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## Dissociation of Methyl Chloride on a Hot Filament\*

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An experimental method for determining directly the bond energies in some polyatomic molecules is suggested, and the experimental data obtained in applying it to the case of carbon-chlorine bond in methyl chloride are presented and discussed. The decomposition of methyl chloride and carbon tetrachloride on hot tungsten is shown to be quite inefficient.

## INTRODUCTION

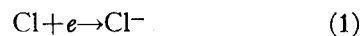
THE bond energy in the case of diatomic molecules has a unique value for it is simply the dissociation energy at absolute zero. For practically all such bond energies spectroscopists have catalogued precise values. Proceeding to the case of polyatomic molecules, the meaning of bond energy becomes less definite. If a polyatomic molecule contains only two atomic species the bond energy could be defined as being equal to the atomic heat of formation divided by the number of bonds in the molecule. For example, the energy necessary to split an  $H_2O$  molecule into one O atom and two H atoms in the ground state is 218.9 kcal. and the O—H bond energy may be assigned a value of 109.5 kcal. It is well known that this value deviates considerably from the true separation energies since 119.5 kcal. are required to remove the first hydrogen from water and 99.4 kcal. to separate the O—H radical.<sup>1</sup> When a polyatomic molecule composed of more than two atomic species is considered, an individual bond energy is usually regarded as the energy of separation of the two parts united by the bond in question; and, indeed, this seems to be almost the only rigorously definable quantity which can be used to fit the general concept.

One must distinguish between bond energy and activation energy. The latter may be larger than, but can never be smaller than, the bond energy. The bond energy we shall take to be the energy difference between the normal molecule

in the ground level and the two separated atoms or radicals in their ground level. This is the energy of the gaseous reaction at 0°K. In only a very few cases is it possible to determine directly the energy required to separate an atom or a radical from a polyatomic molecule. The desire to measure directly this energy of separation in polyatomic molecules led to work reported here.

## OUTLINE OF THE METHOD

In some experiments concerned with measuring electron affinities it has been shown that hydrogen,<sup>2</sup> chlorine,<sup>3</sup> and bromine<sup>4</sup> molecules come to complete thermal equilibrium when they collide with a hot tungsten surface. This is described by stating that the accommodation coefficient for these gases on hot tungsten is unity. In the case of chlorine, for example, all the chlorine molecules hitting the tungsten wire (about 2000°K) would decompose into atoms whereupon the reaction



would occur. By a suitable experimental arrangement it was possible to measure the concentration of Cl and the ratio of chloride ions to electrons. This permitted the calculation of the equilibrium constant and hence the energy (electron affinity) of the above reaction. Incidentally, the fraction of chloride ions in the equilibrium mixture is very small. It was noted in these experiments that stannic chloride also exhibited an accommodation coefficient of unity. In view of this it was hoped that if methyl chloride were passed

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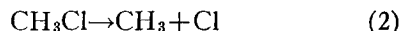
<sup>1</sup> O. Riechmeier, H. Steuftteben, and H. Pastorff, *Ann. d. Physik* **19**, 202 (1934).

<sup>2</sup> P. M. Doty, *J. Chem. Phys.* **11**, 557 (1943).

<sup>3</sup> K. J. McCallum and J. E. Mayer, *J. Chem. Phys.* **11**, 56 (1943).

<sup>4</sup> P. M. Doty and J. E. Mayer, *J. Chem. Phys.* **12**, 323 (1944).

over a hot tungsten filament at low pressure the reaction



would occur on the surface, with an accommodation coefficient of unity, followed by reaction (1). This would allow a determination of the carbon-chlorine bond energy in methyl chloride as follows.

From the measured electron affinity of chlorine (negative of the energy change) one calculates the equilibrium constant  $K_I$ , of reaction (1) over the desired temperature range. Using this relation the pressure of the chlorine atoms on the tungsten surface may be expressed as

$$P_{\text{Cl}} = \frac{1}{K_I} \frac{P_{\text{Cl}^-}}{P_e} \quad (3)$$

The experimental arrangement allows the measurement of the ratio of the chlorine ions to electrons,  $Z_{\text{Cl}^-}/Z_e$ , leaving the filament. Relating this ratio to the pressures of the species by the Langmuir-Knudsen equation changes Eq. (3) into

$$P_{\text{Cl}}(\text{atmos.}) = \frac{1}{K_I} \left( \frac{M_{\text{Cl}^-}}{M_e} \right)^{\frac{1}{2}} \frac{Z_{\text{Cl}^-}}{Z_e} = 254 \frac{Z_{\text{Cl}^-}}{Z_e} \frac{1}{K_I} \quad (4)$$

If we equate the pressure of the chlorine atoms to the pressure of the methyl radicals and use the measured pressure of methyl chloride, the equilibrium constant  $K_{II}$  for reaction (2) may be evaluated. Measuring the equilibrium constant in this way at various temperatures gives data from which the equilibrium constant of reaction (2), the bond energy, may be calculated. This procedure should in general lead to the determination of bond energies for any covalent bond formed by the halogens or oxygen since the electron affinity of these atoms has been determined by the method described.

The accommodation coefficient would have to be unity in order to evaluate reliably the bond energy by this method. In carrying out the experimental work with methyl chloride it soon became apparent, as explained later, that the accommodation coefficient of methyl chloride was far less than unity. The method of this particular application would then appear to break down; therefore, it seems at first remarkable to find that a plot of  $\log K_{I(\text{expt})}$  versus  $1/T$  is a straight line

TABLE I.

Temp. °K	Pres- sure (mi- crons)	$Z_{\text{Cl}^-}/Z_e$	$K_{II}$	$P_{\text{Cl}}(\text{atmos})$	$K_{I(\text{expt})}$
1561	10.0	0.327	$35.1 \times 10^8$	$2.72 \times 10^{-8}$	$0.423 \times 10^{-10}$
1592	10.0	0.256	19.1	3.40	0.879
1630	12.3	0.185	9.55	4.93	1.50
1722	9.6	0.200	2.00	2.54	5.10
1848	11.1	0.0654	0.295	5.63	20.9
1921	11.6	0.369	0.109	8.60	48.5

whose slope yields a reasonable value for the carbon-chlorine bond energy.

### EXPERIMENTAL RESULTS

The apparatus used in the research has been described<sup>4</sup> in a previous publication. In brief, the apparatus consists of a tungsten filament so arranged that methyl chloride at any constant low pressure may pass over the electrically heated filament. Concentric with the filament are, in order, a radial grid, a plate (collector) connected to an FP-54 Dubridge amplifier, and then, outside of the vacuum system, a solenoid. With proper positive potentials electrons and chloride ions go to the plate where they register on the galvanometer attached to the output of the amplifier. When the solenoid is activated the electrons are turned into the grid and the ion current alone is measured. The temperature of the filament is determined by its resistance found by measuring the current and voltage across the filament. A McLeod gauge is used to determine the pressure of methyl chloride.

In Table I the experimental data for methyl chloride are recorded. In the last column of the table is listed the value of

$$\frac{P_{\text{Cl}} P_{\text{CH}_3}}{P_{\text{CH}_3\text{Cl}}} = \frac{P_{\text{Cl}}^2}{P_{\text{CH}_3\text{Cl}}} = K_{I(\text{expt})} \quad (5)$$

in units of atmospheres.

The plot of  $\log K_{I(\text{expt})}$  versus reciprocal absolute temperature as shown in Fig. 1 is a reasonably straight line with a slope corresponding to 74 kcal. per mole. This may be compared with 66.5<sup>5</sup> and 73<sup>6</sup> kcal. per mole, often quoted values of carbon-chlorine bond energy.

<sup>5</sup> O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940).

<sup>6</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, 1941).

Carbon tetrachloride was then used in the apparatus to compare its behavior with that of methyl chloride and stannic chloride. Several measurements were taken at 1560°K and 10 microns pressure. The results of these measurements showed that under the above conditions the ratio of carbon tetrachloride molecules hitting the hot surface to the chlorine atoms formed was about 160. From Fig. 1 the corresponding ratio for methyl chloride at the same temperature and pressure is 920. This indicates that the carbon-chlorine bond in carbon tetrachloride is either weaker than it is in methyl chloride or that the accommodation coefficient is greater than in methyl chloride although it is still far from unity.

#### EFFICIENCY OF THE METHYL CHLORIDE DECOMPOSITION

The incomplete attainment of thermal equilibrium by methyl chloride on hot tungsten is clearly demonstrated by calculating the equi-

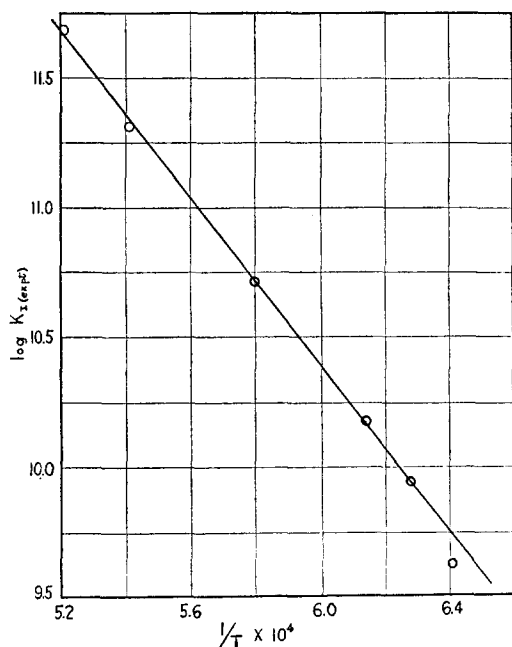


FIG. 1.

librium constant for reaction (1) at 1560°K and comparing it with  $K_{I(\text{expt})}$ . This step requires the calculation of  $\Delta S$  for reaction (1)—a calculation that can be done with moderate accuracy. The entropy of methyl chloride is given by

Stevenson and Beach<sup>7</sup> at 800°, 1000°, and 1200° from which it is easy to extrapolate to 1560°. From the work of Penney<sup>8</sup> and VanVleck<sup>9</sup> it follows that the methyl radical is a planer structure and the frequency assignment, 2850, 3182 (2), 1065, 1383 (2), was obtained by extrapolation methods using the corresponding frequencies of the methyl halides.<sup>9</sup> Using this together with the entropy of the chlorine atom the entropy change at 1560° is found to be 42.3 e.u. This is then used in the relation  $-RT \ln K = \Delta H - T\Delta S$  to obtain for  $K_I$  at 1560° a value of 0.076. When this is compared with the value of  $K_{I(\text{expt})}$  from Table I, it is apparent that the accommodation coefficient is far less than unity. In other words, this calculated equilibrium constant predicts that out of 1000 methyl chloride molecules hitting the hot filament (1560°K) 987 are decomposed according to Eq. (1), whereas actually only about 1 molecule decomposes out of the thousand.

#### CONCLUSION

An experimental method for determining directly the bond energies in some polyatomic molecules has been discussed and the experimental data obtained in the first attempt to apply the method have been presented. The method cannot be applied with certainty and simplicity unless it can be demonstrated that the molecule being investigated comes to thermal equilibrium on a hot filament. This could be shown either by measuring the energy loss of the filament which should equal the energy used in breaking the bonds plus additional translational energy or by determining at higher temperatures the electron affinity of the halogen contained in the compound.

In the case investigated here it is shown that the methyl chloride does not come to equilibrium; yet, by calculating a quasi-equilibrium constant for the decomposition, a reasonable value for the carbon-chlorine bond energy is obtained. This situation is consistent with the kinetic picture that the energy of adsorption of methyl chloride on the hot surface (probably carbon coated) is negligibly small and that only methyl chloride molecules colliding with the

<sup>7</sup> D. P. Stevenson and J. Y. Beach, J. Chem. Phys. 6, 25 (1938).

<sup>8</sup> W. G. Penney, Trans. Faraday Soc. 31, 734 (1935).

<sup>9</sup> J. H. VanVleck, J. Chem. Phys. 1, 219 (1933).

filament at a particularly favorable orientation come to thermal equilibrium with the surface. A small constant accommodation coefficient would follow from this. The postulated circumstances are reminiscent of the interpretation of the hydrogen molecule-hydrogen atom exchange reaction where the hydrogen atom must meet the

hydrogen molecule close to the line of centers for a reaction to be effected.<sup>10</sup>

The author is deeply indebted to Professor Joseph E. Mayer who suggested this problem and continually guided its progress.

<sup>10</sup> J. O. Hirschfelder, H. Eyring, and B. Topley, *J. Chem. Phys.* **4**, 170 (1936).

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## Equilibrium Distribution in Sizes for Linear Polymer Molecules

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Systems of linear polymer molecules are characterized by favorable heats of polymerization counterbalanced by unfavorable entropies of polymerization. Long chains are therefore formed and are stable at low temperatures while at sufficiently high temperature appreciable amounts of monomeric units split off. At any given temperature there exists a definite equilibrium distribution in sizes. This distribution is derived here by statistical methods and proves to be a very simple function of the heat of polymerization.

**P**OLYMERIC materials occurring in nature or produced in the laboratory display a distribution in molecular sizes. The so-called molecular weight distribution curves have been rather intensively investigated in recent years from both the experimental and theoretical viewpoints.

The theoretical studies have been based on statistical or kinetic treatments of the postulated mechanism of formation of the polymers. For example, Flory<sup>1</sup> developed the theory for size distribution in condensation polymers by a statistical treatment. Kuhn,<sup>2</sup> Mark and Simha,<sup>3</sup> Montroll,<sup>4</sup> and others developed the theory for size distributions resulting from chain degradation. Flory<sup>5</sup> and Stockmayer<sup>6</sup> have investigated the theory of size distribution in branched

polymers. Several authors<sup>7-9</sup> have discussed size distributions resulting from postulated chain mechanisms of polymerization by integrating the kinetic equations.

There have been, however, few attempts to discuss quantitatively the equilibrium distribution that must exist between polymerized and unpolymerized material as a function of temperature. It has generally been tacitly assumed that in a certain temperature range polymers will keep growing in size, restricted only by the kinetic situation, until all the monomer and short polymers are incorporated into one giant molecule.

It is, however, well known that polymers, such as polystyrene and many other chain polymers, will break down at high temperatures and give a large percentage of monomeric material. It is also known that polymers formed at high temperatures generally have a lower average molec-

<sup>1</sup> P. J. Flory, *J. Am. Chem. Soc.* **58**, 1877 (1936).

<sup>2</sup> W. Kuhn, *Ber.* **B63**, 1503 (1930).

<sup>3</sup> H. Mark and R. Simha, *Trans. Faraday Soc.* **36**, 611 (1940).

<sup>4</sup> E. W. Montroll and R. Simha, *J. Chem. Phys.* **8**, 721 (1940).

<sup>5</sup> P. J. Flory, *J. Am. Chem. Soc.* **63**, 3083, 3091, 3096 (1941).

<sup>6</sup> W. H. Stockmayer, *J. Chem. Phys.* **11**, 45 (1943); *ibid.* **12**, 125 (1944).

<sup>7</sup> G. V. Schulz, *Zeits. f. physik. Chemie* **B32**, 27 (1936); *ibid.* **B43**, 25 (1939).

<sup>8</sup> E. F. Herrington and A. Robertson, *Trans. Faraday Soc.* **38**, 490 (1942).

<sup>9</sup> Hulbert, Harmon, Tobolsky, and Eyring, *Ann. N. Y. Acad. Sci.* **44**, 371 (1943).