are descendants of those that inhabited the common ancestors of man and monkeys. ROBERT HEGNER

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VELOCITY OF CHEMICAL REACTIONS¹

IT is well known that different chemical reactions progress with greatly different velocities. For examples, the oxidation and drying of linseed oil extends over a period of days, while the explosion of gasoline vapors is completed in a small fraction of a second. In most cases where velocities of reactions are recorded they are expressed as the total mass transformed per unit of time, $\frac{dc}{dt}$, and the absolute time required for the transformation of individual molecules is ignored or can not be estimated because there are very few methods for studying intramolecular mechanics and dynamics. In the case of explosions, however, data are available for the estimation of the time required for the reaction to proceed from molecule to molecule, as the following calculations will show.

When nitroglycerine explodes according to the reaction:

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$$C_3H_5(NO_3)_3 \rightarrow 12 CO_2 + 10 H_2O + 6 N_2 + O_3$$

the explosive wave travels at the rate of five miles per second through the mass.¹ It might be argued that the explosive wave precedes the course of the chemical reaction, but since the exact nature of the former is unknown, it seems reasonable to conclude that it merely measures the progress of the chemical reaction from molecule to molecule. With this assumption the following calculations can be made.

The molecular weight of nitroglycerine is 227.1 and its density is 1.6, giving a molecular volume of 141.9 cc. Assuming this volume of nitroglycerine to be in the form of a cube, each edge will be $\sqrt[3]{141.9}$ cms and will contain $\frac{13}{(6.06)(10)^{23}}$ molecules, or $(1.622)(10)^7$ molecules per linear centimeter. five miles there are $(8.047)(10)^5$ cms, so that a chain of nitroglycerine molecules five miles long, spaced as they are in the liquid, contains (1.305)(10)¹³ molecules. Since the reaction proceeds from the first of these to the last one in one second, the time required for the explosion to go from molecule to molecule is

 $\frac{1}{(1.305)(10)^{13}}$ or (7.661)(10)⁻¹⁴ seconds.

To conceive of this infinitesimal time, let us compare it to one second, which is the time of explosion of the entire mass and also approximately the lowest perceptible time unit. Making this comparison, since one year contains $(3.1536)(10)^7$ seconds, we find that 414,000 years bear the same relation to one second that one second bears to the time between successive

¹ Comey, Seventh Int. Cong., 1909, III b, 30.

explosions. In other words, if a being could take the time of a molecular explosion for his smallest perceptible time unit, then one of our seconds would bear the same relation to his time value that a geologic age does to our second.

In the above reasoning the assumption is made that a molecule of nitroglycerine explodes, sending out a wave of energy which upon striking the next molecule causes its explosion. whereupon the process is repeated: the disruption of the original molecule is assumed to be completed by the time its explosive wave has initiated the explosion of the next molecule; finally, the explosion of each molecule is assumed to be dependent upon energy received from the molecule immediately preceding. Under these conditions the time which we have calculated, namely (7.661)(10)⁻¹⁴ seconds, represents the time required for a molecule both to complete its own explosion and to initiate the explosion of its neighbor through an energy transfer. It is impossible to estimate the relative times required for these two processes: however, it is at least true that the time of the individual molecular reaction is less than the number calculated.

While at present it is impossible to follow the breaking down of such individual molecules, and although thermodynamics as yet can not treat such reaction rates, still it can be concluded that with some chemical reactions their infinitesimal times bear a ratio to the times of human experience that the latter do to geologic and astronomical times.

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