

The Decomposition of Complex Molecules at High Pressures

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(20°C) is illuminated by a Hg(Ne) discharge tube. The following bands occur in fluorescence:

Band Center (cm ⁻¹)	(2536.7)	1	2	3	4
	39421	39330	39268	39213	39152

These diffuse bands are easily visible on the negatives, and the photomicrographs show them clearly. (See Fig. 1.)

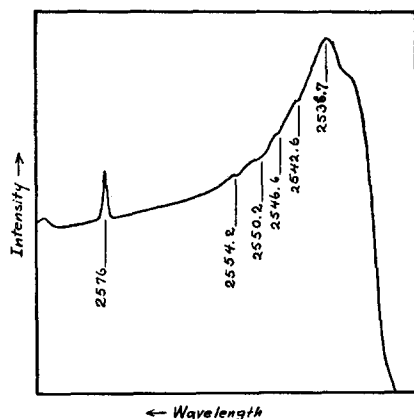


FIG. 1. Diffuse bands in CH₄-Hg mixtures near $\lambda = 2536.7\text{\AA}$.

These bands must be due to quantized states of a mercury complex with methane.² They cannot be due to Raman scattering from methane for the CH bond would produce a vibrational Raman line 3000 cm⁻¹ from the exciting line and the rotational effect would be much closer to the exciting line ($\Delta\gamma_R = 10\text{ cm}^{-1}$).³ Moreover the above bands are obtained in 30 minutes exposure. It has been shown that under the conditions of these experiments it is very unlikely that such bands are due to mercury molecules.¹

The details of this research will be discussed in a future publication.

GEORGE GLOCKLER
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University of Minnesota,
Minneapolis, Minnesota,
November 28, 1933.

² H. Kuhn and O. Oldenberg, Phys. Rev. **41**, 72 (1932).

³ R. G. Dickinson, R. T. Dillon and F. Rasetti, Phys. Rev. **34**, 582 (1929).

Raman Effect of Furane and Furfural

The following lines (cm⁻¹) were found with 4358A Hg line excitation using NaNO₂ filter:¹ *Furane*: 604, 735, 857, 990, 1055, 1139, 1381, 1486 due to the furane ring and 3165 due to the aromatic CH-bond. No line due to C=C is found. *Furfural*: 172, 497, 581, 929 and 1221 due to the alpha-substituted HOC group; 624, 758, 878, 1021, 1078, 1156, 1378, 1467 due to the furane ring. We find the C=C bond in the molecule at 1567 and the C=O bond at 1677. The aliphatic C-H bond (in HC=O) occurs at 2881 and the aromatic CH bond at 3129.

These results favor the centric formula for furane since no double bond is found. However, substitution has a great effect upon the structure of the ring itself. It is seen

that alpha-substitution will cause the appearance of a double bond C=C within the ring. Similar findings have been reported by G. B. Monino (and co-workers²) in pyrrol.

The complete details will be published later.

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B. WIENER

University of Minnesota,
Minneapolis, Minnesota,
December 12, 1933.

¹ A. H. Pfund, Phys. Rev. **42**, 581 (1932).

² G. B. Monino, *et al.*, Zeits. f. physik. Chemie **B22**, 21-44 (1933).

The Decomposition of Complex Molecules at High Pressures

The homogeneous thermal decomposition of gaseous paraldehyde to acetaldehyde has been investigated in this Laboratory from pressures of a few mm of Hg to about 18 atmospheres.^{1,2} (Above this pressure the liquid phase makes its appearance at temperatures where the rate is measurable.) It is believed that no other "simple" first order reaction³ has been studied over as wide a range of pressure and that therefore, the results will be of interest. It is found that the velocity of the reaction slowly diminishes as the initial pressure is increased, the rate constant at 254°, for example, falling from 6×10^{-4} at several mm pressure to about 3×10^{-4} at 18 atmospheres. This result has been checked by different experimental

methods and is therefore believed to be real. The following mechanism is suggested as a possible explanation which may apply generally to the first order decomposition of complex molecules.

If at an activating collision every possible energy dis-

¹ Coffin, Can. J. Research **7**, 75 (1932).

² Geddes and Coffin, Can. J. Research (In press).

³ The decomposition of ethyl ether investigated by Newitt and Vernon (Proc. Roy. Soc. **A135**, 307 (1932)) up to 17 atmospheres pressure is "complex" in that it takes place by two different mechanisms each of which involves several intermediate steps.

tribution throughout the contributory degrees of freedom of a molecule is equally probable no effect of shortened mean free time (i.e., increased pressure) on reaction rate is to be expected since the particular distribution favorable to reaction is as probable as any other. If on the other hand the distributions most probable on collision are not coincident with those favorable to reaction a definite time interval must elapse between activation and decomposition due to the fact that different distributions follow one another at a finite rate. If such be the state of affairs therefore, the longer any one activated molecule is left alone the greater is the probability that it will react; that is to say the shorter the time between collisions (i.e., before deactivation) the smaller the chance of reaction. In other words increase of pressure may be expected to retard the reaction to an extent which is dependent upon the effectiveness with which the "vital" degree of freedom is protected and which will vary inversely as a linear function of the pressure.

This effect is to be expected particularly in the case of complex symmetrical molecules such as the paraldehydes^{1, 2, 4} whose vital degrees of freedom lie well within the periphery presented by the rotating molecule to its

colliding neighbors. Unfortunately in no case is it yet possible to estimate the necessary minimum time interval between the receipt and expenditure of activation energy and to compare its order of magnitude with that of the mean free time. Times of atomic relaxation however are known to be of the order of 10^{-8} sec.—an interval certainly longer than mean free times at pressures of one atmosphere or more—and vibrational excitation and its consequences might be expected to be more sluggish than electronic. Indeed the insulators suggested by O. K. Rice⁵ (see also^{6, 7}) will account for practically any time lag required.

Other reactions are being examined for this effect.

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December 12, 1933.

⁴ Coffin, Can. J. Research (In press).

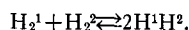
⁵ Rice, Zeits. f. physik. Chemie **B7**, 226 (1930).

⁶ Coffin, Can. J. Research **6**, 417 (1932).

⁷ Coffin, Trans. Roy. Soc. Can. 1933 (In press).

The Equilibrium Between the Three Hydrogens

While studying the dependence of the equilibrium of the hydrogen-iodine reaction on the isotopic composition of the hydrogen,¹ it has been necessary to check the composition of the hydrogen by the mass-spectrographic method.² A sample of the hydrogen iodide used in this work was decomposed by allowing it to react at ordinary temperatures with mercury. Two other samples were the hydrogen produced by the decomposition of hydrogen iodide at 397°C and at 468°C. In determining the deuterium-protium ratio, the relative abundances of the three varieties of hydrogen molecules, H₂², H¹H² and H₂¹ were determined, thus permitting a determination of the equilibrium constants for the reaction,



The equilibrium constant of this reaction has been calculated¹ and thus a check against theory can be secured.

Three samples were analyzed, check determinations being made on each. The results are summarized in Table I.

TABLE I.

Sample	T	Run	H ₂ ²	H ¹ H ²	H ₂ ¹	K (obs.)	K (calc.)
5A	25°C	1	1.00	20.8	132	3.28	3.28
		2	1.00	21.2	137	3.28	
5B	397°C	1	1.00	13.9	46.0	4.20	3.73
		2	1.00	12.6	47.4	3.35	
6B	468°C	1	1.00	2.70	1.91	3.82	3.82
		2	1.00	2.68	1.96	3.68	

The numbers given under the headings H₂², H¹H², and H₂¹ give the relative abundances of the three molecules. At the time 5B was analyzed, the apparatus was fluctuating rather badly. The cause was later traced to variations in the magnetic field. When this trouble was remedied, much more reliable results were secured for 6B. In each case the observed equilibrium constant agrees closely with the calculated values. These are secured by interpolation from the tables previously published.

Samples 5B and 6B were prepared at the temperatures recorded in the table but remained in all glass containers at room temperatures for about twenty-one days before analysis. The fact that the equilibrium constants are those characteristic of the temperature of preparation shows that the exchange reaction does not take place rapidly, and thus that this reaction is similar to the exchange reaction between hydrogen and steam investigated by Crist and Dalin.³ The time between preparation and analysis is not so long as that in the observations on liquid water and hydrogen by Oliphant,⁴ and perhaps the method of analysis is not so sensitive.

¹ H. C. Urey and D. Rittenberg, J. Chem. Phys. **1**, 137 (1933).

² W. Bleakney, Phys. Rev. **41**, 32 (1932). H. S. Taylor, H. A. Gould and W. Bleakney, Phys. Rev. **43**, 496 (1933).

³ R. H. Crist and G. A. Dalin, J. Chem. Phys. **1**, 677 (1933).

⁴ M. L. Oliphant, Nature **132**, 675 (1933).