

ATOMS AND MOLECULES SPECTROSCOPICALLY CONSIDERED *

LET me commence by congratulating you on the circumstance that this School and the Literary Society connected with it are known over a much more extensive area than Whitechapel. It is some time ago since I first heard of the work which you are attempting to do, and which indeed to a large extent you are doing, in this part of London. All friends of Science must deeply sympathise with your efforts, and I looked upon it as my bounden duty to come here and lecture when asked to do so. I have one more remark to offer: as I knew that my audience would consist if not altogether of old students of Science in this school, still of those largely interested in mental culture and in the acquisition of useful knowledge, I thought it right to ask you to follow me into a region which a few men in lands far apart are now investigating—a region which lies outside the known, and which is being explored by means of the spectro-scope. I hope to be able to suggest a few thoughts to some of you, in case you have worked with that instrument, and I hope also to be able to place before those who have not, many facts with which they are already acquainted, in a new point of view.

Now, in the first place, what are Atoms and what are Molecules? A chemist will tell you about the atomic weight of certain elements, and you will hear him talk about molecular volumes, and the like. Here is a definition given by Dr. Frankland in his book on Chemistry ("Lecture Notes," p. 2): "An atom is the smallest proportion by weight in which the element (that is to say the element to which the atom under discussion belongs) enters into or is expelled from a chemical compound." He then points out that when atoms are isolated—that is, when they are separated from other kinds of matter—they do not necessarily exist as atoms in the old sense; they go about in company, generally being associated in pairs. He then defines such a combination of atoms as an elementary molecule. Here, then, is put before us authoritatively a chemist's view of the difference between an atom and a molecule.

Let us now go to the physicist and see if we can gather from him his idea of atoms or molecules. It is remarkable that, in a most admirable book, Prof. Clerk-Maxwell's "Theory of Heat," in which you find nearly all that is known by physicists about molecular theories, the word "atom" is not used at all. We are at once introduced to the word "molecule," which is defined to be "a small mass of matter the parts of which do not part company during the excursions which the molecule makes when the body to which it belongs is hot."

Prof. Clerk-Maxwell goes on to give us ideas about these "molecules," which have resulted from the investigations of himself and others; and if you will allow me, I will read a few extracts from his book (p. 286): "All bodies consist of a number of small parts called molecules. Every molecule consists of a definite quantity of matter, which is exactly the same for all the molecules of the same substance. The mode in which the molecule is bound together is the same for all molecules of the same substance. A molecule may consist of several distinct portions of matter held together by chemical bonds, and may be set in vibration, rotation, or any other kind of relative motion, but so long as the different portions do not part company but travel together in the excursions made by the molecule, our theory calls the whole connected mass a single molecule." Here, then, we have our definition of a molecule enlarged. The next point insisted upon by our author is that *the molecules of all bodies are in a state of continual agitation.*

That this agitation or motion exists in the smallest parts of bodies is partly made clear by the fact that we cannot see the bodies themselves move.

Now in a solid body the molecule never gets beyond a certain distance from its initial position. The path it describes is often within a very small region of space. Prof. Clifford, in a lecture upon atoms, has illustrated this very clearly. He supposes a body in the middle of the room held by elastic bands to the ceiling and the floor, and in the same manner to each side of the room. Now pull the body from its place; it will vibrate, but always about a mean position; it will not travel bodily out of its place. It will always go back again.

We next come to fluids: concerning these we read—

"In fluids, on the other hand, there is no such restriction to the

excursions of a molecule. It is true that the molecule generally can travel but a very small distance before its path is disturbed by an encounter with some other molecule; but after this encounter there is nothing which determines the molecule rather to return towards the place from whence it came than to push its way into new regions. Hence in fluids the path of a molecule is not confined within a limited region, as in the case of solids, but may penetrate to any part of the space occupied by the fluid."

Now we have the motion of the molecule in the solid and the fluid. How about the movement in a gas? "A gaseous body is supposed to consist of a large number of molecules moving very rapidly." For instance, in this room the molecules of the air are travelling about twenty miles in a minute. "During the greater part of their course these molecules are not acted upon by any sensible force, and therefore move in straight lines with uniform velocity. When two molecules come within a certain distance of each other, a mutual action takes place between them which may be compared to the collision of two billiard balls. Each molecule has its course changed and starts in a new path."

The collision between two molecules is defined as an "Encounter;" the course of a molecule between encounters a "Free path." It is then pointed out that "in ordinary gases the free motion of a molecule takes up much more time than is occupied by an encounter. As the density of the gas increases the free path diminishes, and in liquids no part of the course of a molecule can be spoken of as its free path."

Now the kinetic theory of gases, on which theory these statements are made, has this great advantage about it, that it explains certain facts which had been got at experimentally, facts which had been established over and over again, but which lacked explanation altogether, till this molecular theory, which takes for granted the existence of certain small things which are moving rapidly in gases, less rapidly in fluids, and still less in solids, was launched. The theory in fact explains in a most ample manner, many phenomena so well known, that are termed "laws." It explains Boyle's law, and others, well known to students of this school. This theory, which takes for its basis the existence of molecules and their motions, explains pressure by likening it to the bombardment of the sides of the containing vessel by the molecules in motion; or it tells us that the temperature of a gas depends upon the velocity of the agitation of the molecules, and that this velocity of the molecules in the same gas is the same for the same temperature, whatever be the density. When the density varies, the pressure varies in the same proportion. This is Boyle's law. Further, the densities of two gases at the same temperature and pressure are proportional to the masses of their individual molecules, or, when two gases are at the same pressure and temperature, the number of molecules in unit of volume is the same. This is the law of Gay Lussac.

I have now fairly introduced you to the atom of the chemist and the molecule of the physicist; you will see at once that the methods of study employed by chemical and physical investigators are widely different. The chemist never thinks about encounters, and the physicist is careless as to atomic weight; in his mind's eye he sees a perpetual clashing and rushing of particles of matter, and he deals rather with the quality of the various motions than of the material.

Next let me say a little more about these "encounters;" and here I must again refer you to Prof. Clerk-Maxwell's book (p. 306). It is assumed that while the molecule is traversing its free path after an encounter, it vibrates according to its own law, the law being determined by the construction of the molecule, or let us say its chemical nature, so that the vibration of one particle of sodium would be like that of another particle of sodium, but unlike that of a particle of another chemical substance, let us say iron. If the interval between encounters is long, the molecule may have used up its vibrations before the second encounter, and may not vibrate at all for a certain time previous to it. The amplitude of the vibration will depend upon the kind of encounter, and will be independent of the number of encounters.

We can imagine a small number of feeble encounters, a large number of feeble encounters, a small number of strong encounters, and a large number of strong encounters.

In the case of feeble encounters, we pass from a small number to a large one by increasing the density.

In the case of strong encounters we pass from low temperature with small density to high temperature with great density.

Increase of density will reduce "free path."

* Revised from short-hand notes of a Lecture delivered to the Whitechapel Foundation School Literary and Scientific Society, March 10, 1874.

Increase of temperature will increase amplitude.

The shorter the free path the more complex the vibrations.

The greater the amplitude the more will the vibration of the molecule be brought out, not merely the *fundamental vibrations*, as we may term them, which we get in the free path, when it is longest, but the *overtones*.

Now why have I risked wearying you with these detailed statements concerning the vibrations of "molecules?" Because we believe that each molecular vibration disturbs the Ether; that spectra are thus begotten; each wave-length of light being set in vibration by a molecular vibration of corresponding wave-length. The vibration is, in fact, the sender; the spectrum is the receiving instrument, in this new telegraphy.

Now there are two questions which I propose to discuss, and they are these:—What light does the spectroscope throw upon molecular questions? and is there any hope that the spectroscope, as researches with it are extended, may aid the study of a subject which lies at the root of chemical and physical investigation?

I have written down several statements, which I propose to discuss one by one. I shall state the experimental basis, when it exists, on which the statements rest and the methods by which the results have been obtained.

I shall for a time use the word "particle" to represent a small mass of matter, because it does not tie me to the "atom," or the "molecule" of the chemist, or to the "molecule" of the physicist. "Particle" is a neutral term, which I hope none of you will quarrel with.

1. My first proposition is this:—*When particles are aggregated together, so as to form a solid or liquid, they give out rays of light of certain refrangibilities; and the spectrum is continuous as far as it goes.* This was Kirchoff's first generalisation.

It surely is an important fact from the point of view of the molecular theory that all solids and liquids, with their particles moving as already stated, do give you a perfectly distinct spectrum from that which you get when you deal with any rare gas or vapour whatever. A poker put into the fire becomes of a dull red heat, after a time a white heat is arrived at. As far as the vibrations exist they are continuous, there are no breaks in the series of wave-lengths. You may also get a platinum wire, and drive it to incandescence in the same way by means of electricity. Analyse the light by means of the spectroscope, the spectrum is the same as that of the poker. Further, we can go to the sun, and divest it in imagination of the atmosphere which absorbs much of its light, and we know that, with a small exception, we shall get a perfectly continuous spectrum similar to that in the case of the poker or platinum wire. Connected with spectroscopic investigation there is this wonderful fact, that as it deals with matter in the most general way, it is perfectly easy to carry on a line of argument, not by referring to different chemical elements, but to matter, now on the earth, now in the sun, or again in some of the stars. It is a great leveller. In this continuous spectrum we have a spectroscopic fact connected with that kind of molecular motion which physicists attribute to particles so long as they are closely packed together in the solid state, and so long as they have but a small free path as in the fluid state.

2. I now come to my second proposition:—*When particles are in a state of gas or vapour, and are rendered incandescent by high tension electricity, line-spectra are produced in the case of all the chemical elements.*

I have several photographs which I will throw on the screen, showing such spectra as these now in question. We have thus the spectra of the light given off by the vapour of cobalt and of nickel rendered incandescent by means of high-tension electricity. I will next show you the spectra of other chemical elements, such as aluminium and iron compared with nickel and cobalt, pure and impure iron compared with a meteorite. These line-spectra are only to be obtained from gases and vapours, and as a rule only when we employ high-tension electricity.

We get a perfectly distinct spectroscopic result from the one we had before, precisely in the case where according to the physicists we have an enormous motion and agitation of molecules.

3. I now proceed to the next proposition:—*In some cases particles in a state of gas or vapour can be set swinging by heat waves.* I have here some salts of sodium and strontium, these I place in the heat of a Bunsen burner, they are at once dissociated and the particles of the metals are set swinging by the heat waves and we get their longest lines. Now that is not only true for strontium and sodium, but for many other elements. But if I put salts of iron, or of the other heavy metals in the flame, I shall not

get bright lines. Or again, in some other vapours, such as sulphur, we only get a spectrum, not of lines, but continuous over a limited part of the spectrum. In fact I may say that with the exception of those elements which easily reverse themselves, this heat is absolutely incompetent to give me anything like a bright line.

4. *Particles, the amplitudes of vibrations of which may either be so slight that no visible light proceeds from them, or so great that they give out light of their own, absorb light of the same wave-length and of greater amplitude passing through them.*

Consider how beautiful this statement is when you look at it in the light of its teaching with regard to particles. We throw sodium into a flame and get a yellow light; we place it on the poles of our electric lamp and render it incandescent, and its light is rich yellow.

We have similarly incandescent sodium outside the sun, through which the rays of sunlight pass outwards towards the earth, and we may have similar non-luminous sodium vapour in a test-tube; and the vibration which gives the yellow light, in the case of the sun, and which is invisible in the vapour of the tube, instead of giving a bright line gives a dark one. Let me show you some photographs of the solar spectrum, so that as you have seen the bright lines due to radiation, you may see the dark lines in the solar spectrum which are due to absorption.

Our knowledge of the elements existing in the sun and stars depends entirely upon the principle first suggested by Stokes, that particles are set swinging when light waves pass through them with the particular rate of vibration which they effect.

The elements to which a large number of the Fraunhofer lines are due have been determined by means of the vibrations of particles on the earth. Whether a particle vibrates on the earth or on the sun it does not matter to the spectroscope, the vibration is the same, but as the particle is set vibrating at the sun by a greater amplitude of the light passing through it we get a dark line instead of a bright one. To show that in the stars, representing to us other suns, the spectra are very various I will exhibit spectra of the three classes of stars into which most may be grouped. In the middle we have a simple line spectrum, in the centre a more complex one, and at the bottom a channelled spectrum.

5. Next I have to point out to you that *line spectra become more complicated as the particles are brought nearer together, provided the state of gas or vapour be retained.* See the importance of this observed fact in connection with the molecular theory. If in the solid the particles can only oscillate round their mean position, if in the gas they can go through with enormous rapidity a tremendous number of various movements of rotation and vibration, and along their free path; and if spectroscopically we can follow these movements by differences in the phenomenon observed, is it too much to hope that in the coming time we shall have an enormous help in our inquiries? We get a solid or liquid condition, and a continuous spectrum; we get the most tenuous gaseous condition and then the phenomenon is changed, and the spectrum consists of a single line. So far indeed as the visible spectrum goes, it is possible by working with the gas at low pressure, and not too high temperature, to get a spectrum from any gas or vapour of only a single line, and as you increase the density, and thus force the particles closer together, and make the conditions of the gas approximate in the way of aggregation more to those of a solid, so does the spectrum get more and more like that of a solid, till we see at last a bright continuous spectrum. Take, for instance, hydrogen, and use, not an ordinary air-pump, but a Sprengel mercury pump; use this for three or four hours, and observe the spectrum of the gas. It is a single line. Fill the tube again with gas, at ordinary atmospheric pressure, double the pressure, or multiply it ten or more times, and what becomes of the line? Not only does that green line which first appeared get more and more obvious and thick, but more lines appear, and they get thicker, till at last there is such a background of continuous spectrum that these are all invisible as lines. At twenty atmospheres the spectrum is as continuous as that of a solid.

6. Here is my sixth proposition:—*In the case of metals there are two different ways in which the continuous spectrum is approached.* Mind I do not say reached, for there may be much more to learn on this point. To render this clear I must show you some more photographs and explain the method by which they have been obtained. Here I have a coil and a jar, and here the poles. We drive the metal of which these poles are composed into vapour, the vapour is rendered incandescent; the spectrum we should get would therefore be one of bright lines. Now,

instead of bringing the spectroscope close to the poles, in which case, in every part of the spectrum, we should get light from every part of the spark, I prefer to use a lens, by means of which I throw an image of the spark on the slit; then in each strip of the total visible spectrum is the spectrum of some particular part of the vapour. Think the matter over a little for yourselves. These poles are perpetually giving off vapour, which is constantly going away; some of it is being oxidised, some of it is travelling away along the currents of air set up. What follows? There must be more vapour close to the pole than in the interval between the poles; that will be still more true if I make the interval between the two poles longer. In the part between the two poles, if they consist of two different elements, we have three distinct spectra. In the upper part, a region rich in the upper vapour; in the lower, one rich in the lower vapour; between them one which is rich in neither. We have then at least three distinct layers, so to speak, in the spectrum, the spectrum of the vapour of the upper pole the spectrum of the vapour of the lower one, and also of the central region. The number of particles of each vapour will decrease from each pole. You will see in a moment that much the same condition of affairs will be brought about, if, instead of using a spark, I use an electric arc, in which the pure vapour of the substance which is being rendered incandescent

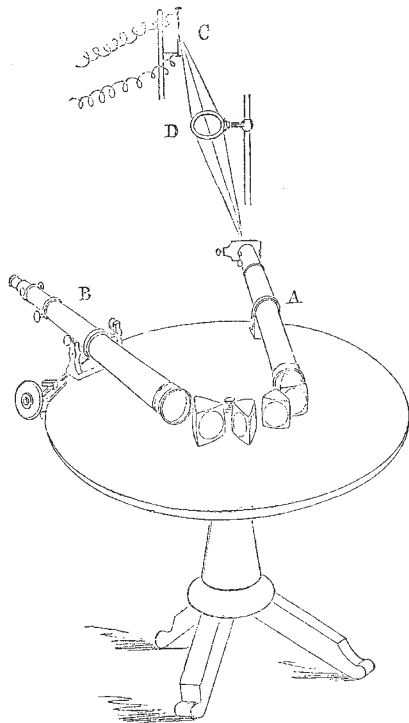


FIG. 1.—C, spark; D, lens; A, collimator; B, observing telescope.

fills the whole interval between the poles, the number of particles being smaller at the sides of the arc. Now I can throw an image of such a horizontal arc on a vertical slit; the slit will give then the spectrum of a section of the arc at right angles to its length. You have a photograph of such a spectrum of iron now before you. I wish to draw your attention to the long and the short lines. The vapour which exists furthest from the core of the arc has a much more simple spectrum than that of the core of the arc itself. The spectrum of the centre consists of a large number of lines; that furthest from the centre consists of one line. If you picture to yourselves the particles getting nearer to each other, as you get nearer the source of supply, you see that the nearer the particles are together the more they hang about and the more lines we get in the spectrum. It is important to notice that vibration once begun always goes on; it never gives place to others, although it may give rise to others; so that you get the largest number of lines in the centre, where the particles are closest together. Now I have specially to refer to the fact that the way in which the continuous

spectrum is built up varies in different substances. Here I have a photograph giving the spectrum of aluminium and calcium compared with that of the Lenarto meteorite. The spectra of calcium and aluminium differ generically from that of the meteorite. I want to draw attention to the thick or winged lines you get in the case of aluminium and calcium. These spectra are good specimens of those which give a continuous spectrum by thickening the lines, while the elements in the meteorite are as good specimens as I could put before you of those which produce a continuous spectrum by increasing the number of their lines. There is another remarkable fact connected with this.

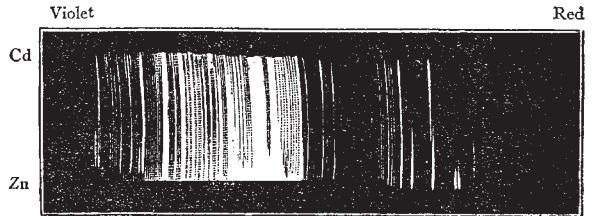


FIG. 2.—Long and short lines of zinc and cadmium.

You see a thin dark line in the centre of the thick bright lines; this is due to the absorption by the rarer cooler vapour lying outside this vapour. This is almost invariably observed in the substances giving us the lines thickening as the continuous spectrum is approached, while iron does not give us any such reversal. It is well to see if one can group facts together. That is the first business of a man of Science. It is extraordinary that in all the substances I have yet examined the question of specific gravity decides whether the substance should have its spectrum complicated by thickening or increasing

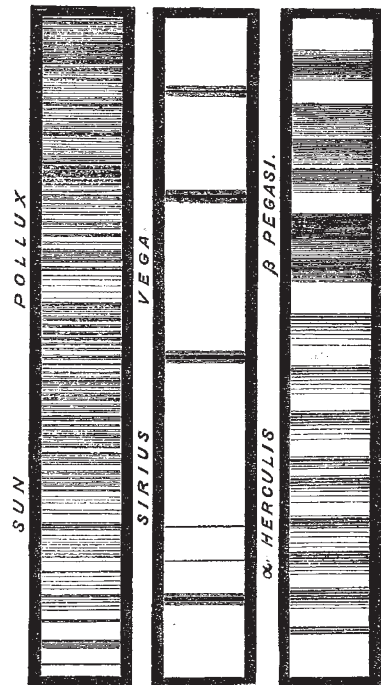


FIG. 3.—Long and short lines of iron.

its lines. You know the specific gravity of iron is high. In the case of aluminium, magnesium, sodium, and others where this is low you have the widening of the lines and the easy reversal.

So much for the continuity of the spectroscopic record of the continually increasing distance of particles from particles. We began with a solid and a continuous spectrum, we end with a tenuous gas and a spectrum of a single line, and we partly bridge over the gap between these states in two different ways.

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(To be continued.)