

upon carrion and fecal matter; apparently, they are likewise forced to obtain their food from unnatural sources due to lack of flowers.

Another explanation may be based on a craving of the moths for salt. It is well known that butterflies alight on people and probe about on the skin with their proboscides as if trying to absorb the free perspiration. It is commonly believed that their object is salt.

Perhaps this region shares in common with certain large areas of Brazil an absence of salt in the soil. It may be of interest to investigate the salt requirement of insects and the power of salt to attract adult insects after they have been deprived of it in the larval stage.

R. C. SHANNON

THE FUNCTIONAL FORM OF THE CONSTANT OF MASS ACTION AND ATOMIC ACTIVATION

It was shown by the writer in a previous paper (*Phil. Mag.*, 5, 263 (1928)) that the constant of mass action of an interacting gaseous mixture may be a function of the volume and masses of the elemental constituents as well as of the temperature. The differential equations of a reacting mixture were subsequently given (*Phil. Mag.*, 5, 620 (1928)) and applied to certain reactions by the help of the orthodox gas equation $pV = MRT$. In a paper that recently appeared (*Phil. Mag.*, 5, 1191 (1928)) it is shown that according to thermodynamics the gas equation should have the form $pV = M\xi RT$, where ξ is a function of the number of mols of the gas, its volume V , and absolute temperature T , which differs inappreciably from unity under ordinary conditions, but which is less than unity when the volume is very large, or the molecular concentration very small. It appears therefore that the law of mass action, as usually understood, breaks down completely if the volume of the gas is sufficiently increased. The pressure at which this begins to take place can not at present be predicted theoretically—probably it is extremely low—and it might therefore form the subject of some interesting experimental investigations.

It also follows from this result that strictly under all conditions the constant of mass action is not only a function of the temperature but also of the volume and masses of the constituents. This indicates that what happens to two molecules in a gas does not depend only on their chance of encounter, but on their previous encounters with other molecules during which they get activated for chemical change. It will therefore be of interest to see if some indirect evidence exists indicating that such activation may take place.

If the temperature of a gas is increased the spectrum emitted undergoes a change. This shows that the emission of the spectrum is associated with molecular collisions and their violence. Some experiments by Liveing and Dewar show besides in a striking way that the light emitted depends on the persistence of the effect of collision, or activation of the molecules. Thus if a small quantity of NaCl is put into a flame its spectrum shows the D lines of sodium sharply defined. On adding more salt the breadth of each line is increased, and on further addition of salt a further broadening of the lines takes place till a stage is reached at which they coalesce into one broad band.

The effect of one kind of atom on the light emitted by another is shown by the spectrum of the carbon arc containing a salt. The lines in the spectrum due to the salt are displaced when the pressure of the air is changed, showing that the effect produced in an atom of a salt molecule through collision with an air molecule persists for a longer time than the period between two consecutive collisions.

A mixture of PH_3 and air explodes if suddenly expanded beyond a certain limit. This remarkable effect was first observed by Houton de Labillardiere and studied in detail by J. V. D. Stadt, and found to be due to the oxygen present. A gaseous mixture of PH_3 and O_2 at ordinary temperatures and pressures does not interact, but if suddenly rarefied combination takes place with explosion. If the mixture is allowed to stand for some time at $50^\circ C$. a gradual decrease in pressure of the mixture takes place till a state is reached at which explosion occurs. The phenomenon possesses other peculiarities, one of which is that water vapor has a retarding effect on the explosion.

Chemical combination between molecules may be induced by ultra-violet and other radiations. The activity thus given to molecules may by contact be imparted to other molecules.

The foregoing results show that a molecule may undergo a temporary change through interaction with other molecules, and in other ways. Chemical interaction must be affected by these changes, and render the constant of mass action of a gaseous mixture in some cases appreciably a function of its volume and masses of the constituents as well as of the temperature. If the pressure undergoes a continual change, the average activation of a molecule at any instant is likely to differ in nature and magnitude from that corresponding to a state of equilibrium, an effect which is probably connected with the experiments with PH_3 described.

R. D. KLEEMAN

SCHENECTADY, N. Y.