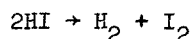


CONNECTION BETWEEN ACTIVATION ENERGY OF THERMAL DISSOCIATION OF MOLECULES IN THE GAS PHASE
AND THE BOND-BREAKING ENERGY

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None of the numerous theories of thermal decay of molecules in the gas phase [1] can still explain the character of the connection between the spectroscopic energy of dissociation and the activation energy for either diatomic or polyatomic molecules. We have therefore attempted to calculate by the Monte Carlo method the activation energy of the process of thermal dissociation of certain molecules.

Diatomic molecules. It is known that the decay of a diatomic molecule sets in when the vibrational energy in the molecule exceeds the dissociation energy. At the same time, the activation energies of molecular-decay processes vary greatly in magnitude. They can be greater than, smaller than, or equal to the values of the spectroscopically-determined dissociation energy. For example, for the thermal decomposition of hydrogen iodide, a reaction thoroughly investigated by Bodenstein,



the rate at 698°K is

$$\sim 1.11 \exp[-44000/RT] \text{ cm}^3/\text{mole-sec},$$

the activation energy at this temperature is $E \approx 44$ kcal/mole, and the energy required to break the I-I bond is 72.4 kcal/mole.

Let us assume that the collisions between molecules are elastic, and that the decay of the diatomic molecule occurs only if the kinetic energy of the molecule after the next collision becomes larger than the bond-breaking energy, and the total collision energy is distributed among the two scattered molecules in random manner.

The latter condition reflects, possible, a certain physical law, since a similar energy distribution occurs in many physical processes. For example, a random energy distribution obtains between the neutrino and the electron produced in beta decay of nuclei, between the products of the dissociation of molecules excited by electron impact, in various nuclear reactions, etc.

The problem for HI molecules at 698°K was solved in the following manner: The interval of collision energies from $E = 36.2$ kcal/mole to $E = \infty$ ¹⁾ was broken up into 10^3 parts in such a way that each part contains the same number of collisions. It was assumed that in each interval the collision energy is equal to the lowest energy in this interval. Thus, in the first variant we considered 10 collisions in each interval, in the second 5, etc.

The energies acquired by the molecules as a result of the collision was determined in

¹⁾ We allow in this case for the fact that particles with kinetic energy larger than the dissociation energy take no part in the collisions. We have shown earlier [2, 3] that the difference in the determination of the dissociation energy E_0 differs by a factor equal to $[1 - \exp(-3E_0/2RT)]$, which is small for large E_0 , as in this problem.

the following manner. We considered some interval in which the collision energy was equal to E_1 . A random number ξ was taken from the random-number table [4] and multiplied by E_1 . It was assumed that the first molecule had after the collision an energy ξE_1 , and the second $E_1 - \xi E_1$. If the quantities ξE_1 or $E_1 - \xi E_1$ were larger than $E = 36.2$ kcal/mole, then this was identified with molecule dissociation. In the opposite case, no dissociation took place. The ratio of the number of all the tried collisions to the number of collisions with molecule dissociation yielded a quantity, with the aid of which the activation energy E_0 was determined. For the HI molecule, this quantity amounted to, according to our calculations, 44.4 kcal/mole. We see that the agreement with the experimental values turned out to be good.

Calculations performed for five variants have shown that the use of 10^4 , 5×10^3 , 10^3 , and 8×10^2 collisions yields the same value of the activation energy. When these quantities are decreased, the calculation accuracy deteriorates. The remaining problems were therefore solved using the variant with 10^3 collisions, which apparently is optimal from the point of view of calculation accuracy and minimum calculation volume.

Similar calculations were performed to determine the activation energy for thermal decay of Br_2 molecules at 473°K. The value obtained was $E_0 = 36.2$ kcal/mole (as against the experimental 38).

Polyatomic molecules. The problem was solved in a manner similar to that used for diatomic molecules, except that in this case an additional condition was imposed, viz., it was assumed that the energy distribution over the bonds in the molecule is random. This condition complicated the solution to some degree, for after trying out the energies acquired by the molecules as a result of the collision, it was necessary to try also the binding energies within the molecule. It was assumed that the molecule dissociates when the tried energy for a definite bond exceeded the energy required to break this bond.

By way of an example, we calculated the activation energy of thermal dissociation of the NOCl molecule. The energy required to break the NO-Cl bond is 27 kcal/mole, and the experimentally determined value of E_0 in the 451 - 567°K interval is 26 kcal/mole. Following an analysis with 10^3 molecule collisions, the activation energy at 550°K was found to be 25.7 kcal/mole.

Thermal decays of polyatomic reactions are usually complicated by the presence of heterogeneous processes, and by a chainlike or complicated decay mechanism. The decay mechanism must therefore be known in order to perform the calculation.

- [1] E. E. Nikitin, *Sovremennye teorii termicheskogo raspada i izomerizatsii molekul v gazovoi faze* (Modern Theories of the Thermal Decay and Molecule Isomerization in the Gas Phase) Nauka, 1964.
- [2] Yu. G. Basov, Dissertation, Moscow State University, 1968.
- [3] G. M. Panchenkov and Yu. G. Basov, *Vestnik, Moscow State Univ. Chem. Series*, No.4, 90 (1968).
- [4] M. Kadyrov, *Tablitsy sluchainykh chisel* (Tables of Random Numbers), Publication of Central-Asia University, Tashkent, 1936.