the vicinity of the appearance potential is asymptotic to the energy axis and the appearance potential is difficult to detect. There are degrees of arbitrariness in the various methods used to decide which point of an ionisation efficiency curve characterises the appearance potential, but methods of cross-checking the results can often be devised. Finally, the voltage actually measured between the filament and the ionisation chamber does not correspond to the mean energy of the electrons, owing to the unknown surface potentials

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[14] Hagstrum, " Mass Spectrometry in Physics Research ", U.S. Dept. of Commerce, Nat. Bur. Stand. Circular No. 522, 1953, p. 193—199.

[15] Bleakney, *Phys. Rev.*, 1930, **35,** 1180; 1932, **40,** 496; Lozier, *ibid.*, 1930, **36,** 1285; Smith and Bleakney, *ibid.*, 1936, **49,** 883; Hagstrum and Tate, *ibid.*, 1941, **59,** 354.

and the complexity of the electric field in the ionisation chamber. To overcome this, a monatomic gas (usually argon) of known ionisation potential is admitted simultaneously with the gas being studied, and the appearance potential of the calibrating gas determined. In this way the zero of the energy scale can be fixed.

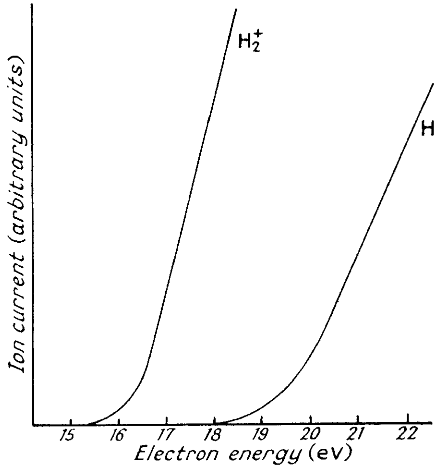

FIG. 6

Appearance potentials and ionisation efficiencies for hydrogen.

Appearance Potentials and Potential Energy Curves.—The significance of the appearance potentials of H_2^+ and H^+ can be discussed with reference to Fig. 7, which shows three potential energy curves[16] for H_2 and the molecular ion H_2^+. Since the Franck–Condon principle applies, electronic transitions induced by electron impact may be represented by vertical lines on the diagram. The ionisation potential of hydrogen is represented by the transition I and the probability of such a transition is dependent on the amplitude (shown by the broken line C in Fig. 7) of the vibrational wave function of the H_2 molecule in its ground state. If the amplitude is appreciable at internuclear distances corresponding to the ground state of the H_2^+ ion, then the appearance potential of H_2^+ will be the ionisation potential of H_2, *i.e.*, $A(H_2^+) = I(H_2)$, where $A(x)$ and $I(x)$ represent the appearance potential and ionisation potential of the species x respectively. If, however, this amplitude at the base of the arrow I is small, the probability of the transition I will be small and the resulting ion current may be undetectable; the appearance potential found experimentally will then correspond to a transition such as II, for which the amplitude, and hence the probability of transition, is larger. In such a case the appearance potential will be greater than the ionisation potential by $E_{\text{vib.}}(H_2^+)$ (represented by y in Fig. 7), the vibrational energy in the upper state, and

$$A(H_2^+) = I(H_2) + E_{\text{vib.}}(H_2^+)$$

whether the appearance potential is greater than or equal to the ionisation

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[16] Bleakney, Condon, and Smith, *J. Phys. Chem.*, 1937, **41**, 197.

potential depends therefore upon the equilibrium nuclear distances r_e and r_e'. For H_2, r_e is 0·74 Å and for H_2^+, r_e' is 1·06 Å, and transitions of type I have small probability. The mass spectrometer must therefore be sufficiently sensitive to detect the ions resulting from this transition, otherwise the experimental appearance potential will correspond to transitions of the more probable type II. Bleakney [15] obtained a value of 15·45 ev for $A(H_2^+)$, very close to the spectroscopic value of 15·43 ev.

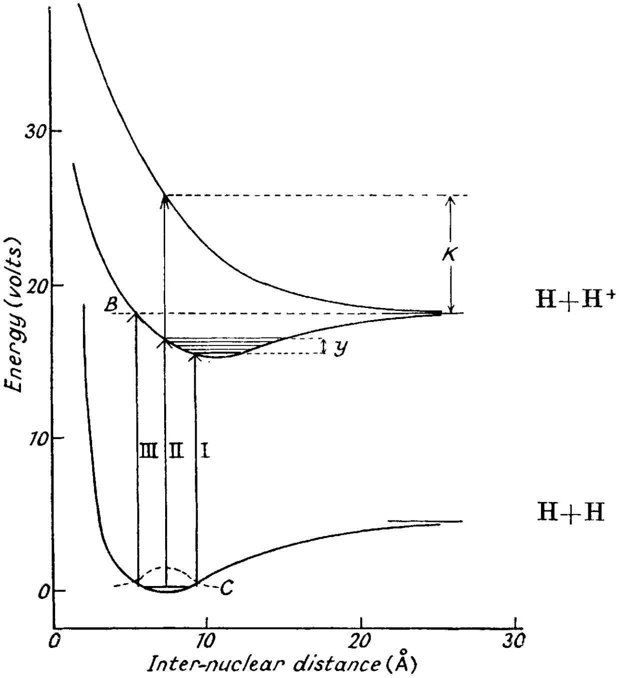

FIG. 7

Potential energy curves for hydrogen and the hydrogen molecule ion.

Protons will be produced by transitions such as III (Fig. 7) to states on the $^2\Sigma_g^+$ curve of H_2^+ which lie at or above the dissociation limit for H_2^+. If transitions to *B* (Fig. 7), the state at the dissociation limit, have an appreciable probability, then the experimental appearance potential is such that

$$A(H^+) = D(H\text{–}H) + I(H)$$

where D(H–H) is the bond dissociation energy of the hydrogen molecule and I(H) is the ionisation potential of the hydrogen atom. Bleakney's [15] value of 18·0 ev for the appearance potential of H^+ is in good agreement with 18·07 ev, the sum of 13·59 ev and 4·478 ev, the spectroscopic values of I(H) and D(H–H). It is, however, possible with some molecules that r_e' in the upper ionised state is not very different from r_e for the neutral molecule and consequently the amplitude of the latter's wave function at internuclear distances corresponding to the state B is small. The probability of such transitions may then be so small that the resulting current of atomic H^+ ions is below the sensitivity of the detecting apparatus.

Transitions (II in Fig. 7) may take place to the repulsive ${}^2\Sigma_u{}^+$ curve. The products H and H^+ then dissociate with kinetic energy $K(H + H^+)$ and

$$A(H^+) = D(H\text{–}H) + I(H) + K(H + H^+)$$

The presence of kinetic energy in the products may be indicated by an abnormal width of the ion peak and the amount of kinetic energy can be determined by a suitable technique[17] involving the use of retarding potentials. It will be clear that, especially in the absence of kinetic energy in the products, the value of $D(H\text{–}H)$, if unknown, could be obtained from a determination of $A(H^+)$ in the mass spectrometer and a knowledge of $I(H)$.

Bond Dissociation Energies of Polyatomic Molecules.—Electron-impact experiments provide a general method of obtaining data related to molecular properties of considerable importance. It succeeds in many cases where other techniques fail and is particularly important in the study of polyatomic molecules for which the optical spectrum is too complex for detailed analysis. Although there is considerable advantage in being able to identify one of the products by its mass-to-charge ratio, there is often the possibility of ambiguity in deciding on the process responsible for the formation of this ion and always the possibility that the dissociation may result in excited products.

The appearance potential $A(R_1{}^+)$ of the radical ion $R_1{}^+$ from the polyatomic molecule R_1R_2 will in general be given by

$$\begin{aligned} A(R_1{}^+) = D(R_1\text{–}R_2) + I(R_1) + E(R_1{}^+) + E(R_2) - E(R_1R_2) \\ + K(R_1{}^+) + K(R_2) - K(R_1R_2) \quad . \quad (3) \end{aligned}$$

where $E(x)$ signifies the internal (electronic, vibrational, and rotational) energy and $K(x)$ the kinetic energy of the species x. Usually $E(R_1{}^+)$ and $E(R_2)$ are small and $E(R_1R_2)$ and $K(R_1R_2)$ can be neglected.[17] In these circumstances

$$A(R_1{}^+) = D(R_1\text{–}R_2) + I(R_1).$$

Stevenson has shown for hydrocarbons that a condition for this equality is that $I(R_1) < I(R_2)$. The " direct method " of obtaining $D(R_1\text{–}R_2)$ is to measure $A(R_1{}^+)$ and subtract the ionisation potential of the radical R_1. In the " indirect method " it is not necessary to know $I(R_1)$, which can be eliminated by using the appearance potentials of $R_1{}^+$ from two different compounds together with thermochemical data.

The ionisation potentials of radicals can be obtained by pyrolysing a suitable compound (*e.g.*, tetramethyl-lead for methyl) in a furnace adjacent to the ion source. The radicals are led into the ionisation chamber by as

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[17] Arnot and Milligan, *Proc. Roy. Soc.*, 1936, *A*, **156**, 538 ; Sloan and Press, *ibid.*, 1938, *A*, **168**, 284 ; Hipple, Fox, and Condon, *Phys. Rev.*, 1945, **68**, 54 ; 1946, **69**, 347 ; Fox and Hipple, *Rev. Sci. Instr.*, 1948, **19**, 462 ; Hagstrum, *Rev. Mod. Phys.*, 1951, **23**, 185.

short a path as possible, and the appearance potential of the radical ion determined. For the process

$$R_1 + e \longrightarrow R_1^+ + 2e$$

$A(R_1^+) = I(R_1)$. In this way $I(R_1)$ for a number of radicals has been determined. Table 1 gives a list of ionisation potentials, some determined in this way, others by alternative routes.

TABLE 1. *Ionisation potentials of radicals*

Methyl [18, 19, 20, 32]	10·08 ± 0·1 9·95 ± 0·03	*iso*Propyl [21]	7·45 ± 0·1
Ethyl [18]	8·66 ± 0·1	*tert.*-Butyl [21]	6·90 ± 0·1
Allyl [19, 20]	8·16 ± 0·03	Benzyl [19, 20]	7·73 ± 0·08
n-Propyl [32]	7·94 ± 0·1	Methylene [22]	11·9 ± 0·2

Hipple and Stevenson [18] found $A(CH_3^+)$ from methane to be 14·52 ± 0·1 which with their value of $I(CH_3)$ gives 4·44 ev for $D(CH_3–H)$. The indirect method can be illustrated with the following example. The heats of formation of CH_4, C_2H_6, C_3H_8, and H give – 5·08 ev as the heat of the reaction

$$CH_4 + C_2H_6 \longrightarrow C_3H_8 + 2H\,; \quad \Delta H = 5{\cdot}08 \text{ ev}$$

By combining this with the appearance potentials of ethyl ion from ethane and propane : [23]

$$\text{(add)} \qquad C_3H_8 \longrightarrow C_2H_5^+ + CH_3\,; \quad A(C_2H_5^+) = 14{\cdot}50 \text{ ev}$$

$$\text{(subtract)} \qquad C_2H_6 \longrightarrow C_2H_5^+ + H\,; \quad A(C_2H_5^+) = 15{\cdot}20 \text{ ev}$$

we obtain $D(CH_3–H) = 4{\cdot}38$ ev. Table 2, due to Stevenson,[21] summarises the results of the various determinations of $D(CH_3–H)$ and includes for comparison the results obtained from the kinetics of photochemical reactions and pyrolyses. The agreement between the values found for $D(CH_3–H)$ means that the excitation and kinetic energy terms in equation 3 are insignificant in the electron-impact processes studied.[29]

It has also proved possible to trace the changes in carbon–hydrogen bond dissociation energy with progressive methyl substitution (see Table 3). Other values which are of interest here are $D(n\text{-}C_3H_7–H) = 4{\cdot}30 \pm 0{\cdot}09$ and $D(n\text{-}C_4H_9–H) = 4{\cdot}38$.

From these data, together with thermochemical data,[30] the heats of formation of radicals may be derived, *e.g.*,

$$Q_f(R) = D(R–H) - Q_f(H) + Q_f(RH)$$

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[18] Hipple and Stevenson, *Phys. Rev.*, 1943, **63,** 121 ; see also Waldron, *Trans. Faraday Soc.*, 1954, **50,** 102.

[19] Lossing, Ingold, and Henderson, Institute of Petroleum Conference on Mass Spectrometry, October, 1953.

[20] *Idem, J. Chem. Phys.*, 1954, **22,** 621.

[21] Stevenson, *Discuss. Faraday Soc.*, 1951, **10,** 35.

[22] Langer and Hipple, *Phys. Rev.*, 1946, **69,** 691 ; Langer, Hipple, and Stevenson, *J. Chem. Phys.*, 1954, **22,** 1836.

TABLE 2. *Determinations of* $D(CH_3–H)$

Method	Process	Ref.	$D(CH_3–H)$ (ev)
Electron impact (direct)	$CH_3 \rightarrow CH_3^+ + e$ with	18	
	$CH_4 \rightarrow CH_3^+ + H + e$ or with	24	4·44 ± 0·2
	$CH_3·OH \rightarrow CH_3^+ + OH$	25	4·48 ± 0·4
Electron impact (indirect)	$C_2H_6 \rightarrow C_2H_5^+ + H + e$ with	23	4·38 ± 0·2
	$C_3H_8 \rightarrow C_2H_5^+ + CH_3 + e$		
	$C_3H_8 \rightarrow C_3H_7^+ + H + e$ with		4·34 ± 0·2
	$isoC_4H_{10} \rightarrow C_3H_7^+ + CH_3 + e$		
	$C_3H_6 \rightarrow C_3H_5^+ + H + e$ with		4·48 ± 0·2
	$isoC_4H_8 \rightarrow C_3H_5 + CH_3 + e$		
	$n\text{-}C_3H_7Cl \rightarrow C_3H_7^+ + Cl + e$ with	26	4·42 ± 0·2
	$n\text{-}C_4H_{10} \rightarrow C_3H_7^+ + CH_3 + e$		
	$CH_3·OH \rightarrow CH_2·OH^+ + H + e$ with	25	4·42 ± 0·2
	$C_2H_5·OH \rightarrow CH_2·OH^+ + CH_3 + e$		
Average for electron impact			4·42 ± 0·04
Photochemical	$CH_4 + Br \rightarrow CH_3 + HBr$	27	4·43 ± 0·05
	$HBr \rightarrow H + Br$		
Pyrolysis	$CH_3I \rightarrow CH_3 + I$	28	4·45 ± ?
	$HI \rightarrow H + I$		

TABLE 3

R	D(R–H) Electron impact (ev)	D(R–H) Pyrolysis [31] (ev)
$CH_3·$	4·42 ± 0·04	4·45
$CH_3CH_2·$	4·20 ± 0·04	4·23
$(CH_3)_2CH·$ . . .	4·07 ± 0·09	3·86
$(CH_3)_3C·$	3·88 ± 0·09	3·73

Then, knowing the heats of formation of radicals and atoms X, further bond dissociation energies may be derived :

$$D(R_1–R_2) = Q_f(R_1) + Q_f(R_2) - Q_f(R_1R_2)$$
$$D(R–X) = Q_f(R) + Q_f(X) - Q_f(RX)$$

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[23] Stevenson, *J. Chem. Phys.*, 1942, **10,** 291.

[24] Smith, *Phys. Rev.*, 1937, **51,** 263.

[25] Cumming and Bleakney, *ibid.*, 1940, **58,** 787.

[26] Stevenson and Hipple, *J. Amer. Chem. Soc.*, 1942, **64,** 2766.

[27] Kistiakowsky *et al.*, *J. Chem. Phys.*, 1942, **10,** 305 ; 1943, **11,** 6 ; 1944, **12,** 469.

[28] Polanyi *et al.*, *Nature,* 1940, **146,** 129, 685 ; *Trans. Faraday Soc.*, 1941, **37,** 648 ; 1943, **39,** 19.

[29] See footnote to p. 869 in Stevenson, *ibid.*, 1953, **49,** 867.

[30] Franklin, *J. Chem. Phys.*, 1953, **21,** 2029.

[31] Polanyi *et al.*, summarised by Steacie, Darwent, and Trost, *Discuss. Faraday Soc.*, 1947, **2,** 80.

In this way $D(CH_3-CH_3)$ is found to be 3·58 ev and $D(C_2H_5-C_2H_5)$ to be 3·37 ev.[32]

Electron-impact measurements have been used to obtain information on the successive bond dissociation energies of methane $D(CH_3-H)$, $D(CH_2-H)$, $D(CH-H)$, and $D(C-H)$.[33] From a knowledge of these values, the heat of atomisation of methane may be derived and thence the latent heat of vaporisation of carbon, $L(C)$, which is of fundamental importance. The results lend support to the lower figure $L(C) \sim 130$ kcal., rather than $L(C) \sim 170$ kcal.[34] Investigations have not been confined to hydrocarbon molecules : Hagstrum [35] has carried out a careful investigation of the molecules CO, N_2, NO, and O_2. He has measured the kinetic energies of the ions and derived values for the bond dissociation energies of these molecules. The value of 4·00 ev for $D(HS-H)$ can be obtained from the appearance potentials of alkyl ions in the mass spectra of alkanethiols [36] and appropriate thermochemical data.[37]

The Significance of Ionisation Potentials.—The theoretical significance of the ionisation potential has been recognised for a long time.[38] Mulliken [39] in his many papers on the electronic structure of molecules made extensive use of it as an orbital characteristic, and used it as a parameter in the empirical correlation of other molecular and bond properties. This approach has been extended and applied in detail by Price [40] and by Walsh.[41] The latter author [42] has, with some success, suggested a possible definition of bond order in terms of ionisation potentials. Some interesting correlations between the ionisation potentials of molecules have been made by Morrison and Nicholson [43] and they have been able, by technical refinements, to resolve the fine structure in ionisation efficiency curves.[44] Further progress along these lines should be of considerable importance in developing quantitatively the recent theoretical work of Lennard-Jones.[45] Hall [46] has reported some preliminary results in the application of these theories to the change in the ionisation potential in the homologous series of normal paraffins.[47]

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[32] Stevenson, *Trans. Faraday Soc.*, 1953, **49**, 867.

[33] Smith, *Phys. Rev.*, 1937, **51**, 263 ; Koffel and Lad, *J. Chem. Phys.*, 1948, **16**, 420 ; Geerk and Neuert, *Z. Naturforsch.*, 1950, **5A**, 502 ; McDowell and Warren, *Discuss. Faraday Soc.*, 1951, **10**, 53.

[34] *Idem, ibid.* ; Field, *J. Chem. Phys.*, 1951, **19**, 793 ; see also ref. 69.

[35] Hagstrum, *Phys. Rev.*, 1947, **72**, 947 ; ref. 17.

[36] Franklin and Lumpkin, *J. Amer. Chem. Soc.*, 1952, **74**, 1023.

[37] Stevenson, ref. 21.

[38] Koopmans, *Physica*, 1933, **1**, 104.

[39] Mulliken, *Phys. Rev.*, 1934, **46**, 551 ; *J. Chem. Phys.*, 1934, **2**, 782 ; 1935, **3**, 514.

[40] Price, *Ann. Rep.*, 1939, **36**, 47 ; *Chem. Rev.*, 1947, **41**, 257.

[41] Walsh, *Quart. Rev.*, 1948, **2**, 73 ; *Ann. Rep.*, 1947, **44**, 32.

[42] *Idem, Trans. Faraday Soc.*, 1946, **42**, 779.

[43] Morrison and Nicholson, *J. Chem. Phys.*, 1952, **20**, 1021.

[44] Morrison, *J. Chem. Phys.*, 1953, **21**, 1767.

[45] Lennard-Jones, *Proc. Roy. Soc.*, 1949, *A*, **198**, 1, 14 ; Lennard-Jones and Hall, *Discuss. Faraday Soc.*, 1951, **10**, 18.

[46] Hall, *Proc. Roy. Soc.*, 1951, *A*, **205**, 541 ; *Trans. Faraday Soc.*, 1954, **50**, 319.

[47] Honig, *J. Chem. Phys.*, 1948, **16**, 105.

Analysis

Analysis of Hydrocarbon and Other Organic Mixtures.[48]—In 1913 J. J. Thomson [3] foresaw the possibilities of using positive rays as a method of chemical analysis. Conrad,[49] seventeen years later, applied the parabola technique to the study of organic molecules, and in 1935 Taylor used a mass spectrometer for this purpose. Since then [50] mass spectrometry has become an important analytical technique, particularly for hydrocarbons.

With electrons of 70 ev, *n*-butane (*M*, 58) disintegrates on impact into about fifty different ions. The ion currents for each of these masses can be measured and a plot of ion beam intensity (" peak height ") against *m/e* (" mass number ") is called the mass spectrum or " cracking pattern ". Table 5 gives a list of the peak heights of the ten most abundant ions in the mass spectra of *n*-butane and *iso*butane. In both cases the ion beam of mass 43 is the most intense ; this base peak is taken as 100 units and the other peak intensities are scaled accordingly. The actual ion intensities are all proportional to the pressure of the hydrocarbon at the inlet and in addition the intensity of the base peak per unit of pressure is given ; this is the " sensitivity ". The manner in which a molecule is ionised and breaks up under electron impact depends upon the structure of the molecule and the " cracking pattern " which results is characteristic of that molecule. Enough relative peak heights are given in Table 5 to show that the two isomeric butanes have quite distinct " mass spectra ", though there are some isomers where the difference is not so marked.

TABLE 5. *Mass spectra at* 70 ev *electron energy*

Mass	*n*-Butane	*iso*Butane	Mass	*n*-Butane	*iso*Butane
58	12·3	2·73	29	44·2	6·16
43	100	100	28	32·6	2·62
42	12·2	33·5	27	37·1	27·8
41	27·8	38·1	26	6·17	2·36
39	12·5	16·5	15	5·3	6·41

Sensitivity of *n*-butane, 39·6 per μ.
Sensitivity of *iso*butane, 46·4 per μ.

The principle of the method of quantitative analysis can be understood by considering a very simple case, the analysis of a mixture of *n*-butane and *iso*butane. The mass spectra and sensitivities of each of the pure components are determined separately (Table 5). If each component in

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[48] Washburn, Mass Spectrometry in " Physical Methods in Chemical Analysis ", New York Acad. Press, 1950, Vol. 1, p. 587 ; Mitchell, Mass Spectroscopy in Hydrocarbon Analysis in " Physical Chemistry of Hydrocarbons ", New York Acad. Press, 1950, Vol. 1, p. 830.

[49] Conrad, *Physikal. Z.*, 1930, **31**, 888.

[50] Hoover and Washburn, *Petroleum Technology*, May, 1940; Washburn, Wiley, and Rock, *Ind. Eng. Chem. Anal.*, 1943, **15**, 541 ; Washburn, Wiley, Rock, and Berry, *ibid.*, 1945, **17**, 74 ; Brewer and Dibeler, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 125.

the mixture contributes independently to every peak height, then the height, H_m, of the peak of mass number m is given by

$$0{\cdot}396h_{mn}p_n + 0{\cdot}464h_{mi}p_i = H_m$$

where p_n and p_i are the partial pressures of *n*- and *iso*-butane at the inlet, h_{mn} and h_{mi} are the relative heights of peak m in the pure samples; the sensitivity coefficients 39·6/100 and 46·6/100 convert the relative heights into intensities. There are two unknowns, p_n and p_i, and as many equations as there are peaks. The extension of the method to more complicated mixtures is clear. Calibration is first carried out with the pure components, *i.e.*, their cracking patterns and sensitivities are determined, then the spectrum of the mixture is obtained. The height of the mth mass peak is given by

$$s_1h_{m1}p_1 + s_2h_{m2}p_2 \ . \ . \ . \ s_nh_{mn}p_n = H_m$$

where s_1, s_2, etc., are the sensitivity coefficients for the first, second, etc., components. The large number of equations available is reduced to a number equal to the number of components in the mixture by selection or a least-squares method, and these equations are solved for the unknowns $p_1, p_2, \ . \ . \ . \ p_n$ by conventional methods.[51, 52] The labour involved in computation will depend upon the complexity and nature of the mixture. The more components there are and the less difference there is in their cracking patterns, the more the computation necessary to obtain an acceptable solution.

Naturally, this lengthy mathematical technique of solving the equations is not always necessary. A common procedure in many cases is to start with the component of highest molecular weight. Its parent peak, as the highest mass in the spectrum of the mixture, is unique and the contributions of this component may be subtracted. Similarly, the contributions of the component of next highest molecular weight may now be subtracted from the remaining spectrum and so on progressively, until all components have been dealt with.

An impression of the accuracy [53] of the technique can be obtained from Table 6, which shows the results of an analysis of a fourteen-component mixture in comparison with its synthetic composition, and from Table 7, which shows a similar comparison for a synthetic blend of higher hydrocarbons. The successful application of the technique rests on the following conditions; (*a*) the mass spectrum of each component is characteristic of that component; (*b*) the intensity of each ion beam resulting from the fragmentation of a component is proportional to the partial pressure of the component at the inlet; (*c*) the mass spectra of the various components

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[51] Hartree, " Numerical Analysis ", Oxford Univ. Press, London, 1952, p. 164.

[52] Johnson, *Analyt. Chem.*, 1947, **19**, 305; Danby, " Mass Spectrometry ", Institute of Petroleum, London, 1952, p. 135.

[53] Washburn, Wiley, Rock, and Berry, ref. 50; Starr and Lane, *Analyt. Chem.*, 1949, **21**, 572; Shepherd, *J. Res. Nat. Bur. Stand.*, 1950, **44**, 509; Nicholson, " Mass Spectrometry ", Institute of Petroleum, London, 1952, p. 99; Powell and Ross; Quayle; Waldron; in ref. 19.

TABLE 6 [54]

	% Composition by			% Composition by	
	Synthesis	Mass spectrometry		Synthesis	Mass spectrometry
H_2	3·0	3·2	*iso*Butene	2·8	1·6
Methane	10·8	10·3	*n*-Butene	2·9	4·1
Ethylene	6·0	5·9	(But-1-ene)	(1·5)	(2·4)
Ethane	6·0	5·8	(But-2-ene)	(1·4)	(1·7)
Propene	11·1	11·1	*n*-Butane	5·0	5·2
Propane	19·2	19·5	*iso*Pentane	10·1	10·2
*iso*Butane	20·1	20·0	Pentenes	3·0	3·1

TABLE 7 [55]

n-Heptane	5·2	4·5	4·9	2-Methylheptane	7·0	7·0	6·9
n-Nonane	3·2	3·9	3·5	3-Methylheptane	6·9	6·4	7·2
n-Octane	74·8	75·3	73·2	4-Methylheptane	2·9	2·9	4·3

of a mixture are linearly additive ; (*d*) the cracking pattern and the sensitivities are stable and constant. When these conditions are satisfied, the mass spectrometer can analyse complex hydrocarbon mixtures accurately and rapidly. The analysis of a mixture such as that in Table 6 required about 2·8 man-hours.

The method compares [56] well with other methods [57] of analysis for hydrocarbons such as infra-red, Raman, and ultra-violet absorption, and fractional distillation. However, it by no means replaces these methods completely. For example, the mass spectrometer cannot determine the individual butenes in a mixture. On the other hand, whilst infra-red spectra of *n*- and monomethyl-alkanes are very similar, the mass spectra are quite characteristic. The various techniques are considered to be complementary and are often used in various combinations. To avoid lengthy computation, it is advantageous to fractionate a complex mixture by distillation into a number of broad cuts and to subject each cut to mass spectrometric analysis.[58]

A sensitive, high-resolution mass spectrometer has been used [59] to analyse petroleum fractions of higher molecular weight. The parent peaks have

[54] Washburn, Wiley, Rock, and Berry, ref. 50.

[55] Friedel and Anderson, *J. Amer. Chem. Soc.*, 1950, **72,** 1215.

[56] Starr and Lane, ref. 53 ; Milsom, Jacoby, and Rescorla, *Analyt. Chem.*, 1949, **21,** 547.

[57] For a summary of other methods see " Light Hydrocarbon Analysis ", ed. Burke, Starr, and Tuemmler, Reinhold, New York, 1951.

[58] Young, *Nat. Petroleum News* (Tech. Section), 1946, **38,** R212 ; Friedel and Anderson, ref. 55 ; Sobcov, *Analyt. Chem.*, 1952, **24,** 1386 ; Friedel, Logar, and Shultz, *Appl. Spectroscopy*, 1952, **6,** 24.

[59] O'Neal, *Analyt. Chem.*, 1951, **23,** 830 ; and in ref. 14, p. 217. Institute of Petroleum Conference on Mass Spectrometry, 1953.

the same masses as the original molecules and give the values of n and z in the molecular formulæ, C_nH_{2n-z}, of the original constituents; z gives the number of ring closures or double bonds. In one example, the mass spectrum of a paraffin wax enabled three distribution curves to be derived, giving the percentages of each molecular weight (C_{18} to C_{30}) of *n*-, *iso*-, and *cyclo*-alkanes. A second method used the intensities of the fragment ions which were found to be characteristic of the hydrocarbon type; a hydrocarbon was analysed into *n*-, *iso*-, non-condensed *cyclo*-, condensed *cyclo*-alkanes, and eighteen aromatic types ranging from benzenes to benzoperylenes.

In principle, mass spectrometric analysis is applicable to volatile mixtures of other types of compounds. However, there are limitations, and it is inadvisable to pass corrosive substances through the instrument; polar compounds are liable to adsorption which may result in serious changes of composition and in " memory " effects, and compounds containing oxygen may affect the filament.[60] Some of these difficulties can be overcome by the use of flushing techniques, heated inlet systems, etc. Hageman and van Katwijk [61] have successfully analysed mixtures of methanol, ethanol, propan-1- and -2-ol, butanol, and water, and mixtures containing nine carboxylic acids. Washburn [62] gives a list of compounds which have been successfully analysed by the mass spectrometer.

Temperature Effect, Metastable Transitions, and Rearrangement Peaks.—Some of the peaks in the mass spectra of hydrocarbons decrease in intensity when the temperature of the ionisation chamber increases.[63] In some cases the decrease is particularly marked for the parent ion; for example, the parent peak of 2 : 2 : 3-trimethylpentane is five times as large at 175° as it is at 225° c. A relatively minor part of the effect is the result of a decrease in gas density at the higher temperature. In a number of cases, it has been found that the temperature effect is larger the smaller the difference between the ionisation potential of the molecular ion and the appearance potential of the fragment ion which results from its dissociation. This suggests (see Fig. 7) that at the higher temperature there may be an increased probability of transitions to states of the molecule ion which are above its dissociation limit.

The stability towards dissociation of the excited molecule ion in such states may be expressed as the " half-life ". If the half-life is less than 10^{-7} second, most of the ions in that state will dissociate before leaving the ionisation chamber, and the resulting ions form the normal peaks of the mass spectrum. If the half-life is about 10^{-6} second, some of the molecule ions will survive long enough to pass out of the chamber and

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[60] Taylor, Brown, Young, and Headington, *Analyt. Chem.*, 1948, **20,** 396; Thomas and Seyfried, *ibid.*, 1949, **21,** 1022; Gifford, Rock, and Comaford, *ibid.*, p. 1026; Langer and Fox, *ibid.*, p. 1032.

[61] Hageman and van Katwijk, in ref. 19.

[62] Washburn, ref. 48.

[63] Fox and Hipple, *J. Chem. Phys.*, 1947, **15,** 208; Stevenson, *ibid.*, 1949, **17,** 101; Berry, *ibid.*, p. 1164; Reese, Dibeler, and Mohler, *J. Res. Nat. Bur. Stand.*, 1951, **46, 79.**

through the ion gun before they dissociate spontaneously. The fragment ion resulting from the dissociation shares with the neutral partner the kinetic energy eV impressed on the parent ion in the gun. If m_0 and m_1 are the masses of the parent ion and the fragment ion, the velocity of the latter after dissociation is $(2eV/m_0)^{\frac{1}{2}}$ and its momentum $m_1(2eV/m_0)^{\frac{1}{2}}$. On entering the magnetic field of the instrument the radius of curvature of its path will be

$$r = \frac{m_1 v}{eH} = \frac{m_1(2eV/m_0)^{\frac{1}{2}}}{eH} = \frac{(2eV.m_1{}^2/m_0)^{\frac{1}{2}}}{eH}$$

The beam of fragment ions will register on the collector slits at a voltage corresponding to the apparent ion mass $m_1{}^2/m_0$. This is usually non-integral. Many examples of such metastable ion transitions are found in the mass spectrum of *n*-butane. The parent ion of mass 58 can dissociate into an ion of mass 43 with a mass loss of 15,

$$58^+ \longrightarrow 43^+ + 15$$

If the dissociation occurs after passing through the gun, the product ion registers at the apparent mass number $43^2/58 = 31{\cdot}9$. Hipple [64] has shown that the number of metastable ions decreases exponentially with time, confirming the view that the dissociation is spontaneous. During dissociation repelling forces may give the fragments kinetic energy of a few volts ; this is partly responsible for the diffuse nature of these peaks.

Most of the ions in a spectrum could arise from the molecule ion by progressive bond cleavage, but some must involve a rearrangement of the atoms. The ion $C_2H_5{}^+$ in the spectrum of *iso*butane is an example. Stevenson and Hipple [65] in this case considered that the rearrangement was an initial isomerisation, *iso*-$C_4H_{10}{}^+ \longrightarrow$ *n*-$C_4H_{10}{}^+$, and Honig [66] using [^{13}C]*iso*-butane reached similar conclusions. The largest peak in the spectrum of *n*-butyric acid is at mass 60. By labelling the [^{13}C]carboxyl group, Happ and Stewart [67] showed that a C_2H_4 and not a CO group was eliminated, with a shift of a hydrogen atom to the remaining $CH_2{\cdot}CO_2H$ fragment.

The study of the temperature effect, metastable transitions, and rearrangement peaks are of importance in understanding the mechanism of ionisation and fragmentation. The first two phenomena are also important in the use of the instrument for analysis. The stability of the mass spectrum is improved considerably if the temperature of the source is controlled to 0·1°. A sharper, " cleaner " spectrum is obtained if the ions resulting from metastable transitions are prevented from reaching the collector by suitable " suppressor " electrodes placed close to it.

[64] Hipple, *J. Phys. Colloid Chem.*, 1948, **52**, 456 ; Hipple and Condon, *Phys. Rev.*, 1945, **68**, 54 ; Hipple, Fox, and Condon, *ibid.*, 1946, **69**, 347 ; Hipple, *ibid.*, 1947, **71**, 594 ; Dibeler, Wise, and Mohler, *ibid.*, p. 381 ; Bloom, Mohler, Lengel, and Wise, *J. Res. Nat. Bur. Stand.*, 1948, **40**, 437 ; *Phys. Rev.*, 1948, **74**, 1222 ; Bloom, Mohler, Wise, and Wells, *J. Res. Nat. Bur. Stand.*, 1949, **43**, 65.

[65] Stevenson and Hipple, *J. Amer. Chem. Soc.*, 1942, **64**, 1588.

[66] Honig, *Phys. Rev.*, 1949, **75**, 1319.

[67] Happ and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 4404 ; Langer, *J. Phys. Colloid Chem.*, 1950, **54**, 618.

Vapour Pressure Measurements.—If a vapour in equilibrium with its liquid or solid is allowed to diffuse through the leak, the variation of the peak height of the parent ion will reflect accurately the change of the vapour pressure with the equilibrium temperature.[68] Since the peak height can be varied by a factor of a thousand or more and still be accurately measurable, the Clausius-Clapeyron relation may be applied over a wide range of temperatures to obtain the heat of vaporisation. The method is particularly applicable to materials of low vapour pressure and to materials which have volatile impurities or decompose easily, since the parent peak measures the partial pressure irrespective of the total pressure.

The method has been applied to an investigation of the *rate* of sublimation of graphite ; [69] this gives not the heat of sublimation but the activation energies for surface emission. Small filaments of graphite heated electrically up to 2300° C were placed close to the ion source ; neutral particles were emitted and subjected to electron bombardment in the ionisation chamber. The ions C_3^+, C_2^+, and C_1^+ were found and it appears that carbon vapour consists mainly of C_3 molecules. From the variations of the peak heights with temperature, heats of activation for the species emitted were obtained and Honig used these values to adduce evidence which points to 170 kcal. per mole, the highest of the allowed spectroscopic values, as the heat of sublimation of atomic carbon.

Mass Spectrometric Analysis of Solids.—Methods of analysis for solids are not highly developed yet there is scope for such techniques. Washburn [70] points out that the mass spectra of metals and alloys would be simpler to interpret than the emission spectra of the metals. The problem lies in the design of a suitable source for producing the ions without discrimination. The high-voltage vacuum-spark ion source is not very suitable though Dempster [71] and Hipple [72] have used it. Metals may be evaporated from a small furnace close to the ion source [73] or a filament of tungsten or tantalum coated with the oxide may be placed behind the first ion slit. When the filament is heated positive ions are evaporated ; no electron beam is necessary. With the alkali metals, ion beams of 10^{-10} A can be obtained without difficulty [74] and less than 10^{-15} g. is detectable.[75]

Quantitative Analysis by Isotope Dilution.—In chemical methods of quantitative analysis, use is made of a reaction which is specific for the substance sought. Such methods are not well suited to the analysis of mixtures of members of homologous series. For instance, the acid hydrolysis of proteins results in mixtures of about 24 α-amino-acids. The isotope

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[68] Tickner and Lossing, *J. Chem. Phys.*, 1950, **18**, 148 ; *J. Phys. Colloid Chem.*, 1951, **55**, 733.

[69] Chupka and Inghram, *J. Chem. Phys.*, 1953, **21**, 371, 1313 ; Honig, *ibid.*, 1954, **22**, 127.

[70] Washburn, ref. 48.

[71] Dempster, *Proc. Amer. Phil. Soc.*, 1935, **75**, 760.

[72] Gorman, Jones, and Hipple, *Analyt. Chem.*, 1951, **23**, 438.

[73] Nier, *Phys. Rev.*, 1938, **53**, 282.

[74] Palmer and Aitken, in ref. 19.

[75] Inghram, in ref. 14, p. 151 (see also Inghram *et al.*, ref. 87).

dilution method avoids the necessity of quantitative isolation and requires only that a small sample be isolated pure.

A development of the techniques of Hevesy and Hobby,[76] it was first applied by Schoenheimer, Ratner, and Rittenberg [77] and by Ussing [78] to protein analysis. Suppose the amount of glycine in an hydrolysate is to be determined. Glycine enriched with ^{15}N (or ^{13}C) is synthesised. A known weight of this isotopic glycine is dissolved in a known amount of the hydrolysate and there mixes with the normal glycine already present. The isotopic glycine cannot be separated from the normal glycine by ordinary chemical procedures. A pure sample of glycine is recovered by an appropriate technique and converted [79] into N_2, and its isotope concentration is determined. The weight, x, of glycine in the original hydrolysate can be calculated [80] from

$$x = a(C_a - C_{a+x})M_x/(C_{a+x} - C_x)M_a \quad . \quad . \quad . \quad (4)$$

where a is the weight of isotopic glycine added, C_a its isotope concentration, C_x and C_{a+x} the isotope concentrations of the normal (*i.e.*, isotopically ordinary) glycine in the hydrolysate and of the recovered mixed glycine, M_x and M_a, the molecular weights of the normal and enriched glycine. Ordinarily C_x will be the isotope concentration of normal nitrogen (or carbon). The quantitative determination of both enantiomorphs of an amino-acid is only slightly more complicated [81] and the method has been applied extensively to proteins.[82] Bloch and Anker,[83] and Berenbom *et al.*[84] have developed simple variations of the method for metabolic studies where the compound sought may have been labelled for tracer purposes and C_x is therefore unknown. In another variation [85] the compounds sought are directly combined with an isotopic reagent.

An interesting application of the isotope dilution principle is in the elementary analysis of organic compounds [86] particularly for oxygen content. In this case, the combustion of a known amount of the compound with a knowna mount of oxygen enriched with ^{18}O is carried out in a platinum tube at 850°. The oxygen contained in the compound and the enriched

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[76] Hevesy and Hobby, *Z. analyt. Chem.*, 1932, **88,** 1.

[77] Schoenheimer, Ratner, and Rittenberg, *J. Biol. Chem.*, 1939, **130,** 703 ; Rittenberg and Foster, *ibid.*, 1940, **133,** 737 ; Rittenberg, *J. Appl. Physics*, 1942, **13,** 561.

[78] Ussing, *Nature*, 1939, **144,** 977.

[79] Rittenberg in " Preparation and Measurement of Isotopic Tracers ", Edwards, Ann Arbor, Michigan, 1947.

[80] Gest, Kamen, and Reiner, *Arch. Biochem.*, 1947, **12,** 273.

[81] Graff, Rittenberg, and Foster, *J. Biol. Chem.*, 1940, **133,** 745 ; Wieland and Paul, *Ber.*, 1944, *B*, **77,** 34 ; Barker, Hughes, and Young, *J.*, 1951, 3047 ; 1952, 1574.

[82] For reviews see Shemin and Foster, *Ann. New York Acad. Sci.*, 1946, **47,** 119 ; Tristram, *Adv. Protein Chemistry*, 1949, **5,** 83.

[83] Bloch and Anker, *Science*, 1948, **107,** 228.

[84] Berenbom, Sober, and White, *Arch. Biochem.*, 1950, **29,** 369.

[85] Keston, Udenfriend, and Cannan, *J. Amer. Chem. Soc.*, 1946, **68,** 1390 ; 1949, **71,** 249.

[86] Grosse, Hindin, and Kirschenbaum, *ibid.*, 1946, **68,** 2119 ; *Analyt. Chem.*, 1949, **21,** 386 ; Hindin and Grosse, *ibid.*, 1949, **20,** 1019 ; Kirschenbaum, Strong, and Grosse, *ibid.*, 1952, **24,** 1361.

oxygen gas come to equilibrium and the carbon dioxide produced is analysed for its content of ^{18}O in the mass spectrometer. Knowing the isotope concentrations in the enriched oxygen, in natural oxygen, and in the carbon dioxide, the oxygen content of the organic compound can be calculated from equation (4).

Trace quantities of uranium and lead have been determined [87] and the power of the isotopic dilution method is illustrated in Table 8 which gives the uranium content of two meteorites and a measurement of the purity of one of the reagents used. Since a supply of the separated isotope must be available, this is not a general method.

TABLE 8

Solid studied	Uranium content, p.p.m.
Norton county stone meteorite . . .	0·0054 ± 0·0002
Modac stone meteorite	0·0105 ± 0·0003
Ammonium nitrate	0·000075 ± 0·000004

Applications to Reaction Kinetics

Analysis of Reaction Mixtures.—Since the mass spectrometer has proved valuable in analysing complex mixtures accurately and rapidly, it is natural that it should be used for following the kinetics of gaseous reactions. The direct identification and the measurement of the concentrations of all stable substances including intermediates is possible. The first requirement is that the instrument be stable, particularly that the sensitivities for various chemical species remain unchanged during the course of the experiment. The second requirement is for some means of transferring a sample of the reaction mixture to the ionisation chamber, where the pressure is about 10^{-4} mm. If the reaction mixture is passed in viscous flow down a fine capillary, only stable products and stable intermediates will survive at the ion source. Alternatively, a small hole in a diaphragm may be used, through which molecular flow occurs. In both cases the gas flow is of the order 0·01—0·05 c.c. at N.T.P. per hour, and so the change in the pressure of the reaction vessel is usually negligible. By recording automatically on a paper chart, the entire mass spectrum can be obtained in intervals of 10—15 minutes. Naturally if only one peak is followed the record can be continuous. If any of the components are adsorbed on the capillary walls or on the electrode surfaces within the ionisation chamber, the response may lag behind the changes in the partial pressure of that component in the reaction mixture. The products of any thermal cracking which may occur on the hot filament must not be allowed to diffuse back into the ionisation chamber, and it is usual to provide extra pumping in the neighbourhood of the filament.

Leifer and Urey [88] were the first to follow the course of a gas reaction

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[87] Hess, Brown, Inghram, Patterson, and Tilton, ref. 14, p. 183.

[88] Leifer and Urey, *J. Amer. Chem. Soc.*, 1942, **64**, 994.

by mass-spectrometric analysis, and in a study of the thermal decomposition of dimethyl ether, small quantities of acetylene were found. With this more sensitive method of analysis, it was possible to follow the changing concentration of the trace of ethane produced in the photolysis of acetaldehyde.[89]

Detection and Measurement of Free Radicals.—A large proportion of chemical reactions in the gas phase are chain reactions in which atoms and free radicals take part as intermediates. Their presence is inferred from the kinetics of the reactions and methods have been devised to give more direct proof of their existence in the reacting mixtures.[90] The Paneth mirror method is limited to low temperatures, low pressures, and systems free from oxygen. Optical spectroscopy [91] has been applied to the detection and study of atoms and radicals such as OH, CH, SO, NH, etc., in flames, but is limited essentially to monatomic and diatomic species. Although it will not give information concerning the excitation of species (say in flames) as optical spectroscopy often can, the mass spectrometer appears to offer many advantages and intriguing possibilities in the study of labile intermediates in gas reactions. Eltenton [92] pioneered this field.

If atoms and free radicals are present in the ionisation chamber, their identities may be decided by the masses and appearance potentials of the corresponding ions. For example, if methyl is present in the ionisation chamber, the ion CH_3^+ will appear at 9·95 ev, the ionisation potential I of the radical. This electron energy is less than the appearance potential A required to form the same ion from a parent molecule CH_3R, by an amount at least equal to the bond dissociation energy $D(CH_3\text{–}R)$. It would thus seem that if the electron energy is adjusted to a suitable value between I and A, any CH_3^+ ion recorded may be attributed to the ionisation of the free radical CH_3 and not to the dissociative ionisation of the parent molecule. Some caution is necessary here since, as a result of the thermal spread of the electron energies, it is possible for the average energy to lie within the limits I and A, and yet a significant, if very small, number of electrons may have energies greater than A. Dissociative ionisation of the parent molecule CH_3R by this " tail " of high-energy electrons will produce a background current of CH_3^+ ions and the lowest concentration of CH_3 radicals which can then be detected in the presence of CH_3R will be such that its contribution to the CH_3^+ ion current can be just distinguished from the background. Eltenton [93] (cf. also Robertson [94]) considered that the limiting concentration at which radicals can be detected is about 10^{-3} %.

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[89] Zemany and Burton, *J. Phys. Colloid Chem.*, 1951, **55,** 949 ; see also Danby and Henderson, *J.*, 1951, 1426.

[90] See Steacie, " Atomic and Free Radical Reactions ", Reinhold, New York, 1946.

[91] Gaydon, " Spectroscopy and Combustion Theory ", Chapman and Hall, London, 1948 ; *idem, Quart. Rev.*, 1950, **4,** 1 ; Lewis and von Elbe, " Combustion, Flames, and Explosions of Gases ", Cambridge Univ. Press, London, 1938 ; Jost, " Explosions- und Verbrennungsvorgänge in Gasen ", Springer, Berlin, 1939.

[92] Eltenton, *J. Chem. Phys.*, 1942, **10,** 403.

[93] *Idem, ibid.*, 1947, **15,** 455 ; *J. Phys. Colloid Chem.*, 1948, **52,** 463.

[94] Robertson, " Mass Spectrometry ", Institute of Petroleum, London, 1952, p. 47.

One of the methods used by Eltenton to study free radicals is illustrated schematically in Fig. 8. The reaction mixture passed down the heated central quartz tube *A* and back along the concentric annular tube *BB*. A small orifice in the diaphragm *C* allowed a very small fraction of the reaction mixture to effuse into the closely adjacent ionisation chamber of the mass spectrometer. In this way reaction intermediates of short life reached the electron beam without colliding with other molecules or with any surfaces, and the rapid expansion of the gas causes a very rapid cooling which " freezes " the reaction. Depending on the rate of flow through the reactor, the reaction mixture spent 10^{-1} to 10^{-3} second in the heated tube *A* before it was sampled at the orifice.

Methyl radicals were identified and appeared to be the only intermediate present when methane was passed through the reactor at temperatures between 800° and 1000°. In other experiments tetramethyl-lead was studied in helium and in other carrier gases such as ethane, ethylene, and propene with which the methyl radical could react.

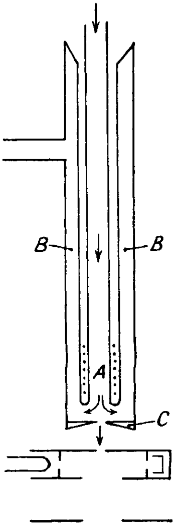

FIG. 8

Schematic diagram of Eltenton's apparatus.

If a reactant gas such as tetramethyl-lead, *tert.*-butyl peroxide, or dimethylmercury is carried in a stream of helium, the height of the parent peak (and hence the partial pressure of the undecomposed reactant which reaches the pinhole after spending a known time in the heated zone) may be used to evaluate the velocity constant, if it is assumed that the decomposition is of the first order. On the other hand, the measurement of the rates of radical reactions, such as combination and disproportionation, involves difficulties which are common to the continuous flow technique whatever method of detection and analysis is used ; the parent substance decomposes progressively along the reactor and the reactions of the radicals produced result in unknown concentration gradients. An ideal technique would enable the radical concentration to be determined by scanning along the length of the heated zone. As a step in this direction, K. U. Ingold and Lossing [95] have described a furnace which can be moved towards and away from the pinhole. Radicals can then be examined at earlier and later stages of their history. It was found that the concentration of methyl radicals is smaller the later the analysis and that an equivalent amount of ethane appears. Eltenton [93] had explored previously the possibilities of such a technique in his investigations of flames. In these, a burner formed a flame just above the pinhole ; by mechanically moving the burner, the flame moved in such a way that the pinhole scanned back and forth along the length of the flame with a certain periodic frequency. Since the composition of the gases varies along the length of the flame the ion currents

[95] Ingold and Lossing, *J. Chem. Phys.*, 1953, **21**, 368.

arising from any one chemical species will fluctuate with the same frequency ; the phase of this fluctuation will depend upon whereabouts in the length of the flame this species reaches its maximum or minimum concentration. Thus, from their relation as regards phase, the maxima and minima of the various species can be placed in sequence along the length and the stages of the flame reaction in which the species are formed or consumed can be decided. As an alternative method to mechanically moving the flame the supply of the reactant gases may be varied in a pulsating manner ; the flame will then contract and expand over the pinhole. By this type of experiment Eltenton obtained some very interesting preliminary results ; for example, in the oxygen–methane flame, the chemical sequence is O_2, CH_3O, CH_2O, CHO, CO, and CH_4.

Foner and Hudson[96] detected H, O, and OH in low pressure H_2–O_2 flames, but the presence of HO_2 radical[97] was not confirmed. Eltenton also studied a number of thermal decompositions on a heated filament placed just in front of the pinhole.[98]

Isotopes and Mass Spectrometry

Analysis of Isotopic Molecules.—In 1913 Hevesy and Paneth[99] labelled lead by adding a little Ra-*D* to it ; the radioactivity could then be used for tracing the lead. Ten years later, Hevesy[100] followed the absorption and distribution of lead and bismuth in animals and plants by this method. These classical experiments pioneered the whole field of isotope tracer research.

Both radioactive and stable isotopes are now used and the choice is often a matter of convenience, each having advantages and disadvantages. The detection of radioactivity by means of a Geiger–Müller counter is convenient, quick, and very sensitive, and the necessary apparatus is not expensive. The high sensitivity of detection permits extensive dilution by factors of the order 10^6 in the course of an experiment. The measurement of the radioactivity of a sample is non-destructive. However, radioactive isotopes with short half-lives are unsuitable for time-consuming experiments and two important elements, oxygen and nitrogen, have no radioactive isotopes of convenient half-life.

The determination of stable isotopes can be carried out in a number of ways. The density,[101, 102] thermal conductivity,[103] infra-red absorp-

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[96] Foner and Hudson, *J. Chem. Phys.*, 1953, **21**, 1375.

[97] Hinshelwood, *Proc. Roy. Soc.*, 1946, *A*, **188**, 1 ; Minkoff, *Discuss. Faraday Soc.*, 1947, **2**, 151.

[98] See Robertson, *Proc. Roy. Soc.*, 1949, *A*, **199**, 394.

[99] Hevesy and Paneth, *Z. anorg. Chem.*, 1913, **82**, 323 ; *Brit. Ass. Rep.*, 1913, 448 ; *Chem. News*, 1913, **108**, 166.

[100] " Radio Elements as Indicators ", McGraw-Hill, New York, 1928.

[101] Cohn, " Preparation and Measurement of Isotopic Tracers ", Edwards, Ann Arbor, Michigan, 1946.

[102] Afinsen, *ibid.*

[103] A. Farkas, " Light and Heavy Hydrogen ", Cambridge Univ. Press, London, 1935.

tion,[104] and microwave-[105] and band-spectra [106] may be used. The most general method of measuring isotope abundances is to use a mass spectrometer. There are, however, considerable difficulties in analysing accurately mixtures of protium and deuterium and mixtures of H_2O and D_2O by this method.[107, 108, 109]

In tracer studies it is often necessary to determine the position of the tracer atom in the molecule. The usual procedure, and the only one for radioactive isotopes, is to degrade the molecule in unequivocal steps and examine the degradation products separately for the isotope. Rearrangements and exchanges are possible during such degradations and may render the information gained invalid. For volatile compounds, mass spectrometry offers an alternative technique, which combines in one operation the chemical degradation and isotopic analysis. The peaks for the isotopic compound can be correlated with those of the normal compound and an examination of their intensities will often decide the position of the isotopic atom. An example will indicate the principles involved. Under electron impact, the dissociation probabilities of the C–C bonds in the propanes C_3H_8, $CH_3{\cdot}CH_2{\cdot}CH_2D$, and $CH_3{\cdot}CHD{\cdot}CH_3$ should be almost equal. On this basis, the peak for mass 30 ($CH_2{\cdot}CH_2D^+$) in the spectrum of $CH_3{\cdot}CH_2{\cdot}CH_2D$ should be half the intensity of the mass 30 peak ($CH_3{\cdot}CHD^+$) in $CH_3{\cdot}CHD{\cdot}CH_3$ and half that of the mass 29 peak ($CH_3.CH_2^+$) in C_3H_8. This is found to be the case.[110] Table 9 gives a selection of peak intensities from the three mass spectra. Considering the peaks at 16 and 15 (CH_2D and CH_3) in a similar way, the mass 16 peak for $CH_3{\cdot}CHD{\cdot}CH_3$ should be zero whilst experimentally it is 3·3. Nevertheless, the mass spectra of the three isotopic compounds are sufficiently characteristic to enable the presence and position of the deuterium to be determined and to allow quantitative analysis of the three propanes in a mixture.

TABLE 9

Mass	45	44	30	29	16	15
C_3H_8	—	100	—	312	—	13·5
$CH_3{\cdot}CH_2{\cdot}CH_2D$.	100	—	151	—	7·4	—
$CH_3{\cdot}CHD{\cdot}CH_3$ . .	100	—	323	—	3·3	—

The isotope dilution method previously described is an example in which complete molecules are traced. Another instance is the use of the mass spectrometer to study the diffusion rates of the molecules $^{14}N^{15}N$, $^{16}O^{18}O$,

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[104] Thornton and Condon, *Analyt. Chem.*, 1950, **22,** 690.

[105] Southern, Morgan, Keilholtz, and Smith, *Phys. Rev.*, 1950, **78,** 639; *Analyt. Chem.*, 1951, **23,** 1000.

[106] Hoch and Weisser, *Helv. Chim. Acta,* 1950, **33,** 2128.

[107] Roth, in ref. 19.

[108] Alfin-Slater, Rock, and Swislocki, *Analyt. Chem.*, 1950, **22,** 421.

[109] von Ubish, *Arkiv Fys.*, 1951, **2,** 517; den Boer and Borg, *Rec. Trav. chim.*, 1952, **71,** 120.

[110] Turkevich, Friedman, Soloman, and Wrightson, *J. Amer. Chem. Soc.*, 1948, **70,** 2638.

and $^{12}C^{16}O^{18}O$ into isotopically normal nitrogen, oxygen, and carbon dioxide respectively.[111] A further example is given by the work of Hunt and Taube,[112] who have measured the rate of exchange when ions hydrated with normal water are dissolved in water enriched with $H_2{}^{18}O$.

One of the first applications of isotopic oxygen to the elucidation of reaction mechanisms was the study of the hydrolysis of amyl acetate by Polanyi and Szabo,[113] who were able to show that the acyl–oxygen bond was split. This work has been followed by similar investigations [114] in many of which the mass spectrometer has been used for isotope assay. An unconventional application of the instrument is to be found in a study by Long and Friedman.[115]

Isotopes and Catalysis.—Tracers are proving particularly valuable in the study of catalysis, though much remains to be done, and the following selected examples are illustrative of the power of the mass spectrometer in the investigation of this field. In the presence of iron synthetic ammonia catalysts, an exchange reaction between molecules of $^{14}N^{14}N$ and $^{15}N^{15}N$ takes place at 500° :

$$^{14}N^{14}N + {}^{15}N^{15}N \rightleftharpoons 2\,{}^{14}N^{15}N$$

Emmett and Kummer [116] found that the reaction went comparatively rapidly on a singly promoted catalyst, and that the rate of exchange was in good agreement with the measured rate of desorption. It would, therefore, seem to follow that the chemisorption of nitrogen on such catalysts involves dissociation into atoms. McGeer and Taylor [117] showed that this nitrogen isotope exchange reaction on rhenium catalysts was accelerated by the presence of hydrogen, and they also studied the exchange of protium and deuterium between NH_3 and ND_3 on the same catalysts. In the exchange reaction between NH_3 and D_2 on evaporated nickel catalysts, Kemball [118] found that the primary product was NH_2D and successive reactions produced NHD_2 and ND_3. There was no evidence of the exchange of more than one hydrogen atom at a time.

In contrast with this conclusion for ammonia, the same author found,[119] in similar experiments with CH_4 and D_2, that in the initial reaction CD_4 was the most abundant product and hence could not have been formed by successive exchanges. Turkevich *et al.*[120] had previously studied the kinetics of the interaction of C_2H_4 and D_2 on nickel at 90°. Detailed analyses for the individual species C_2H_4, C_2H_3D, $C_2H_2D_2$, C_2HD_3, and C_2D_4 as well as for C_2H_6 and the various deuterated ethanes up to C_2D_6 were possible.

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[111] Winter, *Trans. Faraday Soc.*, 1951, **47**, 342.

[112] Hunt and Taube, *J. Chem. Phys.*, 1950, **18**, 757 ; 1951, **19**, 602.

[113] Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508.

[114] See M. Dole, *Chem. Rev.*, 1952, **51**, 288.

[115] Long and Friedman, *J. Amer. Chem. Soc.*, 1950, **72**, 3692.

[116] Emmett and Kummer, *J. Chim. phys.*, 1950, **47**, 67.

[117] McGeer and Taylor, *J. Amer. Chem. Soc.*, 1951, **73**, 2743.

[118] Kemball, *Trans. Faraday Soc.*, 1952, **48**, 254 ; *Proc. Roy. Soc.*, 1952, *A*, **214**, 413.

[119] *Idem, ibid.*, 1951, *A*, **207**, 539.

[120] Turkevich, Bonner, Schissler, and Irsa, *Discuss. Faraday Soc.*, 1950, **8**, 352 ; *J. Phys. Colloid Chem.*, 1951, **55**, 1078.

Beeck and his collaborators [121] have investigated the isomerisation of [1-^{13}C]propane (with 16·7 atom per cent of ^{13}C in the end position) to [2-^{13}C]propane over almost anhydrous aluminium bromide at 25°. The concentrations of [1-^{13}C]propane and [2-^{13}C]propane were determined from the intensities of the peaks at masses 29 and 30, since the first species gives half as many $^{12}C^{13}CH_5^+$ ions as the second species. No molecules with two ^{13}C atoms were found in the products, which implies that the isomerisation is purely intramolecular.

Isotopes and Gaseous Reactions.—As mass spectrometers become more readily available, isotopic tracers are being used to an increasing extent in studies of homogeneous gas kinetics. The advantages to be derived from them and the increased information which they provide can be appreciated from some selected examples. Wall and Moore [122] have pyrolysed mixtures of C_2H_6 and C_2D_6 at temperatures between 510° and 610° and subjected the product to analysis by mass spectrometry. All the methanes, $CH_{4-n}D_n$ ($n = 0, 1, 2, 3,$ or 4), and all the ethanes were found. The amount of $C_2H_2D_4$ in the early stages of the reaction is too low for the isotopic mixing observed to have been produced by the intramolecular reactions

$$C_2D_6 = C_2D_4 + D_2$$
$$C_2D_4 + H_2 = C_2H_2D_4, \text{ etc.}$$

However, the Rice–Herzfeld free-radical chain mechanism does provide a qualitative interpretation of the mixing. Further evidence for this mechanism is provided by the fact that nitric oxide which inhibits the reaction rate also inhibits the extent of the isotopic mixing ; some mixing still remains and it would seem that nitric oxide does not completely inhibit the formation of free radicals.

The photochemical decomposition of a mixture of $CH_3{\cdot}CHO$ and $CD_3{\cdot}CDO$ was studied by Zemany and Burton.[123] If a molecular rearrangement

$$CD_3{\cdot}CDO = CD_4 + CO$$
$$CH_3{\cdot}CHO = CH_4 + CO$$

takes place, then only CD_4 and CH_4 should be formed. If the molecules split into free radicals :

$$CD_3{\cdot}CDO = CD_3 + DCO$$
$$CH_3{\cdot}CHO = CH_3 + HCO$$

followed by

$$CD_3 + CH_3{\cdot}CHO = CHD_3 + CH_3{\cdot}CO, \text{ etc.}$$

then CD_4 and CHD_3, CH_4, and CH_3D should result. Analysis of the products confirms the presence of CHD_3. The corresponding experiment on a mixture of $(CH_3)_2CO$ and $(CD_3)_2CO$ would give exclusively C_2H_6 and C_2D_6 if the acetone dissociated directly into ethane and CO. On the other hand, a free-radical mechanism involving CH_3 and CD_3 would lead to C_2H_6 25%, C_2D_6 25%, and $CH_3{\cdot}CD_3$ 50%. Benson and Falterman [124] found that the

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[121] Beeck, Otvos, Stevenson, and Wagner, *J. Chem. Phys.*, 1948, **16**, 255, 745, 993.

[122] Wall and Moore, *J. Amer. Chem. Soc.*, 1951, **73**, 2840.

[123] Zemany and Burton, *ibid.*, p. 499 ; see also *J. Phys. Colloid Chem.*, 1951, **55**, 949 ; Morris, *J. Amer. Chem. Soc.*, 1944, **66**, 584.

[124] Benson and Falterman, *J. Chem. Phys.*, 1952, **20**, 201.

distribution of the isotopic ethanes was within 2% of that predicted by the free-radical mechanism. The photolysis[125] of the diethyl ketone $(CH_3{\cdot}CD_2)_2CO$ first produces the ethyl radicals $CH_3{\cdot}CD_2$, which then disproportionate to form the ethane $CH_3{\cdot}CHD_2$ and ethylene $CH_2{:}CD_2$. This suggests that the disproportionation proceeds by a " head-to-tail " mechanism

$$CH_3{\cdot}CD_2^- + HCH_2{\cdot}CD_2^- \rightarrow CH_3{\cdot}CD_2H + CH_2{:}CD_2$$

rather than a " head-to-head " mechanism

$$CH_3{\cdot}CD_2^- + {-}DCD{\cdot}CH_3 \rightarrow CH_3{\cdot}CD_3 + \rangle CD{\cdot}CH_3$$

the ethylidene radical isomerising to ethylene.

The use of isotopes in reaction kinetics will prove especially powerful when the effect of reaction variables on the course of the reaction can be followed by detailed isotopic analysis. One factor limiting the application of this method at present is the difficulty of deriving a precise isotopic analysis from the mass spectrum of an isotopically mixed compound without having the mass spectra of the pure isotopic individuals available for comparison. There are, for example, ten deuterated ethanes ; if the individuals are not separately available, the mass spectrum of each can be calculated approximately from that of ethane, but because the probabilities of rupture of the various bonds under electron impact are influenced by the isotopic atoms present in the molecule the approximations are not very good.

Conclusion

In addition to the applications described above, the mass spectrometer has been used extensively in other fields of research of less direct interest to the chemist, and as yet there seems to be no indication that it has reached the limit of its versatility. New types of mass spectrometers are being developed[126] and modifications and improvements in the conventional type may be expected for special applications. Instruments with very high resolution would be of considerable advantage for the analysis of isotopic (*e.g.*, deuterated) compounds and for resolving certain peaks such as the mass 28 peaks. In the determination of appearance potentials, the utilisation of a beam of electrons uniform in energy would assist in the solution of a number of problems and expose the finer structure of the ionisation efficiency curves. Further improvements in the sensitivity of detection of the ion beam may permit other methods of producing dissociation and ionisation to be used, and would also be useful in the investigation of free radicals in reactions less extreme than those at present. In the catalytic field, there has been little work done on the direct examination of surface

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[125] Wijnen and Steacie, *Canad. J. Chem.*, 1951, **29**, 1093.

[126] Stephens, *Phys. Rev.*, 1946, **69**, 691 ; Cameron and Eggers, *Rev. Sci. Instr.*, 1948, **19**, 605 ; Roth, *J. Phys. Radiol.*, 1949, **10**, 17 ; Keller, *Helv. Chim. Acta*, 1949, **22**, 386 ; Hipple and Thomas, *Phys. Rev.*, 1949, **75**, 1616 ; Boyd, *Nature*, 1950, **165**, 142 ; Hays, Richards, and Goudsmit, *Phys. Rev.*, 1951, **84**, 824 ; Smith, *ibid.*, p. 295 ; *Rev. Sci. Instr.*, 1951, **22**, 115 ; Schissel, *J. Appl. Phys.*, 1951, **22**, 680 ; Hipple and Sommer, *Phys. Rev.*, 1952, **85**, 712.

reactions, though for the chemist the field is of considerable interest. Mass spectrometry has given rise to many phenomena which merit theoretical study; factors which decide the relative intensities of the ions in mass spectra[127] and the stabilities of ions would be a fruitful field of research.

Thanks are offered to Mr. A. J. Shipman for assistance in the preparation of the manuscript.

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[127] Magat and Viallard, *J. Chim. phys.*, 1951, **48,** 485; Magat, *Discuss. Faraday Soc.*, 1951, **10,** 113; Thompson, in ref. 19.