

TABLE V
CHARACTERISTIC PARAMETERS FOR HIGH POLYMERS

	T/\bar{T}	$N_{AV}^*/s/n, cc./mole$	$N_A \epsilon^*/s/n, kcal./mole$	n/s	$3c/n$
Polymethylene	5402	15.8	0.17	2.7	3/6.3
Polytetrafluoroethylene	4791	22.4	.15	2.5	3/6.4
Polystyrene	6450	46.8	.64	8.9	3/2.0
Polydimethylsiloxane	4004	33.8	.40	4.7	3/2.0

The relative magnitudes of the van der Waals volumes v^* are as expected. From Table V we conclude, for example, that 5 CH_2^- units are approximately equal in size to one $\text{CH}-\text{C}_6\text{H}_5^-$ unit. Similarly, the maximum energies of attraction represented by column 4 indicate that about 6.5 CH_2^- units are equivalent to one $\text{CH}-\text{C}_6\text{H}_5^-$ unit. Also, the position of the fluorocarbons is expected. The difference between dimethylsiloxane and methylene is consistent with the somewhat lower observed c.e.d. and considerably larger V^* for the former. The values in column 5 which are the result of equating intra- and intermolecular distances between segments on the effective lattice are reasonable.

The differences and similarities in the last column are noteworthy. We have previously commented on the reasons for the large values for polystyrene and polydimethylsiloxane. It is, furthermore, interesting to note the similarity between polymethylene and polyperfluoromethylene, which is contrary to the common characterization of the latter as more rigid. An interpretation of fluorine nuclear spin resonance experiments on perfluorocyclohexane, however, suggests⁴⁴ that conformational isomerizations in noncyclic fluorocarbons above C_2F_6 are facilitated by a 1,3-F-F interaction which would manifest itself in an increased c -value

(44) G. V. D. Tiers, *Proc. Chem. Soc.*, 389 (1960).

Moreover, we are comparing here frequencies of small amplitude oscillations rather than rotation barriers. The c -values for polymethylene are in approximate accord with deductions from root-mean-square chain dimensions.⁴⁵

It will be seen in Fig. 4 that the phosphonitrilic fluorides satisfy the principle of corresponding states obeyed by the other systems in spite of their markedly different structure. Their detailed characterization must await data on the high polymer and additional oligomers. Similarly, in Fig. 3 the polyoxyethylenes do not appear different from the other series. The volume shifts are, as always, linear in n and yield the least square result $N_{AV}^*/B = 12.02$, $A = 0.409$. The temperature shifts, however, vary but slightly with n . For $n = 4$, $T/\bar{T} = 4855$ and for $n = 10$, $T/\bar{T} = 4903$, and finally $(T/\bar{T})_\infty = 5760$. While it is formally possible to represent these results by eq. 7, the parameter values obtained are meaningless in terms of the underlying lattice model. It is suggestive to ascribe this behavior to hydrogen bond formation between terminal hydroxyl groups, which must be particularly important in the low molecular weight range. Two factors are significant. First, the actual and apparent molecular weight, resulting from association, differ significantly. Second, copolymeric structures are formed, which change composition with increasing molecular weight. These effects can be eliminated by means of volume-temperature data for the methylated oligomers in combination with results for the high polymer.

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(45) W. J. Taylor, *J. Chem. Phys.*, **16**, 257 (1948).

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Ortho- and Paratritium¹

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The conversion of ortho-paratritium in the homogeneous gas and solid phases has been studied. The extent of conversion was measured by a heat conductivity cell cooled with liquid neon to 27.2°K. The gas phase conversion was observed at 27.2°K., at which temperature the equilibrium concentration is approximately one part ortho- to one part paratritium. The role of an ion mechanism in this conversion is discussed. In the solid phase, the rate of conversion of tritium exceeds that of hydrogen by two orders of magnitude. Consideration of the kinetic data for hydrogen, deuterium, and tritium in the solid phase and adsorbed phase indicates that a more favorable energy transfer process may be operative for tritium and deuterium.

Introduction

Because of the existence of the ortho and para modifications of hydrogen, not only the different physical properties of these modifications but also their interconversion reactions by the atomic mechanism $\text{H} + \text{H}_2(\text{para}) \rightarrow \text{H} + \text{H}_2(\text{ortho})$ ^{2,3} and by ionizing radiation^{4,5} became available for study. After the discovery of deuterium,⁶ in addition to the ortho-paradeuterium

(1) The research reported in this paper has been sponsored by the National Aeronautics and Space Administration, Washington, D. C. Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1963.

(2) (a) K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 113 (1929); (b) A. Farkas, *Z. Elektrochem.*, **36**, 782 (1930); *Z. physik. Chem.*, **B10**, 419 (1930).

(3) K. H. Geib and P. Harteck, *ibid.*, *Bodensteinband*, 849 (1931).

(4) P. C. Capron, *Ann. soc. sci. Bruxelles*, **55**, 222 (1935).

(5) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479, 570 (1936).

(6) H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Phys. Rev.*, **39**, 164, 864 (1932).

system, the chemical exchange between hydrogen and deuterium could be studied. At first glance, one might be therefore lead to believe that very little new or basic knowledge could be acquired by investigating the ortho-paratritium system. Actually it appears that refined kinetic understanding may be achieved by the investigation of the ortho-paratritium system and mixtures of tritium with hydrogen and deuterium which could not be accomplished with hydrogen and deuterium alone.

In an earlier paper⁷ the conversion of normal tritium into paratritium was reported using a coconut charcoal as a catalyst. The conversion of the normal tritium (three parts ortho- and one part paratritium) was made at liquid neon temperature (27.2°K.), obtaining the equilibrium concentration of approximately 50% paratritium. By cooling the charcoal with liquid

(7) E. W. Albers, P. Harteck, and R. R. Reeves, *Z. Naturforsch.*, **18a**, 197 (1963).

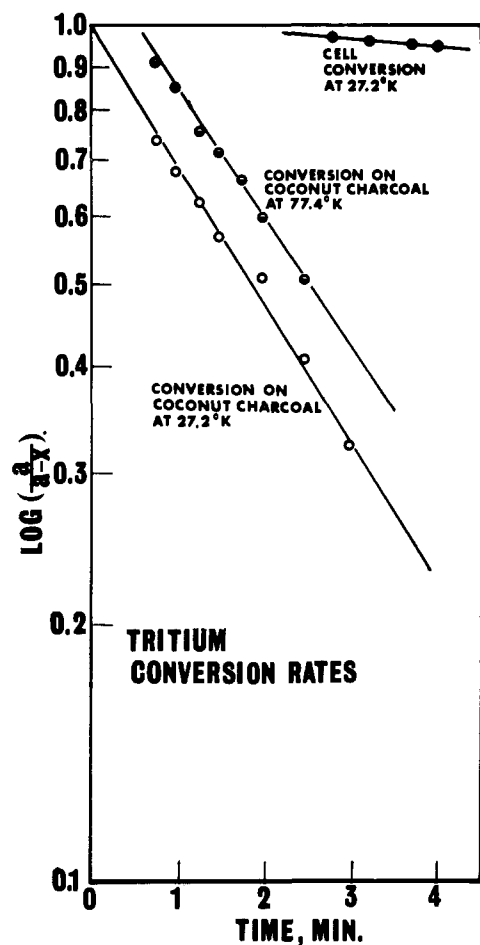


Figure 1.

helium, practically 100% paratritium could be obtained (see Table I). The concentration of paratritium was measured by the heat conductivity method of Bonhoeffer and Harteck.^{2,8} The measured forward and reverse processes at the boiling point of liquid neon and the boiling point of liquid nitrogen gave half lifetimes on coconut charcoal of 0.92 and 1.0 min., respectively (see Fig. 1). As will be discussed below, this was an order of magnitude faster than expected when compared with the rate of conversion of normal hydrogen on the same charcoal under identical conditions.

TABLE I
EQUILIBRIUM ORTHO-PARATRITIUM CONCENTRATIONS^a

T, °K.	Ortho, %	Para, %	T, °K.	Ortho, %	Para, %
0	0.0	100.0	30	56.7	43.3
5	0.0	100.0	40	66.8	33.2
10	2.8	97.2	50	71.3	28.7
15	16.4	83.6	75	74.5	25.5
20	33.8	66.2	100	74.9	25.1
25	47.4	52.6			

^a This table may also be used to compute the ortho-paratritium equilibrium concentration by multiplying the above temperatures by a factor of three.

Conversion was also obtained without a catalyst by freezing the tritium with liquid helium. This solid phase conversion occurred with a 17-min. half lifetime which exceeded the expected rate by two orders of magnitude.

Since tritium is radioactive and emits β -particles with a half-life of 12.5 years⁹ and an average energy of 5.69 kev., the possibility of β n reactions must be

(8) K. Bonhoeffer and P. Harteck, *Sitzber. Preuss. Akad. Wiss.*, **103**, (1929); *Naturwiss.*, **17**, 182 (1929).

(9) L. Alvarez and R. Cornog, *Phys. Rev.*, **56**, 613 (1939); **58**, 197 (1940).

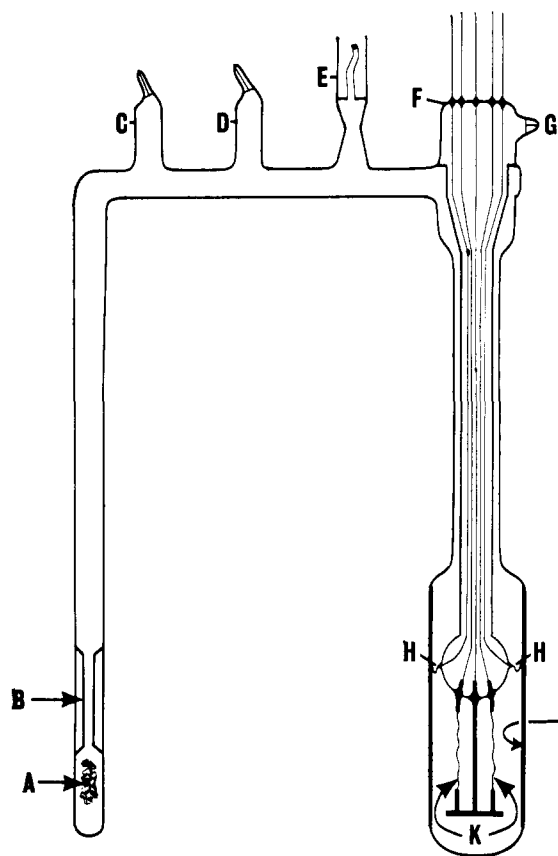


Figure 2.

considered for the conversion of ortho- and paratritium. As will be shown, while the ions do not play an important part in the ortho-para conversion on charcoal, they cause conversion in the gas phase. The effect of the ions on the solid conversion needs to be investigated further.

Experimental

In the conversion experiments of normal hydrogen to parahydrogen, measurements could be made each time with a fresh charge of hydrogen which was then discarded. Because of the radioactive nature of tritium, however, it was not possible to follow exactly this same technique. Instead a sealed Pyrex apparatus was fabricated as a single unit within which one could convert the tritium to paratritium and back again to normal tritium, measuring the degree of conversion by the heat conductivity method in the closed system as used by Bonhoeffer and Harteck.⁸

In order to study the effect of ions in the gas phase a modified apparatus was constructed where an electric field could be applied within the cell. In Fig. 2 a schematic drawing is shown for this arrangement. Bulb A contains approximately 0.5 g. of coconut charcoal. As before a 1 mm. capillary section B was incorporated to minimize back diffusion. The septums C, D, and E were used for baking out, filling, and final disposal of the tritium. Septum G shown in the sealed condition was used for evacuating the space containing the 38-gage copper lead wires. The region noted by F simply indicates the physical arrangement which proved to be practical for the five 22-gage nickel leads. Number 38 gage copper leads were then soft soldered to their respective nickel leads at the top and bottom of this section. The filaments labeled K were 2- μ diameter platinum Wollaston wires. Only one wire was used during measurements; the second was a spare since we were working with a sealed system.

In order to produce an electric field within the heat conductivity cell it was plated with two electrodes by depositing platinum metal on the inside wall in two strips 12.5 cm. \times 7 mm.

The heat conductivity cell described previously⁷ was later modified, replacing the 22 gage tungsten with 38 gage copper wires and 2- μ Wollaston wire as mentioned above for the study of ion removal in an electric field. The new arrangement was identical with that in our original paper except that the heat conductivity cell was an exact duplicate of that in Fig. 2 without the two additional electrodes (platinum strips) for maintaining an electric field.

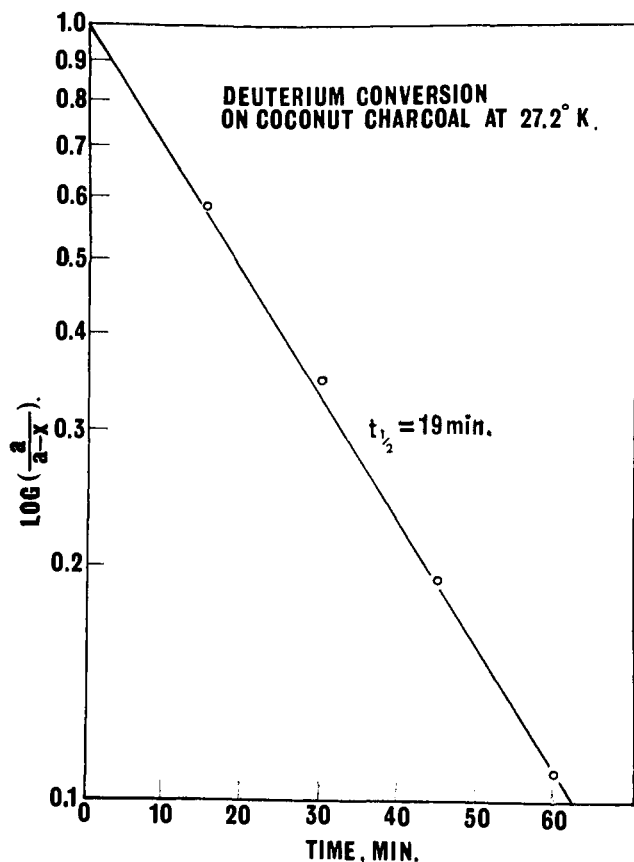


Figure 3.

At the low pressures used in this paper the heat conductivity cell operated also to a certain extent as a Pirani gage, which means that it will be sensitive to pressure changes as will occur when the level of the liquid neon decreases or if the room temperature changes. This becomes important if transformation phenomena are investigated which occur over a longer period of time since slight changes of the liquid neon level or changes in room temperature will correspondingly vary the pressure, effecting the reading of the gage and therefore care must be taken to avoid undue errors.

Results and Discussion

Conversion on Coconut Charcoal.—The conversion on coconut charcoal was reported in the previous paper. It is advisable, however, to summarize here pertinent aspects in order to introduce the discussion of the work reported in this paper.

Since the half lifetime for the conversion of tritium was unexpectedly faster, compared with that for the conversion of hydrogen, three possible reasons appeared likely: (a) Because of the difference in zero point energy, the average interaction distance between a tritium molecule and the surface of the charcoal may become affected. (b) While in the adsorbed state, the ions produced by the β -decay of tritium would be sufficiently mobile to enhance the conversion by a chain mechanism. (c) Compared with hydrogen, the smaller difference in rotational quanta for tritium between the $J = 1$ and $J = 0$ states may facilitate the conversion of tritium in the adsorbed and solid states.

As we have shown, the contribution from (a) can be at the most minor; and the semiconducting property of charcoal would negate the ion process mentioned in (b). Consequently, the ease of energy transfer in (c) appears probable. Moreover, subsequent to our first paper, the conversion of deuterium was studied since it offered an opportunity to study a system which was intermediate between hydrogen and tritium as well as free from the influence of ions.

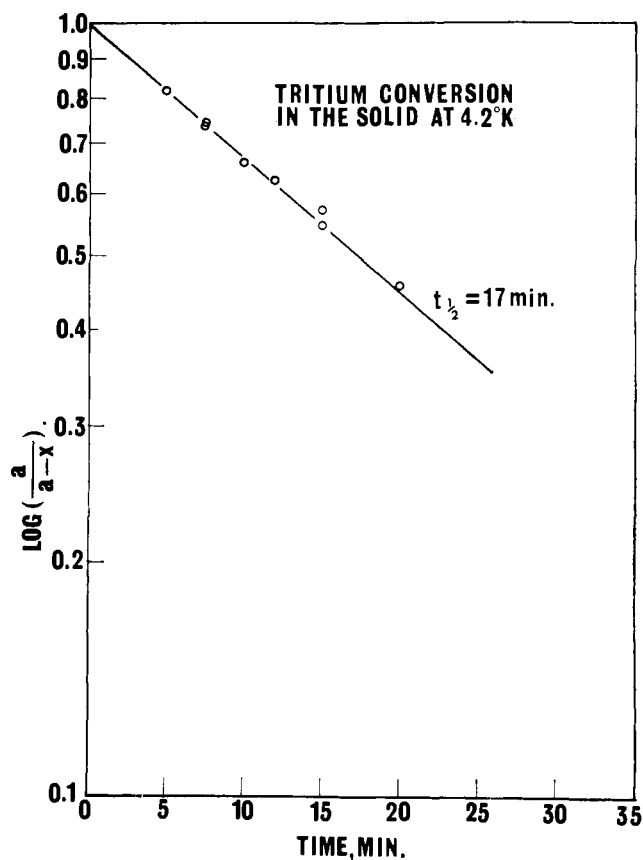


Figure 4.

As will be shown below, the deuterium conversion in the adsorbed state under identical conditions was faster than anticipated too.

Additional information was obtained by studying the conversion rate of deuterium on the same charcoal under identical conditions. In Fig. 3 the kinetic data for the conversion of deuterium are reported; the graph represents the fractional decrease in paradeuterium normalized between room temperature and 27.2°K. as a function of time. The measurement of the slope yields a half lifetime of 19 min. If one considers the half lifetime for hydrogen, deuterium, and tritium with due allowance being made for difference in the nuclear magnetic moment an interesting relationship becomes apparent. In Table II it may be seen that deuterium and tritium convert four and eight times faster, respectively, compared to hydrogen under identical conditions. The marked departure of deuterium and tritium may very well be due to a more favorable energy transfer.

Conversion in Solid Phase.—Bonhoeffer and Harteck⁸ have shown that while the ortho-para conversion of normal hydrogen does not occur on freezing or melting it proceeds in the liquid phase at a rate of 1%/hr. These studies on the liquid and solid phases clearly established the existence of freely rotating molecules. Subsequently, exact measurements for the transformation in the solid phase were made by Cremer and Polanyi.¹⁰ Recently, Motizuki and Nagamiya¹¹ have treated the conversion in the solid theoretically. They find nearly exact agreement between their calculated half lifetimes and the half lifetime of 60 hr. measured by Cremer and Polanyi, a value which is 210 times as large as the half lifetime value of 17 min. for the solid phase conversion of pure tritium reported in Fig. 4.

(10) D. Cremer and M. Polanyi, *Z. physik. Chem.*, **B21**, 459 (1933).

(11) K. Motizuki and T. Nagamiya, *J. Phys. Soc. Japan*, **11**, 93 (1956) **11**, 654 (1956); **12**, 163 (1957).

The rate of conversion varies directly with the mass of the converting species; therefore the conversion of tritium would be expected to occur three times as fast rather than 210 times as fast as the conversion of hydrogen. The somewhat unexpected behavior of tritium may, however, be explained either by a more favorable energy transfer or an ion mechanism. In Table III the Debye characteristic temperature for each isotope and the corresponding rotational temperatures are given. It should be noted that the rotational temperatures are smaller than the Debye temperatures for deuterium and tritium, whereas for hydrogen the rotational temperature is substantially higher than the Debye temperature. Therefore, for deuterium and tritium the energy transfer may be more favorable than in the case of hydrogen.

TABLE II
CONVERSION OF HYDROGEN, DEUTERIUM, AND TRITIUM ON
COCONUT CHARCOAL

	Obsd. half lifetime, min.	$k_{\text{obsd.}}$ min. ⁻¹	$\frac{(\mu^2 M)_{\text{D or T}}}{(\mu^2 M)_{\text{H}}}$ ^a	$k_{\text{calcd.}}$ min. ⁻¹	$k_{\text{obsd.}}/k_{\text{calcd.}}$
H ₂	27	0.026	1.00	(0.026)	1
D ₂	19	.036	0.199	.0051	3.9 ^b
T ₂	1.0	.69	3.42	.088	8

^a Using Wigner's¹² expression for the ortho-para transition probability, it may be seen that the calculated rate constants for deuterium and tritium relative to hydrogen are proportional to $(\mu^2 M)_{\text{D or T}}$ which is the product of the square of the nuclear magnetic moment and the mass of deuterium or tritium. ^b The factor $(3/4)^2$ must be included to account for the unequal nuclear spins of hydrogen and deuterium¹³ (H₂ and T₂, $S = 1/2$; D₂, $S = 1$).

Conversion at 27.2°K. in the Gas Phase.—A slow conversion of normal tritium to the equilibrium concentration at liquid neon temperature 27.2°K. could be observed as shown in Fig. 1 (cell conversion). This conversion must have occurred in the neon-cooled thermal conductivity cell in the gas phase because under the experimental conditions used any conversion due to van der Waals adsorption or due to the glass walls should be negligible. Oxygen frozen on the walls is known to cause ortho-para conversion in hydrogen (for details see Farkas).¹⁴ Therefore a platinum wire was heated to 1000°K. which would convert even traces of oxygen to T₂O while in liquid N₂. Subsequent recoiling of the cell in liquid neon, however, still re-

TABLE III
ENERGY TRANSFER PARAMETERS

	Debye temperature, θ_{D} ^a	Rotational temperature, θ_{R} ^b ($J = 0 \rightarrow J = 1$)
Hydrogen	91	172
Deuterium	89	86
Tritium	(72-87) ^c	57

^a $\theta_{\text{D}} = h\nu/k$. ^b $\theta_{\text{R}} = \sigma h^2/8\pi^2 I k$; σ denotes the symmetry number; h , I , and k are Planck's constant, the moment of inertia, and Boltzmann's constant, respectively. ^c The Debye characteristic temperature for hydrogen and deuterium has been measured directly^{15,16}; to our knowledge the Debye characteristic temperature for tritium has not been measured. Since hydrogen and deuterium behave anomalously, it is difficult to extrapolate the value for tritium and therefore we give large limits of error.

sulted in exactly the same rate of conversion indicating the conversion was not due to oxygen. Since the

(12) E. P. Wigner, *Z. physik. Chem.*, **B19**, 203 (1932).

(13) F. Kalckar and E. Teller, *Proc. Roy. Soc. (London)*, **A150**, 520 (1935).

(14) A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, London, 1935.

(15) F. Simon, K. Mendelssohn, and M. Ruhemann, *Naturwiss.*, **18**, 34 (1930).

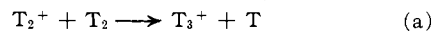
(16) K. Clusius and E. Bartholome, *ibid.*, **22**, 526 (1934).

liquid neon will freeze all impurities except the hydrogen isotopes and inert helium, the system will be extremely clean. The ions produced by the radioactive tritium cause conversion by virtue of this relatively long life since they will only be destroyed by ion-electron recombination on the wall or in the gas phase.¹⁷

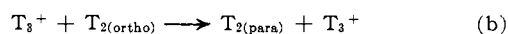
Tritium atoms resulting from ion-electron recombination cannot cause additional conversion according to the reaction $\text{T} + \text{T}_{2(\text{ortho})} \rightarrow \text{T}_{2(\text{para})} + \text{T}$, since the heat of activation of this reaction is probably higher than that of the analogous hydrogen reaction $\text{H} + \text{H}_{2(\text{para})} \rightarrow \text{H}_{2(\text{ortho})} + \text{H}$ which is 7 kcal.¹⁸ The relatively low heat of activation for the exchange reaction is due to the zero point energy of the hydrogen molecule and to the tunneling effect for this exchange reaction as theoretical analysis has shown. But since the zero point energy of tritium is 2.56 kcal./mole less than that of the hydrogen (see Table III) and the tunneling effect in the case of tritium exchange reactions is almost negligible, the apparent heat of activation for the tritium reaction will exceed 7 kcal. To be sure, even an activation energy of 7 kcal. would suppress any reaction at 27.2°K.

In the course of our studies, a series of experimental arrangements provided with somewhat different heat conductivity cell designs were used. Each cell had characteristic rates for the ortho-para conversion which could be reproduced; the rate of conversion involved approximately first-order kinetics. Since the conversion by atom reactions and by paramagnetic oxygen molecules could not be operative, ion reactions were considered to explain this conversion.

The primarily formed T₂⁺ ion may react with T₂



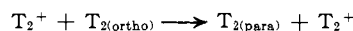
which is analogous to the hydrogen ion reaction expected with hydrogen.¹⁷ The T₃⁺ ion can then bring about conversion *via*



which may proceed with a long chain length before destruction of the T₂⁺ ion occurs.

The conversion tends to an equilibrium corresponding to the temperature of the cell at 27.2°K., as shown by the observation that both pure paratritium and normal tritium convert to the equilibrium mixture of 1 part ortho- to 1 part paratritium. This conversion must proceed *via* reactions such as (a) and (b) with virtually no heat of activation.

If reactions (a) or (b) should have a heat of activation of only 1 kcal., the rate of the reaction would be negligible at 27.2°K. under the conditions of the experiments. In particular, if a heat of activation of about 1 kcal. or more should exist for reaction (a) then the T₂⁺ could react with T₂, and might be the chain carrier *via*



The ion effect will dominate in the cell cooled with liquid neon since at 27.2°K. the particle density of tritium is ten times as high as the density at room temperature. Not only is 70 to 90% of T₂ in the cell, but ions producing conversion will be in much higher concentration at the low temperature because of the ten times greater concentration of tritium. The ion production will be proportional to the density of the

(17) In addition to hydrogen, helium, and neon, the other volatile gases to be considered at the temperature of liquid neon are nitrogen, carbon monoxide, and argon. The partial pressures at this temperature are: N₂, 3.1×10^{-6} ; CO, 6×10^{-7} ; Ar, 2×10^{-8} mm. Therefore ion-exchange reactions incorporating these three gases may be disregarded. At these low pressures diffusion to the walls is more likely.

(18) A. Farkas, *Z. Elektrochem.*, **36**, 782 (1930); *Z. physik. Chem.*, **B10**, 419 (1930); K. Geib and P. Harteck, *ibid.*, *Bodensteinband*, 849 (1931).

number of particles of radioactive tritium which disintegrate, and proportional to the cross section or particle density of tritium in this pressure range. Also, at 27.2°K. the recombination of the ions will at neon temperature also be less because diffusion to the wall, the site of recombination, is decreased by the higher particle density and the low temperature. The recombination in the gas phase is minor because of the relatively rapid diffusion to the wall not only of the positive ions but especially of the electrons before they are thermalized.

An electric field was applied across the cell using internal platinum electrodes. The current measured indicated about 10% of the β -energy released in the gas phase. The chain length then is in the order of 10^{15} .¹⁹

Changes in the characteristics of the wall could be expected to be more or less effective in destroying the ions. It was found that faster conversion occurred in a glass system, while the presence of platinum electrodes (provided to measure the effect of electric field) slowed down the conversion considerably (see Table IV). The glass walls of the cell could repel or reflect a fraction of the ions on collision where the metal surfaces would recombine the ions with a higher recombination efficiency. It would be possible by these techniques to obtain an insight into the recombination characteristics of ions for different surfaces at these low temperatures. Research on these lines are in progress.

TABLE IV
OBSERVED HALF LIFETIMES FOR THE DIFFERENT HEAT
CONDUCTIVITY CELLS

Cell description	Obsd. half lifetime, min.
Minimum metal surface	15
Tungsten leads extending throughout cell envelope (see ref. 7)	60
Platinum electrodes without voltage applied (Fig. 2)	27
Platinum electrodes with voltage applied (Fig. 2)	33

Thompson and Schaeffer²⁰ have proposed an ion chain mechanism for hydrogen and deuterium exchange when subjected to α -radiation, in the absence of impurities. Long chains could be obtained since chain-terminating charge transfer reactions with an impurity with a lower ionization potential were avoided. Under the conditions used in the present work, the liquid neon quantitatively froze out all interfering gas impurities. Therefore, charge transfer reactions with an impurity with a lower ionization potential are also avoided.

In the ion chain mechanism of Thompson and Schaeffer for the exchange between hydrogen and deuterium certain steps of the chain must have a heat of activation because the different species have different amounts of zero point energy; these reactions could not be expected to occur at 27.2°K. In our case, however, there is the distinct possibility to observe a reaction chain, where each link of the chain is operative without any heat of activation and the length of the chain is then determined by the rate of consumption of the ions which may be due to recombination in the gas phase or on the walls.

In a mixture of hydrogen and tritium the gas phase conversion could not be observed for the tritium and it was postulated that a chain termination step might occur. The reaction $H_2^+ + T_2 \rightarrow H_2 + T_2^+$ would be endothermic to the extent of 1.24 kcal. considering the differences in zero point energy; hence, at 27.2°K.

(19) More exact measurements of the ion production and chain length under various experimental conditions are in progress.

(20) S. O. Thompson and O. A. Schaeffer, *J. Am. Chem. Soc.*, **80**, 553 (1958); *Radiation Research*, **10**, 671 (1959).

reaction would not occur. Table V shows similar reactions and their corresponding heats of reaction calculated according to the zero point energies listed in Table VI. All of these reactions are endothermic and will not occur before ion recombination at 27.2°K. under our conditions.

TABLE V
HYDROGEN, DEUTERIUM, AND TRITIUM ION REACTIONS^a

	ΔE_0^0 , kcal./mole
$H_2^+ + T_2 \rightarrow H_2 + T_2^+$	+1.21
$H_2^+ + T_2 \rightarrow HT + HT^+$	+0.87
$H_2^+ + HT \rightarrow H_2 + HT^+$	+ .51
$HT^+ + T_2 \rightarrow HT + T_2^+$	+ .70
$H_2^+ + D_2 \rightarrow H_2 + D_2^+$	+ .84
$H_2^+ + D_2 \rightarrow HD + HD^+$	+ .53
$H_2^+ + HD \rightarrow H_2 + HD^+$	+ .38
$HD^+ + D_2 \rightarrow HD + D_2^+$	+ .46

^a Zero point energy differences may also be reflected in small differences of the ionization potentials of deuterated or tritiated compounds. Some have been measured, e.g., $ND_3 = 11.52$ e.v. and $ND_2H = 11.47$ e.v.²¹ For more examples see Lind.²²

The triatomic ions H_3^+ , H_2T^+ , HT_2^+ , and T_3^+ may also interact with H_2 , HT , and T_2 . The zero point energies of these ions are not known, but the differences should be analogous to those indicated for the diatomic ions. It means they may have relatively lower vibrational frequencies per degree of freedom than the uncharged diatomic species; also, the sum of the zero point energies will decrease with the tritium content of these species. All reactions involving a triatomic ion and uncharged diatomic molecules will tend therefore to go in the direction where the triatomic ions contain preferably hydrogen, and in the diatomic molecules preferably tritium. Consequently, ortho-paratritium conversion over long chains will not occur. Since the ions resulting from these reactions would not be tritium ions, but ions containing hydrogen and tritium, and never revert to pure tritium ions at these low temperatures, conversion becomes correspondingly hindered.

TABLE VI
ZERO POINT ENERGIES,^a KCAL./MOLE

H_2	6.20	H_2^+	3.24
HD	5.38	HD^+	2.80
HT	5.09	HT^+	2.64
D_2	4.41	D_2^+	2.29
DT	4.01	DT^+	2.09
T_2	3.62	T_2^+	1.87

^a These values were calculated from the spectral data reported by Herzberg.²³

Gas Phase Conversion in the Presence of a Paramagnetic Gas.—According to the formula of Wigner¹² a paramagnetic gas can cause conversion of parahydrogen to orthohydrogen. By means of this type of conversion, the relative magnetic moments of hydrogen and deuterium were determined with oxygen as a paramagnetic gas.²⁴ Similarly we have observed the relative conversion rates for hydrogen and tritium using nitric oxide in this case as the paramagnetic gas. The use of oxygen would have been less favorable in our experimental arrangement.

(21) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

(22) S. C. Lind, "Radiation Chemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1961, p. 270.

(23) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I. D. Van Nostrand Co., Inc., New York, N. Y., 1950.

(24) L. Parkas and H. Sachsse, *Sitzber. Preuss. Akad. Wiss.*, 268 (1933); *Z. physik. Chem.*, **B23**, 1, 19 (1933).

Nitric oxide has been used previously for ortho-para conversion of hydrogen.²² Of the lowest states of NO the ${}^2\Pi_{1/2}$ state is 345 cal. above the ${}^2\Pi_{1/2}$ ground state. The upper state is paramagnetic, whereas the lower state is not. Therefore, at room temperature a high percentage of the NO is paramagnetic while at liquid neon temperatures it is not only frozen out, but over 99% of the NO will be in the lower diamagnetic state.

The observed half lifetime for paratritium of 17 min. for a partial pressure of 100 mm. of NO was within 10% in agreement with the prediction of Wigner's formula¹²; thus, this result adds support to the validity of this equation for gas phase conversion, where the interacting distance is assumed unchanged.

Conclusions

In the preceding paper⁷ we have shown that it is possible to convert normal tritium to paratritium on charcoal in the temperature region of liquid neon and liquid helium. Hydrogen and tritium have the spin $1/2$ and follow therefore the same statistics. In addition they have almost the same nuclear magnetic moment. It is therefore of major interest to compare the kinetic data of the ortho-para conversion of these two hydrogen species. From the results obtained, we have been able to show that: (1) On a coconut charcoal

under the same conditions the ortho-para transformation of tritium was 27 times faster than that of hydrogen. (2) In the solid phase the ortho-paratritium conversion has a half lifetime of 17 min. which corresponds to a rate 210 times as fast as the rate of conversion of hydrogen. (3) Concerning the occurrence of conversion reactions by ions the following conclusions could be drawn: (a) During the conversion experiments in the gas phase the heat conductivity cell remained always cooled with liquid neon; therefore the tritium gas was extremely pure. It seems that under these conditions the ortho-para conversion occurs over an ion mechanism with practically zero heat of activation. (b) Metal surfaces enhanced the ion recombination process and thereby decreased the rate of conversion. (c) The application of an electric field to part of the cooled experimental arrangement removed some of the ions and decreased the rate of conversion. (d) In the adsorbed phase on semiconducting charcoal, ions do not seem to play a role in the catalysis.

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The Infrared Spectra of Some Alkyl-Substituted Pentavalent Antimony Compounds

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A number of antimony compounds of the type R_3SbX_2 , where R is methyl or ethyl and X is a halogen, NO_3 , OH, or $0.5SO_4$ have been prepared. Attempts to prepare compounds of the type R_3SbXOH have failed, and the existence of such compounds is doubtful. However, compounds of the type $[R_3SbX]_2O$ are readily prepared. The infrared spectra of these compounds have been determined. The spectra of the dihalides are consistent with the trigonal bipyramid structure, suggested by other workers. Trimethylantimony dinitrate contains the Me_3Sb^{++} ion. In trimethyl- and triethylantimony sulfates the sulfate groups are covalently bonded, but the exact structure is uncertain. Oxybis-[trimethylantimony] diperchlorate and dichloride are clearly ionic and contain the $[(Me_3Sb)_2O]^{++}$ ion.

The structure of trialkyl- and triarylantimony dihalides has been established by the work of several investigators. Wells, on the basis of X-ray diffraction studies, demonstrated that trimethylantimony dihalides exist as trigonal bipyramids with the methyl groups in the plane of the antimony atom and the halogens at the apices.¹ The antimony-halogen distance is somewhat longer than expected for covalent bonds; this finding led Wells to suggest that the halogen-antimony bonds might be intermediate in character between covalent and ionic bonds. Jensen obtained zero dipole moment values for triphenylantimony dichloride and dihydroxide and assigned the trigonal bipyramid structure to these compounds.² This structure was recently confirmed for triphenylantimony dichloride by means of X-ray diffraction studies.³ It has also been demonstrated that triphenyl- and tribenzylantimony dichlorides do not conduct an electric current in acetonitrile solution.⁴ It has thus been clearly established that both triaryl- and trialkylantimony dihalides contain a pentavalent antimony atom.

In addition to the dihalides, a number of similar antimony compounds have been reported. These include such compounds as trialkyl- and triarylantimony sulfates, dinitrates, hydroxychlorides, hydroxynitrates, etc. It is by no means clear that all or any of such compounds contain a pentavalent antimony atom. In fact a trialkyl- or triarylantimony sulfate with a trigonal bipyramid structure, in which a sulfato group is bonded to any two corner positions of the bipyramid, would involve a highly strained structure. For this reason we have prepared a series of trialkylantimony compounds and examined their infrared spectra in the hope of elucidating the structure of such compounds. The compounds prepared, together with the analytical results, are given in Table I. The results of the spectral studies are reported later in this paper.

In addition to the structural problem discussed above, we have also attempted to clear up several rather puzzling findings reported in the literature dealing with the trialkylantimony dihalides. Hantzsch and Hibbert were the first to demonstrate that compounds of the type R_3MBr_2 (where R is an alkyl group and M is P, As, or Sb) are extensively hydrolyzed in aqueous solution.⁵ This work was subsequently extended by Nylen, who made a detailed study of the hydrolysis of trialkylar-

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