tions at room temperature. Hence the excited molecules have ample probability of encountering oxygen molecules before they fluoresce even at a concentration of oxygen of 10^{-3} M.

It is interesting to point out that the above described theory has certain points in common with previous theories proposed by Kautsky and Weiss. Kautsky[31] explained the quenching action of oxygen by assuming an energy transfer from the excited molecule to the oxygen molecule, resulting in an excitation of oxygen from its ground state to its low ${}^1\Sigma_g{}^+$ or ${}^1\Delta_g$ state, accompanied by intersystem crossing in the organic molecule from a singlet to a triplet state. In this way the multiplicity of the system is held constant. This theory is in agreement with the present one in emphasizing the role of the triplet ground state of oxygen. But, in the present theory, the energy difference between the singlet and triplet states of the donor is dissipated as thermal energy (vibrational at first), and no excitation of the oxygen molecule to its metastable states is necessarily involved.

Weiss,[32] on the other hand, explained the quenching action by electron transfer of the type

$$D^* + O_2 \longrightarrow D^+ + O_2^-$$

with dissociation of the ions, mostly followed by subsequent chemical reaction. This theory has one feature in common with the present one in relating the quenching action of oxygen to charge transfer. However, although in aqueous solutions and with certain dye molecules the process proposed by Weiss seems to occur, such a complete electron transfer as he proposes is very unlikely in non-polar solutions, where the present theory of the mechanism of quenching seems to be much more adequate.[33]

Acknowledgments.—Technical assistance by Mr. J. M. Kliegman and Mr. R. P. Lang for the experimental part of the present work is gratefully acknowledged.

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(31) H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).

(32) J. Weiss, *ibid.*, **35**, 48 (1939); *ibid.*, **152**, 133 (1946).

(33) After the manuscript of this paper had been sent to the *Journal*, we learned of a paper by G. J. Hoijtink, *Mol. Physics*, **3**, 67 (1960), in which he discussed the effect of oxygen on the T–N bands of organic molecules. He took into account only the matrix element between the states we call ${}^3G$ and ${}^3F$, which we find to have smaller effect than the interaction of these states through ${}^3CT$. See also the reference to recent work by J. N. Murrell in ref. 22.

[Contribution from the Department of Chemistry of the University of Notre Dame, Notre Dame, Indiana]

Diffusion Kinetics in the Photolysis of Hydrogen Iodide in Hydrocarbon Solutions from 25° to −196°[1]

By J. R. Nash, R. R. Williams, Jr., and W. H. Hamill

Received April 21, 1960

The quantum yield of hydrogen from hydrogen iodide in *n*-hexane or 3-methylpentane is unity at 2537 Å. and 25°. It decreases steadily with decreasing temperature, to −196°, although the solvent is a rigid glass at the lowest temperatures. At each reduced temperature $\Phi(H_2)$ increases with increasing concentrations of hydrogen iodide, and this can be accounted for in terms of diffusion controlled intervention of HI in the geminate recombination of H + I. This effect has been correlated with the temperature-dependent free volume.

The phenomenon of diffusion-controlled recombination of free radical pairs in the liquid state within times of *ca.* 10^{-10} sec. after formation has been examined both theoretically and experimentally.[2-4] When the reaction between radical pairs competes with a radical-scavenger reaction, we have found repeatedly[5] that

$$\log (1 - W) = -P_1(5.75\ \gamma\rho_0)^{-1} + P_1P_2{}^{1/2}(3.24\ \gamma^2)^{-1}X^{1/2} \qquad (1)$$

where W is the probability of recombination in the presence of radical scavenger at mole fraction X; γ and ρ_0 represent mean free path for diffusion and initial separation in units of collision diameters; P_1 and P_2 are reaction probabilities for recombination and scavenging.

The photolysis of hydrogen iodide in non-ionizing solvents might be expected to illustrate these effects and the results of Warburg and Rump seemed to agree,[6] *viz.*, a quantum yield of hydrogen less than unity, increasing as the square root of the concentration of hydrogen iodide. In this system hydrogen iodide itself should act as a scavenger for hydrogen atoms and the mechanism to be expected is

$$HI + h\nu \longrightarrow (H + I) \qquad (2)$$

$$(H + I) \longrightarrow HI \qquad (3)$$

$$\longrightarrow H + I \qquad (4)$$

$$(H + I) + HI \longrightarrow H_2 + I + I \qquad (5)$$

$$H + HI \longrightarrow H_2 + I \qquad (6)$$

$$H + I_2 \longrightarrow HI + I \qquad (7)$$

$$I + I \longrightarrow I_2 \qquad (8)$$

Parentheses denote particles within the diffusion zone. Step 3 represents recombination of atoms by diffusion. Primary recombination (prior to diffusion) will be found to be unimportant. Step 4 represents escape of atoms into the stationary state. Step 5 represents intervention by hydrogen iodide, preventing possible recombination by diffusion and

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(1) From the doctoral dissertation of J. R. Nash, University of Notre Dame, June 1958. Presented at the 133rd meeting of the American Chemical Society, San Francisco, April, 1958. The work was carried out under the auspices of the Radiation Project, Department of Chemistry, The University of Notre Dame, supported in part by the U. S. Atomic Energy Commission under contract AT(11-1)-38 and Navy Department Contract Nonr-06900.

(2) R. M. Noyes, This Journal, **77**, 2042 (1955).

(3) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

(4) J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, This Journal, **76**, 3274 (1954); **77**, 2953 (1955).

(5) For the most recent example see R. F. Pottie, W. H. Hamill and R. R. Williams, *ibid.*, **80**, 4224 (1958).

(6) E. Warburg and W. Rump, *Z. physik*, **47**, 35 (1928).

increasing the quantum yield of hydrogen, Φ_{H_2}, which we identify with $1 - W$ of eq. 1. That is, Φ_{H_2} is expected to be less than unity because of step 3 and increasing the concentration of hydrogen iodide will raise Φ_{H_2} toward unity because of step 5.

One important complication has not been included. The hot hydrogen atom **H** is known to react efficiently in the gas phase[7,8] and will presumably do likewise in the liquid phase. This reaction will also produce H_2 or HD, with quantum yields $\Phi^*_{H_2}$, Φ_{HD}, in hydrogenous solvents RH or RD

$$\mathbf{H} + RH \longrightarrow H_2 + R\cdot \quad (9)$$

$$\mathbf{H} + RD \longrightarrow HD + R\cdot \quad (10)$$

$$R\cdot + HI \longrightarrow RH + I \quad (11)$$

and will consume 2HI per event. In order to measure and allow for this effect, it was decided to use deuterated hydrocarbon solvents because of the severe difficulties of avoiding extensive and irreproducible isotopic dilution with deuterium iodide.

Experimental

Hydrogen iodide was prepared from phosphoric acid and potassium iodide, twice distilled from trap to trap at −70°, then condensed and outgassed at −196°. It was liquefied, dried with P_2O_5 and condensed into and thereafter maintained in a storage bulb at −70°.

Phillips "pure grade" *n*-hexane and 3-methylpentane were treated first with sulfuric acid, then repeatedly with 35% fuming sulfuric acid, washed with 5% NaOH, dried with anhydrous calcium chloride and distilled through a 4 ft. glass helix-packed column at a reflux ratio of 15–1. The constant boiling middle fraction was used. Solvents showed substantially 100% transmission at 2500 Å.

3-Methylpentane was deuterated by isotopic exchange with D_2 on an alumina-supported platinum catalyst at 80°. The deuterated hydrocarbon was distilled into sulfuric acid and thoroughly shaken, then distilled onto vacuum-distilled sodium. The isotopic composition of the deuterated solvent was determined by mass spectrometric analysis and also by extensively decomposing the vapor with a Tesla discharge, with subsequent analysis of the resulting hydrogen. It was impractical to continue isotopic exchange beyond *ca.* 80% deuteration.

The light source was a Hanovia SC-2537 mercury resonance lamp in the form of a helix, supplied by a 5000-v. transformer. The secondary current was held constant at 60 ma. and the lamp was allowed at least 30 min. to reach operating temperature before a run. The temperature in the lamp housing was kept at 35° by a stream of air.

Cylindrical Vycor (Corning 7910) cells were 19 mm. o.d. and contained 5-ml. liquid samples. For measurements at 25° two cells were positioned reproducibly in a block, with 8 × 25 mm. slits and a shutter, affixed to the lamp housing. One cell contained solutions of hydrogen iodide or uranyl oxalate, the other contained gaseous hydrogen iodide at 1 atm. as a monitor. Throughout this work the output of the lamp remained constant, the average variation of the light flux amounting to 2%. Quantum yields were established with stirred solutions of uranyl oxalate[9] in the same cell and with the same geometry as those employed for solutions of hydrogen iodide. The minor long wave length component of the light flux which is measured by uranyl oxalate (but not absorbed by hydrogen iodide) was measured, using a Pyrex filter, and allowed for. Differences in interface reflections for the various types of systems also were estimated and corrections applied. The average light flux through the sample was 4.67×10^{17} quanta min.$^{-1}$.

For photolyses at reduced temperatures as low as −150° a 13 mm. o.d. Vycor cell was suspended within a vacuum-jacketed Vycor tube in a rapid stream of nitrogen which had passed through a copper coil immersed in a suitable refrigerant. The cell temperatures, measured with an iron-constantan thermocouple, differed by only 3° over the length of the filled portion and remained constant within ± 3° during a run. Because samples were viscous at low temperatures, the cell was rotated 90° every minute during photolysis. Runs at −196° were performed with the cell immersed in liquid nitrogen.

Light and heavy hydrocarbons were outgassed on the vacuum line and twice dried over freshly distilled sodium. The concentration of hydrogen iodide was determined by its pressure in the photolytic cell. It then was frozen immediately, the solvent condensed into the cell, the contents melted, frozen and pumped and the cell sealed.

Following photolysis, cells containing hydrogen iodide were sealed to the vacuum line, opened *via* break-off seals, and contents volatile at −196° were collected and measured in a modified Saunder–Taylor apparatus, then subjected to mass spectrometric analysis. Deuterated solvent was recovered by distilling the solution totally into a cell containing copper wire. After hydrogen evolution ceased the solvent was treated with clean sodium as before.

The specific volume of 3-methylpentane was measured at six temperatures between 25 and −150° with a reliability approximating 0.5%. The dependence was quite linear, corresponding to −0.110% deg.$^{-1}$ referred to the volume at 25°.

Results

Warburg and Rump found a five-fold increase in quantum yield when the solutions were stirred. No such effect was found in this work and, except for a few preliminary experiments, solutions were not stirred. Initial trials in cyclohexane were discontinued when it was found that iodine absorbs strongly in this solvent at 2537Å.[10] In contrast, iodine and hydrogen iodide have comparable extinction coefficients at this wave length in *n*-hexane, for which Φ_{H_2} at several concentrations of hydrogen iodide is given in Table I, based upon uranyl oxalate actinometry. There is clearly no trend in Φ_{H_2} with concentration of hydrogen iodide and no evidence of appreciable primary or secondary diffusion recombination (Franck–Rabinowitch recombination). Two additional runs with 0.04 *M* hydrogen iodide in *n*-hexane at the same temperature were performed, using gaseous hydrogen iodide as an actinometer ($\Phi_{H_2} = 1.00$). They led to a value of $\Phi_{H_2} = 0.90$ after correcting for interface reflections. This method involves only a comparison of pressures of hydrogen from sample and actinometer and, together with indirect evidence, indicates that Φ_{H_2} under these conditions in solution may be somewhat less than unity.

TABLE I

PHOTOLYSIS OF HYDROGEN IODIDE IN *n*-HEXANE AT 25°

Initial HI, mole/l.	Product H_2, mole × 10^6	Product I_2, mole × 10^6	Φ_{H_2}
0.030	6.34	7.0	1.00
.033	6.58	6.5	0.97
.038	5.61	..	1.00
.076	7.49	7.3	0.99
.100	9.04	9.2	0.96
.114	12.3	11.5	1.02

To obtain a measure of the relative rate constants k_6 and k_7, several runs with added iodine in 3-methylpentane (27% D) were performed at 25° and results appear in Table II.

In Table III are summarized the results of other runs at several temperatures and different concen-

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(7) H. A. Schwarz, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **74**, 6008 (1952).

(8) R. J. Carter, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **77** 6457 (1955).

(9) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

(10) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *ibid.*, **75**, 2900 (1953).

Table II

Photolysis of HI with Added I_2 in 27% Deuterated 3-Methylpentane

I_2, mole/l. × 10^3	HI, mole/l. × 10^2	Product, H_2/HD
0	3.84	11.6
1.44	7.20	9.31
2.70	3.86	7.46
1.78	2.00	6.74
2.50	1.84	5.65

Table III

Photolysis of Hydrogen Iodide in Deuterated 3-Methylpentane at Various Temperatures

Solvent, atom % D	HI, mole/l.	Φ_{HD}	Φ_{H_2}	H_2/HD	$t°$	F_{100}
27	0.026	..	..	11.6	25	0.296
68	.024	0.19	0.81	4.12	25	.288
68	.033	..	..	4.10	25	.289
68	.035	..	..	4.14	25	286
68	.088	..	..	5.08	25	241
68	.089	0.17	0.83	4.67	25	.259
68	.094	..	..	4.90	25	.250
68	.180	0.15	0.84	5.53	25	.228
76	.207	.17	.90	4.64	25	.233
76	.284	.15	.83	4.85	25	.225
79	.100	.21	.79	3.74	25	.271
76	.031	.15	.60	3.41	−25	.299
76	.210	.17	.80	4.12	−25	.257
76	.284	.17	.83	4.12	−25	.246
68	.035	.13	.44	3.35	−60	.338
68	.033	.13	.31	2.36	−100	.434
68	.021	.14	.24	1.76	−125	.438
68	.032	.13	.21	1.67	−125	.551
68	.083	.11	.22	1.98	−125	.493
68	.147	.15	.35	2.31	−125	.449
68	.180	.14	.36	2.59	−125	.414
68	.030	.12	.17	1.40	−150	.612
79	.018	..	..	0.79	−196	.708
79	.048	..	..	1.11	−196	.600
79	.106	..	..	1.16	−196	.585

trations of hydrogen iodide. The last column lists values F = moles HD/(moles HD + moles H_2), linearly extrapolated to 100% deuterated solvent, using $F = F_{100}$ (%D) where F_{100} is the value of F in 100% deuterated solvent. The first four entries are relatively free of a complicating dependence upon the concentration of hydrogen iodide and clearly support this extrapolation. Whether or not the extrapolation is fully justified is immaterial, since, in practice, it actually serves only to interpolate from 68 to 79% D. Only the first run in this table was performed with the cell in the block, as for runs reported in Tables I and II. For consistency, all other runs employed the vacuum jacket. Cells were positioned reproducibly for all runs with reported quantum yields. Quantum yields for total hydrogen at reduced temperatures are based upon a value of unity at 25° and constant geometry and light flux. Concentrations given for hydrogen iodide were those measured at *ca.* 20°. Quantum yields of H_2 and HD in 76% solvent have been normalized to correspond with results for 68% solvent. No allowance has been made for light absorption by iodine or for interference by reaction 7. Quantum yields at reduced temperatures are based upon the yield of HD from the hot H-atom reaction, for which Φ_{HD} is taken to be independent of temperature. In some runs at the lowest temperatures, formation of frost on the outer surface of the vacuum jacket could not be prevented altogether; no correction has been attempted.

Discussion

The quantum yield of H_2 in *n*-hexane and the combined yield of H_2 and HD from deuterated 3-methylpentane is substantially unity at 25° and independent of the concentration of hydrogen iodide. We conclude that there is little or no primary or secondary recombination of H and I. This is consistent with the small size of the H-atom and the relatively open structure of the solvents. For runs with added iodine (Table II), there are six parameters: k_6, k_7, Φ_4, Φ_{10} and two rate constants for H and D abstraction from solvent by thermal reaction. It can only be concluded from these results that there is qualitative evidence for $k_6 \sim k_7$, as might have been expected *a priori*. There is no reason to expect that small yields of iodine from photolysis will interfere significantly with H_2-formation, upon which the interpretation of the results of Table III depends.

The marked decrease in Φ_{H_2} with decreasing temperature is evidence for enhanced geminate recombination of H and I atoms. This interpretation is confirmed by the effect of increasing concentrations of hydrogen iodide, at and below −25°, which increases Φ_{H_2}. This effect is accounted for by step 5 in the mechanism and by equation 1.

The ratio H_2/HD increases with increasing concentration of hydrogen iodide in 68% solvent at 25°. Since the quantum yield of combined H_2 and HD is already substantially unity, this trend is interpreted as a suppression by hydrogen iodide of a thermal reaction of H-atoms with solvent. At least four parameters are involved and the data are insufficient for kinetic analysis. The effect is not to be expected at or below −25° since the activation energy is *ca.* 6 kcal./mole.[8,11]

In the absence of thermal reaction at reduced temperatures, it is plausible to assign HD formation to the hot reaction 10. Over the limited range of isotopic composition involved we may normalize results from different solvents by the approximation $\Phi_{HD} = \Phi_{HD} f_D^{-1}$ where f_D is atom fraction of D in the solvent. The average value of Φ^*_{HD} from −25 to −150° so obtained was 0.20 with an a.d. ± 0.01. There is no trend with temperature nor, at one temperature, with concentration of hydrogen iodide. It is therefore permissible to use HD as an internal actinometer. The subsequent calculations of Φ_{H_2} are based upon Φ^*_{HD} and even runs with samples immersed in liquid nitrogen, for which the solvents had glassed and cracked, can be compared reliably with others performed under different conditions. It was also important in this work to be able to measure precisely small, systematic changes in Φ_{H_2}. Since this now becomes essentially a measurement of H_2/HD, the precision is greatly enhanced.

In order to apply equation 1 to the effect upon Φ_{H_2} of increasing the concentration of hydrogen

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(11) B. de B. Darwent and R. Roberts, *Discussions Faraday Soc.*, **14**, 55 (1953).

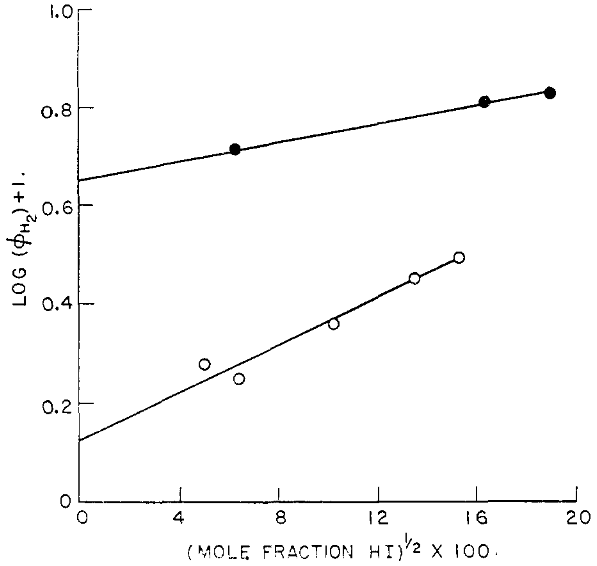

Fig. 1.—The quantum yield of hydrogen from hydrogen iodide dissolved in 3-methylpentane at 148°K. (○) and at 248°K. (●) as a function of the concentration.

iodide we must correlate 1-W, the probability that geminate recombination does not occur, with the measured quantum yields. We assume that H atoms which reacted hot would have been distributed between recombination and escape processes in the same proportion as those which failed to react hot. From the preceding mechanism $1 - W = \Phi_4/[1 - (\Phi_9 + \Phi_{10})]$ or $1 - W = 1.25\Phi_4$ if $\Phi_9 + \Phi_{10} \cong 0.20$. The individual yields are

$$\begin{aligned}\Phi_{H_2} &= \Phi_4 + \Phi_9\\ &= \Phi_4 + 0.20\,(1 - f_D)\\ \Phi_{HD} &= \Phi_{10} = 0.20\,f_D\end{aligned}$$

and their ratio is

$$\Phi_{H_2}/\Phi_{HD} = r = [\Phi_4 + 0.20(1 - f_D)]/0.20f_D$$

Since

$$\Phi_4 = 0.20[f_D(1 + r) - 1]$$

we obtain

$$1 - W = \Phi'_{H_2} = 0.25[f_D(1 + r) - 1]$$

where Φ'_{H_2} is the yield of hydrogen corrected for hot reaction.

The graphs of log Φ'_{H_2} *vs.* $X_{HI}{}^{1/2}$ in Fig. 1, for runs at −25° and −125°, give a measure of $P_1P_2{}^{1/2}\gamma^{-2}$ and of $P_1\gamma^{-1}\rho_0{}^{-1}$ at these two temperatures. The slopes and intercepts are 2.47 and 0.87 at 148°K. and 0.94 and 0.35 at 248°K. It is generally accepted that the activation energy is zero for reaction 3, and it is plausible that $P_1 = 1$. The temperature dependence of the intercept in Fig. 1 therefore is due presumably to the decrease of $\gamma\rho_0$ with decreasing temperature. The slope, which is proportional to $P_1P_2{}^{1/2}\gamma^{-2}$, also increases with decreasing temperature, and the temperature coefficient equals that for the intercept. These facts strongly suggest, although they do not establish, that the temperature dependence of the slope is related to γ^2 and not $P_2{}^{1/2}$.

Whether or not P_2 is temperature dependent, we must expect both γ and ρ_0 to decrease as the solvent contracts. Specifically, we may expect a correlation to exist between these parameters and the free volume, V_f, for which we choose the definition[12]

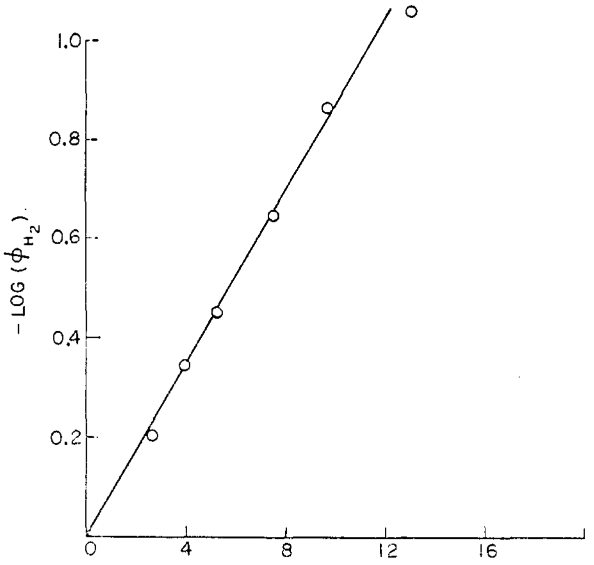

Fig. 2.—The quantum yield of hydrogen from hydrogen iodide in 3-methylpentane, extrapolated to zero concentration, as a function of the temperature-dependent free volume in terms of $\lambda = (V^{1/3} - V_0{}^{1/3})/2r$ where r is the Bohr radius.

$$V_f = \alpha^3(V^{1/3} - V_0{}^{1/3})^3$$

where V_0 is the incompressible volume and α is a constant between 1 and 2 dependent upon the type of packing. For the present purpose it is adequate to let V_0 be the linearly extrapolated volume of the solvent at 0°K. and 1 atm. This is plausible *a priori* and is supported by the fact that H atoms are stable at 4°K. in Ar and CH_4 matrices but not at slightly higher temperatures.[13,14]

Let $\gamma^* = P_1{}^{-1/2}P_2{}^{-1/4}\gamma$ and let $\lambda = (V^{1/3} - V_0{}^{1/3})/2r$, where r is the Bohr radius. From Fig. 1 $\gamma^* = 0.59$ at −25° and $\gamma^* = 0.36$ at −125°. These results, together with $\gamma^* = 0$ at −273°, are described by the empirical relation $\gamma^* = 1.14\ \lambda$. That is, if we suppose that $\gamma^* \cong \gamma$, then the mean free path for diffusion of the H atom at these temperatures approximates the cube root of the free volume in units of $2r$.

By virtue of the empirical relation $\gamma^* = 1.14\lambda$ it is now possible to predict the slope of the diffusion equation 1 at any other temperature and, from even a single measurement of Φ_{H_2}, to obtain the limiting yield, for which $\log \Phi_{H_2},\ _{X=0} = -P_1(5.75\gamma\rho_0)^{-1}$. This evaluation is free of any assumptions about the values of P_1 and P_2 or their temperature dependence. One may expect that the initial separation of H–I, following the primary act, will also be a function of the free volume. The simplest, plausible dependence would be $\rho_0 \propto \lambda$ and therefore $\log \Phi_{H_2} \propto \lambda^{-2}$ at $X = 0$. A graphical test of this relation in Fig. 2 is quite successful. From Figs. 1, 2, we obtain ρ_0 =

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[12] R. J. Buehler, R. H. Wentorf, Jr., J. O. Hirschfelder and C. F. Curtiss, *J. Chem. Phys.*, **19**, 61 (1951).

[13] C. J. Jen, S. N. Foner, E. L. Cochran and V. A. Bowers, *Phys. Rev.*, **104**, 846 (1956).

[14] B. Smaller and M. S. Matheson, *J. Chem. Phys.*. **28**, 11596 (1958).

$1.76P_1^{1/2}P_2^{-1/4}\lambda$ or $\rho_0 = 1.5P_2^{-1/2}\gamma$; this relation depends only upon the adequacy of the three relationships involved to describe the facts. In terms of our interpretation of equation 1, however, we must expect ρ_0 to be greater than γ, so that $P_2^{1/2}$ must be less than 1.5. This is consistent with the derivation of the equation, in which $P_2 \lesssim 1$ is the probability of reaction of H and HI upon encounter. For P_2 to be appreciably less than unity would make ρ_0 correspondingly greater than γ, which seems unlikely. The evidence suggests that $P_2 \sim 1$ from -25 to $-196°$.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA]

Bond Angles and the Spatial Correlation of Electrons[1]

BY R. J. GILLESPIE

RECEIVED MAY 21, 1960

Bond angles in various series of related molecules such as the hydrides and halides of Groups V and VI are discussed in terms of the spatial correlation of electron pairs that results from the operation of the Pauli exclusion principle. It is shown that a number of apparent anomalies can be understood in terms of the strong repulsions between electron pairs in the completely filled valency shells of first-row elements in contrast to the weaker repulsions associated with incompletely filled valency shells of other elements.

It has long been a problem to explain why the bond angles in the water and ammonia molecules are so close to the tetrahedral angle of 109.5° while the bond angles in phosphine, hydrogen sulfide and the other hydrides of these groups approach closely to 90°. Other related observations that have not been explained satisfactorily include the facts that, in contrast to the corresponding hydrides, the bond angle in NF_3 is smaller than in PF_3, that the fluorides of elements such as P and As have anomalously large bond angles when compared with the other halides of these elements and that the valency angle at an oxygen atom is, in a variety of molecules, considerably larger than at the sulfur atom in the corresponding molecule. It is the purpose of this paper to show that some understanding of these bond angle variations can be obtained by considering the spatial correlation of electron pairs in valency shells which arises mainly from the operation of the Pauli Exclusion Principle.

The Hydrides of Groups V and VI.—The valence-bond theory in its simplest form assumes that the bonds in molecules such as NH_3 and H_2O are formed by p orbitals on the central atom and it predicts therefore that the bond angles in these molecules should be 90°.[2] The bond angles in PH_3 and H_2S and the higher members of both groups of molecules are in reasonably good agreement with this predicted value, being generally just a few degrees larger than 90°, but the bond angles in the water and ammonia molecules are very much larger and approach the tetrahedral angle (Table I).[3,4] Repulsions between the hydrogen atoms and partial hybridization of the orbitals of the central atom have been put forward as explanations of these apparently anomalous bond angles in NH_3 and H_2O, but neither is completely satisfactory.[2,5,6] It is not altogether clear why these same factors are not also important in the higher members of each group: indeed, hybridization might be expected to become an increasingly important factor as the energy difference between s and p orbitals becomes smaller with increasing atomic number of the central atom.

TABLE I

HYDRIDES OF GROUPS V AND VI

Molecule	Bond angle	Ref.	Molecule	Bond angle	Ref.
H_3N	107.3	3	H_2O	104.5	3
H_3P	93.3	3	H_2S	92.2	3
H_3As	91.8	3	H_2Se	91.0	4a
H_3Sb	91.3	3	H_2Te	89.5	4b

An alternative explanation of the shapes of these molecules has been put forward recently based on the idea that the arrangement of all the electron pairs (bonding pairs *and* lone pairs) in the valency shell of the central atom is determined by the operation of the Pauli exclusion principle,[7,8] as a consequence of which the electrons in a valency shell arrange themselves in close pairs of opposite spin which keep as far apart as possible. For four electron pairs this leads to a tetrahedral arrangement,[7] and this is the most probable arrangement of the four pairs of electrons in the outer or valency shells of the ions C^{4-}, N^{3-} and O^{2-}. These electron pairs may to a reasonable approximation be regarded as each independently occupying one of four tetrahedrally directed equivalent segments of a sphere surrounding the nucleus and inner electron shells, which may be conveniently described as tetrahedral orbitals and are essentially the sp^3 hybrid orbitals introduced in the valence-bond theory.[2] Figure 1 shows the most

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(1) Presented at the 138th meeting of the American Chemical Society in New York, September 1960.

(2) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 108-124.

(3) L. E. Sutton, "Interatomic Distances," Chemical Society Special Publication No. 11, 1958.

(4) (a) A. W. Jache, P. W. Moser and W. Gordy, *J. Chem. Phys.*, **25**, 209 (1956); (b) K. Rossman and J. W. Straley, *ibid.*, **24**, 1276 (1956).

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