

However, the entropy, as calculated above, cannot be used for chemical purposes without reference to the entropy of mixing of isotopes. This entropy of mixing is $\frac{3}{2} R \ln 2$ per mole, while for the free atoms (or for HBr, for example) it is $R \ln 2$ per mole. If, by convention, the entropy of mixing of the atoms is to be excluded, the value for the entropy which we have calculated must be reduced by $\frac{1}{2} R \ln 2$. For bromine gas in its standard state this results in the value $S_{298.1}^{\circ} = 58.63$ E. U. The value is thus the same as if the additional entropy of $\text{Br}_2^{79,81}$ resulting from its additional states had been considered as a part of the entropy of mixing of isotopes. This places Br_2 on the same basis as HBr, the entropy of which has been calculated from band spectrum data by Giauque.⁷

The equilibrium constants for the dissociation of bromine at high temperatures, calculated by means of the Gibson and Heitler⁸ equation and the band spectrum constants, are in poor agreement with the experimental values of Bodenstein.⁹ The discrepancy, for which no explanation is offered, amounts to 0.15 in $\log K$ and is constant with temperature. The writer plans a further check on the entropy of bromine through the use of the experimental data for the dissociation of iodine bromide. An analysis of the iodine bromide absorption bands, which will provide the necessary spectroscopic data, is now in progress. *

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⁷ Giauque, *THIS JOURNAL*, **50**, 2193 (1928).

⁸ Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

⁹ Bodenstein, *Z. Elektrochem.*, **22**, 327 (1916).

The Recombination of Hydrogen Atoms

BY GEORGE E. KIMBALL

In a recent paper Steiner¹ has made some very interesting calculations on the rate of recombination of hydrogen atoms by triple collisions with hydrogen atoms and molecules as third bodies. He assumes that the recombination takes place in two steps: (1) the formation of an atom pair, or quasi-molecule, and (2) the stabilization of the energy-rich atom pair by collision with a third body during its lifetime τ . Throughout this work Steiner has overlooked the fact that there is another, equally probable, mechanism for the recombination. This mechanism may also be divided into two steps, but these are now: (1') collision of a hydrogen atom with a hydrogen molecule, and (2') collision of this quasi-molecule with a new hydrogen atom to form two hydrogen molecules.

Steiner finds theoretically that the diameter of a hydrogen atom in (1)

¹ Steiner, *Z. Physik. Chem.*, **B15**, 249 (1932).

is $2.5\text{--}3.5 \times 10^{-8}$ cm., and that the lifetime τ of the atom pair is $2.5\text{--}4.5 \times 10^{-14}$ sec. By comparison of the theory with experiment he then finds that the effective diameter of H_2 as a stabilizing third body must be $6.7\text{--}12.5 \times 10^{-8}$ cm. By considering the mechanism (1'), (2') we find that the required diameter of the molecule H_2 is a much more reasonable value.

The rate of process (1') is given by

$$Z_{AM} = 2 \sqrt{2\pi} N_L^2 \sigma_1^2 \left(\frac{3RT}{2M} \right)^{1/2} [C_H][C_{H_2}] \quad (1)$$

and the stationary concentration of the quasi-molecules H_3 is given by

$$[C_{H_3}] = \frac{Z_{AM} \bar{\tau}}{N_L} = 2 \sqrt{2\pi} N_L \sigma_1^2 \left(\frac{3RT}{2M} \right)^{1/2} [C_H][C_{H_2}] \bar{\tau} \quad (2)$$

The symbols used in these equations are those used by Steiner, except that σ_1 is the collision diameter for a hydrogen atom colliding with a hydrogen molecule, and $\bar{\tau}$ is now the mean life of the quasi-molecule H_3 . The number of three-body collisions of this type is then given by

$$\begin{aligned} Z_3 &= 2 \sqrt{2\pi} N_L^2 \sigma_2^2 \left(\frac{4RT}{3M} \right)^{1/2} [C_H][C_{H_3}] \\ &= 8\pi \sqrt{2} N_L^3 \frac{RT}{M} \sigma_1^2 \sigma_2^2 \tau [C_H]^2 [C_{H_2}] \end{aligned} \quad (3)$$

or, on introducing the statistical weight factor $1/4$

$$Z_3^* = 2\pi \sqrt{2} N_L^3 \frac{RT}{M} \sigma_2^2 \sigma_1^2 \bar{\tau} [C_H]^2 [C_{H_2}] \quad (4)$$

where σ_2 is the effective diameter for the collisions of H with H_3 .

We may safely assume that σ_1 is about the same as Steiner's σ_{AA} , that is, $2.5\text{--}3.5 \times 10^{-8}$ cm. The value of $\bar{\tau}$ is, however, different. In order to estimate the value of $\bar{\tau}$ we must know the potential energy curve for three hydrogen atoms. Such a curve has been calculated by Eyring and Slater (to appear in THIS JOURNAL). The theoretical curve found by these authors agrees well with the empirical curves given by Lennard-Jones.² The curve consists of the coulombic energy, less one-half the interchange energy, plus the van der Waals energy for two hydrogen atoms. There is no minimum in this curve such as that in the curve for two hydrogen atoms, and any definition of the collision distance is somewhat arbitrary. A hydrogen atom with the mean thermal energy of 600 cal. will be at a distance of 2.35×10^{-8} cm. from the hydrogen molecule when it is brought to rest. If we assume that the molecule and atom are in contact when the potential energy between them is one-tenth of its maximum value of 600 cal. a simple calculation shows that the time of contact is 6.58×10^{-14} sec.

We may now use the values we have found for σ_1 and $\bar{\tau}$ to calculate σ_2 from the experimentally found rate of reaction. If we assume that all

² Cf. Fowler, "Statistical Mechanics," Cambridge, 1929, Chap. X.

of the recombination with H_2 as the third body takes place by this mechanism we find that σ_2 lies between 3.6 and 5.5×10^{-8} cm. Since the recombination probably takes place by both this mechanism and Steiner's the true value of the diameter σ_2 is somewhat smaller.

On the other hand, if we assume σ_2 to be equal to Steiner's σ_{AM} , which is not unreasonable, we find that our mechanism will go at a rate three to six times the rate of Steiner's mechanism.

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A STUDY OF MOLECULAR ORGANIC COMPOUNDS. IV.¹ THE MOLECULAR ORGANIC COMPOUNDS OF PHENOL, THEIR PARACHORS AND REFRACTIVITIES²

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The molecular organic compounds of phenol, as a group, represent one of the simplest types. These compounds, although possessing fairly sharp melting points, decompose so readily into the original components that attempts to gain any information as to their structure by chemical methods have been unsuccessful. In the present investigation two physical methods have been applied to the study of the structure of some of these molecular compounds.

In Table I are listed the compounds which have been isolated and studied. Most of these have only previously been shown to exist by their freezing point curves. Worthy of note are the great number of them, the usual molecular ratios of 1:1 and 2:1 and the fact that the second components all contain amino groups.

The parachors as determined, both for some of the components and their molecular compounds, by the formula of Sugden³ are given in Tables II and III. Among the components it is to be noted that the observed parachors are lower than the calculated values and with increasing temperature a steady rise occurs much in the same way as with the alcohols and fatty acids.⁴ The same relation exists among the molecular compounds although the temperature coefficients and the differences between

¹ Contribution III, THIS JOURNAL, 53, 4094 (1931).

² Parts of this paper are taken from the Masters' Theses presented by David C. Hull and E. C. Erwin at the University of Tennessee.

³ Sugden, "The Parachor and Valency," George Routledge and Sons, Ltd., London, 1930, p. 30.

⁴ Sugden, Ref. 3, p. 167.