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The Para-Ortho Hydrogen Conversion by the Hydrogen Iodide Reaction and by Iodine Atoms

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The rate of conversion of para to ortho hydrogen was determined in the presence of equilibrium concentrations of hydrogen iodide and iodine. From these data, velocity constants and collision efficiencies for the conversion by iodine atoms were calculated. The results are in agreement with a theoretical equation derived by Wigner.

ON the basis of experiment there is no evidence of any appreciable difference between the velocity constant of a reaction involving ortho hydrogen and that of the corresponding reaction involving the para modification. Therefore, in any reversible reaction involving hydrogen in which the hydrogen is not in equilibrium with respect to its two modifications, the para and ortho modifications are removed by the reaction in the proportion existing in the reacting mixture, while the hydrogen formed by the reverse reaction is composed of para and ortho hydrogen in the equilibrium ratio, which is 1 : 3 if the reaction is taking place at a temperature above 250°A. If the hydrogen present at the start of a reaction contains a fraction of para hydrogen larger than the equilibrium proportion of $\frac{1}{4}$, the rate at which the fraction of para hydrogen changes can be related to the velocities of the forward and reverse reactions.

A method for determining the velocity constants of a reaction at equilibrium is thus made possible, at least in principle. A reaction suitable for experiment must satisfy several conditions: the equilibrium concentration of hydrogen must be large enough to allow the withdrawal of samples for analyses; the reaction must proceed with a moderate velocity in a temperature range below 750°A, where a thermal reaction becomes important; and the conversion reaction must not be catalyzed directly by any component of the reacting mixture.

At the inception of this investigation the hydrogen iodide reaction seemed an excellent example which satisfied these conditions. Moreover, reliable data on the velocity constants of this reaction were available and a simple and reasonable mechanism had been proposed to explain these data.

When the results of the experiments here reported had been analyzed, it was found that the values of the velocity constants of the hydrogen iodide reaction which were obtained were so much larger than those which had been obtained by Bodenstein[1] that it was necessary to look for an additional conversion mechanism. Experiments showed that the hydrogen iodide and iodine molecules had no catalytic effect. It was known that hydrogen atoms could effect the conversion of para to ortho hydrogen, but the equilibrium concentrations of hydrogen atoms at the temperatures at which the experiments had been performed were far too small to account for the large velocity constants. Similarly, any possible catalytic effect of the walls of the reaction tubes was not large enough to account for the observed rate of conversion.

The iodine atoms, the only remaining component of the reacting mixture, were tentatively considered to be responsible for the catalysis. This consideration was greatly strengthened by the appearance of a series of papers which showed, both theoretically and experimentally, that paramagnetic solids, gases and solutions are effective in catalyzing the para-ortho hydrogen

[1] Bodenstein, Zeits. f. physik. Chemie **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).

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conversion.[2] Since iodine atoms are paramagnetic, it seemed reasonable to ascribe to them the additional rate of conversion beyond that calculated from Bodenstein's data. The experimental results are consistent with this assumption.

With this assumption, it is necessary to consider a mechanism involving two processes in accounting for the observed rate of conversion of para to ortho hydrogen:

$$H_2^p + I_2 \rightarrow 2HI \rightarrow H_2^0 + I_2$$

and

$$H_2^p + I \rightarrow H_2^0 + I.$$

The rate at which para hydrogen is removed by both processes is

$$-d[H_2^p]/dt = (K_1/2)[H_2^p][I_2] + K_2[H_2^p][I]. \tag{1}$$

K_1 as used here is the velocity constant of the formation of hydrogen iodide:

$$d[HI]/dt = -2d[H_2]/dt.$$

The rate at which para hydrogen is formed is

$$d[H_2^p]/dt = (K_1'/8)[HI]^2 + K_2'[H_2^0][I]. \tag{2}$$

The factor $\frac{1}{8}$ appears in the first term of the right side of Eq. (2) because only $\frac{1}{4}$ of all the hydrogen molecules formed are of the para modification. The net rate at which para hydrogen is removed is

$$-d[H_2^p]/dt = (K_1/2)[H_2^p][I_2] - (K_1'/8)[HI]^2 + (K_2[H_2^p] - K_2'[H_2^0])[I]. \tag{3}$$

When this is divided by the total concentration of hydrogen, and the following relationships are introduced:

$$\frac{[HI]^2}{[H_2][I_2]} = \frac{K_1}{K_1'} \quad \text{and} \quad \frac{K_2'}{K_2 + K_2'} = \frac{1}{4}$$

(since $K_2 = 3K_2'$ above room temperature), then Eq. (3) becomes

$$-dN_p/dt = (K_1/2)[I_2](N_p - \tfrac{1}{4}) + 4K_2'(N_p - \tfrac{1}{4})[I], \tag{4}$$

in which N_p is the mol fraction of para hydrogen. When Eq. (4) is integrated, there is obtained

$$N_p = \tfrac{1}{4} + (N_{p_0} - \tfrac{1}{4}) \exp\{-((K_1/2)[I_2] + 4K_2'[I])t\}. \tag{5}$$

With N_p and t measured, N_{p_0} known from the temperature of the charcoal catalyst, K_1 obtained from Bodenstein's data, and $[I]$ calculated from $[I_2]$ by the use of the equilibrium constant of the reaction $I_2 \rightleftharpoons 2I$, this equation can be solved for K_2, the velocity constant for the para to ortho hydrogen conversion:

$$K_2 = -\frac{3}{4[I]}\left\{\frac{\ln(4N_p - 1)}{t} + \frac{K_1}{2}[I_2]\right\}. \tag{6}$$

At the highest temperature used an additional process, due to the equilibrium concentration of hydrogen atoms, is effective in converting para to ortho hydrogen:

$$H + H_2^p \rightarrow H + H_2^0; \quad -dN_p/dt = K_3(N_p - \tfrac{1}{4})[H].$$

The inclusion of this process leads to the integrated equation

$$N_p = \tfrac{1}{4} + (N_{p_0} - \tfrac{1}{4}) \exp\{-((K_1/2)[I_2] + 4K_2'[I] + K_3[H])t\}. \tag{7}$$

The values of $K_3[H]$ were determined from blank experiments in which 1 : 1 para-ortho hydrogen only was heated.

[2] Farkas and Sachsse, Zeits. f. physik. Chemie **B23**, 1 (1933). Wigner, ibid. 28 (1933). Taylor and Diamond, J. Am. Chem. Soc. **55**, 2613 (1933). Taylor and Eyring, Proc. Am. Phil. Soc. **72**, 255 (1933).

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Experimental

Mixtures of equilibrium proportions of 1 : 1 para-ortho hydrogen, hydrogen iodide and iodine were sealed into Pyrex reaction tubes, heated at a constant temperature for a measured length of time, and then rapidly cooled. The hydrogen iodide and iodine were frozen out with liquid nitrogen, each tube was opened and the hydrogen was analyzed for its ortho-para composition in a thermal conductivity cell.

Commercial electrolytic hydrogen was purified by passing it through a heated palladium tube, *F* in Fig. 1. C.P. iodine was resublimed and stored over phosphorus pentoxide. To obtain dry hydrogen iodide, a colorless concentrated solution of hydrogen iodide was dropped on phosphorus pentoxide in an evacuated generator *I*, and the gas was passed through a phosphorus pentoxide trap.

The form of the thermal conductivity cell adopted was essentially that used by other investigators. The principal difference lay in the fact that the spreader for the heated wire was held by a glass rod attached at the top of the cell to the electrode seal. The resistance of the cell wire (a 0.01 mm Wollaston wire) was measured by a very sensitive Wheatstone bridge. The wires used had resistances in the range 80–115 ohms at operating temperature.

The furnace was of the resistance type, with a large heat capacity. An iron jacket surrounded the reaction tube. Because of its high thermal conductivity this metal lining made the temperature of the reaction zone of the furnace uniform to within 1°. The temperature was measured with a calibrated chromel-alumel thermocouple and a potentiometer. It was possible to hold the temperature constant to within 1°.

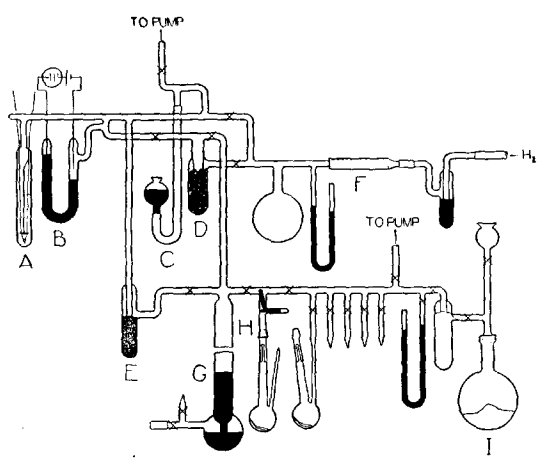

Fig. 1. Vacuum line. *A* is the thermal conductivity cell, *B* is a mercury manometer, *C* is a mercury piston, *D* is the activated charcoal catalyst, *E* is a trap, *F* is a palladium tube, *G* is a Toepler pump, *H* is an interchangeable ground glass joint and *I* is the hydrogen iodide generator.

The form and dimensions of the reaction tubes were chosen to give a volume large enough for duplicate analyses of the hydrogen, together with a small length to insure uniformity of temperature throughout the tube. A vacuum-tight connection was made between each of the reaction tubes and the vacuum line by means of an interchangeable ground joint *H*. The neck of each tube was closed off by a thin glass bubble which could be broken by releasing a weight with a small solenoid. A piece of capillary tubing in the side arm which was used to fill each reaction tube made negligible the effect of diffusion to the heated area when the tubes were sealed off.

The calculated equilibrium amounts of iodine were contained in capsules with capillary tips. To prepare one of these capsules an open capillary tip was drawn on a piece of 2 mm tubing. After this piece of tubing was weighed, an approximate amount of iodine was introduced into it and it was purged thoroughly with dry hydrogen while the capillary was kept in contact with solid carbon dioxide to prevent excessive loss of iodine. With the hydrogen flowing, the capillary and the other end of the capsule were successively sealed a few centimeters from the iodine. The capsule was weighed together with the rest of the original piece of tubing, and the weight of the iodine was obtained by difference. A capsule was sealed into each reaction tube (except those used for blanks); the tubes were sealed on the line and were evacuated to a pressure of 10^{-4} mm or lower.

A 1 : 1 para-ortho hydrogen mixture was obtained by placing liquid nitrogen around the tube *D* which contained degassed activated charcoal, and allowing the charcoal to adsorb hydrogen until the pressure above the charcoal was about 20 cm. After an interval of an hour, some of the hydrogen was pumped away; then the reaction tubes were filled to a desired pressure

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of 1 : 1 para-ortho hydrogen by means of the Toepler pump G. The stopcocks on the tubes were closed, the hydrogen remaining in the line was pumped out, and hydrogen iodide was added to each tube until the desired total pressure was reached. An effort was made to have each stopcock attached to a reaction tube open for as short a time as possible to prevent diffusion of hydrogen. The reaction tubes were sealed off at a previously prepared constriction and the capillaries of the iodine capsules were broken by shaking the tubes. The tubes were then ready to be placed in the furnace.

After a tube was heated for a measured length of time, it was removed from the furnace and cooled as quickly as possible in the air current of an electric fan. The grind on the tube was fitted into the one on the line H and the line was evacuated while the reaction tube was immersed in liquid nitrogen to condense the iodine and hydrogen iodide. The breaker was released to open the tube and a sample of hydrogen was pumped with the Toepler pump into the thermal conductivity cell A through the trap E immersed in liquid nitrogen to prevent traces of iodine and hydrogen iodide from reaching the cell. The pressure of hydrogen in the cell was adjusted with a mercury piston to a value of approximately 40 mm, which was reproducible to 0.02 mm. The thermal conductivity cell was always covered with liquid nitrogen, the level of which was kept constant. After the current had been regulated, the resistance of the cell was measured.

Results

With the final composition of the hydrogen N_p determined this value could be substituted in Eq. (6), and since the other quantities were known, K_2 could be calculated. By using the average value of K_2 for each temperature, the mol fraction of para hydrogen could be recalculated and compared with the experimental value. The data obtained are compiled in Table I, from which the agreement between the calculated and observed values can be seen.

No changes were noticed in the blank experiments carried out at a temperature of 716°A or lower.

The errors in the pressures of hydrogen and hydrogen iodide were less than 0.5 percent. The volumes of the reaction tubes were measured to within 1 percent. The iodine was weighed by difference; the weighing error varied from 0.3 to 4 percent. An error in the concentration of iodine did not cause an equal error in the observed value of N_p, however, because of the logarithmic relationship between the iodine concentration and N_p and the fact that the equilibrium concentration of iodine is established during the heating period. The intense heat required to seal off the tubes caused a slight amount of conversion which was reduced to a negligible value by the use of capillary tubing in the side arm of the reaction tubes. The temperatures of the reaction tubes were within one degree of the reported temperatures.

A possible source of error is the catalytic effect of the Pyrex walls of the reaction tubes. H. A. Taylor[3] found a relatively small variation in the decomposition velocity constant with surface-volume ratio, using crushed glass to increase the

TABLE I.

I_2 (moles/cc) 10^7	Time (sec.)	N_p Calc.	N_p Obs.
Temperature 753°A Mean constant 9960 cc/mol sec.			
2.54	7860	0.289	0.283
3.33	7500	.281	.292
1.95	5120	.340	.326
1.14	4380	.383	.392
1.88	5280	.339	.351
2.84	4500	.329	.326
3.84	6500	.284	.284
0.91	5480	.376	.368
Blank	7200		.466
Blank	7200		.446
Blank	7200		.462
Temperature 716°A Mean constant 3690 cc/mol sec.			
4.27	7020	0.407	0.417
6.92	7220	.377	.375
10.3	7770	.343	.348
6.18	8080	.374	.376
7.60	9200	.348	.343
10.4	7730	.343	.348
6.12	9800	.358	.358
4.79	6260	.409	.407
10.3	7770	.343	.348
Temperature 693°A Mean constant 2600 cc/mol sec.			
6.20	9660	0.424	0.426
7.34	13610	.391	.402
6.94	5770	.448	.439
7.46	8030	.428	.429

[3] H. A. Taylor, J. Phys. Chem. **28**, 984 (1924).

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surface. In the present work, however, the surface-volume ratio was smaller than any in Taylor's work, approximately 1.4 cm^{-1}, and the walls were smooth. That the condition of the wall had no marked effect on the reaction velocity was shown by a comparison between reaction tubes which had not been cleaned carefully and those which had been cleaned with hot $K_2Cr_2O_7-H_2SO_4$ solution just before sealing off.

Discussion

It can be seen that the use of the mean velocity constant leads to calculated values of N_p which are in agreement with the data. The consistency of the data can also be judged from the deviation from the mean of the individual values of the velocity constant which is less than 15 percent with the exception of two values, one of which deviates by 30 percent, the other by 25 percent. In view of the fact that each determination involves a considerable number of manipulations and that the desired constant is obtained as a difference, this degree of concordance is as high as could be expected.

From the values of the velocity constants, the collision efficiency can be calculated for each temperature. In particular, the collision efficiency for the para to ortho hydrogen conversion can be obtained by dividing the product of the corresponding velocity constant, the concentration of para hydrogen molecules and the concentration of iodine atoms by the total number of collisions between para hydrogen molecules and iodine atoms. The calculation of this total number of collisions depends on an assumed value for the closest distance of approach between a hydrogen molecule and an iodine atom, since this quantity has not been determined. With an assumed distance of approach of 2A, the collision efficiency for the para to ortho hydrogen conversion is found to be 9.4×10^{-12}, 13×10^{-12} and 34×10^{-12} at 693, 716 and 753°A, respectively.

It is of interest to compare these values with some obtained from a theoretical equation of Wigner[4] and with experimental data obtained by Farkas and Sachsse[4] for other reactions. By an application of quantum mechanics, Wigner has derived expressions for the probability of a para to ortho conversion in those collisions in which the required energy is present:

$$P_{j\to j+1}=1.1\times10^{-17}\frac{\mu^2}{a^6T}\frac{j+1}{2j+1}$$

$$P_{j\to j-1}=1.1\times10^{-17}\frac{\mu^2}{a^6T}\frac{j}{2j+1}$$

in which μ is the magnetic moment of the paramagnetic particle (in this case the iodine atom), a is the effective minimum distance of approach, T is the absolute temperature, j is the rotational quantum number of the hydrogen molecule, and the factor 1.1×10^{-17} contains only universal constants and the square of the magnetic moment of the proton.

The normal state of the iodine atom is $^2P_{3/2}$. Its magnetic moment, calculated from the expression $\mu=[g^2j(j+1)]^{\frac{1}{2}}$ (g, the Lande splitting factor) is 2.58 Bohr units or 2.38×10^{-20} gauss cm. It is unnecessary here to consider any excited state of the iodine atom, since the fraction of atoms in the first excited state, $^2P_{1/2}$, is only 3×10^{-7} at 750°A.

In the complete absence of any information about the quantity a, we may assume, with Farkas and Sachsse, a value of 1A. It should be observed that this distance need not coincide with the kinetic theory distance of closest approach, usually obtained from viscosity data, which was used to calculate collision efficiencies from experimental data.

When these values are introduced into Wigner's expressions and the effective value of the factor involving j is obtained by summing over five[5] rotational states of the hydrogen molecule, the probability, and thus the collision efficiency, of para to ortho transitions is found to be 6.2×10^{-12}, 6.0×10^{-12} and 5.8×10^{-12} at 693, 716 and 753°A, respectively.

It is evident that so far as the order of magnitude of the collision efficiency is concerned, the theory is in agreement with the experimental data. However, the theoretical equation of Wigner requires a very small negative temperature coefficient, while the temperature coefficient of collision efficiency obtained experimentally has a small positive value. It is not surprising that the

[4] See reference 2.

[5] The fraction of molecules with a j value of 5 is only 0.035.

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agreement is less good at the higher temperatures since the theory was designed to fit a lower temperature range.

The results of Farkas and Sachsse for a number of paramagnetic substances are also in agreement with Wigner's equation. In particular, the order of magnitude they obtained for the collision efficiency of NO(2×10^{-12}) is approximately the same as that found in the present work with iodine atoms. They, too, found a positive temperature coefficient in the temperature range 600–750°A.

It might be worth while to mention at this point a confirmation of a result obtained by a previous investigator. A. Farkas,[6] in the study of the thermal conversion of para to ortho hydrogen, determined values for the velocity constant for this reaction which have a small temperature coefficient and from which the extrapolated value at 750°A is approximately 9×10^{11} cc/mol sec. From the blank experiments at 753°A, $K_3[\mathrm{H}]=2.6\times10^{-5}$. The hydrogen atom concentration at this temperature calculated from the equilibrium constant is 2.3×10^{-17} mols/cc. From these data the value of K_3 is

$$(2.6\times10^{-5})/(2.3\times10^{-17})=11\times10^{11}$$

which confirms the values obtained by Farkas.

[6] A. Farkas, Zeits. f. physik. Chemie **B10**, 419 (1930).

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