DYNAMICS OF A DISSOCIATING GAS

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It will perhaps suffice for a half-hour's lecture to speak of the dynamics of one much-discussed dissociating gas, namely oxygen. The oxygen molecule can exist in an enormous number of states. It consists of sixteen electrons, grouped about two nuclei whose combined mass is thirty-seven hundred times as great. The different states can therefore, to a close approximation—the Born and Oppenheimer approximation—be described as follows. First, if the nuclei are considered fixed, a certain set of states for the electrons is possible, whose energies $V_1(r)$, $V_2(r)$, $V_3(r)$, ... depend only on the distance between the two nuclei. Superimposed on any such electronic state is a state of motion of the two nuclei, regarded as particles attracting or repelling one another with the potential $V_n(r)$. Some of these potentials possess a minimum for a certain value of r, which means that states are possible in which r oscillates about that minimum, so that the states may be described as stable. Each such state of motion in the nuclei can, to a close approximation, be regarded as a combination of a state of rotation of the system about its mass-centre, and a state of linear vibration under the potential $V_n(r)$. The energies of the rotational states are very thickly spaced; but by contrast there are rather large jumps of energy from one vibrational state to the next.

For the lowest electronic state of O_2 the potential is something like the lowest curve in Fig. 1, and about 50 vibrational states exist; the horizontal lines on the curve indicate the energy levels and the approximate amplitude of vibration in each of the four lowest vibrational states. Different states are occupied in numbers proportional to $e^{-\epsilon/kT}$, where ϵ is the energy of the state and k is Boltzmann's constant. Now, if we measure energies ϵ from that of the *ground* state as zero, then ϵ/k for the next vibrational state is 2230°K, and ϵ/k for the state in which the nuclei are separated and we have two oxygen atoms each in their ground state is 59,000°K. It follows that at ordinary temperatures the great majority of molecules are in their ground state, and that it takes an energy k (59,000) to dissociate them into atoms. It takes just the same energy to raise them first to the second, third or fourth stable electronic state and then dissociate them. The fifth state, however, dissociates into atoms of which only one is in its ground state and the other in a higher electronic state, so transition to this state followed by dissociation would require more energy.
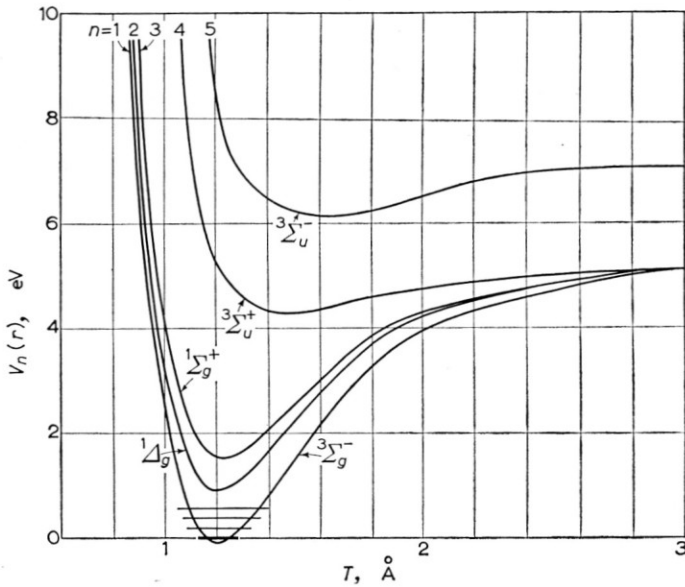
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FIG. 1. Potential energy curves for O_2 (for information on the derivation of the curves *see* Gaydon[9]).

Two main mechanisms of dissociation exist. One is by collision with other particles, which may or may not be oxygen molecules. The other is by the absorption of a photon of light whose energy $h\nu$ (where ν is the frequency) is equal to the jump from the lowest to the fifth electronic state (which is the only transition between any two of these states which has a non-vanishing dipole moment and therefore a reasonable probability of happening). When it gets there it has an energy above the dissociation level and flies apart into atoms. The frequencies of light required are in the ultraviolet range, especially from 1300 to 1750 Å.

The sun shines powerfully in this frequency range, but if one is interested in flight below about 60 km altitude, there is practically no light of these frequencies present, having all been absorbed by the same mechanism higher up, where it has led to the presence of regions where almost all the oxygen is in the form of free atoms. Similarly, in the absorption experiments of Ladenburg *et al.* [1] from which Stueckelberg[2] deduced the form of the upper potential curve, the oxygen in his ultraviolet absorption tube rapidly disappeared by combination of the free atoms with the material of the tube.

At low altitudes dissociation takes place entirely by collisions. Such collisions must be between an oxygen molecule and some other body, such that the combined excess energy of both bodies over their ground

state energies is greater than the dissociation energy D (which I gave as k (59,000)). When the colliding body is another molecule many different types of energy may be involved, vibrational energy of both molecules, rotational energy of both and the combined translational energy of both relative to their mass centre. This large choice of degrees of freedom increases the possible number of pairs of colliding molecules which satisfy the required condition on total excess energy. In fact, a proportion

$$\frac{e^{-D/kT}(D/kT)^{n/2-1}}{(\frac{1}{2}n-1)!} \tag{1}$$

of collisions will do so, where n is the number of degrees of freedom involved. The suggested enumeration gives $n = 7$.

Measurements of dissociation rate by Byron[3] indicate that a slightly better fit is obtained with $n = 6$, perhaps because if one oxygen molecule is rotating one way it is only rotation of the other in the opposite sense that can help to give up energy for the benefit of dissociation—if angular momentum is to be conserved—whence really only 3 degrees of rotational freedom contribute. With $n = 6$ he finds that results for temperatures from 2500°K to 3500°K are well fitted by the supposition that a quarter of those collisions with sufficient excess energy are successful in producing dissociation.

Atoms produced by dissociation may recombine again in two ways, which are the inverses of those I have discussed. The inverse of collisional dissociation is so-called three-body recombination, in which two atoms collide and simultaneously a third body hits them, leaving again unaltered except for having acquired some of the energy which they gave up on recombining. The third body is necessary because otherwise the atoms would simply approach one another, buzz round and fly off again. Similarly, the inverse of photo-dissociation is two-body recombination with emission of light. This is possible only if one of the atoms is in the higher electronic state which makes them able, on approaching one another, to follow the highest curve in Fig. 1, emitting a photon and dropping to the lowest state when they are on the left-hand arm of the curve. At sufficiently low densities this mode of recombination must become dominant, because triple encounters become so rare. For this to be so, however, the density would have to be below 10^{-8}g/c^3, so that in regions where aerodynamic forces are important most recombination takes place by triple encounters. On the other hand, as a source of heat transfer to the surface of a body, with high temperature oxygen near it, the radiation of light by transitions from all points on this upper curve, particularly those with lowest energy, becomes important, and this radiation has been observed recently by Gaydon (unpublished).

We may turn now to how dissociation is produced by bodies moving at high speed. Another useful way of expressing the energy required to dissociate one molecule of oxygen is to say that it is the kinetic energy

which the molecule would have if its speed were 5·5 km/sec. It follows that if a body travels through oxygen at such a speed it can dissociate a large fraction of the molecules that come near it. More precisely, the resulting flow can be regarded, relative to the body, as a steady flow around the body with upstream velocity of 5·5 km/sec. Then all the oxygen which goes close enough to the body for its speed to be reduced to a low value will lose enough energy to dissociate it completely. Of course, not all the energy will actually be *used* to do this; some of this will go into increasing the mean translational, rotational and vibrational energy of the molecules; but still 66% dissociation can be reached at this speed if the density is around 10^{-4}g/c³. Let us look a little more closely, however, at the details of how this is obtained.

When a body moves faster than sound it notoriously pushes a shock-wave ahead of it, which in steady motion becomes fixed relative to the body. The air approaching the body then remains completely undisturbed until it encounters this shock wave, at which its pressure and temperature rise abruptly and its velocity falls, both in a very, very short time, only enough time for a molecule to make a few collisions, which it does every 10^{-10} sec at n.t.p.

It is important to see clearly why this result must still be true even though the rise in temperature causes dissociation, a process which requires many, many collisions, owing to the fact that such a small fraction of them are effective. Basically the shock wave appears because any compressive waveform has the well-known tendency to steepen itself owing to the higher velocity of propagation of the rear portions. This steepening has to increase until it is resisted sufficiently strongly by diffusive forces like viscosity and heat conduction, or by dissipations resulting from lag in the attainment of thermal equilibrium, such lag resulting for example from the slow rate of excitation of higher vibrational states, or of collisional dissociation.

Now there is a limit to the amount of dissipation that such lags can produce. As the wave form steepens, the dissipation resisting steepening goes on increasing up to a maximum when the duration of the pulse is about equal to the time lag. If this amount of dissipation is still insufficient then steepening continues further, but is less and less impeded, at least until viscous diffusion takes over at pulse durations of a few collisions. So we end up as before, with a very, very thin shock wave, so thin that no slow adjustments like dissociation occur, followed by a thicker region in which the degree of dissociation and that of vibrational excitation find their equilibrium level.

For example, at an oncoming speed of 5·5 km/sec, the state immediately behind the shock wave is one in which the large oncoming kinetic energy has almost entirely been converted into translational and rotational energy of the molecules relative to the mean flow; the temperature is then 16,500°K. Dissociation at once begins at a great rate, almost a twentieth

of all collisions being effective in producing it. However, when the equilibrium state with 66% dissociation which I mentioned before is reached, so much translational and rotational energy of molecules and atoms has been absorbed in dissociating collisions that the temperature has fallen to 4300°K. Therefore in the final stages of the dissociation a much smaller fraction of collisions, about 1 in 40,000, is being effective. In the intermediate stage when the gas is 33% dissociated, the temperature is 9000°K, and 1 in 120 collisions is effective.

We see then that the departures from equilibrium do not die off exponentially with time; rather, equilibrium is approached rapidly at first and then less and less rapidly, leaving a long trail of not quite equilibrated gas. The changes in rate of dissociation with distance behind the shock wave are, in fact, so rapid that no direct measurement of this rate has satisfactory accuracy. It is better to assume a definite formula for it and determine the constants therein by fitting the inferred density distribution behind the shock wave, which is obtained by solving the equations of one-dimensional motion, to that observed by interferometry.

A good approximation for solving these equations of one-dimensional motion quickly is to take the pressure constant behind the shock wave; this is nearly correct because almost all the rate of transport of momentum in the oncoming stream is converted into pressure, not more than about 10% rise of pressure occurring as the flow beyond the shock wave slows down further. Since, however, the temperature is dropping substantially, it follows that the density increases by a factor of more than 2 during dissociation, and this is observed.

The effect of this increased density on the flow about bluff bodies that Professor Hayes was so effectively analysing, is to reduce the thickness of the compressed-air cap between shock wave and body. The so-called Newton–Busemann theory has now been worked out by Freeman[4] for the case when the dissociation rate process behind the initial shock wave is taken into account according to an equation of the general form (1), while the recombination process is taken to be that three-body process which, together with the assumed dissociation process, gives the correct equilibrium state determined by statistical mechanics. Freeman shows how the stand-off distance of the shock wave decreases with a parameter $\rho_0 d/U$, which relates the time, taken for gas to pass by a body of length d with velocity U, to the average collision time. For large enough $\rho_0 d/U$ dissociation becomes complete in a distance small compared with the stand-off distance, and the whole compressed-air cap is at high density and is correspondingly thin. For very small $\rho_0 d/U$ little dissociation occurs and there is a thicker cap corresponding to $\gamma = 1\cdot4$. Of course, for such low densities the Reynolds number is small and the boundary layer thickness is comparable to the thickness of the compressed-air cap. In this case a recognizable viscous boundary layer may well extend right up to the shock wave. Recent calculations by Herring[5] and others of this

regime, using approximations similar to those of the Newton–Busemann theory, but with viscous terms included, have faced the interesting mathematical problem of solving the boundary layer equations with the outer boundary condition not at infinity but at an unknown, as it were "free" surface, the shock wave. One interesting conclusion was that, if the surface is cooled to a temperature not much above that of the undisturbed stream, then the effect of the boundary layer is to decrease the stand-off distance more and more as the Reynolds number decreases, that is as the boundary layer grows. We may say that the cooled boundary layer has negative displacement thickness.

On the other hand, at ordinary densities, for example of the order of one-hundredth of the sea-level density, the boundary layer is much thinner and the problem is rather how the dissociated gas outside the boundary layer affects it, particularly if the wall is maintained at a temperature cool enough to cause the atoms to recombine if equilibrium is reached. Regarding this important issue, two points have been fully stressed in the literature. One is that, despite the thinness of the boundary layer, atoms take quite a long time to cross it, during which they can have the necessary triple encounters which will enable them to recombine; these do not become less probable as the gas gets cool since they do not require any excess energy. Atoms cross the boundary layer by diffusion, in fact, and the time they take to do so is about the same as the time that a portion of gas takes to be convected round the surface of the body. Hence if there is time for equilibrium to be reached in the flow outside the boundary layer, there should also be time for it to be reached inside the boundary layer.

A second point is that the rates of diffusion of all the different modes of energy are of the same order of magnitude—including what we may call the "dissociation mode", that is, the fact that the energy of two atoms exceeds that of one molecule. Atoms and molecules interdiffuse with approximately the same diffusion coefficient as heat. It follows that from a given oncoming speed, and therefore a given specific enthalpy outside the layer, the rate of heat transfer to the surface will not be altered in order of magnitude by the process of dissociation.

Two further points may be made in connection with attempts to calculate the effect more precisely. One is that many estimates assume a "Lewis number" (that is, the ratio of the diffusivity of atoms through molecules to the diffusivity of heat) which is constant at around 1·4, on the basis of the kinetic theory of gas mixtures. However this value is truly indicated by the theory only when the gas is slightly dissociated, and the Lewis number probably drops to around 0·7 for fully dissociated gas.

A second point, due to Clarke[6] is that, if recombination does not produce equilibrium in the boundary layer, the heat transfer will be reduced. For the theories which suggest the contrary have assumed a so-called "fully catalytic" wall, where the equilibrium condition *is* satisfied. Clarke points out that the most catalytic wall of all possible walls would be

one which caused instantaneously the recombination of every atom hitting it. But since there is only a finite rate of collision of atoms with the wall, there is only a finite rate of recombination there, and hence a measurable degree of departure from equilibrium is still found.

As I said at the beginning, I have had to select only a few aspects of the subject for a half-hour lecture and even then it was impossible to go into details (but see Lighthill[7] [8] for a fuller treatment). The aim could only be to indicate the spirit of the investigations. To sum up, I think their spirit consists of a determination not to look at the problem obstinately "as a fluid dynamicist" or "as a chemical kineticist", but to try to pour out a nicely-matured blend of the two.

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