A Sketch for a History of THE KINETIC THEORY OF GASES

By E. Mendoza

THE ideas that solids are composed of compact arrays of atoms, while gases are composed of atoms or molecules in very rapid translational motion, are so obvious that we accept them nowadays without question; in teaching textbooks they are stated as if they were axioms. In its most elementary form, without any sophisticated calculations about the distribution of velocities, with only the one assumption that the impacts of the molecules on the walls of the containing vessel produce the pressure, a very simple calculation gives the equation

$$pV = \tfrac{1}{3}\, mNc^2 \qquad (1)$$

where m and N are the mass of a molecule and the number per unit volume, and c is a velocity; p is the pressure and V the volume of the gas.

This formula poses something of a historical puzzle. For comparing it with $pV = RT$, there is the strong implication that the temperature—and therefore the heat content of a gas whose specific heat is constant with temperature—is proportional to the kinetic energy of translation of the molecules, and hence that heat is a form of motion. It is stated in every textbook that this kinetic theory originated with Daniel Bernoulli in the middle of the eighteenth century. But it is equally well known that the dynamical theory of heat was not accepted till a whole century later. On the face of it, therefore, scientists seem to have been singularly obtuse not to have recognized the straightforward implications of Eq. (1) for so long.

But in reality it seems that the kinetic theory of gases is quite a modern development. It was not at all obviously correct; it was not accepted into physics until it had overcome some formidable opposition. The outline of the story will be given here.

The Static Theory of Gases

IT is quite true that Bernoulli did give an excellent account of the kinetic theory in his book on hydrodynamics published in 1738. But I have never been able to trace a single reference to this theory in any paper or book published in France or England during the first half of the nineteenth century; it was piously disinterred in 1859. The influence that Bernoulli's kinetic theory had on other physicists during the critical period was nil; it might just as well never have been written.

Most scientists in France and Britain adopted instead the *static* theory of gases. According to this, the forces which held atoms together in a solid were attractive forces which gave the solid its cohesion, but in a gas these changed into repulsions. The atoms tried to get as far from one another as they could, and this purely static effect produced the pressure. A gas was therefore merely a highly expanded solid; except for accidental effects like convection, the atoms in a gas were quite stationary.

This theory originated with Newton but Laplace refined it in several authoritative papers published around 1824. The origin of the repulsive forces was taken to be the short-range repulsions of the caloric atoms inside the gas molecules. Lengthy calculations showed that whatever the law of force

$$\text{Pressure} = (\text{constant})\ \rho^2 q^2$$

where ρ was the gas density, q the charge of caloric in each molecule. Considering the dynamic equilibrium of emission and absorption of the caloric and taking the temperature to be proportional to the density of caloric atoms in transit, he found

$$\text{Temperature} = (\text{constant})\ \rho\, q^2$$

and hence the gas laws followed. These papers are deeply impressive, but they leave the nasty impression that the abstractness of the mathematics was a sign of decadence. The fact that the quantity of heat appears squared in both these formulae seems to conceal some basic confusion, hidden somewhere under the mathematics.

In England Newton's theory was widely taught, but

E. Mendoza is senior lecturer in physics at Manchester University, England. His "Sketch for a History of Early Thermodynamics" appeared in the February 1961 issue of *Physics Today*, p. 32.

The first practical steam carriage to p along English roads, between Bath ar London, in 1829. John Herapath is t front. (Information kindly supplied t Spencer D. Herapath of London.)

not everyone was in agreement. When Davy wrote his *Elements of Chemical Philosophy* in 1812, he inclined quite strongly towards the dynamical theory of heat and proposed that in solids the motion was a vibration or undulation of the atoms, but that in gases the atoms also *rotated* about their axes. He seems to have had a glimmering of the idea of the partition of energy between the rotational and vibrational modes, and to have tried to explain the latent heat of boiling in this way. The idea that gas atoms revolved on their axes made a great impression on Davy's contemporaries. For combined with the orthodox static theory of gases it allowed a precise model to be made of the origin of the repulsive force between gas molecules—namely the centrifugal force of the revolving atomic atmospheres. This idea was later taken up by Joule and Rankine.

In this discussion it is important to realize that there were several possible concepts of atoms. They could be point centers of force—the forces could have a finite range or could extend an infinite distance—or they could be particles with definite shapes. There were difficulties in imagining the collisions between atomic *particles* to be perfectly elastic, however; for a body could deform elastically only if its parts moved relatively to one another, whereas an atom was usually held to be an indivisible elementary particle and therefore without substructure. For the same reason, Davy's idea of atoms with revolving atmospheres offended some purists. But I get the impression that different scientists had quite private views on such questions which they rarely bothered to state explicitly.

Herapath's Hypothesis

JOHN Herapath, a self-taught schoolmaster from Bristol, originated the kinetic theory of gases as we know it. He had a genius for distorting irrelevant facts to fit incorrect theories; but if we take the cruel but realistic criterion that the most important scientists are those whose ideas have influenced others, who have proposed theories which are in the main stream of scientific thought, then Herapath is among the most important; the kinetic theory of gases is firmly founded on "Herapath's hypothesis".

He began by noting a small discrepancy in some observations on the motion of the moon, and proposed that Newton's constant of gravitation was not in fact a constant but varied with the temperature of the planet concerned. Thus he was led to a study of Newton's *model* of the gravific ether, the gas whose pressure produced the gravitational force—though Newton himself had of course stressed that the model was not very important. Hence Herapath was led to study the properties of gases in general. He tried to deduce them from the caloric theory and made no progress; then he accepted Newton's theory of static atoms with mutual repulsions but could not see

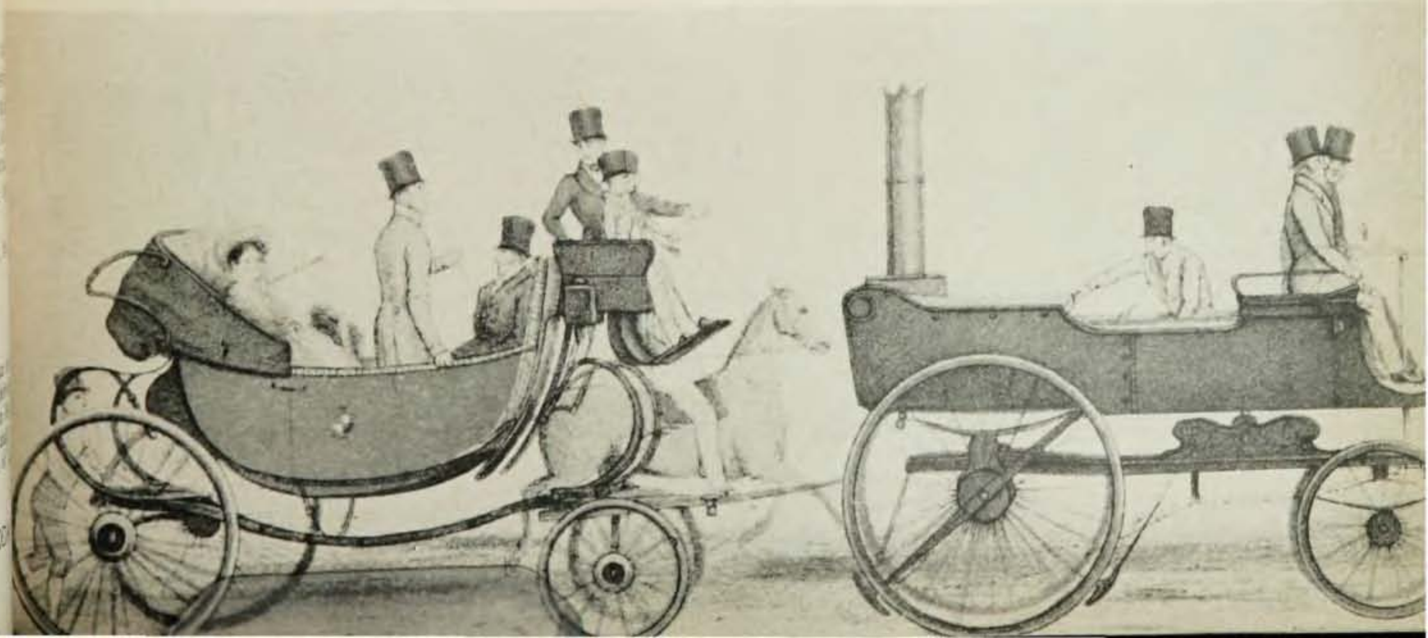
> . . . how any intestine motion could augment or diminish this repulsive power. But it struck me that if gases were made up of particles or atoms mutually impinging on one another and on the sides of the vessel containing them . . .

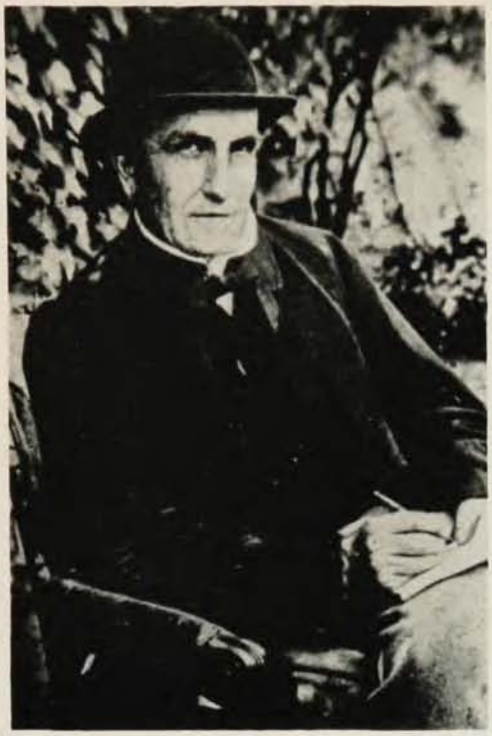
the theory would be more simple, consistent, and easy. After very many pages of quite impenetrable verbal arguments, exhibiting an astonishing confusion about the meaning of the law of conservation of momentum, he eventually reached a set of propositions which are roughly equivalent to Eq. (1) above.

He then gave experimental proofs that his hypothesis was correct. In a thermal mixing experiment in a calorimeter, he said, quantity of motion was conserved; and quantity of motion, as everyone knew, was momentum. Since momentum depended on the first power of the velocity whereas Eq. (1) implied that the absolute temperature varied as the square, he predicted that when equal masses of the same substance at absolute temperatures T_1 and T_2 were mixed, they would reach equilibrium at T_3 where

$$\sqrt{T_1} + \sqrt{T_2} = 2\sqrt{T_3}.$$

Water at 0°C and 100°C should reach equilibrium not at 50°C but at 48°C. He could not perform the experi-





Waterston as he appeared at the age of 46. (Courtesy Oliver & Boyd Ltd. from *The Collected Scientific Papers of J. J. Waterston*, edited by J. B. S. Haldane.)

ment himself for lack of good thermometers, so he searched the literature. Crawford, he found, had determined the equilibrium temperature to be 50.0°C; but this result, said Herapath, was the *expected* one, it was therefore suspect and should be rejected. (Actually it is within 0.05° of the correct value.) De Luc, on the other hand, had found 48.3°C. This confirmed Herapath's theory. But there was another proof, equally convincing, that his theory of gravity was correct. For it was well known that the acceleration of gravity at the earth's surface varied from equator to pole in a way which did not conform to the known ellipticity of the earth. But Herapath could now explain this in terms of the influence of the temperature at the two latitudes on Newton's "constant" of gravitation. Again his theory was in agreement with observation.

These papers were published in 1821, to be followed by long drawn-out disputes, attacks, refutations, and denials. But after they died down, there were *three* rival theories of gases—Newton's static theory, Davy's rotational model, and Herapath's hypothesis.

Joule and Others

IF Herapath remains a comic figure in spite of his real achievement, John James Waterston was a man whose genius was dogged by tragic ill luck. In 1843, while a schoolteacher for the East India Company in Bombay, he had a book published in Edinburgh—anonymously—entitled *Thoughts on the Mental Functions*, an attempt to explain human behavior in mathematical and physical terms. In a note at the end, he gave a full and accurate account of the kinetic theory of gases. But nobody read the book. Two years later he sent a paper to the Royal Society on the physics of media composed of free and perfectly elastic molecules in a state of motion; he wrote that he hoped that "although the fundamental hypothesis [of perfect elasticity] is likely to be repulsive to mathematicians, they will not reject it without a fair trial". But the referee reported that it was "nothing but nonsense" and only a short abstract was published, in another journal. Waterston not only developed the basic ideas precisely and was the first to see the relevance of Graham's recently published law of the effusion of gases through small holes, but he also stated the principle of equipartition of energy, introduced the concept of the mean free path (the "impinging distance") and proposed modifications of the model to represent imperfect gases. But his work was passed over and his influence on the main stream of science was negligible compared with that of the gregarious Mr. Herapath.

Joule favored Davy's rotational hypothesis at first. In a paper on electrolysis (1844) he spoke of revolving atmospheres of electricity and later he used the same idea to explain radiation. In his paper on the rarefaction of air he said that the centrifugal force of the revolving atmospheres was the sole cause of the expansion of a gas when the pressure was removed. But his main interest was to calculate the specific heats of gases. In one of his notebooks is to be found the rough draft of a lecture in which he drew a block of a substance

> . . . containing a number of atoms each of which revolves rapidly on its axis in the direction of the hands of a watch. Suppose now a number of fine cords to be rolled round each of these atoms and to pass over a wheel. It is evident that the force of the atoms will be diminished in winding up the weight *W*. This diminution of the velocity of the atoms is what we generally call a diminution of temperature. . . .

But shortly afterwards he realized that both rotational and translational motion could give the result that the vis viva of the atoms was proportional to the heat content. In 1848 he wrote that since Herapath's hypothesis was simpler, he would use it in preference to Davy's. He calculated the molecular velocities in several gases and also some specific heats. These were the first definite numbers ever to emerge from the kinetic theory of gases (except for those in Waterston's papers). Thus the kinetic theory of gases and the dynamical theory of heat were developed at the same time and largely by the same people.

Rankine developed the rotational (or vortex) theory to its highest refinement shortly *after* this. The essence of his method was to divide up each revolving atmosphere into concentric shells, typically of area $4\pi r^2$

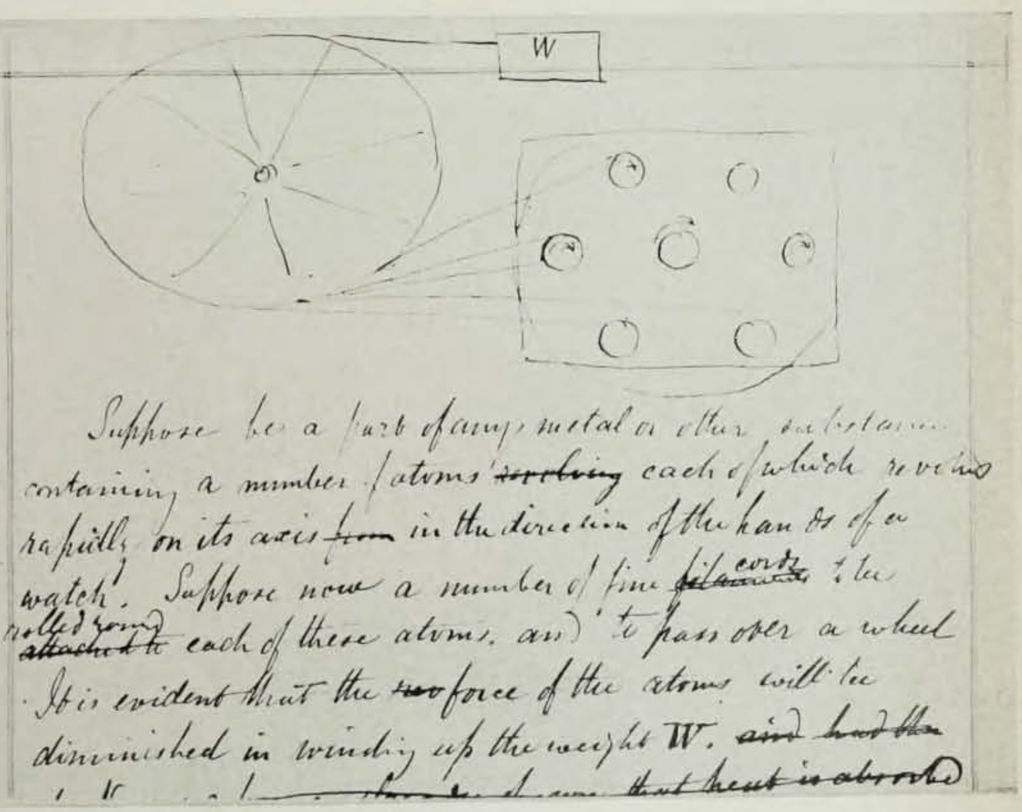
and acted upon by a centrifugal force of the type mc^2/r; the pressure p was therefore of the type $mc^2/4\pi r^3$. The total volume V of N such atoms was $\frac{4}{3}\pi r^3 N$. Substituting, one arrives again at Eq. (1). Rankine extended this to arbitrarily shaped vortices and again reached the same result—as must always be for any form of motion because of the implicit assumption of the equipartition of energy. This was an interesting situation, for no experiment could ever decide which was the correct model. But within a few years Herapath's hypothesis gained almost universal acceptance. Even Waterston managed to get a paper published on it in 1851. The German scientists Krönig and Clausius evolved just the same ideas independently in 1856 and 1857 (though Clausius certainly knew of Joule's results on molecular velocities). Two years later, a German translation of Bernoulli's old paper was published. Within a short time even British scientists were writing of "Bernoulli's theory lately revived by Mr. Herapath" and it was not long before Herapath's name was almost forgotten.

The vortex model persisted for a long time, however, in various guises. Maxwell dismissed it for an ordinary gas, in preference to Herapath's hypothesis, because he thought the rigidity would be too high. But he used it, as is well known, as the basis of his model of the electromagnetic ether. Later still, Kelvin made smoke-ring models of atoms to explain spectra. His calculations of the modes of oscillation of such systems have a very modern sound.

Conclusion

THE outstanding feature of this story is that—like the dynamical theory of heat—the kinetic theory of gases had first to break the grip of an abstruse and authoritative mathematical theory before the simple basic physical ideas could be accepted. These difficulties should, perhaps, be presented in their proper perspectives in our teaching textbooks.

Above all, these episodes accentuate the problem of communication in science. The records of the Royal Society and the French Academy of Sciences are blotted again and again by the rejection of outstanding discoveries. On the other hand, a hypothesis like Herapath's, published in a journal with less stringent refereeing, was embedded amid so much nonsense-writing that it took the instinct and genius of a man like Joule to uncover the one idea worth preserving. When the amateur historian descends into the stacks of a library he can contemplate the yards and yards of dusty volumes, records of decades of busy scientific activity. On the average, perhaps one short paragraph out of the huge output of any one year was *really* worth writing. Scientific researches are like fishes' eggs—only one in thousands ever reaches maturity. It is a chastening thought.



A sketch (drawn sideways to save space) from one of Joule's private notebooks. It illustrates his idea of the rotating atom theory.