

## GAS REACTIONS

## Neutral Beam Kinetics

from our Molecular Physics Correspondent

THE prolonged and, at times, painful evolution of chemical kinetics into an exact science has been measured, not so much by theoretical advance as by the growing determination of experimentalists to stop heating things in a pot and concentrate on the crucial problem of fixing the fundamental action of collision between reagent molecules in some form of direct observation. Although they will surely never see this act with the ease of a nuclear physicist observing particle tracks, the past decade has brought remarkable progress towards liberating experimental gas kinetics from the pervasive and sometimes cruel deceptions caused by trace impurities, the walls of the container, secondary reactions and, not least, the Boltzmann distribution of energies itself.

Two instruments, the molecular beam apparatus and its relative the mass spectrometer, have contributed more than any others to this movement; indeed it has long been realized that anybody ingenious enough to couple both these into a single instrument for reaction and analysis would have something like the answer to the kineticist's prayer. What is perhaps the first really successful application of the combined system to the study of neutral atom-molecule reactions now seems to have been achieved by S. N. Foner and R. L. Hudson, of Johns Hopkins University (*J. Chem. Phys.*, **53**, 4377; 1970).

In the ideal molecular beam apparatus reactive molecules or atoms would be fired at each other in streams which are highly defined in both position and velocity and almost innocent of all self-collisions. To the extent that this can be achieved in an actual apparatus, the statistical noise in the outcome can be treated in terms of the dynamics of the reactive scattering alone, while, at the same time, the product particles can be whisked into an analyser with little chance of secondary reaction. Measurement of the identity, recoil velocity, and angular spread of the products can then be attempted. Unhappily, although this sequence sounds straightforward on paper, there is much bitter experience on both sides of the Atlantic to show that, unless the beam definition and intensity and the detector selectivity and signal/noise ratio combine to a certain threshold, all the elaborate vacuum and electronic engineering necessary will be in vain. Although most workers in the field have always looked to the mass spectrometer for their salvation, the intensities of beam available with neutral molecules have never been sufficient to allow a further loss of signal by a factor of perhaps a thousand in ionization at the

mass spectrometer stage. As a result ion-molecule reactions have gained a somewhat undeserved prominence and those laboratories remaining faithful to neutral systems have developed an unhealthy dependence on the few beam reactions which can be run with unsophisticated detectors, chiefly those of alkali metals and halogen compounds.

The apparatus of Foner and Hudson, developed out of many years' experience with the mass spectrometry of unstable species, brings a variety of ordinary atom-molecule reactions within the scope of crossed-beam mass-spectrometric detection for the first time. This is achieved by crossing two relatively ill defined beams at high intensity and making a calculated sacrifice of the scattering-angle information usually sought, for the sake of increased detector efficiency. This is hardly too great a price to pay, for, with a consequent increase of a factor  $10^4$  in detector signal over that obtained in conventional crossed beam arrangements and with products discriminated by both

mass and ionization potential, the information to be gained is still very considerable. Foner and Hudson describe a whole gamut of reactions, resulting from Cl, O or H atoms in one beam and hydrocarbons, hydrazines or oxides of nitrogen in the other. The different butyl radicals are produced in a very clean reaction of chlorine atoms with butanes, the classic reaction of H with  $\text{NO}_2$  is re-examined and a bizarre reaction of O atoms with hydrazine is reported in which the oxygen makes off with two hydrogens abstracted simultaneously from opposite ends of the molecule. In all cases ionization energies of the species involved are obtained at no extra cost.

Although much remains to be learned about the physics of these processes, it is gratifying that some of the elementary atom and free radical reactions which are familiar only as equations in the complicated hypothetical schemes of the textbooks should now be under scrutiny as truly elementary events.

## Why do Magnetic Anomalies Weaken?

THE magnetic evidence for seafloor spreading is based on the pattern of the linear magnetic anomalies which lie over and to the sides of mid-oceanic ridges. This pattern correlates well with the dated polarity-time scale from continental rocks up to about 4 million years old; and, because the latter must be produced by reversals of the Earth's magnetic field, there is no reason to suppose that the older marine anomalies are not also reflexions of geomagnetic field behaviour. For this particular exercise, however, the amplitudes of the anomalies are unimportant—it is the wavelengths alone which decide the issue.

The anomaly amplitudes, in fact, are not constant but generally decrease with distance from a ridge. But why? There has been no shortage of possible explanations for this phenomenon; but so far nobody has succeeded in pinning it down to one. One of the earliest suggestions was that the rocks producing the older anomalies are deeper and have a thicker sediment cover and thus are partially shielded magnetically. But it seems probable that this is altogether a too facile explanation; and, in any case, there does not seem to be a correlation of amplitude with sediment thickness where such a possibility has been investigated in detail.

Other suggestions have been more sophisticated but notably short on evidence. Matthews and Bath (*Geophys. J.*, **13**, 349; 1967), for example, thought that the central ridge block might be injected slightly asymmetrically and thus "contaminate" the blocks of opposite polarity on either side. But Harrison (*J. Geophys. Res.*, **73**, 2137; 1968) soon

put an end to this idea by pointing out that this process would almost certainly have obliterated the short magnetic events which are visible in the anomaly pattern.

The most popular explanations invoke some sort of decay of the magnetization in the ocean floor basalt. Chemical alteration is a widely touted mechanism for this; and it is not difficult to imagine what seawater and high pressures might do in this line. But imagination is not enough. Proponents of chemical alteration have always been intuitively convincing but short on specific proof. The problem of decay has, of course, bedevilled palaeomagnetism for many a year; but nobody has been able to explain it properly in physical terms. Indeed, at one stage the whole question was in danger of becoming a universal palaeomagnetic pessimism; but the pessimists were firmly routed by the discovery, from rock magnetism, that at times during the Pre-Cambrian the Earth's magnetic field was as strong as, if not stronger than, it is now.

But in spite of all this, the older marine magnetic anomalies are self-evidently weaker—and some explanation is still required. In next Monday's *Nature Physical Science* S. K. Banerjee, fully appreciating the history of this problem, puts forward a new possibility—decay of magnetization by diffusion of ferrous ions but without chemical alteration. Banerjee's argument is highly theoretical and heavily dependent on uncertain estimates of several physical parameters. For this reason it will be very difficult to obtain direct proof. On the other hand, it does not suffer from the obvious disadvantages of the simpler, perhaps more naive, explanations.