sequence in which the points were obtained. It is seen that any *P–T* value within the loop could be obtained by suitable temperature manipulation. This is consistent with the explanation that the loops are caused by lack of equilibrium between two solid hydride phases, so that the observed pressure is dependent on the relative amounts of the two phases as well as on the temperature. The situation may be summarized by saying that the observed pressure within the region of the hysteresis loops is dependent on the immediate past history of the sample. The ends of the loops, when they were observable, were fairly reproducible upon continued cycling, but it should be pointed out that the loop ends were not defined exactly by the data and depend somewhat on how one chooses to draw the *P–T* curves. This lack of precision is not important to the interpretation as long as the loop ends are taken to be observed phase boundaries rather than equilibrium boundaries.

From the foregoing it is evident that the conditions for the equilibrium transformation of plutonium hydride from a cubic to a hexagonal structure are not yet precisely defined. It has not been possible to observe a sharp transformation, and it is not clear what circumstances will be required to accomplish this. It might be assumed that the transformation becomes thermodynamically possible when the composition reaches a certain value and that if the composition can be maintained at a suitable value and the temperature raised high enough (by keeping a high hydrogen pressure over the specimen), the transformation will be sufficiently rapid to permit equilibrium to be reached. This is not entirely true, however, because exactly this experiment has been tried without making any apparent difference in the hysteresis. We believe that hysteresis behavior may be inherent in some hydride systems and that its explanation will have to come from a detailed elucidation of the solid-state physics involved.

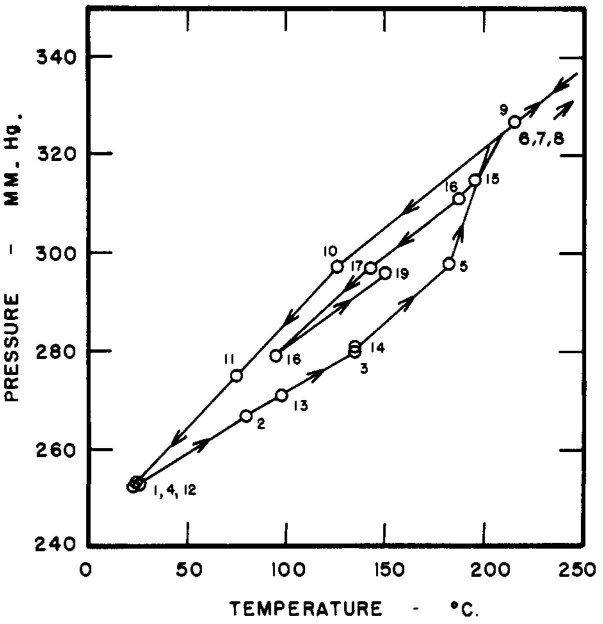

Fig. 7.—Portion of *P–T* curve from Fig. 1.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Kinetics of the Reaction of Hydrogen Chloride with Glass[1]

BY JAMES E. BOGGS AND HELENE P. MOSHER

RECEIVED FEBRUARY 2, 1956

The reaction of hydrogen chloride gas with Pyrex #7220 glass wool to form NaCl and water was studied between 295 and 385°. The reaction is primarily controlled by diffusion through the glass, but the rate is slightly affected by variations in HCl pressure.

During a recent investigation of the kinetics of chlorine isotope exchange between HCl and the compounds CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl in the gas phase,[2] several observations indicated that an extensive chemical reaction may occur between HCl gas and Pyrex glass. In the case of CH_3Cl and CH_2FCl, the exchange with HCl is heterogeneous and very strongly dependent on the previous treatment of the glass container. Reproducible results could be obtained only after extensive baking of the glass *in vacuo*. Similar surface effects were reported by Peri and Daniels[3] in their study of bromine isotope exchange between HBr and C_2H_5Br in Pyrex vessels. Crespi and Moles[4] have shown that small quantities of HCl gas are absorbed into the bulk of glass vessels at room temperature in addition to the amount which is adsorbed on the surface.

The present study was undertaken to determine the nature of the reaction of HCl gas with Pyrex glass, and to study the conditions under which it occurs. The results of such a study should be of importance in connection with kinetic studies of chemical reactions involving HCl gas in Pyrex containers and especially isotope exchange reactions which might occur through a mechanism involving exchange with reaction products on the wall.

Experimental

Hydrogen chloride was prepared in an all-glass generator by dropping concd. sulfuric acid solution onto solid sodium

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[1] This work was supported by grant No. 443 from The University of Texas Research Institute. Portions of it were presented before the Eleventh Southwest Regional Meeting of the American Chemical Society, Houston, Texas, December 1–3, 1955.

(2) J. E. Boggs and L. O. Brockway, THIS JOURNAL, **77**, 3444 (1955).

(3) J. B. Peri and F. Daniels, *ibid.*, **72**, 424 (1950).

(4) M. Crespi and E. Moles, *Anal. Soc. Españ. fís. quím.*, **29**, 146 (1931).

chloride. The gas was then dried and purified by vacuum distillation.

Corning Pyrex #7220 glass wool was used for the reactive surface. The fibers were of reasonably uniform size and had an average diameter of 6.3×10^{-4} cm. as measured from electron microscope photographs. No special treatment was given to the surface to remove surface films, since the reaction studied was one of the bulk material rather than of the surface layers.

Sufficient glass wool to have a surface area in the vicinity of 10^4 cm.^{2} was contained in a Pyrex reactor which was heated in an electric tube furnace. The temperature of the furnace was determined with a chromel–alumel thermocouple, and maintained constant to ±0.5° by an automatic controller. A storage bulb was filled with HCl to a pressure higher than that at which the experiment was to be run. Gas was then admitted to the reactor at the desired pressure. As HCl was consumed in the reaction, more was admitted from the storage bulb to keep the gas pressure in the reactor constant throughout the experiment. The rate of the reaction was followed by pressure readings on a manometer attached to the storage bulb. Water which was produced in the reaction was frozen out at −78° in a trap connected to the reactor. The level of the cooling bath was maintained at a constant height so that the pressure readings would not be affected by variations in the volume cooled. The entire apparatus was connected to a vacuum line with facilities for preparing and storing the HCl.

Results

The interaction between HCl and Pyrex in the temperature range between 295 and 385° is not one of surface adsorption, but rather a true chemical reaction. Electron micrographs of the glass fibers before reaction showed a perfectly smooth surface; the appearance after extensive reaction is shown in Fig. 1. Water was formed as one of the products and electron diffraction pictures of the reacted fibers showed clear patterns of NaCl. No other reaction products could be found, either in the gas state or in the diffraction pattern from the solid.

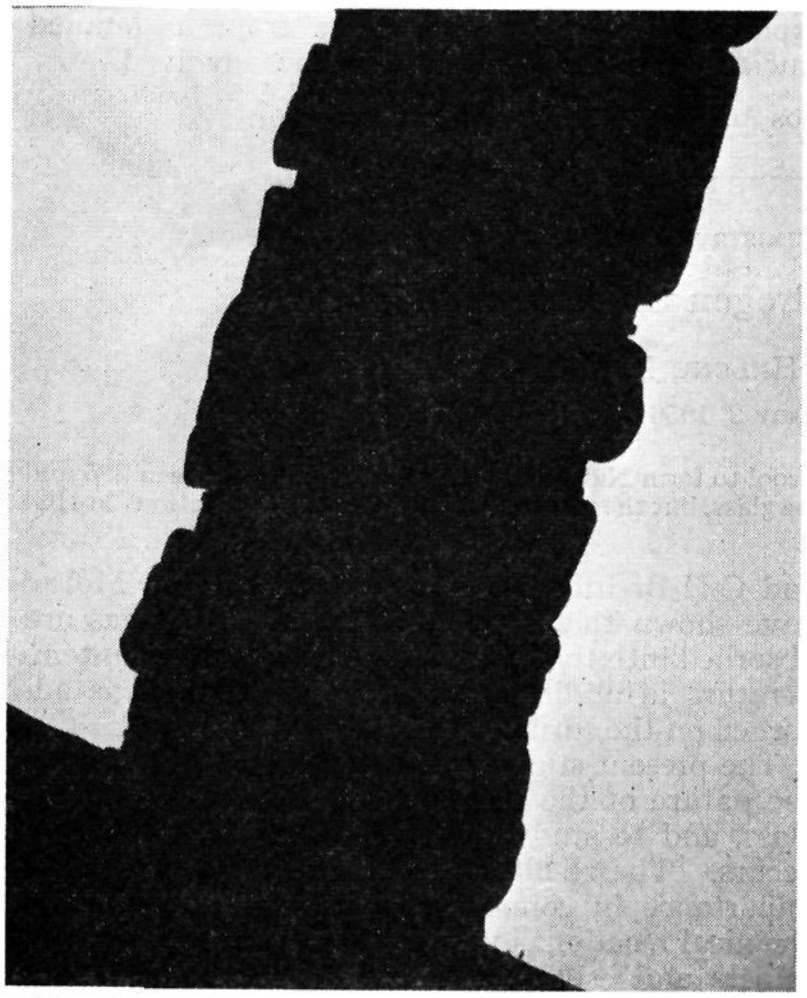

Fig. 1.—Electron micrograph of glass fiber after reaction with HCl. Before reaction, an electron micrograph showed a perfectly smooth surface.

The rate-controlling step in the reaction of HCl with glass appears to be a diffusion process through the glass. The rate of diffusion would be expected to be inversely proportional to the thickness of the layer of reaction products. Thus $dx/dt = -k/(a - x)$, where x is the number of moles of HCl in the reaction vessel per cm.^{2} of glass surface and $(a - x)$ is the quantity which has already reacted. Integrating, the rate constant would be $k = (a - x)^2/2t$.

Figure 2 shows a plot of $(a - x)^2$ against t for three different temperatures. Each line is the result of two or three separate runs with different quantities of glass wool and is drawn from an average of 42 experimental points. The average deviation of the observed points from the recorded line is $\pm 0.1 \times 10^{-14}$ (moles cm.$^{-2}$)^2. It will be noted that a straight line results after a brief initial period of more rapid reaction. The surface layers of glass will have a different composition than the interior and may be covered with adsorbed foreign materials, either of which factors might account for the initial faster reaction.

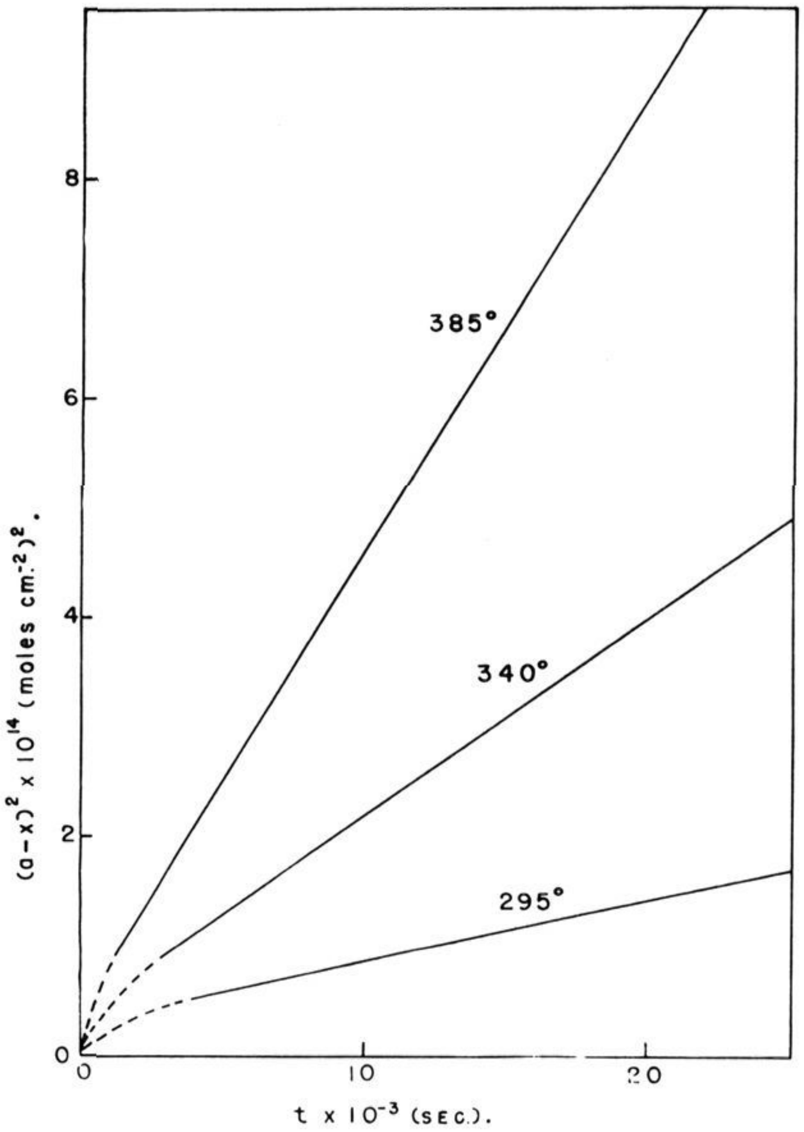

Fig. 2.—Variation of extent of reaction with time at three different temperatures.

At a pressure of 500 mm., the reaction rate constant, k, is 21×10^{-19} (moles cm.$^{-2}$)^2 sec.$^{-1}$ at 385°, 9.0×10^{-19} at 340°, and 2.8×10^{-19} at 295°. From an Arrhenius-type plot of these values, the reaction is found to have an activation energy of 17 kcal./mole.

Although the reaction of HCl with Pyrex is primarily diffusion-controlled, there is a small pressure effect. A series of runs was made at a temperature of 385°, keeping the HCl pressure constant for each run, but changing it between runs. The rate constant, k, is 21×10^{-19} (moles cm.$^{-2}$)^2 sec.$^{-1}$ at 500 mm., 16.5×10^{-19} at 100 mm., and 14.5×10^{-19} at 30 mm. Thus a 17-fold increase in pressure increases the constant by only about 45%. In Fig. 3, the value of the rate constant, k, is plotted against the HCl pressure. It will be noted that with increasing pressure the rate appears to be approaching a steady value. At the lower pressures, the small initial rapid reaction is less pronounced.

Conclusions

Although the kinetics of the reaction of HCl with Pyrex indicate that the rate-determining step involves a diffusion process through the glass, the identity of the diffusing substance has not been established. There are three distinct possibilities: (1) HCl may be diffusing from the surface to the interior, (2) Na_2O (*i.e.*, sodium ions accompanied by an equivalent number of oxide ions) may be diffusing from the interior to the surface, or (3) HCl may dissolve in a layer of adsorbed water on the surface of the glass fibers, followed by a counter diffusion of H^+ ions into the glass and Na^+ ions to the surface.[5] Considering the temperature range in which the reaction is observed, the last of these possibilities seems most likely.

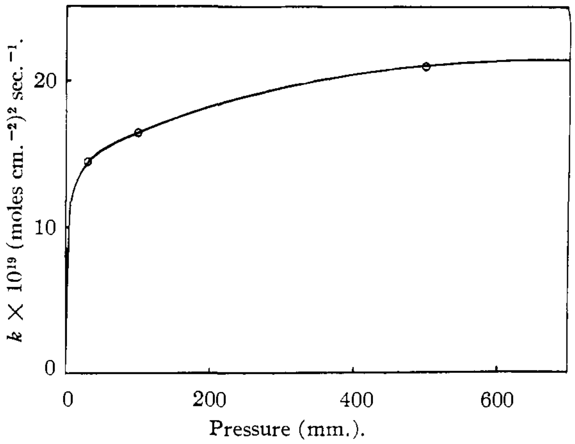

Fig. 3.—Variation of the specific reaction rate constant with HCl pressure.

Several studies of halogen isotope exchange reactions using hydrogen halides have been made in Pyrex vessels.[2,3] In such cases the formation of sodium halide on the reaction vessel surface may play an important role in the mechanism of exchange. Since Na_2O tends to migrate to the surface when glass is heated,[6] glassware which has been exposed to glassblowing operations might be expected to have a higher surface concentration of Na_2O than do the fibers studied in this work.

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[5] R. W. Douglas and J. O. Isard, *J. Soc. Glass Tech.*, **33**, 289T (1949).

[6] H. S. Williams and W. A. Weyl, *Glass Ind.*, **26**, 275 (1945).

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Energy Transfer Processes in the Unimolecular Decomposition of Nitryl Chloride[1]

BY MILTON VOLPE AND HAROLD S. JOHNSTON

RECEIVED MARCH 23, 1956

The decomposition of nitryl chloride has been studied at 203° in the presence of each of 16 foreign gases at total pressures between 3 and 9 mm. As shown previously[2] the rate under such conditions is the rate of activation of nitryl chloride by collision. This paper lists relative rate constants for activation by the various foreign gases as well as the relative efficiency of energy transfer, collision per collision. As noted before,[2-4] deactivation does *not* occur upon every collision. The relative efficiency of energy transfer shows several strong empirical correlations with molecular interaction parameters such as boiling point and the constants from the Lennard-Jones potential function, and gases with permanent dipole moments are all more efficient than comparable non-polar molecules. On the other hand these results indicate, somewhat surprisingly, very little or no correlation with the number of atoms or the number of oscillators in the foreign gas.

Schumacher and Sprenger[5] studied the decomposition of nitryl chloride and proposed the mechanism

$$NO_2Cl = NO_2 + Cl \qquad (1)$$

$$NO_2Cl + Cl = NO_2 + Cl_2 \qquad (2)$$

Thus they proposed their observed rate to be twice that of the elementary unimolecular decomposition. Our recent reinvestigation[2] confirmed all of these features and also demonstrated that the unimolecular reaction was essentially within its second-order region below 5 mm. Therefore the observed rate of reaction is the rate of activation according to the Lindemann[6] mechanism

$$\begin{aligned} A + M &\xrightarrow{a_{mi}} A_i^* + M \qquad (3)\\ A_i^* + M &\xrightarrow{b_{mi}} A + M \\ A_i^* &\xrightarrow{c_i} \text{products} \end{aligned}$$

where * denotes internal energy above the critical energy, i denotes some activated state of the reac-

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[1] Presented at the 128th meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1955. Submitted to Stanford University in partial fulfillment of the requirements for the Ph.D. degree 1956.

[2] H. F. Cordes and H. S. Johnston, THIS JOURNAL, **76**, 4264 (1954).

[3] D. J. Wilson and H. S. Johnston, *ibid.*, **75**, 5763 (1953).

[4] H. S. Johnston, *ibid.*, **75**, 1567 (1953).

[5] H. J. Schumacher and G. Sprenger, *Z. Elektrochem.*, **35**, 653 (1929); *Z. physik. Chem.*, **B12**, 115 (1931). H. J. Schumacher, "Chemische Gas Reactionen," Edward Bros., Inc., Ann Arbor, Mich., 1943 (Photolithoprint reproduction), pp. 127–130.

[6] F. A. Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).