357. *The Surface Chemistry of Germanium. Part II.* Erosion by Chlorine.*

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The rate of reaction of chlorine with germanium samples of known crystallographic and electronic properties is determined by a manometric method over a range of temperatures. The entropy factor for the reaction is found to correspond to full surface coverage, with a probability factor of unity. The measured activation energy indicates that the supply of positive holes to the surface is not rate-limiting.

Studies of heterogeneous reactions on solids have usually suffered from the difficulty of obtaining a uniform solid and a simple surface. The use of large single-crystal specimens of known crystallographic orientation affords reproducibility as well as detailed physical information on the atomic and electronic conditions at the surface. Such studies are of current interest in the field of semiconductor surface physics.

Most of the solid–gas reactions for which rate measurements are available are of the "tarnishing reaction" type: their rates are determined by diffusional or electrolytic transport of reactants through a solid phase of products, and therefore yield little information on the electronic processes at the gas–solid interface. Reactions of this type have been discussed by Wagner,[1] Mott,[2] and Gulbransen.[3] Gasification reactions, on the other hand, appear to have received little attention, with the notable exception [4] of the gasification of carbon by steam or oxygen. Some studies have been reported [5] of high-temperature metal–halogen reactions. At temperatures high enough to volatilize the halide,

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* Part I, *J.*, 1956, 3726.

[1] Wagner, *Z. phys. Chem.*, 1933, *B*, **21**, 25; 1936, *B*, **32**, 447.

[2] Mott and Cabrera, *Rep. Progr. Phys.*, 1948—49, **12**, 163.

[3] Gulbransen, *Trans. Electrochem. Soc.*, 1943, **83**, 301.

[4] Hinshelwood *et al.*, *Proc. Roy. Soc.*, 1946, *A*, **187**, 129; 1948, *A*, **193**, 357, 377.

[5] Frommer and Polanyi, *Z. phys. Chem.*, 1928, *A*, **137**, 201; McKinley and Shuler, *J. Chem. Phys.*, 1958, **28**, 1207.

these are found to be of first order in halogen pressure, indicating that the reaction is taking place on a nearly bare surface, and to be non-activated. Law and Meigs [6] have studied the reaction between monocrystalline germanium and oxygen at temperatures high enough to evaporate germanium monoxide. This reaction is retarded by products so as to become of zero order, and the inverse pressure-dependence of the rate indicates rate-limitation by the diffusion of germanium monoxide away from the site of reaction. In the present paper the far simpler reaction between chlorine and monocrystalline germanium (in the temperature range 175—260° C and at pressures below 130 mm. Hg) is discussed. The reaction is found to be of zero order in chlorine pressure with no evidence of retardation by products, and the rate obeys the equation:

$$\text{Rate} = 10^{27 \pm 1} \exp\,[(-25{,}000 \pm 1000)/\boldsymbol{R}T] \text{ molecules sec.}^{-1}\text{ cm.}^{-2}$$

The observed rates are shown to correspond to a mechanism in which the supply of positive holes at the surface does not limit the reaction rate.

EXPERIMENTAL

Materials.—Chlorine gas was led from a cylinder of commercial liquid to the purification assembly (Fig. 1) through silver-plated copper tubing, purified by bulb-to-bulb vacuum-distillation and stored in 2-l. flasks. Immediately before use the gas was given one further fractionation. Germanium slices were cut in the (111) plane from a monocrystalline bar of zone-refined and zone-levelled *n*-type germanium of uniform resistivity (2 ohm-cm.) and lifetime of minority carriers (150 microsec.), lapped on a glass plate with 900-grade corundum powder and water, and finally etched in a mixture of nitric, hydrofluoric, and acetic acid (45, 25, 30 ml. respectively) to complete removal of mechanical damage, as shown by the attainment of a constant etching rate. The B.E.T. area of surfaces thus prepared has been determined,[7] and leads to a value of 1·4 for the surface roughness. Since the surface density of germanium atoms in a (111) plane is $7{\cdot}3 \times 10^{14}$ cm.$^{-2}$, the samples exposed $\simeq 1{\cdot}0 \times 10^{15}$ atoms of metal per cm.^{2} of apparent surface area.

Apparatus.—*Pressure-following system.* The rate of reaction of chlorine with the germanium surface was measured by following the change with time of the chlorine pressure, which was transmitted to a mercury manometer by a servo-mechanism operated by a spoon gauge (Fig. 1). The spoon gauge was fitted with a pair of platinum contacts connected by 40-gauge enamelled copper wires to tungsten lead-in wires. A reduction in pressure inside the spoon gauge opens the contacts and thus actuates a Thyratron relay controlling an on-off, magnetically operated, vacuum valve in series with an adjustable throttle. This causes a reduction in pressure outside the spoon gauge as long as the contacts remain open. To enable the system to follow both increases and decreases in pressure, an air-leak controlled by a needle valve is included in the ("slave") external system, so that the pressure in the latter continuously fluctuates about the static pressure in the ("master") system of reaction chamber and spoon gauge. Initial chamber pressures between 5 and 760 mm. Hg can be balanced by appropriate relative settings of the vacuum and air-leak throttles. Coarse settings make it possible to follow rapid changes in pressure (up to ~30 cm. min.$^{-1}$) but give rise to excessive pressure oscillations in the slave system. With fine settings it is possible to smooth the movement of the mercury column so that the pressure can be measured with a cathetometer to 0·02 mm. A 10-l. ballast reservoir associated with the slave system also helps to minimize pressure fluctuations. The manometer (15 mm. bore), spoon gauge chamber, and ballast reservoir were housed in air thermostats, and dead spaces were kept to a minimum.

Chlorine reaction chamber. The chamber (Fig. 1) consisted of a horizontal vapour-jacketed glass tube of internal diameter such that it just supported the germanium slice by its edges. The loading stopper and the taps immediately adjacent to the chamber were lubricated with Fluorube grease (B.D.H. Ltd.), grease A on the taps and W on the joint. This grease was found to be entirely inert towards chlorine. The reaction chamber was connected to the vacuum manifold by a short length of 10-mm. tubing to permit thorough outgassing. An alternative

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[6] Law and Meigs, *J. Electrochem. Soc.*, 1957, **104**, 154.

[7] Law, *J. Phys. Chem.*, 1955, **59**, 543.

" slow " connection to the chamber was provided, in the form of 1-mm. bore capillary tubing, to enable the chamber to be filled, or evacuated, without overloading the servo-mechanism. The reaction temperature was controlled by circulating in the outer jacket the vapour of a high-boiling liquid (*o*-dichlorobenzene, decalin, benzyl alcohol, or 1-chloronaphthalene). After the system had been evacuated for several hours by means of a diffusion pump backed by a rotary pump, chlorine was introduced into the manifold, and thence into the reaction chamber through the capillary tube. Measurements of pressure were begun as soon as the chamber had been filled to the required pressure of chlorine.

Calculation of Rate Constants.—If it is assumed that chlorine and germanium tetrachloride form an ideal-gas mixture, and since one molecule of germanium tetrachloride is produced for every two molecules of chlorine consumed, the pressure of chlorine at any instant, P_{Cl}, is given by $P_{\mathrm{Cl}} = 2P_t - P_0$, where P_t is the measured total pressure and P_0 is the initial pressure of chlorine, provided that the extent of the reaction is restricted to a pressure of germanium tetrachloride below its saturation value at room temperature, to prevent the appearance of a liquid phase on the cooler parts of the reaction chamber–spoon gauge system. An exact measurement of P_0 cannot be made by the present technique, because several minutes are needed to fill the chamber to the required pressure of chlorine. However, this proves to be immaterial since the total pressure P_t is found to vary with time at a constant rate: hence, $P_t = kt$, so that $P_{\mathrm{Cl}} = 2kt - P_0$, and the reaction rate is not a function of P_0, *i.e.*, $\mathrm{d}P_{\mathrm{Cl}}/\mathrm{d}t = 2k$.

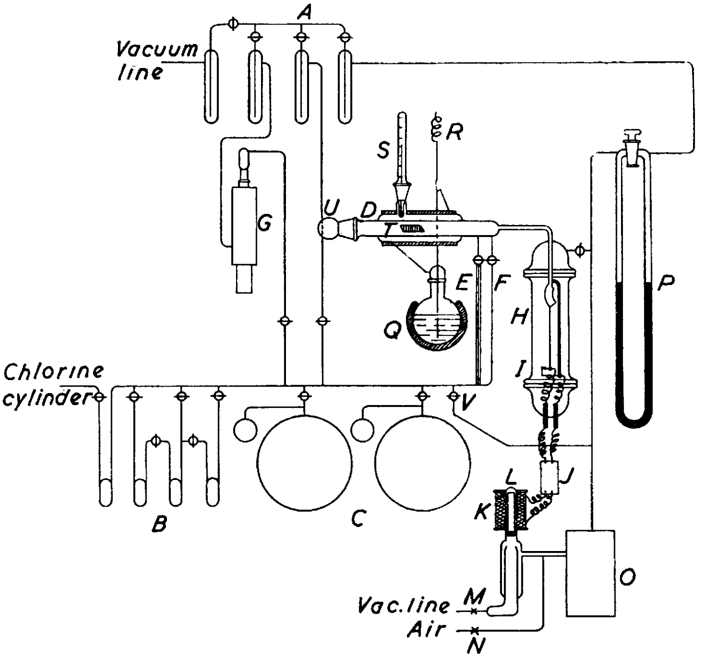


FIG. 1. *Apparatus for erosion rate measurement.*

A, Vacuum manifold.
B, Purification train.
C, Storage flasks.
D, Reaction chamber.
E, "Slow" connection to chamber.
F, " Fast " connection to chamber.
G, Diffusion pump.
H, Spoon gauge.
I, Spoon gauge contacts.
J, Relay.
K, Solenoid.
L, Soft-iron plunger.
M, Needle valve (vacuum).
N, Needle valve (air leak).
O, Ballast tank.
P, Mercury manometer.
Q, Boiler for vapour thermostat.
R, Reflux condenser.
S, Thermometer.
T, Germanium specimen.
U, Loading stopper.
V. Spoon gauge by-pass.

This behaviour is typical of zero-order kinetics (Fig. 2).

Reproducible reaction rates were obtained once the surface showed the characteristic etch pattern for the reaction under 250 × magnification: an array of interlacing equilateral triangles for the lower temperatures and a finer-textured velvety appearance for the higher temperatures. It is not thought, however, that the increase in surface roughness amounted to as much as a factor of three. The rate constants per cm.^{2} of surface were therefore calculated on the assumption that no appreciable change in surface area with temperature took place. The fact that the order is zero over the entire reaction permits a theoretical interpretation of the results even though only part of the reaction chamber was thermostatically controlled: the specimen surface is covered with a layer of chemisorbed chlorine with which it is in intimate thermal contact. The corresponding reaction of bromine could not be investigated in the present apparatus because the rate showed a pressure-dependence.

The factor of 7 × 10^{16} for converting the experimental reaction rates (cm. Hg min.$^{-1}$) into molecular units (molecules sec.$^{-1}$ cm.$^{-2}$) was obtained from the chamber volume (63 cm.^{3}), the surface area of the specimens (4·0 cm.^{2}), and the assumed mean temperature for the gas inside and outside the thermostat vapour jacket (100°). This factor need be known only to the nearest power of ten for the purpose of estimating the entropy factor by extrapolating the results to infinite temperature. The results obtained at four levels of temperature, plotted in Fig. 3, correspond to the rate equation

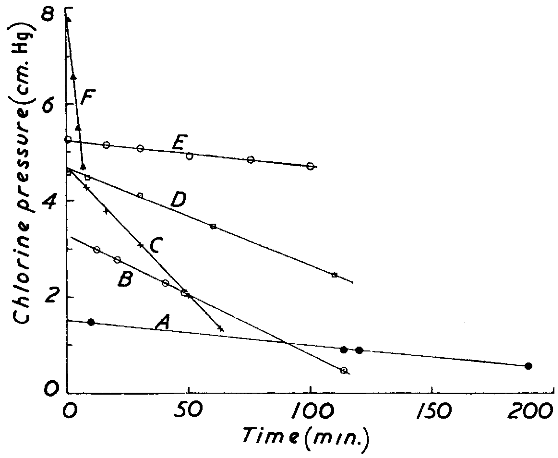


FIG. 2. *Zero-order plots for the erosion of germanium by chlorine.*

(Curve *A*, $T = 177°$; *B*, 189°; *C*, 205°; *D*, 189°; *E*, 175°; *F*, 258°.)

$$\text{Rate} = 10^{27 \pm 1} \exp\,[(-25{,}000 \pm 1000)/\boldsymbol{R}T] \text{ molecule sec.}^{-1} \text{ cm.}^{-2}$$

RESULTS AND DISCUSSION

The rates of reaction of chlorine with a (111) germanium surface, measured at four levels of temperature and over a range of initial chlorine pressures, P_0, are shown in Table 1. The slices used were about 1 mm. thick; the amount consumed in an actual experiment was of the order of 0·1 mm.

TABLE 1.

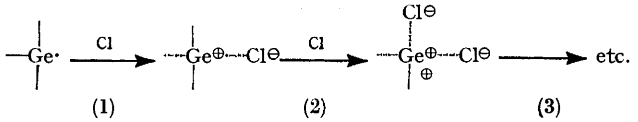
Run no.	P_0 (cm.)	T	Rate (min.$^{-1}$ cm.)	10^{-15} × Rate (molecule sec.$^{-1}$ cm.$^{-2}$)	Run no.	P_0 (cm.)	T	Rate (min.$^{-1}$ cm.)	10^{-15} × Rate (molecule sec.$^{-1}$ cm.$^{-2}$)
17	5·14	175°	0·00875	0·61	16	3·33	191°	0·0230	1·61
12	5·22	175	0·00607	0·43	13	4·70	205	0·0537	3·76
18	1·51	177	0·00508	0·35	15	11·62	205	0·0462	3·24
19 *	1·83	175	0·00516	0·36	28	9·14	258	0·562	39·4
7	4·54	189	0·0210	1·48	29	7·75	258	0·611	42·8
8	3·26	189	0·0238	1·67	30	8·80	258	0·579	40·6

* In this run water vapour at a partial pressure of 0·5 mm. was added with the chlorine.

The runs obeyed zero-order kinetics, and showed no evidence of retardation by products (Fig. 2), thus indicating full surface coverage. The Arrhenius plot for the reaction (Fig. 3) yields an activation energy of 25 ± 1 kcal. mole^{-1} and an infinite-temperature intercept ($\simeq 10^{28}$ molecules sec.$^{-1}$ cm.$^{-2}$) which is sensibly equal to the product of the surface density of germanium atoms for this crystallographic plane with a roughness factor of 1·4 (10^{15} cm.$^{-2}$) and of their vibrational frequency (10^{13} sec.$^{-1}$).

This suggests that the partition functions of the transition state and of the chemisorbed complex are approximately equal, a result not unexpected in view of the simple nature of the reactants. We can infer that the transition-state structure differs from that of the chemisorbed complex only in its electronic configuration and hence affects the reaction rate only through the activation-energy term. For the same reason entropy-controlling processes, such as diffusional transport of reactants and end-products, are not rate-limiting.

The electronic structure of the chemisorbed state has been shown (Part I) to be at least partially ionic by studies of the influence of oxidizing environments upon the electrical properties of the surface.[8] These suggest that charge-transfer can take place, between the bulk of the semiconductor and the adsorbate, in the form of delocalized positive holes just below the germanium surface and negative charges on the adsorbate. We shall now suppose that the localization of a positive hole ($\oplus$) on a surface atom leads to the formation of the transition state. A reaction mechanism of the following kind is consistent with the above observations:



$$-\mathrm{Ge}\cdot \xrightarrow{\mathrm{Cl}} -\mathrm{Ge}^{\oplus}\cdots\mathrm{Cl}^{\ominus} \xrightarrow{\mathrm{Cl}} \overset{\mathrm{Cl}^{\ominus}}{\underset{\oplus}{-\mathrm{Ge}^{\oplus}}}\cdots\mathrm{Cl}^{\ominus} \longrightarrow \text{etc.}$$

Each stage involves localization of a hole and adsorption of a chlorine atom; hole localization may be identified with heterolysis, and the rate at which holes can be localized may, in certain circumstances, limit the reaction rate. Successive stages will, however, involve a progressively higher energy barrier, on account of electrostatic repulsive forces. A calculation of the reaction rate based on availability of holes therefore seems out of the question except in cases where the repulsive forces can be minimized by external solvent interactions.

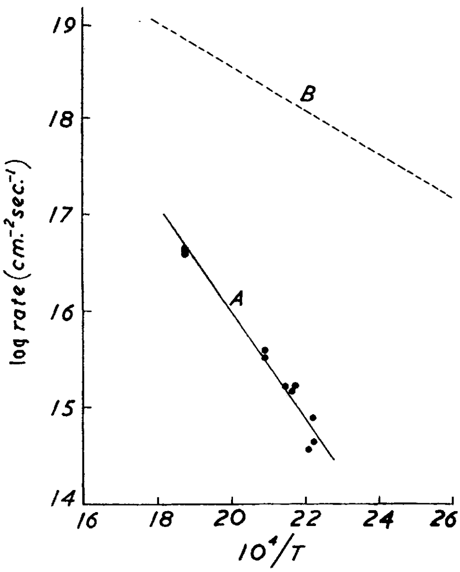


FIG. 3. *Arrhenius plots.*

[Curve *A*, chlorine erosion (exptl.). Curve *B*, availability of bulk-generated positive holes in intrinsic region (calc.).]

The activation energy for stage (1) can be identified with that attending the supply of positive holes to the surface, $E_{\oplus}$, and this can be evaluated from solid-state theory. If further stages are involved, the energy barrier is increased by $\sum_i E_{R,i} - E_S$ where E_R is the repulsion energy for each of these stages, and E_S is the solvation energy. In strongly solvating media this energy-increase term may be expected to vanish, and the activation energy controlling the reaction will then be simply $E_{\oplus}$. As is shown below, the gaseous reaction medium can contribute little solvation energy, and results in an activation energy well in excess of $E_{\oplus}$. Reactions involving solids, in which electrons and holes may play a

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[8] Carasso and Stelzer, *J.*, 1956, 3726.

kinetic rôle and limit the rate by a kind of concentration polarization, are now becoming generally recognized.[9] Our present reaction, utilizing germanium of known crystallographic and electrical parameters, lends itself well to a comparison of the measured reaction rate with the calculated limiting diffusion current of positive holes from the bulk to the surface. For the case when the surface acts as a perfect sink, semiconductor theory indicates [9] that the maximum diffusion current of holes to the surface, I_{ps} is given by

$$I_{ps} = p_0 V \text{ holes cm.}^{-2} \text{ sec.}^{-1}$$

where p_0 is the equilibrium concentration of holes in the bulk, and the rate constant V, dimensionally a velocity, has the value

$$V = s + \sqrt{(D_p/\tau_p)} \text{ cm. sec.}^{-1}$$

D_p is the diffusion constant for positive holes; s (" surface recombination velocity ") and $1/\tau_p$ (reciprocal " lifetime of positive holes ") are the first-order velocity constants for the generation of positive holes at the surface and in the bulk respectively; thus,

$$g_{\text{surf}} = sp \text{ holes cm.}^{-2} \text{ sec.}^{-1}$$

$$g_{\text{bulk}} = p/\tau_p \text{ holes cm.}^{-3} \text{ sec.}^{-1}$$

Calculation shows that, throughout the temperature range of the chlorine-erosion experiments, the samples, having a room temperature resistivity of 2 ohm-cm., *n*-type, are in the range of intrinsic conduction. If the contribution to I_{ps} due to surface generation is neglected in comparison with that due to bulk generation, a lower limit for the rate of arrival of holes at the surface of the intrinsic sample is given by

$$(I_{ps})_{\text{bulk}} = p_i \sqrt{(D_p/\tau_i)}$$

in which p_i is the equilibrium density of holes, and τ_i their lifetime, in the intrinsic germanium. Expressions are available for all three quantities in the right-hand side of the above equation: D is related to the mobility, μ, by Einstein's relation $D = \mu \mathbf{k} T/q$, and μ_p is given by $\mu_p = 8{\cdot}9 \times 10^6 \times T^{-\frac{3}{2}}$ cm.^{2} volt^{-1} sec.$^{-1}$ in the high-temperature (lattice scattering) region.[10] Therefore

$$D_p = 7{\cdot}7 \times 10^2 \times T^{-\frac{1}{2}} \text{ cm.}^{-2} \text{ sec.}^{-1}$$

The intrinsic carrier density is given [10] by

$$p_i = n_i = 9{\cdot}7 \times 10^{15} \times T^{\frac{3}{2}} \times \exp(-4350/T) \text{ cm.}^{-3}$$

The hole lifetime in the intrinsic region can be derived from Shockley and Read's general expression [11] which becomes, for the intrinsic case

$$\tau_i = \tfrac{1}{2}\tau_{p0}(1 + n_1/n_{i0}) + \tfrac{1}{2}\tau_{n0}(1 + p_1/p_i)$$

τ_{p0} and τ_{n0} are defined by Shockley and Read and are insensitive functions of temperature; n_1 and p_1, the concentrations of electrons and holes for material in which the Fermi level passes through the trap level,[11] can be expressed by the classical approximation as an exponential function of the difference in energy between the trap level E_t and the Fermi level for intrinsic material E_i. The expression thus reduces to

$$\tau_i = \tfrac{1}{2}\tau_{p0}\left[1 + \exp\left(\frac{E_t - E_i}{\mathbf{k}T}\right)\right] + \tfrac{1}{2}\tau_{n0}\left[1 + \exp\left(\frac{E_i - E_t}{\mathbf{k}T}\right)\right]$$

Introducing the empirical values for τ_{p0} and τ_{n0} and for $(E_t - E_i)$ determined by Burton

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[9] Brattain and Garrett, *Bell System Tech. J.*, 1955, **34**, 129; Hauffe, " Semiconductor Surface Physics " (Ed. by R. H. Kingston), Univ. Pennsylvania Press, Philadelphia, 1957, p. 259; Schwab, *op. cit.*, p. 283.

[10] Conwell, *Proc. Inst. Radio Engineers*, 1952, **40**, 1327.

[11] Shockley and Read, *Phys. Rev.*, 1952, **87**, 835.

et al.[12] for high-grade germanium crystals, we obtain the following approximate numerical expression for the intrinsic lifetime:

$$\tau_i = 2{\cdot}5 \times 10^{-5}[11 + 10 \exp(622/T)] \text{ sec.}$$

Ignoring all but the fastest temperature variation, we can evaluate the limiting diffusion current of bulk-generated positive holes, over the experimentally accessible temperature range (average 475° K), as

$$I_{ps} = p_i\sqrt{(D_p/\tau_i)} = 1{\cdot}6 \times 10^{22} \times \exp(-8700/\boldsymbol{R}T) \text{ holes cm.}^{-2}\text{ sec.}^{-1}$$

It can be seen from the plot of this expression (curve *B*, Fig. 3) that the rate of arrival of bulk-generated positive holes alone exceeds the rate of reaction of germanium with chlorine by several powers of ten over the whole experimental temperature range. There is some justification, therefore, despite the uncertainties which attach to the above calculation, for the conclusion that the supply of positive holes does not limit the rate of reaction of germanium with gaseous chlorine, and that the process of hole localization, summarized by the following series of reactions, is fast compared with subsequent electronic rearrangements leading to the transition state. The symbols $\ominus_{\text{cond.}}$ and $\oplus_{\text{val.}}$ represent, respectively, a conduction-band electron and a valence-band (*i.e.*, delocalized) positive hole.

Carrier generation	$\text{Thermal energy} \longrightarrow \ominus_{\text{cond.}} + \oplus_{\text{val.}}$
Adsorption	$\text{Ge} + \tfrac{1}{2}\text{Cl}_2 \longrightarrow \text{Ge—Cl}$
" Electron gas " equilibrium	$\text{Ge—Cl} + \ominus_{\text{cond.}} \longrightarrow \text{Ge—Cl}^{\ominus}$
Hole localization	$\text{Ge—Cl}^{\ominus} + \oplus_{\text{val.}} \longrightarrow \text{Ge}^{\oplus}\text{—Cl}^{\ominus}$

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[12] Burton, Hull, Morin, and Severiens, *J. Phys. Chem.*, 1953, **57**, 853.