SHOCK WAVES

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SHOCK waves arise in air because a compressive disturbance can become more and more sudden as time goes on, owing to the faster propagation of the high-pressure parts of the disturbance. Weak shock waves are produced by the clap of a hand or the crack of a whip; strong shock waves are equally familiar to us, and are associated with, for example, thunder, the motion of supersonic aircraft and projectiles, and with explosions of all kinds. The way in which a shock wave builds up can be shown by considering the motion of a wave in which the pressure variation is initially sinusoidal. We consider the disturbance entering a gas at the left-hand side of Fig. 1 and travelling towards the right. Any small pressure disturbance is propagated through the medium with the local velocity of sound, and it is a property of any fluid that the velocity of sound increases with pressure. Thus, the more intense parts of the disturbance will travel more quickly than the weaker parts, so that the wave-form of the pressure variation as it passes through any point in the gas will be a distorted sine wave. This distortion increases, until after a sufficient distance, the high- and low-pressure disturbances arrive simultaneously, *i.e.*, the pressure rise becomes instantaneous; this is a shock wave. In fact, all sound waves will degenerate into small periodic shock waves after travelling a few hundred wavelengths unless sufficiently attenuated by dissipative effects (*i.e.*, diffusion and thermal conduction from the wave). Whilst this effect is of little practical concern, a knowledge of the properties of shock waves is of crucial importance in other fields of technology, most of them military; like several other techniques in physical chemistry, the use of shock waves has filtered through as a by-product of military necessity.

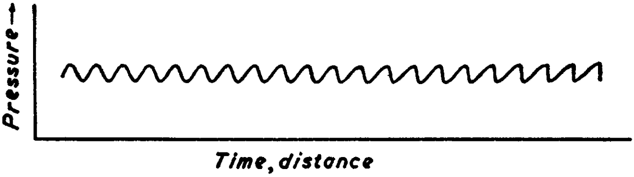

FIG. 1

The shock tube

The behaviour of shock waves is most conveniently studied by using a shock tube. The design of such tubes varies, but one suitable for kinetic studies might consist of a metal tube about 6 in. in diameter, and, say, 20 feet long. It is divided into a high-pressure and a low-pressure compartment by a thin diaphragm (Fig. 2); this diaphragm may be of metal foil, celluloid, cellophane, or some similar material depending on the pressure difference it is required to withstand. A plane shock wave moving into the low-pressure region can then be generated by bursting the diaphragm, either with a suitably controlled needle, or by increasing the driving pressure. A shock tube in this form seems first to have been used by Vieille in 1899, but both experimental and theoretical work on shock waves go back much earlier than this.[1] In Fig. 3 are plotted, one behind the other, successive pressure profiles along the tube. If the diaphragm broke instantaneously the pressure wave would be a shock from the beginning. However, diaphragms take of the order of a millisecond to burst,[2] and there is some turbulence at the pressure front. The second profile shows that some of the driver gas has flowed into the low-pressure section, pushing the low-pressure gas before it; there is little mixing between the two gases and there is a boundary maintained throughout the experiment. The pressure profile at this instant is not yet discontinuous owing to the slow bursting of the diaphragm, but because of the more rapid propagation of the higher-pressure disturbance, it becomes sharper, until, in the sixth profile, we have a shock wave. This shock continues to travel along the tube in a uniform manner provided the internal walls of the tube are not too rough.

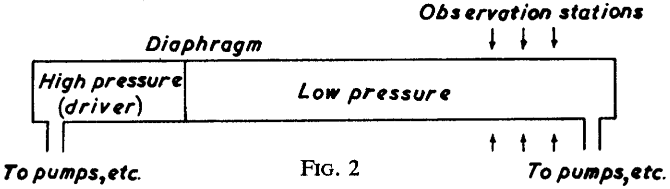

FIG. 2

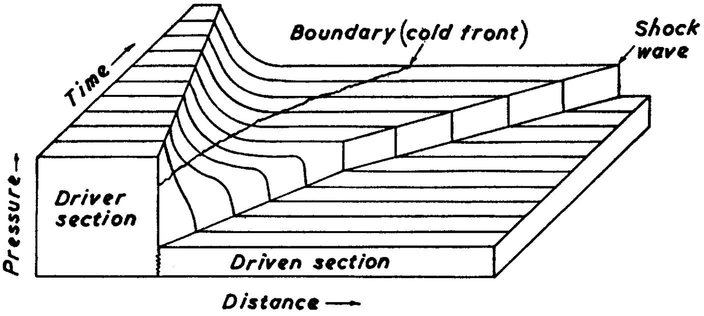

FIG. 3

At any instant during the experiment, there are four distinct regions in which the local conditions differ very markedly. If we consider the final profile, there are the two regions in which the gases are stationary and in the same condition as they were before the experiment started, *i.e.*, the as yet unexpanded driver gas at the extreme left and the as yet uncompressed

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[1] See Payman and Shepherd, *Proc. Roy. Soc.*, 1946, *A*, **186**, 293, for historical references.
[2] White, *J. Fluid Mechanics*, 1958, **4**, 585.

gas at the extreme right. These two regions may be characterised thermodynamically by their pressure, density and temperature, so that we have $P_i^{(d)}$, $\rho_i^{(d)}$, $T_i^{(d)}$ and P_i, ρ_i, T_i, respectively, where the initial temperatures of the driver $T_i^{(d)}$ and the driven gas T_i are usually the same. We then have a region to the left of the composition boundary which consists of expanded driver gas, characterised by $P_f^{(d)}$, $\rho_f^{(d)}$, $T_f^{(d)}$. Finally, there is the region which consists of gas which has been compressed, characterised by P_f, ρ_f, T_f, with $P_f = P_f^{(d)}$; this is the region in which we are interested. This gas has been suddenly compressed, and its temperature has risen. The magnitude of the temperature rise can be calculated from the Rankine–Hugoniot relations,[1,3] which are a consequence of the fact that mass, momentum, and energy must be conserved across the shock front; *i.e.*, if we consider a frame of reference which moves along with the shock front, then the mass, momentum, and energy of the unshocked gas entering from the right must be the same as for the shocked gas leaving to the left. In essence

$$\frac{T_f}{T_i} = \xi \cdot \frac{\xi + \phi}{\xi\phi + 1} = \xi \frac{\rho_i}{\rho_f}$$

where ξ is the "pressure ratio" P_f/P_i and ϕ is a linear function of the average specific heat of the gas between the two temperatures T_i and T_f; in the case of a monatomic gas, ϕ is independent of time, and the pressure ratio ξ can be eliminated if the velocity V of the shock wave is known, since

$$V^2 = \frac{P_i}{\rho_i} \frac{\xi\phi + 1}{\phi - 1}$$

For a weak shock ($\xi \approx 1$), V is only a little greater than the velocity of sound in the unshocked gas, but for strong shocks ($\xi \gg 1$), V can be several times the speed of sound, and is usually described by a Mach number (*i.e.*, a number of multiples of the velocity of sound in the unshocked gas). Thus if we know the specific-heat function ϕ and the initial state, P_i, ρ_i, T_i, of the unshocked gas, we can calculate the final temperature if we measure the velocity V of the shock wave; this is one use for the observation stations at the right-hand end of the tube in Fig. 2.

The energy which causes the rise in temperature is derived from the energy of flow of the driver gas down the tube, and anything which increases the speed of flow of the driver into the low-pressure section will result in a higher value of $P_f^{(d)}$ (and therefore ξ) and consequently a bigger temperature rise. To some extent, increasing the driver gas pressure is advantageous, but it causes difficulties with diaphragm materials, etc.

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[3] The relevant equations are given in a number of places, *e.g.*:
(*a*) Bleakney and Taub, *Rev. Mod. Phys.*, 1949, **21**, 584;
(*b*) Bleakney, Weimer, and Fletcher, *Rev. Sci. Inst.*, 1949, **20**, 807;
(*c*) Penney and Pike, *Rep. Progr. Phys.*, 1950, **13**, 46;
(*d*) Griffith and Bleakney, *Amer. J. Phys.*, 1954, **22**, 597;
(*e*) Hirschfelder, Curtiss, and Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1954.

Increasing the actual velocity of the driver gas molecules is also useful, so that hydrogen or helium is the most efficient driver: and it is possible to gain a little extra by heating the driver gas to a high temperature beforehand; this can be done either physically (*e.g.*, an electric heater inside the high-pressure chamber) or chemically (the ignition of a mixture of hydrogen and oxygen in the driver section has been used to initiate the flow[4]) Another device which roughly doubles the temperature rise is to allow the shock wave to be reflected at the right-hand closed end of the tube, whereupon it then begins to move leftwards through the already shocked gas, and raises its temperature again; the quantitative interpretations of reflected shock studies are, however, open to some criticism.[5]

We can now see what considerations determine the size of the two compartments in a chemical shock tube. Owing to the non-ideal bursting of the diaphragm, a good shock is not produced until the compression has moved several diameters down the tube. Then, if we wish to study chemical reactions taking place in the hot zone behind the shock, sufficient gas must be shock-heated so that the necessary observations can be made before the cold front arrives at the observation post. This determines the length of the low-pressure section, and in consequence the driver section must be sufficiently long for the left-moving rarefaction wave not to be reflected back down the tube so as to interfere with the observations.

The scope of shock-tube measurements

If an inert gas, say argon, is shocked, we have a sharp rise in the temperature, pressure, and density across the shock front, and then a uniform region of hot gas. The discontinuity is very sharp, and the distance between uniform unshocked gas and uniform shocked gas is only a few mean-free-paths; *i.e.*, the shock front is only of the order of a micron thick. As the shock strength is increased, the shock velocity and the temperature increase until, at about Mach 10, the temperature is about 8000°K (Fig. 4). For stronger shocks, however, the temperature tails off

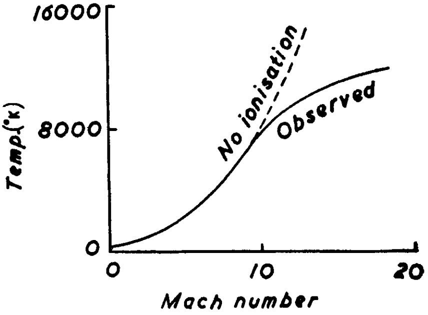

FIG. 4

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[4] Resler, Lin, and Kantrowitz, *J. Appl. Phys.*, 1952, **23**, 1390.

[5] Strehlow and Cohen, *J. Chem. Phys.*, 1959, **30**, 257.

because of the thermal ionisation of the argon atoms; at higher temperatures still, doubly ionised atoms have been observed in thermal equilibrium with their surroundings. Thus, the specific heat of the gas (and the function ϕ) increases by successive steps as the successive ionisation processes become important.

If the gas is diatomic, other things can happen. Starting with a weak shock, travelling only a little faster than sound, we can observe effects due to the sort of processes which cause anomalous dispersion in sound waves, *e.g.*, rotational and vibrational relaxation. The gas is heated suddenly to a new temperature, but it takes many collisions before the molecular rotation and vibration come to thermal equilibrium with the translational motion. Thus, the gas behind the shock does not become uniform immediately, and by measuring the thickness of this non-uniform region, the rate of these equilibration processes can be inferred. At stronger shock strengths, temperatures are reached where the diatomic molecule begins to dissociate; this is again a slow process, and the rate can sometimes be studied under suitable conditions. It may also be possible to study the further reactions of these atoms once they have been produced. At higher temperatures still, ionisation again occurs, and even this is a slow process; however, although rates of ionisation (about 1 μsec. at 1 cm. pressure) and recombination have been measured[4,6] these are not quantities which have yet found their way into chemical thinking. In addition, there is radiation of energy from the shocked gas at most temperatures, so that spectral information can be obtained.

Shock-tube instrumentation

Apart from the obvious pressure-measuring and pumping equipment, most of the instrumentation is concerned with the detection of the shock wave, the measurement of its velocity, and following the variations behind it. If the shock front can be detected and its arrival at the observation post converted into an electrical pulse, then the measurement of the velocity simply reduces to the need for a suitable device to time the progress between two adjacent stations. Since the velocity of the shock front is of the order of 10^5 cm./sec., and the two observation stations may be 10 cm. apart, we have to time an interval of about 10^{-4} sec.; thus, to obtain the velocity to better than 1% needs sub-microsecond electronic techniques. One interesting technique for strong shocks and blast waves is to direct 3 cm. radar waves upstream at the approaching shock, and measure the Doppler change in frequency of those waves reflected back by the ions in the shock front.[7]

There are a great variety of methods available for the detection of the arrival of the shock front; they depend on observing the sharp change

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[6] (*a*) Niblett and Blackman, *J. Fluid Mechanics*, 1958, **4**, 194; (*b*) Manheimer-Timnat and Low, *J. Fluid Mechanics*, 1959, **6**, 449; (*c*) Lamb and Lin, *J. Appl. Phys.*, 1957, **28**, 754; (*d*) Toennies and Greene, *J. Chem. Phys.*, 1957, **26**, 655.

[7] Cook, Doran, and Morris, *J. Appl. Phys.*, 1955, **26**, 426.

in temperature, pressure, density, or, in strong shocks, conductivity, associated with the shock. The detection of a change in electrical conductivity can be particularly simple, requiring only a couple of electrodes with a potential across them and a suitable amplifier;[8] automobile sparking plugs can even be used. The method works down to temperatures of 700°K, where there should be no thermal ionisation, but the reason for this is not known.[9] On the other hand, the measurement of the temperature change across the shock is not easy, but thin films of platinum or gold sputtered on a Pyrex surface have been used as resistance thermometers;[10] the particular thermometers described have time lags of less than 1 μsec. Nor is the measurement of the pressure change particularly easy, but piezoelectric microphones, hot-wire anemometers, and mechanical pressure switches have been successfully used.

Most of the methods of detection (and measurement) make use of the change in density. There are two optical techniques which give essentially direct pictures of the shock front—the shadowgraph and the schlieren method. In the former method, all that is necessary is to trigger an intense flash of light as the shock passes the observation post; the light is collimated so as to be parallel when passing through the shock tube and then falls directly on a photographic plate. A shadow is cast by those regions in which the optical depth (*i.e.*, density) has a non-zero second derivative in the plane perpendicular to the light beam.[11] In the schlieren method, the light from the triggered flash is focused on a second slit after passing through the shock tube, and then into a camera; if there are regions in the optical path in which the optical depth (density) has a non-zero first derivative,[11] light will be deviated from the observation slit and so cause a shadow to be cast on the photographic record. These two techniques give good qualitative representations of the density change in the shock wave, but are of little use for quantitative purposes. However, with a third optical technique, it is possible to measure the actual change in density across the shock: this is the Mach–Zehnder interferometer.[12] In this case, the light from the triggered spark is collimated and then split into two parallel beams by use of half-silvered mirrors; half the light passes through the shock tube, and half through a dummy sample of the unshocked gas. The two beams are then recombined and interference fringes are obtained. When the density in the shock tube changes, the fringes will move, and the position of the shock front is therefore indicated by a sharp discontinuity in the fringes. If the beam is off-set so as to make an angle of 1° or 2° with the shock front, the discontinuity is spread out, and it is

[8] Knight and Duff, *Rev. Sci. Inst.*, 1955, **26**, 257.

[9] Manheimer and Nahmani, *Rev. Sci. Inst.*, 1956, **27**, 174.

[10] (*a*) Blackman, *J. Fluid Mechanics*, 1956, **1**, 61; (*b*) Rabinowicz, Jessey, and Burtsch, *J. Appl. Phys.*, 1956, **27**, 97.

[11] Liepmann and Puckett, "Introduction to the Aerodynamics of a Compressible Fluid", Wiley, New York, 1947.

[12] Winckler, *Rev. Sci. Inst.*, 1948, **19**, 307; Curtiss, Emrich, and Mack, *Rev. Sci. Inst.*, 1954, **25**, 679.

possible to trace the individual fringes through the shock, thus giving an absolute measure of the change in density. Excellent examples of photographs taken by all these three techniques are given in refs. 3(*a*), 3(*b*), and 3(*d*), and in many of the other references quoted in this Review.

Another important method of measuring density changes was developed in the study of detonation waves.[13] This depends on the change in attenuation of *X*-rays by a gas as the density changes, and by using a triggered *X*-ray flash, it is possible[14] to measure the ratio of the densities on the two sides of the shock to about ±1%.

All these methods work with transparent gases. Clearly, if the shocked gas is coloured, *e.g.*, a halogen, relatively simple photometric methods will work; these, however, will be discussed in relation to the particular problem involved.

Spectra and shock waves

Since very high temperatures can be attained in strong shocks, molecular fragments may be formed in states of high excitation, and they will then emit radiation as they fall back to the ground state. For example, strong shocks in methane and ammonia emit the spectra of C_2 and CN, presumably formed *via* C and N atoms.[15] If fine dusts (*e.g.*, MgO, Al_2O_3) are present in the tube, even quite moderate shocks (2000°K) will excite the diatomic molecular spectra, but much stronger shocks are usually required before the atomic lines appear;[16] such spectra are of interest for comparison with the emission of meteoric dusts. Quite often, spectra are produced from trace impurities in the shocked gas: for example, strong shocks in argon or krypton have been known to give the Swan bands of carbon, and the spectra of CN, Hg, Ca, and Na; the mercury lines appear at a later time than the C_2 or CN bands, indicating that electronic excitation of mercury atoms by collision is a relatively slow process.[17] The sodium-atom spectrum is fairly easily excited, and the emission has been used to measure the temperature as a check on the shock-tube equations for the temperature rise.[18] In very strong shocks, *e.g.*, argon at 18,000°K, the atomic lines suffer broadening and a red shift due to the perturbation of neighbouring ions and electrons.[19] Strong shocks in the inert gases also give rise to a continuous spectrum, which is emitted after an induction period of some tens of microseconds. This induction period is temperature dependent, and in the case of xenon, the temperature coefficient over the range 6000—11,000°K, corresponds

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[13] Kistiakowsky and Kydd, *J. Chem. Phys.*, 1956, **25**, 824.

[14] Knight and Venable, *Rev. Sci. Inst.*, 1958, **29**, 92.

[15] Charatis, Doherty, and Wilkerson, *J. Chem. Phys.*, 1957, **27**, 1415.

[16] Nicholls and Parkinson, *J. Chem. Phys.*, 1957, **26**, 423.

[17] Turner and Rose, *Phys. Rev.*, 1955, **99**, 633; Rose, quoted in Clouston and Gaydon, *Spectrochim. Acta.*, 1959, **14**, 56.

[18] (*a*) Losev, *Proc. Acad. Sci.* (*U.S.S.R.*) *Phys. Chem. Sect.*, 1959, **120**, 467; (*b*) Clouston, Gaydon, and Glass, *Proc. Roy. Soc.*, 1958, *A*, **248**, 429.

[19] Petschek, Rose, Glick, Kane, and Kantrowitz, *J. Appl. Phys.*, 1955, **26**, 83.

to an activation energy of 8·3 ev, which is the excitation potential of one of the excited states of the xenon atom. These observations are interpreted[20] to mean that the Xe atom is excited by collision to $Xe^*(5s^2 5p^5 6s)$ and that a stable excited state of Xe_2 is formed by the reaction $Xe^* + Xe \rightarrow Xe_2^*$; this then falls back to its ground state Xe_2 which is repulsive, and consequently the radiation emitted must be continuous. The same phenomenon occurs in argon, but the excited state is more than 11 ev above the ground state.

A continuous spectrum is also emitted from shocks in bromine between 1300° and 2300°K at pressures of 1—2 atm.[21] This arises from a two-body recombination of bromine atoms; no radiation is observed which arises from the normal three-body recombination. Two processes, *i.e.*, $Br(^2P_{3/2}) + Br(^2P_{1/2})$ and $Br(^2P_{3/2}) + Br(^2P_{3/2})$ appear to be important; they lead to the formation of excited states of the bromine molecule, and these emit continuous radiation in falling back to the ground state. A study of the temperature coefficient of the emission at various wavelengths leads to some information on the actual form of the potential-energy curves for these excited states.

Emission, however, is not confined to the visible and the ultraviolet region. Radiation has been observed in the infrared, but measurements are much more difficult because of the lack of suitably fast infrared detectors. However, with a lead sulphide detector of 30 μsec. response time, the infrared emission of the $2 \rightarrow 0$ band in CO has been studied at $2{\cdot}35\mu$.[22] The emission builds up rather slowly in pure CO (relaxation time of 77 μsec. at 0·24 atm. and 1470°K) but it is not possible, because of the experimental difficulties, to decide whether the excitation takes place directly, *i.e.*, $\nu = 0 \rightarrow 2$, or stepwise, *i.e.*, $\nu = 0 \rightarrow 1 \rightarrow 2$. As is common to many of these relaxation processes, there is a considerable acceleration by traces of water.

Spectral measurements on shocked gases can also be made in absorption. For example, air in the range 2000—6000°K shows the Schumann–Runge bands in absorption,[23] and at the higher temperature, can be shown to contain about 5% of NO.[24] Shocks in hydrocarbon–oxygen mixtures exhibit absorption corresponding to C_2 and CH for the first 30 μsec., but after this, only the absorption spectrum of OH persists; on the other hand, in shocks using oxygenated compounds, *e.g.*, acetaldehyde, the C_2 and CH spectra do not appear until after the OH has disappeared.[25] Such observations will help in the interpretation of combustion and explosion processes; clearly, they are complementary to the study of spectra in flame gases and explosion products.

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[20] Roth and Gloersen, *J. Chem. Phys.*, 1958, **29**, 820.
[21] Palmer, *J. Chem. Phys.*, 1957, **26**, 648.
[22] Windsor, Davidson, and Taylor, *J. Chem. Phys.*, 1957, **27**, 315.
[23] Wurster, Treanor, and Glick, *J. Chem. Phys.*, 1958, **29**, 250.
[24] Wurster and Glick, *J. Chem. Phys.*, 1957, **27**, 1218.
[25] Campbell and Johnson, *J. Chem. Phys.*, 1957, **27**, 316.

Vibrational and rotational relaxation in shock waves

As mentioned earlier, it is possible to study relaxation processes by measuring the thickness of the shock front. In light diatomic molecules, the conversion of translational energy into rotational energy may be observed; in more complicated molecules, the equilibration between translational and vibrational energy is important in the shock front. If the rotations were not easily excited, the density profile across the shock would be represented by curve 1 in Fig. 5. On the other hand, if the rotations take up their energy immediately, we have a larger specific heat; thus the temperature rise is not so great and so, for the same pressure ratio, there is a greater increase in density, as in curve 3. In diatomic molecules, the rotations come to thermal equilibrium in less than 150 collisions, and the density profile is represented by curve 2; we have an initial rise in density similar to that in curve 1, followed by a gradual cooling, *i.e.*, a further gradual increase in density, until the final state represented by curve 3 is reached. The same happens in the case of vibrational equilibration. In both processes, the shock front, or region of non-uniform density, becomes extended, and in the case of vibrational relaxation in very weak shocks, may even extend over the better part of a centimetre.[26]

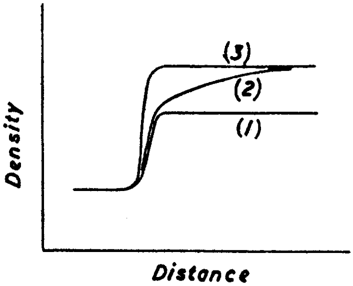

FIG. 5

Three methods have been used to measure the thickness of the front. If it is reasonably thick, then the standard interference fringe method can be used,[10a,26,27] with the light beam, of course, being exactly perpendicular to the motion of the shock. The second method, which has been used fairly extensively, is to measure the reflection of a light beam projected at grazing angle to the shock front;[28] in the steady state, no light is reflected into the detector (apart from some scattering), but there is substantial scattering by the shock front, and the duration of this reflection pulse, together with the known speed of the shock, gives the thickness. The third method, which has been used at low densities, makes use of the attenuation of an electron beam directed across the tube.[29]

[26] Griffith and Kenny, *J. Fluid Mechanics*, 1957, **3**, 286.

[27] (*a*) Griffith, Brickl, and Blackman, *Phys. Rev.*, 1956, **102**, 1209; (*b*) Smiley, Winkler, and Slawsky, *J. Chem. Phys.*, 1952, **20**, 923; 1954, **22**, 2018.

[28] Greene, Cowan, and Hornig, *J. Chem. Phys.*, 1951, **19**, 427; Greene and Hornig, *ibid.*, 1953, **21**, 617; Anderson and Hornig, *ibid.*, 1956, **24**, 767.

[29] Ballard and Venable, *Physics of Fluids*, 1958, **1**, 225.

The results obtained by these methods are in general agreement with those obtained by other measurements, *i.e.*, ultrasonic dispersion, projectile studies, and impact or pitot-tube measurements. Rotational relaxation in hydrogen takes about 150 collisions, and less in other molecules, *e.g.*, about 20 collisions in nitrogen or oxygen. Vibrational relaxation in simple molecules is very slow, *e.g.*, many thousands of collisions in N_2, O_2, CO_2, N_2O, etc., but relatively fast in more complex molecules such as CH_4 or CF_2Cl_2. Again, the well-known catalytic effect of water is found, but it is suggested[27a] that this effect is confined to bending modes of vibration only; it has long been thought that relaxation occurs *via* the lowest vibrational mode in the molecule, and this would seem to fit in with that idea.

Chemical reactions in shock waves

The problem of studying a chemical reaction in a shock wave is, in general, one stage more difficult than the experiments so far described. It is not sufficient just to study the density change; it is necessary to follow the fate of one individual species in the shocked gas, and, except in the special cases of molecules with relatively intense absorption spectra, this is very difficult indeed.

One of the earliest reactions to be studied by light absorption was the thermal decomposition $N_2O_4 \rightleftharpoons 2NO_2$;[30] this reaction had previously been investigated by ultrasonic dispersion measurements. The shocked gas consisted of a mixture of N_2 at 1 atm., containing about 1% of N_2O_4. Although pure N_2O_4 could, in principle, be used, admixture with a large excess of a permanent gas means that the shock is moving through an almost perfect gas, and this is more convenient because the shock-tube equations in their simplest form apply to perfect gases; the properties of shocks in nitrogen are readily calculable, and the presence of 1% of N_2O_4 causes only minor corrections to the expected temperature rise. When 2 atm. of N_2 was used as the driver, a shock of Mach 1·12 was obtained, giving a temperature rise of about 25°. The light absorption was measured with a photomultiplier using mercury radiation at about 4000 Å. In order to get a reasonable signal to noise ratio, it was necessary to use a beam of 1 mm. width, and this sets a lower limit on the time resolution attainable: at Mach 1, the shock passes a 1 mm. beam in about 3 μsec., so that any processes taking place in less than 3 μsec. are not observable. As the N_2O_4 is heated, its vibrations are excited very quickly, and then it begins to dissociate to NO_2 which is coloured and causes a response on the photomultiplier. Above 30°C, this rate of dissociation is too fast to measure, and the whole shock tube was cooled to -35°C before the beginning of each experiment: then, over the range of about 20° either side of 0°C, it was possible to follow the appearance of NO_2 over a time measured in a few tens of microseconds. The rate of dissociation was given by $k[N_2O_4][N_2]$

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[30] Carrington and Davidson, *J. Phys. Chem.*, 1953, **57**, 418.

with an activation energy of 11·0±0·6 kcal./mole: the dissociation energy of N_2O_4 is 13 kcal./mole, but as we shall see, it is common in kinetic dissociation measurements for the activation energy to be rather less than the heat of the reaction. The rate of this dissociation has since been confirmed by expansion of N_2O_4 at a supersonic nozzle.[31]

The dissociation of halogen molecules has been studied by very similar techniques. Iodine,[32] for example, in high dilution with inert gases, dissociates at a convenient rate in the temperature range 1000—1600°K, the rate of dissociation being measured by the decrease in light absorption. The change in light absorption at an observation station, as shown on an oscilloscope, is represented diagrammatically in Fig. 6. The current before the shock is determined by the initial I_2 concentration; as the shock arrives, the absorption rises sharply owing to the compression of the gas, and thereafter begins to fall relatively slowly as the iodine molecules dissociate, the rate of dissociation being determined from the initial slope θ. The problem, however, is not quite as simple as this. The absorption coefficient of any molecule is temperature dependent, and it is therefore necessary to measure the variation of absorption with temperature; this can be done by conventional methods at relatively low temperatures, but the necessary high-temperature coefficients are obtained from the shock tube traces on the (reasonably valid) assumption that the iodine comes to vibrational equilibrium with its surroundings before it begins to dissociate. In addition, allowance has to be made for the fact that, as the gas dissociates, it cools, giving rise to an increase in density and so an increase in absorption; at high I_2 concentrations, this can more than offset the decrease due to the reduction in the number of absorbing molecules.[33] A correction has also to be made for the contraction which occurs in the time scale: at some instant after the shock has passed, we are observing a body of gas which was heated, not when the shock passed the slit system, but at some earlier

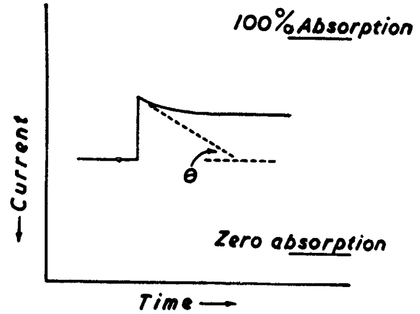

FIG. 6

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[31] Wegener, Marte, and Thiele, *J. Aeronautical Sciences*, 1958, **25**, 205; Wegener, *J. Chem. Phys.*, 1958, **28**, 724.

[32] Britton, Davidson, and Schott, *Discuss. Faraday Soc.*, 1954, **17**, 58; Britton, Davidson, Gehman, and Schott, *J. Chem. Phys.*, 1956, **25**, 804.

[33] Palmer and Hornig, *J. Chem. Phys.*, 1957, **26**, 98.

time, because the gas is moving very rapidly along the tube behind the shock; thus, gas which was heated about 600 μsec. previously will show up on the oscilloscope trace only about 200 μsec. after the shock has passed.

The initial rate of dissociation is given by

$$k_{\mathrm{A}}[\mathrm{I}_2]\,[\mathrm{A}] + k_{\mathrm{I}_2}[\mathrm{I}_2]^2$$

where k_{A} is the rate constant for dissociation by collision with argon, and k_{I_2} is that for dissociation by collision with another iodine molecule; extrapolation to zero $[\mathrm{I}_2]$ gives k_{A} and k_{I_2}. As is to be expected from our previous knowledge of collision efficiencies (flash photolysis and other kinetic energy-transfer studies), collisions with iodine are more effective in bringing about dissociation than are collisions with argon. Other gases can be used as diluents, and their relative efficiencies measured. The activation energy for the dissociation of iodine comes out to be rather (about 4 kcal.) less than the dissociation energy. Similar measurements have been made on bromine,[33,34] and again the activation energy (31 kcal.) for dissociation is substantially less than the dissociation energy (45 kcal.); oxygen also shows this type of behaviour, the rate of dissociation being 150 times the maximum rate it could have if the activation energy were equal to the endothermicity.[18a]

This phenomenon of dissociation with less activation energy than the heat of the reaction appears to be quite common, and one suggestion is that the energy of activation need not be solely concentrated in the molecular vibration for the dissociation to take place,[33] *i.e.*, some molecules can dissociate by rotation. If we don't specify any particular energy division, the probability that we will find an iodine molecule after a collision with an argon atom having the dissociation energy D concentrated in a specified number n of "effective oscillators" is

$$e^{-D/RT}\sum_{r=0}^{n-1}\frac{1}{r!}\left(\frac{D}{RT}\right)^r$$

(2 rotations $\equiv$ 1 effective oscillator). The Arrhenius temperature dependence of an expression like this is substantially lower than D if n is at all appreciable; in the simple collision we have considered, n is very limited, but if we consider collisions between pairs of diatomic molecules and allow all their degrees of freedom to contribute to the dissociation of one of them, then there is more latitude. Even so, it is necessary to strain somewhat the number of important vibrations and rotations in order to get numerical agreement with experiment.

An alternative approach to the problem is to consider the mechanism of the reverse reaction, *i.e.*, the recombination of the atoms. These have been studied by flash photolysis at lower temperatures, and have been shown to have negative temperature coefficients. If we take the shock-wave

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[34] Britton and Davidson, *J. Chem. Phys.*, 1956, **25**, 810.

data, and assume a reversible system, then the ratio of the forward and reverse rate constants is the equilibrium constant of the reaction, and the heat of the reaction is the difference between the two activation energies; since E for dissociation is less than D, then E for combination must be negative. However, the value obtained from shock measurements at high temperatures is much more negative than that obtained at low temperatures from flash photolysis (see Fig. 7). The observed activation energy is the difference in average energy between those molecules which react and all those which are present in the system; therefore, the meaning of a negative activation energy is that those molecules which react have a lower average energy than the average energy of all the molecules in the system. In a reaction $I + I + M \rightarrow I_2 + M$, the third body M has to carry some energy away to bring the relative I + I energy below the dissociation limit; thus, the more energetic the collision between I + I, the more energy M must take away. But M is much more likely to take away only a small amount of energy than a large amount. If we make the very simple assumption that M can only take away very small amounts of energy, then the average energy of the reacting I atoms is approximately zero; on the other hand, the average energy of all the I atoms is $\boldsymbol{R}T$, *i.e.*, 4 kcal. at 2000°K and 1 kcal. at 500°K—hence E at 2000°K is about —4 kcal., and at 500°K about —1 kcal. The Arrhenius curve for such a system has the *shape* of the broken line in Fig. 7, which is in qualitative agreement with the experimental results, but the predicted activation energies are rather small,[35] especially in the bromine case. We see that neither theoretical approach to this problem is really satisfactory, and there is considerable scope for further investigation, both in its theoretical and its experimental aspects.

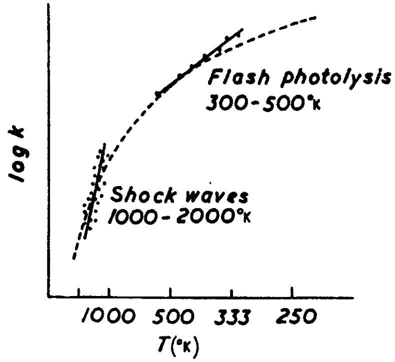

FIG. 7

Several other dissociation reactions have been investigated directly by light absorption, *e.g.*, the dissociation of N_2O_5 to $NO_2 + NO_3$,[36] of NO_2

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[35] Husain and Pritchard, *J. Chem. Phys.*, 1959, **30**, 1101.

[36] Schott and Davidson, *J. Amer. Chem. Soc.*, 1958, **80**, 1841.

to NO and O,[37] and of O_3 into O_2 and O;[38] in all these three studies data were also accumulated on some of the subsequent reactions of the dissociation products (*e.g.*, $NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$; $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$; $NO_2 + O \rightarrow NO + O_2$; $O_3 + O \rightarrow 2O_2$).

In many cases, it may not be convenient to study a dissociation reaction by light absorption, but nevertheless, there are ways in which some relevant information can be obtained. For example, it is possible to measure the heat of dissociation, as opposed to the activation energy. If the shock is strong enough to dissociate all the molecules, then the dissociation energy becomes part of the specific heat function ϕ and thereby affects the shock velocity. Thus, by measuring the effect of the dissociating gas on the velocity of shocks in, say, argon, one can calculate the contribution the dissociation makes to the high-temperature specific heat, and so get the dissociation energy. This has been done for F_2, N_2, and CO where the accepted values have been in doubt until recently, and values of ~ 31,[39] ~ 225,[6d] and ~ 256[6d,40] kcal. respectively were obtained.

Alternatively, one may quench the shock and analyse the products by standard chemical methods. This can be done simply by allowing the shock to expand into a large vessel at the end of the shock tube, or better, after a sufficient reaction time, opening the tube up to a very large evacuated tank by bursting a second diaphragm, thereby quenching the reaction by an expansion wave. This method has been used in the study of the pyrolysis of simple hydrocarbons; it has been found that methane cracks with an activation energy of about 101 kcal.[41] (*i.e.*, $CH_4 \rightarrow CH_3 + H$, $D \approx 102$ kcal.) and also that some curious molecular reactions take place fairly easily,[42] *e.g.*, $2C_2H_2 \rightarrow C_4H_2 + H_2$ ($E \approx 30$ kcal.) and $2CH_4 \rightarrow C_2H_6 + H_2$. Also, in reflected shocks the method has been used in the study of the reaction $N_2 + O_2 \rightleftharpoons 2NO$ at high temperatures.[43] It appears that the reaction is a chain reaction; oxygen, having much the lower dissociation energy, decomposes into atoms, and the rate-determining step is $O + N_2 \rightarrow NO + N$; this reaction has an activation energy of about 74 ± 5 kcal., compared with the endothermicity of about 76 kcal. at 2500°K.

This technique of shocking a mixture of gases, one of which has a much lower dissociation energy than the other, lends itself to the study of atomic reactions, and has been used to study the reaction $Br + H_2$ by using bromine–hydrogen mixtures.[44] Similarly, in using hydrogen–oxygen mixtures,[45] the hydrogen dissociation predominates and it is possible to follow the rate of formation of OH radicals by the reaction $H + O_2 \rightarrow OH$

[37] Huffman and Davidson, personal communication.

[38] Jones and Davidson, personal communication.

[39] Wray and Hornig, *J. Chem. Phys.*, 1956, **24**, 1271.

[40] Knight and Pink, *J. Chem. Phys.*, 1958, **29**, 449.

[41] Skinner and Ruehrwein, *J. Phys. Chem.*, 1959, **63**, 1736.

[42] Greene, Taylor, and Patterson, *J. Phys. Chem.*, 1958, **62**, 238.

[43] Glick, Klein, and Squire, *J. Chem. Phys.*, 1957, **27**, 850.

[44] Britton and Davidson, *J. Chem. Phys.*, 1955, **23**, 2461.

[45] Schott and Kinsey, *J. Chem. Phys.*, 1958, **29**, 1177.

+ O. There is an induction period before the radicals are detected, but this is not an induction period in the true sense: the concentration of radicals is followed by their ultraviolet absorption, and it takes time for this concentration to build up to 1×10^{-6} mole/l., which is the minimum detectable; from the subsequent build-up, the activation energy for H atom attack on oxygen molecules was found to be 17 kcal. The close relation of this experiment to detonation studies need hardly be emphasised.

Although it is possible, as we have seen, to study a number of chemical reactions, some of which cannot be investigated by other methods, or alternatively can only be observed in some other temperature range, yet these experiments are fairly tedious and subject to considerable inaccuracies. For one thing, it is not easy to estimate concentrations very precisely from cathode-ray tube traces, and the mainly electronic problem of time resolution is aggravated somewhat by the time contraction which occurs. Mention has already been made of the variation of spectral absorption coefficients with temperature, and the cooling effect the reaction may have if it is dissociative. In addition, suppose that it is possible to measure the shock velocity to ±1%, which is about as good as can be expected: the temperature rise depends roughly on the square of the velocity, *i.e.*, we have an uncertainty of about 2%, which on a temperature rise of 1500° is ±30°. This makes the temperature scale for activation energy plots a little less precise, and in some such experiment as, say, the reaction of H with O_2, the calculated H atom concentration is subject to significant uncertainty. Finally, mention should be made of the simple physical difficulty of making a large metal shock tube vacuum-tight, and the length of time it takes to pump it out to, say, 10^{-3} mm. before each experiment can begin. These limitations, however, have not prevented the accumulation of a substantial body of important information.

Other applications of shock waves

So far in this Review, our attention has been confined to shock waves in gases. Shocks can also be propagated through liquids and solids, and have been used to measure compressibilities and derive equations of state. One of the more interesting chemical aspects of shocks in solids is the possibility of so compressing a non-metallic solid that it becomes metallic —for example, at shock pressures of 250,000 atm., phosphorus shows an electrical conductivity characteristic of a metal;[46] a similar observation has been made with sulphur.[47] A further application of shock waves in solids is in the production of what are known as "tactical" nuclear weapons. An amount of fissionable material which is less than the critical mass is surrounded with a shell of trinitrotoluene. When the conventional explosive is detonated, a shock wave moves towards the centre of the

[46] Alder and Christian, *Discuss. Faraday Soc.*, 1956, **22**, 441.

[47] David and Hamann, *J. Chem. Phys.*, 1958, **28**, 1006.

system and compresses the fissionable material above its critical density, so causing a sub-critical amount of material to explode.[48]

Mention has already been made of the crucial importance of a knowledge of the behaviour of shocks caused by supersonic aircraft and rocket nose-cones, and of the importance of knowing how hot (and how corroded) the structure will become as a result of its interaction with the hot nitrogen and oxygen ions or atoms which are produced.[49] Other war-time studies were concerned with the effect of blast waves on buildings and upon animal and human life—for example, to find out what sort of shock pressures cause the collapse of an ear-drum, or hæmorrhage of the lungs.[3c]

In astrophysics, the coalescence of masses of interstellar gas appears to lead to shock waves, and it is possible that solar flares are some sort of shock phenomenon; an attempt has been made to explain the difference in electronic and kinetic temperatures of the sun in such terms.[50]

Finally, mention should be made of the field of magnetohydrodynamics, and the production of very strong shocks. Supposing we have a glass tube with a single-turn copper coil around it,[6a] and discharge a suitable condenser through the coil. A rapidly varying magnetic field is produced ($\mathrm{d}H/\mathrm{d}t \approx 70{,}000$ gauss/μsec.) and this induces an electric field which is intense enough to ionise the gas inside the tube. The resulting current of ions is then accelerated by the intense magnetic field to very high velocities, up to about Mach 90 in the experiment quoted. The production of these very high Mach numbers leads to the possibility of thermonuclear fusion reactions taking place in a shock tube. Attempts are being made to reach temperatures of several million degrees in this kind of way, by producing an ionised gas (plasma) and subjecting it to an intense magnetic shock. One of the technical problems involved is to get a sufficiently fast build-up of the magnetic field, say to 1500 gauss in 0·2 μsec.; this requires electrical circuits of sufficiently low impedance for the current to build up at the rate of 10^6 amp./μsec. or more. These and other related problems are discussed in the first few papers of the Conference on Extremely High Temperatures held in Boston in March 1958.[51]

[48] Pauling, "No More War!", Dodd, Mead, New York, 1958.

[49] Hertzberg, *Jet Propulsion*, 1956, **26**, 549.

[50] Sen, *Phys. Rev.*, 1953, **92**, 861.

[51] Fischer and Mansur (editors), Conference on Extremely High Temperatures, Wiley, New York, 1958.