Chapter 11
Thermodynamics and the Kinetic Theory

Abstract From 1859 the kinetic theory gained considerable support from experiment, yielding a range of known phenomena such as the gas laws and predicting new phenomena such as the independence of the viscosity of a gas from its density. Alongside these developments was the rise of thermodynamics, which explained a range of phenomena without any assumptions about the underlying structure of matter and which also received considerable experimental support. Thermodynamics yielded two results, an account of thermal dissociation and a measure of chemical affinities, in areas that had troubled atomists. Two basic problems faced the kinetic theory, its clash with measurements of the specific heats of gases and the problem posed by irreversible processes implied by the second law of thermodynamics. The latter problem was solved by appeal to statistical fluctuations, so that the inverse of apparently irreversible processes became unlikely rather than impossible. There was no independent evidence in support of this move in the nineteenth century.

11.1 Introduction

I have argued that nineteenth-century chemistry made less experimental contact with atoms than is typically supposed. It is time to turn our attention away from chemistry to nineteenth-century physics. Two approaches to the study of heat made considerable progress in the second half of the nineteenth century, but they were very different in kind and the relationship between them was problematic. One approach became consolidated into what has become known as phenomenological thermodynamics. The term 'phenomenological' is designed to capture the extent to which the theory dealt with measurable entities such as temperature and quantity of heat in a way that was independent of any theory about the underlying structure of matter. The approach involved in the kinetic theory of gases, by contrast, was just about the opposite, insofar as that theory was based on quite specific assumptions about molecular motions and collisions.

As we shall see, both thermodynamics and the kinetic theory were borne out by a range of experiments. The former theory was able to make progress in two areas that had posed problems for the atomic programme, namely, the measurement of chemical affinities and understanding the 'anomalous' vapour densities of some

gases. The kinetic theory also had its early successes, but there were also some very basic problems, recognised as such by the proponents of the theory, that it took twentieth-century developments to solve. Both theories had ramifications for chemistry, chemical thermodynamics making possible the study of chemical affinity, speeds of reaction and thermal dissociation and the kinetic theory gave evidence for the molecules that atomic chemistry needed and yielded Avogadro's hypothesis and the di-atomicity of common gases such as oxygen, hydrogen and nitrogen.

Some nineteenth-century scientists, such as Rudolph Clausius, Clerk Maxwell and William Gibbs, worked with and contributed to both theories, recognising and struggling with the tensions between them. Others, such as Pierre Duhem, Wilhelm Ostwald and a young Max Planck, took phenomenological thermodynamics to be a paradigm of good science and ruled out, or were suspicious of, theories such as the kinetic theory that invoked atoms or molecules lying behind the measurable phenomena. Those that took a stand against the atomic theories of the time took strength from their perception that in the last decades of the nineteenth century the kinetic theory was not making headway with the problems that beset it and was proving unable to emulate its early successes. The basic problems faced by the kinetic theory were overcome early in the twentieth century as we shall see in the next chapter. By that time it was possible to make experimental contact with atoms, and the achievement marks the end of the story as far as my book is concerned.

11.2 The Rise of Thermodynamics

Those who formulated and contributed to the spectacular success of thermodynamics in the second half of the nineteenth century, from Clausius and Maxwell through to Gibbs and then Planck, quite explicitly saw themselves as developing a theory that abstracted from and was independent of any views about the underlying structure of matter or heat. Maxwell (1965, Vol. 2, pp. 664–665) for instance, defined thermodynamics as 'the investigation of the dynamical and thermal properties of bodies, deduced entirely from what are called the First and Second laws of Thermodynamics, without any hypotheses as to the molecular constitution of bodies'. These formulations drew on a century of work on heat which had involved various hypotheses, involving such things as caloric or atomic motions, but consciously abstracted from those earlier theories. The aim was to construct a general theory that could learn from the success of earlier theories but jettison from those earlier theories hypotheses that were unsubstantiated and unnecessary. The resulting theory, based on the conservation of energy (the first law) and the increase of entropy (the second law), was remarkably successful and led to a range of novel discoveries.

Joseph Black, in the second half of the eighteenth century, formulated the notions of specific heat and latent heat in the context of a caloric theory. Specific heat is a property of a substance measuring the amount of heat necessary to raise the temperature of unit mass of a substance one degree. Latent heat is a measure of the amount of heat required to change the state of unit mass of a substance without change of temperature. The heat that enters a liquid to vaporise it is latent (hidden)

in the sense that it is absorbed without a corresponding rise in temperature. This was commonly understood in terms of a chemical combination of the heated substance with heat (caloric). Lavoisier, a proponent of the caloric theory, listed caloric as one of his chemical elements. Black's innovations, and the clear distinction between amount of heat and degree of temperature that they involve, became the basis of calorimetry. Changes that involve a mere redistribution of heat in an isolated system are such that the amount of heat in conserved. If a known mass of a hot liquid with a known specific heat and specified temperature is added to a given mass of water with a known specific heat and at a specified temperature, then the temperature of the resulting mixture can be calculated from the fact that the heat lost by the liquid must equal the heat gained by the water.

Early defenders of the caloric theory, such as Laplace and, as we have already had occasion to mention, Dalton, specified much detail. They assumed that particles of a gas are surrounded by atmospheres of caloric and attributed the pressure of a gas to the repulsive effects of the caloric. It was this repulsive effect that accounted for the expansion of a gas when it is heated, that is, when more caloric is added. It is not difficult to see how calorimetry and other common heat phenomena can be captured with the idea that heat is a something that is conserved in a wide range of changes and which flows from a hot to a cold body. Joseph Fourier developed an account of heat conduction that abstracted from the caloric theory in this way. Sadi Carnot also went some way towards abstracting from details of the caloric theory in his theoretical treatment of heat engines that was a major step towards the formulation of thermodynamics.

Carnot understood the performance of work by a heat engine as resulting from the falling of heat from a high to a low temperature. He imagined the quantity of heat (caloric) to be conserved in the process. He introduced the device of considering infinitesimal cyclic processes which involve the returning of a system to its original state, in which case any internal changes in the working substance can be ignored. He considered an ideal, reversible sequence of infinitesimal changes involving two isothermal and two adiabatic transformations (transformations taking place at constant temperature and without heat loss or gain respectively) that brought the working substance back to its original state. Carnot showed that the work performed in the execution of the cycle represented a maximum that could not be exceeded by any real, and hence irreversible, change. Otherwise, an indefinite amount of work could be extracted from a cyclic process by having the ideal engine drive a real one around the cycle. Carnot's considerations also led to a straightforwardly testable prediction, that the difference between the specific heat at constant pressure and the specific heat at constant volume of a gas be a constant.

Carnot's results were published in 1824. They were viewed in a somewhat different light a quarter of a century later, because, by that time, the law of conservation of energy had been formulated and generally accepted. There was a tension between Carnot's analysis and the conservation of energy. An understanding of work as the result of a mere transfer of heat from a high to a low temperature suggested to Rudolph Clausius that there would be a steady loss of working power in nature, which he regarded as implausible. In the 1850s he transformed Carnot's theory by

dropping the idea that heat is conserved and recognising the conversion of heat into work (mechanical energy) for which there was mounting experimental evidence, exemplified, for example, in the work of James Joule. Clausius's reworking of Carnot's analysis of his cyclic changes led to a version of the second law of thermodynamics, 'heat can never pass from a colder to a warmer body without some other change connected therewith occurring at the same time'[1].

The 'mechanical theory of heat' as formulated by Clausius was transformed into what became known as 'phenomenological thermodynamics' by casting principles of conservation of energy and increase of entropy in a general form free of any assumptions about hidden structures of the systems possessing energy and entropy. Gibbs and Planck were the major contributors to that move. The former's work, in particular, made possible the extension of thermodynamic considerations to chemistry.

Thermodynamics was confirmed in a way that conforms to the view of confirmation adopted in this book. A variety of experimentally testable predictions were made in an uncontrived way and vindicated. However, there is a qualification to be made about the extent to which thermodynamics led to natural consequences. Because of the very general form of the laws of thermodynamics those laws alone had scarcely any testable content. Predictions were extracted from them only by adding known empirical laws. This can be seen in the case of two early successes of thermodynamics, the prediction that the difference between the two specific heats of a gas is a constant, and the prediction that the freezing point of water decreases with pressure. Derivation of the first requires the addition of the gas laws to the laws of thermodynamics, whilst thermodynamic reasoning yields the second given the empirical observation that ice is less dense than water at the same temperature. Clark (1976) has pointed out that what he calls the heuristic of thermodynamics was weak. It yielded predictions only by way of the empirical regularities fed into it. Nevertheless, the regularities predicted in this way were natural consequences of thermodynamics plus the independently vindicated empirical knowledge fed in, so there is a strong sense in which the phenomenological theory was confirmed.

11.3 Thermal Dissociation and Affinities

Experiments on a number if gases reveal that they do not obey the gas laws in a straightforward way. Nitrogen peroxide is an example. As was suspected from the early 1860's, the 'anomalous' behaviour is due to the fact that the gases exist in more than one form, the relative proportions of each form depending on the temperature. From 1875 Gibbs treated this problem from the point of view of thermodynamics. He assumed that each component separately obeys the gas laws, used the equations of the component substances to deduce their relative densities, (so that NO_2 is half as dense as N_2O_4) and found the temperature-dependence of the relative proportions of each gas in the mixture from the fact that the equilibrium condition will correspond to maximum entropy. The argument was entirely phenomenological. (We have already seen that the use of formulae need not involve a commitment to atomism.)

Gibbs' predictions were confirmed by experiments by Henri Deville and his student L. J. Troost. In this way, a problem that stood in the way of the determination of relative atomic weights via vapour densities was removed. Clark (1976, pp. 71–72) notes that Boltzmann attempted to derive the equilibrium conditions within the kinetic theory, and succeeded in 1896, but only in an ad hoc way by adapting his assumptions to the known results.

Chemical affinity is a measure of the facility with which chemical substances combine. A theory of affinities should be able to determine the rate and direction of a chemical reaction. Many spontaneous chemical reactions involve the release of heat. A natural assumption informing early thermodynamic treatments of affinity was that chemical reactions take place spontaneously in a way that involves a maximum release of heat. This is not borne out empirically. There are spontaneous chemical reactions that result in cooling and there are reactions involving the release of heat that do not take place spontaneously. Helmholtz, in 1882, followed by van't Hoff and Duhem, developed a theory of affinity and rates of reaction that took account of entropy as well as energy changes. As with the case of thermal dissociation, the arguments were purely thermodynamical and they were borne out by experiment.

In the second half of the nineteenth century, then, thermodynamics was making impressive progress, some of it in territory that had proved problematic for atomists. It is time to switch our attention to developments in the kinetic theory that were taking place concurrently. Did atomism in the form of the kinetic theory lead to experimentally-confirmed knowledge in an especially significant way?

11.4 Early Versions of the Kinetic Theory

An early version of the kinetic theory of gases was proposed by Daniel Bernoulli in 1738. His description of the theory occupied just 5 pages in his book on hydrodynamics, published in Latin.[2] The basic idea that gas pressure is due to the elastic impact of gas particles moving freely and bodily through the volume of the gas was present and Bernoulli in effect showed that his basic assumptions could explain the gas laws. Indeed, insofar as the theory predicted the dependence of volume and pressure on temperature, Bernoulli's theory actually *predicted* the gas laws.

Bernoulli noted that the number of particles striking a piston bounding the surface of a gas, and hence the gas pressure, will be proportional to the gas density. That is, the theory explains Boyle's law. Bernoulli further reasoned that the contribution to pressure of the impact of a particle would be proportional to the mass of the particle and to the square of its velocity. Velocity affects the pressure in two ways. The greater the velocity the greater the impact and the greater the velocity the faster the particle will traverse the gas volume and so the more frequently will it strike the piston. Hence we have the dependence of pressure on the square of the velocity. The further assumption, that temperature is related to the square of the velocity, yields the proportionality of both pressure and volume to temperature.

There are a number of reasons why Bernoulli's version of the kinetic theory cannot be considered to have been well-confirmed at the time. Thermometry was

in its infancy in the early decades of the eighteenth century, and it was to be some time before the laws relating the volume and pressure of a fixed quantity of gas to its temperature were to be regarded as well confirmed experimental laws. If Bernoulli's theory is accepted then the persistence of the state of a well insulated gas implies that the mean velocity of the particles persists undiminished. This in turn implies that their collisions are perfectly elastic and that they experience no resistance to their motion through the body of the gas. These are strong assumptions far from obviously true, and an atomist who favoured a Newtonian model involving a static array of atoms repelling each other with short range forces inversely proportional to their separation and perhaps vibrating about equilibrium positions, must have seemed more plausible at the time. While the basic idea of the cause of pressure as presented by Bernoulli seems straightforward enough, there are problems in the detail. Not all particles can be moving at the same velocity nor can they be moving always normally to the surface on which they impact because of the results of collisions of particles with each other and with the walls of the containing vessel. The fact that particle motions will yield stable averages and produce a steady pressure obeying the gas law was something that needed to be argued for. Further, there is something ad hoc about the assumption that temperature is related to the square of the velocity. That relation is chosen in order to fit the known phenomena to some extent. Further, precisely which function involving the square of the temperature to choose is under-determined in Bernoulli's theory. From Bernoulli's discussion it is natural to identify temperature T with the average value of v^2. Later it was found necessary to identify it with the mean value of the kinetic energy, $1/2mv^2$.

Versions of the kinetic theory similar to that of Bernoulli appeared in the first half of the nineteenth century, in papers by John Herapath and John Waterston. Like Bernoulli, they were able to show how the theory yielded the gas laws, which by then were well established experimentally. However, the theory presented by Herepath and Waterston were not free of the difficulties I have indicated in connection with Bernoulli's version proposed a century earlier. I suggest there is an analogy between the situation with respect to these early versions of the kinetic theory and Dalton's atomic theory. Just as Dalton's theory could explain the laws of proportion so the kinetic theory could explain the gas laws. But (i) were they explanations that could be vindicated by experiment in the way that had come to be demanded of scientific theories and (ii) could the respective theories be defended in the face of obvious objections (for example, how can two like atoms combine to form a molecule, in the Dalton case, how can atomic motions persist and stable averages emerge in the case of the kinetic theory)?

A paper by Karl Kronig summarising the simple version of the kinetic theory was published in the *Annalen der Physik* in 1856 and attracted much more attention than those of Herepath or Waterston. His version did not progress beyond the earlier ones, but by 1856 the scene had changed in a significant way. By then the conservation of energy, and the appreciation that a quantity of heat is equivalent to a definite amount of mechanical energy, was well appreciated, and this made the identification of heat with the mechanical energy of moving molecules more plausible and attractive than it had been hitherto.

Rudolph Clausius and James Clerk Maxwell were soon to produce versions of the kinetic theory that were significant improvements on the simple version. Clausius recognised that most gas molecules, being complexes of atoms, could not be smooth spheres and so would be set in rotation by collisions. Taking into account the rotational and translational energy, he arrived at a novel empirical prediction of the kinetic theory, namely a value for the ratio of the principal specific heats of a gas, the specific heat at constant pressure and the specific heat at constant volume. (The fact that the prediction did not altogether match the empirical data was to prove one of the chief difficulties for the theory as is discussed below.) He also established a method of estimating the mean velocity of molecular motions, the result being velocities on a par with the velocity of sound. These high speeds posed a difficulty for the theory. If molecules in a gas move so quickly why does it take so long for a gas to diffuse through another? Why does it take a few minutes before the students at the back of a lecture room can smell the ammonia emerging from a freshly opened bottle at the front? Clausius responded by introducing the notion of the mean free path. A molecule progresses slowly in spite of its high velocity in between collisions because of the many changes in direction occasioned by those collisions. From Bernoulli onwards, supporters of the kinetic theory had assumed molecules to be of a volume negligible compared with the volume of gas which were aggregates of them. The mean free path is a function of their size, and it was necessary for Clausius to assume a size consistent with observed diffusion rates. There is a strong sense in which, at this stage, the kinetic theory was accommodated to rather than supported by observable rates of diffusion.

11.5 The Statistical Kinetic Theory

From 1859 onwards Clerk Maxwell set about investigating the scope and merits of the kinetic theory and was soon to considerably improve it. A reflection of the fact that, in 1859, the theory, though promising, was far from confirmed, is evident in Maxwell's early attitude to it. Writing to Stokes about his early work on the theory, inspired by Clausius's efforts, Maxwell made it clear that he regarded the theory as speculative and that it might well be refuted by experiment. He clearly recognised that the early form of the theory 'is wrong' but set about investigating it anyway 'as an exercise in mechanics'. Here are some of his own words:

> I do not know how far such speculations may be found to agree with facts, even if they do not it is well to know that Clausius' (or rather Herepath's) theory is wrong and at any rate as I found myself able and willing to deduce the laws of motion of systems of particles acting on each other only by impact, I have done so as an exercise in mechanics. Now do you think there is any so complete a refutation of this theory of gases as would make it absurd to investigate it further so as to found arguments upon measurements of strictly 'molecular' quantities before we know whether there be any molecules?[3]

Maxwell's doubts about the kinetic theory, and even about the existence of molecules, notwithstanding, he was soon able to greatly improve the status of the theory and invoke more empirical support for it. A key move was the introduction of

statistics to deal with the net effect of the motions of systems of moving and collid-ing molecules. In Maxwell's 1859 version of the theory the velocities of molecules, constantly changing through collisions, were randomly distributed about a mean. Using his statistics and the notion of mean free path Maxwell was able to analyse how local groupings of molecules and their velocities would spread through the body of a gas in equilibrium, and in this way was able to offer explanations of diffusion, viscosity and heat conduction. His first paper on the kinetic theory made possible a striking confirmation of it. The statistical theory yielded the result that the viscosity of a gas is independent of its density, so a pendulum swinging in a region evacuated by an air pump would experience no less resistance than one swinging in atmospheric air at the same temperature! Counter-intuitive or not, the prediction was confirmed by experiment. It is possible to comprehend, in a qualitative way, why resistance to motion in a gas should be independent of its density according to the kinetic theory. An object moving through a gas experiences resistance because its motion needs to set in motion the adjoining gas. The *more* dense the gas, the more molecules there are adjacent to a moving object, and so the greater the resistance to the motion spreading. However, on the kinetic theory the moving molecules are in random motion, and molecules set in motion by a moving object will have a tendency to migrate in a direction transverse to the moving object by virtue of the randomising effect of molecular collisions. This tendency for velocity to be trans-mitted through a gas will be greater the greater the mean free path, and that in turn is greater the *less* the density. The two factors affecting the spread of velocity, the one increasing and the other decreasing with density, cancel each other out. Incidentally, on the rival theory that construes a gas as a static array of molecules held together by forces, it is difficult to see how viscosity could fail to increase with density. So the experimental test was a crucial one in favour of the kinetic theory.

Early versions of the kinetic theory were idealisations that assumed that the volume occupied by the molecules themselves is vanishingly small compared to that of the gases they form, that the time spent in collision is negligible and that molecules interact only when colliding. These assumptions needed to be relaxed in order to predict the detailed behaviour of real gases. The kinetic theory met with some success in this direction. A notable one was due to the work of J. D. Van der Waals. He took into account intermolecular forces and the finite volume occupied by the molecules themselves to arrive at a modification of the ideal gas law. The modified law took the form

$$(P + a/V^2)(V - b) = RT$$

This equation proved to be in conformity with detailed experiments on carbon diox-ide at temperatures near and far from its point of liquefaction, although some other gases did not fit so well, especially under high pressure.

Phenomena predicted by the kinetic theory did not permit the determination of the absolute dimensions, weights and numbers of the molecules that it presupposed. The mean free path of molecules could be calculated, for example from the rate of diffusion of gases or from their viscosity. Various ways were devised to add one

other consideration to enable the absolute magnitudes to be determined. Loschmidt added such a relationship by supposing, for example, that the volume occupied by the molecules in a gas equals the volume occupied by that gas when it is liquefied. This yielded a value for NV, the number of molecules in a volume times the volume of each molecule. This relationship in conjunction with the expression for mean free path derived from the kinetic theory enabled the absolute magnitudes to be estimated. It yielded, for example, a value for Avogadro's number, the number of molecules in a gram molecule of gas. The constant b in Van der Waals equation was also related to molecular volume and measuring it gave another way of estimating Avogadro's number. Yet a third way was opened up from a study of thin films, the measurable thickness of which put an upper limit on the size of molecules. The fact that these various methods yielded values for Avogadro's number that were of the same order of magnitude was evidence in favour of the kinetic theory. The values for Avogadro's number were not contrived in the sense that they were consequences of the results of measurements, of the volume of a sample of gas when liquefied, of the thickness of an oil film and of the constant b in Van der Waals equation derived from measurements of the pressure and volume of a gas as a function of temperature. The approximate agreement of the numbers calculated from basic assumptions of the kinetic theory was genuine evidence, if not conclusive evidence, for those assumptions.

Maxwell stressed the central role in the kinetic theory played by the equipartition of energy. The interchange of energy between colliding molecules leads, on average, to an equalisation of kinetic energy. So, if velocities in one direction should happen to exceed those in another direction, collisions would soon ensure that the slower ones gain more energy than the faster ones lose in collisions, thus equalising the average velocity in each direction. Similarly, in a mixture of two gases, collisions will lead to the average kinetic energy of the molecules of each gas becoming equalised. Avogadro's hypothesis follows straightforwardly from this. Our analysis of developments in organic chemistry has shown how support for Avogadro's hypothesis followed from the formulae and molecular weight determinations that those developments made possible. The extent to which the kinetic theory was able to yield that result in an uncontrived way therefore constituted support for the theory. However, the equipartition of energy ran into trouble by clashing with specific heat measurements, as we shall see in the next section.

11.6 Problems with the Kinetic Theory

The basic assumptions of the kinetic theory were borne out through their ability to yield both known laws and novel ones in a natural way. They yielded the gas laws, Avogadro's hypothesis, the independence of the viscosity of a gas and its density and various interconnections between macroscopic properties such as diffusion, viscosity and heat conductivity, where estimates of mean free path by reference to one of these phenomena made possible quantitative predictions in one of the others. There is no doubt that the basic assumptions of the theory received important empirical

support. However, as we have noted in our discussion of the contribution of Van der Waals, the basic kinetic theory involved assumptions, such as the small size of molecules and the extremely short range and elastic character of their interactions, that were known to be violated by real gases. Progress of the theory beyond its initial qualitative successes required its development in the direction of being able to cope with the more complicated situations present in real gases.

Some of the moves to deal with the complications met with some success. The contribution of Van der Waals is a case in point. Others were not so clear-cut. Consider, for example, the variation of the viscosity of a gas with temperature. Experiment shows viscosity to be proportional to absolute temperature. The basic theory predicted that the viscosity be proportional to average velocity and hence to the square root of the absolute temperature. Maxwell attempted to remove the difficulty by introducing an effect of temperature in addition to its effect on the mean free path through an increase in velocity. He argued that the effective diameter of a molecule would also be a function of temperature, since the faster a molecule was moving the more effectively it could counter the repulsive forces of a neighbouring molecule and so the closer it could approach it. Maxwell found that by assuming a repulsive force between two molecules to be inversely proportional to the fifth power of their separation the kinetic theory yielded a value for the viscosity that was proportional to temperature, in accordance with experimental results. This should be classified as an accommodation to rather than confirmation by experiment.

A serious problem with the kinetic theory was posed by measurements of the two specific heats of gases. As Maxwell, most notably, appreciated, these measurements threatened to undermine the equipartition of energy, an assumption at the basis of the theory. It was known from chemistry, and indeed, from the implications of Avogadro's hypothesis now derivable from the kinetic theory, that very few molecules consisted of one atom and so had a structure that could not be spherically symmetric. Molecules made up of atoms must be able to rotate and to be subject to internal vibrations. As far as the latter are concerned, atomists were forced to conclude from the line spectra of gases that their molecules most be capable of a range of modes of vibration. Once molecules are capable of rotation and vibration, collisions of two of them cannot in general be perfectly elastic in the sense that the sum of their kinetic energy is equal before and after collision. If, for instance, a colliding molecule encounters a component atom of a molecule with which it collides as that atom moves towards it, because of rotation or vibration internal to the molecule, then it will receive a boost to its kinetic energy at the expense of the rotational or vibrational energy of the molecule it has struck. This was dealt with within the kinetic theory by assuming the setting up of an equilibrium between the three modes of energy, translational, rotational and vibrational, with equal amounts of energy, on average, being possessed by each degree of freedom of a molecule. This in general will consist of three translational modes along three mutually perpendicular directions, three rotational modes about three mutually perpendicular axes, and a range of vibrational modes. On the assumption of equal partition of energy amongst the degrees of freedom the kinetic theory yields a value of $(n+2)/n$

for the ratio of the specific heat at constant pressure to the specific heat at constant volume for a gas whose molecules have n degrees of freedom.

This formula was not in general borne out by measurements of the specific heats of gases. The formula predicts 1.33 for the ratio for diatomic gases if we take into account the three rotational modes in addition to the three translational modes *and ignore the vibrational modes*, conflicting with the value of 1.4 measured by experiment. As John Nyhof (1988) has stressed, things were not quite as bad as this result suggests. Both R. Bosanquet (1877) and Ludwig Botlzmann (1877) independently proposed that if diatomic molecules involved the combination of two perfectly smooth spheres then any rotation that they possessed about an axis joining the two spheres could not be changed by collisions so that this degree of freedom could be ignored in calculating specific heats. A diatomic molecule on this picture has five degrees of freedom, yielding a predicted value of 1.4 for the ratio of specific heats, conforming precisely to the measured value. Experiments on mercury vapour, a monatomic gas, lent support to this point of view. If atoms are perfectly smooth spheres then molecules of a monatomic gas should have no rotational degrees of freedom, leaving just three translational degrees of freedom if vibrations are ignored. This yields 1.67 for the predicted ratio of specific heats, and this was precisely the value for the specific heat of monatomic mercury vapour, measured by Kundt and Warburg (1876).

However promising this resolution of the specific heats problem may have appeared it remained deeply problematic, as Maxwell for one was well aware. The assumption of perfectly smooth atoms had no independent support so there was a degree of ad hocness about it. More serious is the ignoring of degrees of freedom associated with vibration. As we have mentioned, line spectra indicate that atoms and molecules vibrate in specific modes (and mercury vapour is no exception), and so the degrees of freedom involved in these modes should be taken into account in calculations of specific heat. Once this is done, and once it is recognised that molecules must possess a number of vibrational modes, the predicted value for the ratio of the specific heats of all gases approaches unity. Maxwell frequently expressed his awareness of the seriousness of the problem from his 1860 paper onwards. Maxwell (1877, p. 245) put the point in no uncertain words when, discussing the results of specific heat measurements, he wrote:

> Some of these, no doubt, are very satisfactory to us in our present state of opinion about the constitution of bodies, but there are others which are likely to startle us out of our complacency, and perhaps ultimately drive us out of all the hypotheses in which we have hitherto found refuge into that state of thoroughly conscious ignorance which is the prelude to every real advance in knowledge.

We now know that the classical kinetic theory cannot remove the specific heats problem. The reason why vibrational modes cannot be activated at low temperatures is fundamentally quantum mechanical. The quotation from Maxwell can be seen to be quite prophetic in retrospect.

A second central problem for the kinetic theory stems from the irreversibility of most processes in nature. Newtonian systems, provided they do not involve forces

such as frictional forces that are themselves asymmetrical under time inversion, are invariant under time reversal. The time inverse of any such Newtonian system is also a Newtonian system. For instance, a system of colliding billiard balls free of frictional forces is time-reversible. A film of such a system played backwards shows motions that would indeed occur if all the moving billiard balls could be turned back on their tracks. Macroscopic phenomena are not in general like that. The inverse of the wave radiating out from the point of entry of a stone in a pond, the diffusion of sugar in one's coffee, the cooling of a hot body are all processes such that their time-inverses run counter to what occurs in nature. In general, it is quite easy to discern that a film is being run backwards. However, if the world consists entirely of molecules executing friction-free motions governed by Newton's laws, then the time-inverse of any happening should also be a possible happening. The time asymmetry in evidence in the world clashes with the time-symmetric kinetic theory.

Proponents of the kinetic theory such as Maxwell and Boltzmann were able to rise to this challenge to a considerable degree. They could appeal to statistics to explain the asymmetry. There are innumerable ways of distributing the molecules in a cubic centimetre of ammonia at atmospheric pressure around a laboratory, and considerably less ways of arranging the molecules so that they are confined to a small region near the demonstration desk at the front. Given the basic assumption that molecular motions are random, the probability of the ammonia staying near the desk once released is negligible. Its diffusion through the room is virtually inevitable. This explanation of irreversibility is not ad hoc. It hinges on the randomness of the molecular motions that formed part of the basic assumptions of the theory from Maxwell's 1860 paper onwards. However, this did not dispose of the problem to the satisfaction of those that were most worried by it. An implication of the statistical explanation of time irreversibility is that that irreversibility is merely an improbability rather than an impossibility. This circumstance clashes with the second law of thermodynamics taken literally. The spontaneous congregation of ammonia dispersed throughout a laboratory into a small region near the demonstration desk, with a resulting increase in entropy, is an improbability rather than an impossibility according to the kinetic theory. The power and success of thermodynamics based on the first and second laws that we have already described provided a strong case for taking those laws as fundamental truths. Explanation of time-irreversability by the kinetic theory clashed head-on with that position. It is important to appreciate, in this connection, that there was no evidence available in the nineteenth century for the statistical nature of apparently time-irreversible processes such as diffusion. This became available only with Jean Perrin's experiments on Brownian motion in 1908.

I have highlighted specific heats and irreversibility as the source of two key difficulties for the kinetic theory. A third problem stems from the mathematical complexity of the statistical theory. Progression from the basic theory, that treated gases in equilibrium whose molecules interacted elastically in negligible time whilst occupying a negligible amount of the volume of the gas, needed to be relaxed in order to deduce predictions that could stand comparison with experiments on real gases. In a

wide variety of cases the problems proved intractable. Various approximations were made, yielding conflicting results for such things as diffusion and heat conduction, and with no way of testing the superiority of one set of approximations over another. Clark (1976, pp. 86–88) has characterised the problem in this way and described Boltzmann's ineffective struggles with it, and cites contemporaries of Boltzmann such as Planck who read the problem in just this way. Boltzmann's frustration with these problems was probably a contributing cause to his suicide in 1906.

11.7 The Status of the Kinetic Theory in 1900

In the second half of the nineteenth century the kinetic theory received strong support. It yielded at least approximate predictions of known laws such as the gas laws, successfully explained and exploited departures from them, predicted novel phenomena such as the independence of the viscosity of a gas and its density and gave a natural explanation of many of the time-asymmetries in nature. There was genuine experimental support for the theory that was not contrived. There surely had to be something right about the theory. What is more, the success of the kinetic theory could not be reproduced by bracketing off assumptions about the existence of molecules in the way in which the success of nineteenth-century chemistry could be retained by bracketing off atoms. There is no doubt, then, that the development and testing of the kinetic theory improved the case for atoms and molecules.

However, it must be recognised that the theory had basic problems, problems that had become recalcitrant by the last decade of the nineteenth century. The specific heats problem could be offset only by restricting the application of the equipartition of energy, a principle which was otherwise a central and crucial part of the theory. The claim that the second law of thermodynamics was only statistically true had not been supported by independent evidence and showed no prospects of being so. Partly because of formidable mathematical difficulties, little new evidence for the kinetic theory came to light in the last two decades of the nineteenth-century.

It is not inconceivable that, given the state of play in the late nineteenth-century, molecules might have gone the same way as the aether. From Fresnel to Maxwell and beyond the aether had figured prominently in well-confirmed theories. Most scientists saw a range of phenomena involving diffraction, interference and polarisation of light as establishing that light is a transverse wave in an elastic aether. Maxwell was encouraged to reduce electromagnetism to the mechanics of that aether and succeeded in giving an electromagnetic theory of light that successfully predicted that the ratio of the electromagnetic unit of charge to the electrostatic unit be equal to the velocity of light. The eventual confirmation of Maxwell's theory by Hertz in 1888, with the production of the radio waves that it predicted, was seen by many scientists as establishing the existence of the aether. FitzGerald made the point emphatically when reporting on Hertz's experiment to a meeting of the British Association in Bath in 1888.

> Henceforth I hope no learner will fail to be impressed with the theory – hypothesis no
> longer – that the electromagnetic actions are due to a medium pervading all space, and that
> it is the same medium as the one by which light is propagated.[4]

In spite of the evidence in its favour the aether was, in a sense, banished from science in the first decade of the twentieth century. But only in a sense. The electromagnetic field pervading all space has persisted. The aether has been rejected, but only by being replaced by something that can duplicate its role in the successful predictions of the nineteenth century that had supported it. The molecule of the nineteenth-century kinetic theory may not have survived. After all, as we have seen, the theory faced fundamental difficulties of various kinds. But any replacement would have been required to account for the empirical success of that theory, success that was too diverse to have come about by accident.

Much of the literature on attitudes to assumptions about atoms and molecules in the late nineteenth century assumes that avoidance of or refusal to commit to such notions amounted to positivism. So, for instance, Einstein attributed the opposition to atomism of scientists such as Ostwald and Mach to 'their positivistic philosophical views' a position echoed by Stephen Brush.

> Those scientists who did suggest that the kinetic theory be abandoned in the later 19th
> Century did so not because of empirical difficulties but because of a more deep-seated
> purely philosophical objection. For those who believed in a positivist methodology any
> theory based on invisible and undetectable atoms was unacceptable.[5]

There is no doubt that some scientists who were suspicious of or inclined to reject the claims of atomism invoked philosophical positions that are positivist in some reasonably strong sense. Take, for instance, the following remark made by Mach in 1872 in the context of a denial that it has been established that heat can be attributed to the motion of molecules.

> One thing we maintain, and that is, that in the investigation of nature, we have to deal only
> with knowledge of the connections of appearances with one another. What we represent to
> ourselves behind the appearances exists *only* in our understanding, and has for us only the
> value of a *memoria technical* or a formula, whose form, because it is arbitrary and irrelevant,
> varies very easily with the standpoint of our culture.[6]

Insofar as objections to the kinetic theory appeal to a positivist philosophy they can be rejected along with that philosophy. Appeal to the conservation of energy or the undulatory character of light, endorsed by Mach himself, go beyond the appearances, as do common sense assumptions about tables and chairs. Science in general, not just atomism, clashes with positivism. The clash gives no specific reason to reject atomism and perhaps every reason to reject positivism.

Other philosophical objections to atomism appealed to considerations that are best described as instrumentalist rather than positivist.[7] Pierre Duhem raised objections of this kind. An instrumentalist can endorse theory in science and can recognise that theories involve conceptions, such as energy and mass, that abstract from and go beyond the deliverances of the senses. However, an advocate of this position, like Duhem, insists that scientific theories are adequate to the extent that they adequately order phenomena. There may be a reality behind the phenomena

accessible to observation and measurement, but science is not capable of revealing it. Duhem denied that science can 'strip reality of appearances covering it like a veil, in order to see the bare reality itself'. A physical theory, according to Duhem (1962, p. 19), is not an explanation of the phenomena. Rather, it is 'a system of mathematical propositions which aim to represent as simply, as completely, and as exactly as possible a set of experimental laws'.

As with positivism, it can be argued that this philosophical position clashes with science. Indeed, the general claim that science is not explanatory clashes with Duhem's own science. Duhem was a pioneer of the extension of thermodynamics into chemistry and, as we have seen, one of the merits of thermodynamics was that it could *explain* such phenomena as anomalous vapour densities where atomism had failed.

Objections to the kinetic theory based on positivist or instrumentalist philosophies stand or fall with those philosophies. A scientist impressed with the progress of the kinetic theory might well take that success as one reason among others for rejecting positivism or instrumentalism. If a philosophy cannot accommodate the kinetic theory so much the worse for that philosophy.

As we have seen, then, objections to atomism by the likes of Mach, Ostwald, Duhem and many lesser figures were sometimes couched in general philosophical terms and can be rejected along with the philosophies they presuppose. However, I think it would be a mistake to leave matters there. There were a range of other kinds of objections to atomism in the late nineteenth century that were more closely tied to science itself and not to some positivist or instrumentalist philosophy. Many of them were explicitly invoked by critics of atomism like Mach and Duhem. In the following I extract some of the lines of argument that had something going for them.

All three of the critics of atomism mentioned in the previous paragraph frequently linked their opposition to atomism to an opposition to mechanism. There are aspects of this criticism that cannot be readily dismissed along with positivism. From the mechanical philosophers of the seventeenth century through to many practising scientists of the nineteenth century there was a widespread assumption that the material world is in some strong and narrow sense mechanical. One version of mechanism identifies the mechanisms assumed to underlie phenomena as atomic mechanisms, either systems of atoms with shape, size and motion like Boyle's or as centres of Newtonian force like Newton's or those of Boscovich. After the introduction of the conservation of energy, a weaker version of mechanism assumed all energy to be mechanical energy, without necessarily assuming that energy be borne by discrete moving atoms. (Maxwell, for example, who was a mechanist in the weaker sense, assumed electromagnetic energy to be located in the motions and strains of a continuous aether.) Mach, Duhem and Ostwald all objected to mechanism in this sense, arguing that it went beyond what was implied by or necessary for science.

From a scientific point of view, the possibility of reducing a branch of science to mechanics is to be supported by achieving such a reduction rather than by philosophical decree. Not only had this not been accomplished in several areas of science but it could be argued that things were moving in a contrary direction. For instance, mechanists assumed light to involve transverse vibrations in an aether. After Maxwell,

light became understood as fluctuating electro-magnetic fields. So the first major substantiated reduction in physics was the reduction of optics to electromagnetism. It wasn't a mechanical reduction at all! It is true that Maxwell and his followers believed electric and magnetic fields to be the manifestations of motions and strains in a mechanical aether. But as opponents of mechanism such as Duhem and Ostwald were able to point out, the mechanical models involved were contrived and became increasingly implausible and unsubstantiated as the nineteenth century progressed. It can be argued that not only did progress in electromagnetism move away from mechanical reduction but also that that progress owed nothing to mechanism.[8]

Chemistry was another area providing fertile ground for opposition to mechanism. We have seen in detail that the success of nineteenth-century chemistry could be made sense of via an interpretation of chemical formulae that dispenses with atoms, a point made in detail by Duhem around the turn of the century. Even if the hypothesis of chemical atoms is entertained, as most chemists of the late nineteenth century admittedly did, those atoms could not be mechanical atoms as traditionally conceived. Those atoms needed to possess valency and to combine in various ways that no mechanical atomic theory of the time was able to come close to explaining. Chemical atomism could not be regarded as a vindication of mechanical atomism.

As we have seen, there were specific problems with the kinetic theory stemming from specific heats and irreversibility. They pointed to genuine problems that the theory needed to overcome. However, to take the difficulties as sufficient reason to reject the theory was inappropriate and ignored the significant successes of the theory. So, for instance, the rejection by Ostwald (1896, pp. 345–346) of the kinetic theory on the grounds that it clashes with irreversibility paid inadequate attention to the resources that the theory had for meeting the objection. Those opponents of atomism who favoured outright rejection of it were ill-advised and had at least failed to appreciate the successes of the kinetic theory. On the other hand, in denying that the successes of atomism were a victory for mechanism, questioning the extent to which chemical atomism had been vindicated, stressing the non-mechanical aspects of chemical atoms and arguing that developments in electromagnetism were moving in a direction away from mechanism and atomism towards a theory involving continuous fields and electric charge as primitives, the anti-atomists were on defendable ground.

In the next chapter we will see how new experiments were to leave little scope for a denial of atoms, and those who claimed that atoms could have no place in science in principle were simply shown to be wrong. However, we shall also see that some important aspects of the case against mechanical atomism were vindicated rather than undermined by these developments.

Notes

1. As cited by Clark (1976, p. 65).
2. An English translation of the key part of Bernoulli's paper is in Brush (1965, pp. 52–65).
3. See Brush (1965, pp. 26–27).

4. As cited by Hunt (1991, p. 160).
5. Both quotations are cited in Clark (1976, p. 42).
6. As cited in Nyhof (1988, p. 88). The emphases are Mach's.
7. Nyhof (1988) makes this distinction.
8. I have argued the case that Maxwell's progress in electromagnetism owed little to mechanism in Chalmers (2001). Ostwald (1896) explicitly invoked the history of electromagnetism and optics as part of his case against mechanism.