only and independent of the temperature of the enclosure. This division into absorption and radiation is to some extent artificial and will have to be revised when the phenomena of radiation are placed on a mechanical basis. For our present purpose it is only necessary to point out the difficulty involved in the assumption that the radiation of a body is independent of the temperature of the enclosure. The present writer drew attention to this difficulty as far back as 1881,@@1 when he pointed out that the different intensities of different spectral lines need not involve the consequence that in an enclosure of uniform temperature the energy is unequally partitioned between the corresponding degrees of freedom. When the molecule is losing energy the intensity of each kind of radiation depends principally on the rapidity with which it can be renewed by molecular impacts. The unequal intensities observed indicate a difference in the effectiveness of the channels through which energy is lost, and this need not be connected with the ultimate state of equilibrium when the body is kept at a uniform temperature. For our immediate purpose these considerations are of importance inasmuch as they bear on the question how far the spectra emitted by gases are thermal effects only. We generally observe spectra under conditions in which dissipation of energy takes place, and it is not obvious that we possess a definition of temperature which is strictly applicable to these cases. When, for instance, we observe the relation of the gas contained in a Plücker tube through which an electric discharge is passing, there can be little doubt that the partition of energy is very different from what it would be in thermal equilibrium. In consequence the question as to the connexion of the spectrum with the temperature of the gas seems to the present writer to lose some of its force. We might define temperature in the case of a flame or vacuum tube by the temperature which a small totally reflecting body would tend to take up if placed at the spot, but this definition would fail in the case of a spark discharge. Adopting the definition we should have no difficulty in proving that in a vacuum tube gases may be luminous at very low temperatures, but we are doubtful whether such a conclusion is very helpful towards the elucidation of our problem. Radia- tion is a molecular process, and we can speak of the radiation of a molecule but not of its temperature. When we are trying to bring radiation into connexion with temperature, we must therefore take a sufficiently large group of molecules and compare their average energies with the average radiation. The question arises whether in a vacuum discharge, in which only a comparatively small proportion of the molecules are affected, we are to take the average radiation of the affected portion or include the whole lot of molecules, which at any moment are not concerned in the discharge at all. The two processes would lead to entirely different results. The problem, which, in the opinion of the present writer, is the one of interest and has more or less definitely been in the minds of those who have discussed the subject, is whether the type of wave sent out by a molecule only depends on the internal energy of that molecule, or on other considerations such as the mode of excitement. The average energy of a medium containing a mixture of dissimilar elements possesses in this respect only a very secondary interest.

We must now inquire a little more closely into the mechanical conception of radiation. According to present ideas, the wave originates in a disturbance of electrons within the molecules. The electrons responsible for the radiation are probably few and not directly involved in the structure of the atom, which according to the view at present in favour, is itself made up of electrons. As there is undoubtedly a connexion between thermal motion and radiation, the energy of these electrons within the atom must be supposed to increase with temperature. But we know also that in the complete radiation of a white body the radiative energy increases with the fourth power of the absolute temperature. Hence a part of what must be included in thermal energy is not simply proportional to temperature as is commonly assumed. The energy of radiation resides in the medium and not in the molecule. Even at the

highest temperatures at our command it is small compared with the energy of translatory motion, but as the temperature increases, it must ultimately gain the upper hand, and if there is anywhere such a temperature as that of several million degrees, the greater part of the total energy of a body will be outside the atom and molecular motion ultimately becomes negligible compared with it. But these speculations, interesting and important as they are, lead us away from our main subject.

Considering the great variety of spectra, which one and the same body may possess, the idea lies near that free electrons may temporarily attach themselves to a molecule or detach themselves from it, thereby altering the constitution of the vibrating system. This is most likely to occur in a discharge through a vacuum tube and it is just there that the greatest variety of spectra is observed.

It has been denied by some that pure thermal motion can ever give rise to line spectra, but that either chemical action or impact of electrons is necessary to excite the regular oscillations which give rise to line spectra. There is no doubt that the impact of electrons is likely to be effective in this respect, but it must be remembered that all bodies raised to a sufficient temperature are found to eject electrons, so that the presence of the free electrons is itself a consequence of temperature. The view that visible radiation must be excited by the impact of such an electron is therefore quite consistent with the view that there is no essential difference between the excitement due to chemical or electrical action and that resulting from a sufficient increase of temperature.

Chemical action has frequently been suggested as being a necessary factor in the luminosity of flame, not only in the sense that it causes a sufficient rise of temperature but as furnishing some special and peculiar though undefined stimulus. An important experiment by C. Günther @@2 seems however to show that the radiation of metallic salts in a flame has an intensity equal to that belonging to it in virtue of its temperature.

If a short length of platinum wire be inserted vertically into a lighted Bunsen burner the luminous line may be used as a slit and viewed directly through a prism. When now a small bead of a salt of sodium or lithium is placed in the flame the spectrum of the white hot platinum is traversed by the dark absorption of the D lines. This is consistent with Kirchhoff’s law and shows that the sodium in a flame possesses the same relative radiation and absorption as sodium vapour heated thermally to the temperature of the flames. According to independent experiments by Paschen the radiation of the D fine sent out by the sodium flame of sufficient density is nearly equal to that of a black body at the same temperature. @@3 Other more recent experiments confirm the idea that the radiation of flames is mainly determined by their temperature.

The definition of temperature given above, though difficult in the case of a flame and perhaps still admissible in the case of an electric arc, becomes precarious when applied to the disruptive phenomena of a spark discharge. The only sense in which we might be justified in using the word temperature here is by taking account of the energy set free in each discharge and distributing it between the amount of matter to which the energy is supplied. With a guess at the specific heat we might then calculate the maximum temperature to which the substance might be raised, if there were no loss by radiation or otherwise. But the molecules affected by a spark discharge are not in any sense in equilibrium as regards their partition of energy and the word “ temperature ” cannot therefore be applied to them in the ordinary sense. We might probably with advantage find some definition of what may be called “ radiation temperature ” based on the relation between radiation and absorption in Kirchhoff’s sense, but further information based on experimental investigation is required.

7. *Limits of Homogeneity and Structure of Lines.—*As a first approximation we may say that gases send out homogeneous

*@@@l Phil. Mag.* (1881), 12, p. 261.

*@@@2 Wied. Ann.* (1877), 2, p. 477.

@@@3 lbid. (1894), 51, p. 40.