

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE CATALYTIC DECOMPOSITION OF GERMANE

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Langmuir's concept of contact catalysis has given the most concrete and promising basis for the interpretation of velocities of reactions catalyzed by solid surfaces. Its initial success with the carbon monoxide-oxygen reaction as studied by Langmuir<sup>1</sup> has led to many applications of this theory with some degree of confidence.<sup>2</sup> In many cases it has not offered an entirely unequivocal explanation of the phenomena observed, yet, in the main, the later results have served to increase confidence in Langmuir's general concept of the nature of surface catalysis.

One would expect that this theory could be best applied to the simple decomposition reactions. Such reactions have been studied by Bodenstein and Kranendieck<sup>3</sup> with ammonia and by Stock and Bodenstein,<sup>4</sup> who interpreted the results of Stock, Gomolka and Heynemann<sup>5</sup> on the rate of decomposition of stibine on antimony surfaces. Some of these reactions have been interpreted with moderate success on the assumption that each decomposing molecule has two contact points common with the surface.

The methane analogs of the fourth group elements can be predicted to decompose heterogeneously because of the relatively few degrees of freedom possessed by their molecules and it is conceivable that their rates of decomposition might behave differently from those of the hydrides of the fifth group elements of the periodic system. Of the fourth group hydrides, germane,  $\text{GeH}_4$ , is the best suited for this purpose. It was first prepared by Voegelen,<sup>6</sup> who observed the formation of a metal mirror in the analogous Marsh test, an observation which has been verified qualitatively by later workers. No quantitative measurements have thus far been made on the rate of decomposition of this compound, so in view of the bearing that such studies might have upon the present adsorption theory, we undertook this investigation.

### Experimental

**General Method.**—The thermal decomposition of germane takes place as follows



<sup>1</sup> Langmuir, *Trans. Faraday Soc.*, **17**, (21) (1921).

<sup>2</sup> See Taylor, *Reaction Velocities in Heterogeneous Systems*. "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, 1931.

<sup>3</sup> Bodenstein and Kranendieck, *Nernst Festschrift*, p. 99.

<sup>4</sup> Stock and Bodenstein, *Ber.*, **40**, 570 (1907).

<sup>5</sup> Stock, Gomolka and Heynemann, *ibid.*, **40**, 532 (1907).

<sup>6</sup> Voegelen, *Z. anorg. Chem.*, **30**, 324 (1902).

The hydride exists as a gas at room temperature, boiling point  $-90^{\circ}$ , and undergoes decomposition very slowly at temperatures below  $280^{\circ}$ . Accordingly all experiments were carried out at temperatures exceeding this value. Since hydrogen is the only gaseous constituent resulting from the decomposition, the rate of the reaction was followed by observing the total pressure of the system at different intervals of time. From the total pressure one may readily calculate the pressure of the undecomposed hydride and the pressure of the hydrogen resulting from decomposition.

**Apparatus.**—The apparatus is shown diagrammatically in Fig. 1. The chamber A, about 300 cc. capacity, serves as a container for the reaction. It is inner-sealed into a larger chamber B, 85 mm. in diameter and about 250 mm. in length, which contains approximately 100 cc. of mercury as the heating material. The entire chamber B is inserted in the larger container C which is filled with insulating material. The mercury in B is heated by coils of resistance wire placed in lower regions of C (not shown in the figure). A is connected to the capillary manometer D, the mercury column of which is agitated during the pressure readings by a small doorbell buzzer. E leads to the vacuum pumps and also to the containers for the germane. F represents a Chromel-X-Copel thermocouple to measure the temperature of the reaction chamber. The e. m. f. of this couple was determined with a White potentiometer. G leads to a constant pressure regulator, not shown in the figure, similar in design to that described previously by Smith.<sup>7</sup> The mercury is boiled continuously in B as far as condenser H during the progress of a run in order to ensure a constant temperature in the entire reaction chamber. The pressure regulator was found very satisfactory for maintaining a constant pressure of mercury vapor; no difficulty was experienced in establishing a pressure constant to 0.1 mm., which corresponds to a temperature regulation of  $\pm 0.02^{\circ}$  at  $300^{\circ}$ .

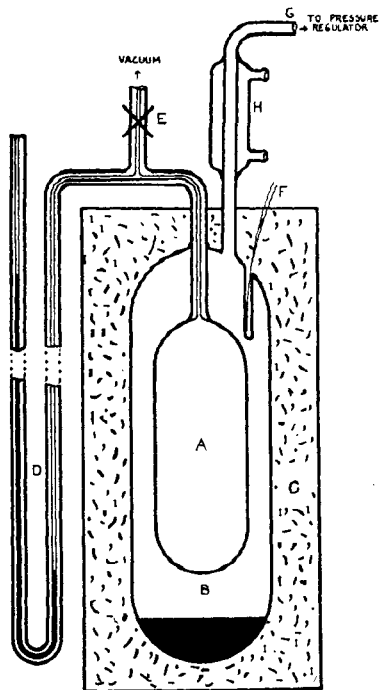


Fig. 1.—Apparatus.

For the higher temperatures, in the neighborhood of the normal boiling point of mercury, the reaction tube was heated directly with a furnace. The temperature of the furnace did not vary more than  $0.5^{\circ}$  over the short period of time required to complete the reaction.

**Preparation of Materials.**—The germane was prepared in liquid ammonia by the reaction of magnesium germanide,  $Mg_2Ge$ , with ammonium bromide.<sup>8</sup> The hydride was collected over water, then dried by passing through a phosphorus pentoxide tube and finally solidified at liquid air temperatures. The hydrogen present with the hydride was removed by the pumps at this low temperature. Since some higher boiling products,

<sup>7</sup> Smith, *Ind. Eng. Chem.*, **16**, 22 (1924).

<sup>8</sup> E. Seaton Carney, Thesis, Brown University, 1928.

presumably higher hydrides of germanium, remained with the germane, the mixture was fractionally distilled at  $-80^{\circ}$  to ensure a pure sample of  $\text{GeH}_4$ . The molecular weight of the purified gas was found to be 76.0, which value increased to 76.5 after the sample was subjected to a second distillation.

Two samples of the hydride were decomposed for analytical purposes, one at  $320^{\circ}$  and the second at  $354^{\circ}$ , with the result that the final gas pressure was practically twice that of the original. Molecular weight determinations of the products in each of these two cases gave a value of  $2.2 \pm 0.1$ .

Approximately three liters of the purified germane were stored in a large flask at about atmospheric pressure. When a reaction was to be carried out, a portion of the hydride was condensed at liquid air temperature in a small volume adjacent to the reaction chamber. The liquid air bath was removed and the hydride was distilled as rapidly as possible into the apparatus; the time for such a distillation usually did not exceed one minute. At the higher temperatures, where the rate of decomposition of the hydride is very rapid, it was found impossible to obtain a pressure reading before an appreciable amount of the germane had dissociated. This difficulty did not appear at lower temperatures.

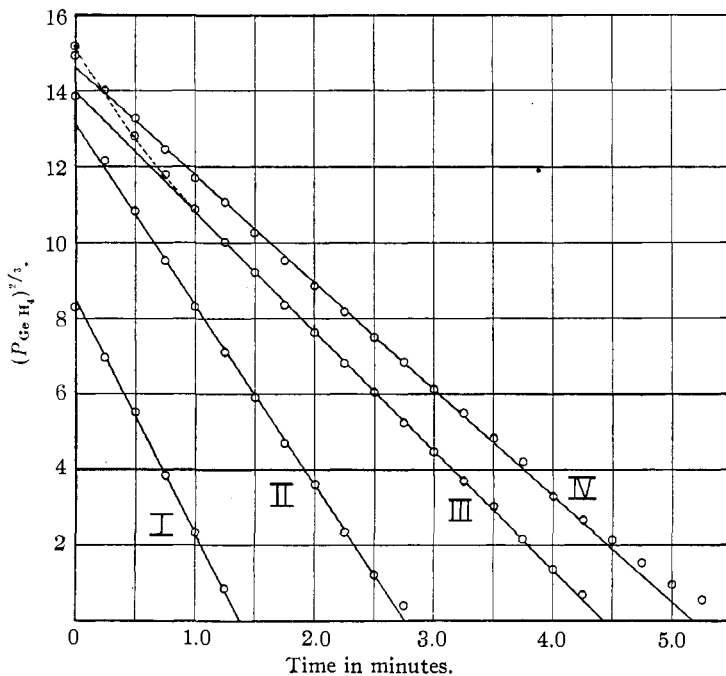


Fig. 2.

## Results

The results of the investigation are shown graphically in Figs. 2, 3 and 4, in which the pressure of the undecomposed germane to the two-thirds power is plotted against the time. It is readily observed that this type of plot follows a straight line, within the limits of experimental error, at the

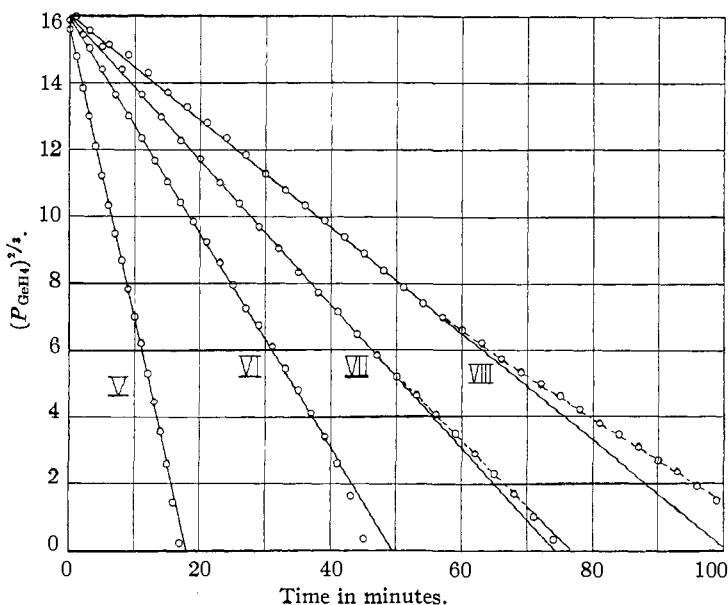


Fig. 3.

higher temperatures and also at the lower temperatures for low germanium hydride pressures. In other words

$$-\frac{dp^{3/4}}{dt} = K \quad (1)$$

or

$$-\frac{dp}{dt} = 3/2 K p^{1/4} \quad (2)$$

The slopes of these lines are given in Table I, designated by  $K$ , expressed in centimeters of germane to the two-thirds power per minute.

TABLE I  
DATA FOR THE DECOMPOSITION OF GERMANE AT DIFFERENT TEMPERATURES

Run	Temperature °C.	°K.	$1/T \times 10^3$	Initial press. GeH <sub>4</sub> , cm.	$K$	$\log K$
I	374	647	1.546	23.9	6.50	0.813
II	364	637	1.570	51.4	4.73	.675
III	360	633	1.580	59.2	3.16	.500
IV	354	627	1.595	57.7	2.95	.447
V	330	603	1.658	61.9	0.845	-.073
VI	319	592	1.689	65.1	.343	-.465
VII	309	582	1.718	64.8	.215	-.668
VIII	301	574	1.742	63.4	.153	-.815
IX <sup>a</sup>	283	556	1.798	69.0	.040	-1.400

Figure 5 shows  $\log K$  plotted against  $1/T \times 10^3$ .

<sup>a</sup> Runs X, XI and XII were carried out with initial germane pressures of 39.95, 19.70 and 10.80 cm., respectively, and at the same temperature as for Run IX.

Theoretical

To represent the experimental results of the decomposition of germane by the theory of Langmuir, certain assumptions regarding the rate of adsorption, the rate of evaporation and the decomposition rates of this compound on the germanium surface are necessary, assumptions which are different for each case to which the theory is applied. We shall assume (1) that three points of condensation are required, all of which must be simultaneously activated if evaporation is to take place, (2) that the rate of evaporation is much greater than the rate of decomposition, (3) that one-point activation of the bond will produce instability and rapid decomposition, and (4) that hydrogen inhibits at low temperatures but less as the temperature is elevated.

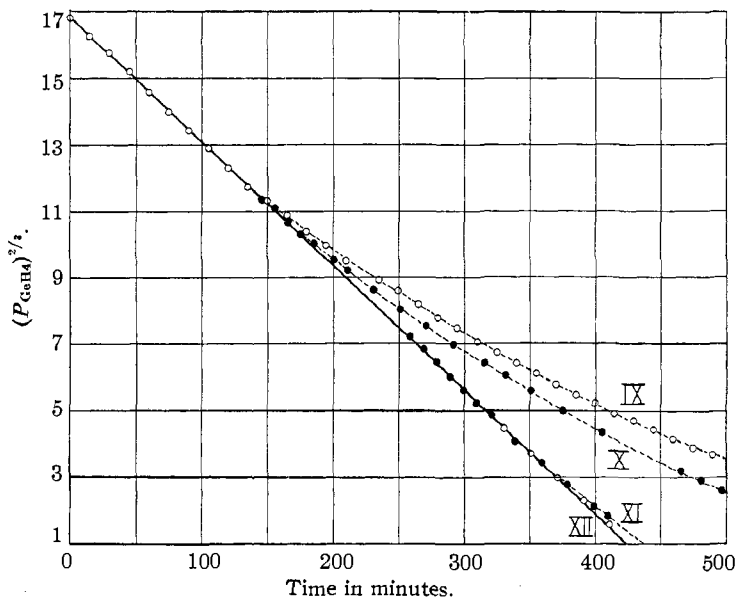


Fig. 4.

With these assumptions we obtain

$$\alpha_1 \mu_1 \Theta^3 = \nu_1 \Theta_1^3 \tag{3}$$

$$\alpha_2 \mu_2 \Theta^n = \nu_2 \Theta_2^n \tag{4}$$

$$w = K_1 \Theta_1 \tag{5}$$

where  $\alpha_1$  and  $\alpha_2$  are the accommodation coefficients for germane and hydrogen, respectively,  $\Theta_1$  and  $\Theta_2$  the fractions of the surface covered by germane and hydrogen and  $\Theta$  the uncovered surface;  $\mu_1$  and  $\mu_2$  represent the number of molecules striking the surface in unit time;  $\nu_1$  and  $\nu_2$ , the specific rates of evaporation of these two gases; and  $K_1$ , the specific decomposition velocity.  $w$  is the rate of decomposition and  $n$  represents the number of

contact points for the hydrogen molecule. Using the above equations together with

$$\theta + \theta_1 + \theta_2 = 1 \quad (6)$$

we obtain

$$w = \frac{K_1 \left( \frac{\alpha_1 \mu_1}{\nu_1} \right)^{1/3}}{1 + \left( \frac{\alpha_1 \mu_1}{\nu_1} \right)^{1/3} + \left( \frac{\alpha_2 \mu_2}{\nu_2} \right)^{1/n}} \quad (7)$$

Since  $\mu$  is proportional to the pressure, we may let  $\left( \frac{\alpha_1 \mu_1}{\nu_1} \right)^{1/3} = A_1^{1/3} p_1^{1/3}$  and

$\left( \frac{\alpha_2 \mu_2}{\nu_2} \right)^{1/n} = A_2^{1/n} p_2^{1/n}$ . We then obtain

$$w = \frac{K_1 A_1^{1/3} p_1^{1/3}}{1 + A_1^{1/3} p_1^{1/3} + A_2^{1/n} p_2^{1/n}} \quad (8)$$

Using equation (8) under conditions where the inhibiting effect of hydrogen is negligible, we may let  $A_2^{1/n} p_2^{1/n}$  be equal to zero. If  $A_1^{1/3} p_1^{1/3}$  is small as compared with unity, the rate becomes

$$w = K_1 A_1^{1/3} p_1^{1/3} \quad (9)$$

which corresponds to equation (2) and represents the results of our experiments. If suitable units are chosen for  $w$ ,  $K_1 A_1^{1/3}$  becomes equal to  $K$  of

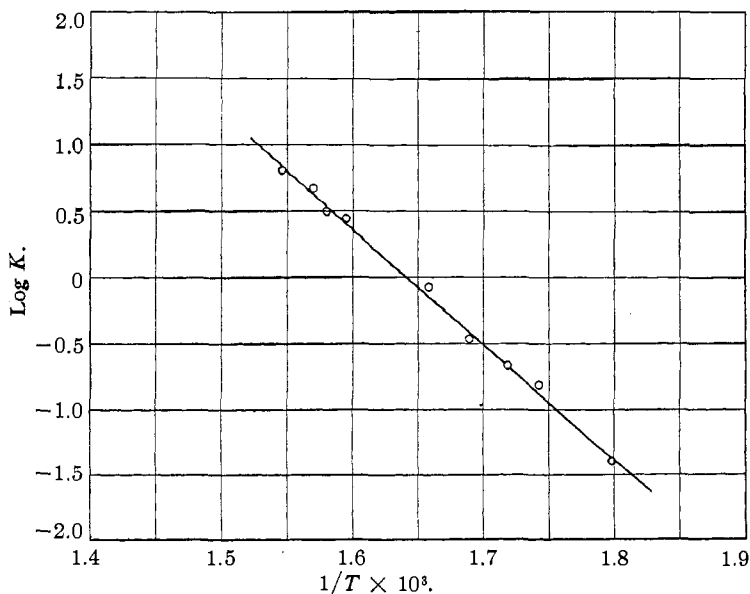


Fig. 5.

equations (1) and (2). Making  $A_1^{1/3} p_1^{1/3}$  small is equivalent to assuming that the specific rate of evaporation is great as compared with the rate at which the molecules condense. In other words, the amount of surface occupied by the germane molecules is relatively small.

**The Inhibiting Effect of Hydrogen.**—With increasing temperature the specific rate of evaporation of hydrogen should increase proportionately to  $e^{-q_2/kT}$ , while the rate of adsorption increases as  $T^{1/3} e^{-r/kT}$ , where  $r$  is the heat of activation of adsorption of hydrogen. Adsorption is here considered in its general sense. It is not implied that this energy  $r$  is that for "secondary" adsorption.<sup>10</sup>  $A_2$  should then be proportional to  $T^{1/3} e^{-(r-q_2)/kT}$ , where  $r-q_2$  is the difference between the heats of activation of adsorption and evaporation of the hydrogen molecules on a germanium surface, and corresponds to the heat of adsorption. Since this is a negative quantity, we conclude that  $A_2^{1/n}$  decreases rapidly with increasing temperature as would be expected, and at higher temperatures this term in equation (8) should become negligible.

For higher temperatures the reaction velocity should follow equation (9) over a longer range of pressures, that is, hydrogen should show a smaller inhibiting effect. Examination of the curves in Figs. 2 and 3 shows clearly that this is the case. We have not added hydrogen to the germane initially to determine its effect since any such condition could be achieved by beginning with different pressures of germane. Unfortunately we have not been able to determine the value of  $n$  without ambiguity inasmuch as this analysis requires the slope of a curve which in itself is derived from the slope of another curve. The uncertainty of any such procedure with rate data is at once apparent. Such analyses of this kind as we did make gave values of  $1/n$  somewhat greater than 1; yet, on account of this uncertainty, we hesitate to give the inhibiting effect of hydrogen a definite numerical value.

**Temperature Coefficient and the Heat of Activation.**—The temperature coefficient of the reaction is that for the specific reaction rate  $K_1 A_1^{1/3}$  of equation (9). This value, as shown in Table I, is for 300 sq. cm. of apparent catalytic surface.  $A_1$  is proportional to  $e^{-H/RT}$ , or  $A_1^{1/3}$ , to  $e^{-H/3RT}$  where, by the same argument as given previously for  $A_2$ ,  $H$  is the heat of adsorption of one mole of germane on germanium.  $K_1$  is proportional to  $e^{-Q/RT}$  where  $Q$  is the heat of activation of the decomposition of one mole of the hydride.  $K_1 A_1^{1/3}$  is then proportional to  $e^{-(Q+H/3)/RT}$  or

$$K_1 A_1^{1/3} = K_0 e^{-(Q+H/3)/RT} \quad (10)$$

We have defined  $H$  as the heat of *adsorption*.  $Q$  and  $H$  are of opposite signs;  $Q$  represents heat absorbed and  $H$  heat evolved.  $Q + H/3$  may also be considered as the difference between the heat of activation and one-third the heat of *evaporation (desorption)*.

Plotting  $\log K_1 A_1^{1/3}$  or  $\log K$  (equations (1) and (2)) against  $1/T$ , we obtain the value of an activation energy which, according to our interpretation, is equal to  $Q + H/3$  (Fig. 5). The value of this quantity is calculated from the slope of the curve and is found to be  $39.7 \pm 2$  kilogram

<sup>10</sup> See Taylor, THIS JOURNAL, 53, 578 (1931).

calories per mole. Thus it is possible to express the rate of the reaction as follows

$$w = 0.935 \times 10^{12} e^{-20,000/T} p^{1/3} \text{ (cm. Hg)}^{3/3} / \text{min. sq. cm.} \quad (11)$$

The rate given in this equation is for 1 sq. cm. of apparent catalytic surface.

### Discussion

The theory for the mechanism of the catalytic decomposition of germane was developed only after it was shown that no other rate law than the one described could represent the data for all pressures and temperatures. The decomposition time plotted against both  $p^{1/3}$  and  $\log p$  gave no consistent results. Plotting  $\log p$  against  $\log t$ , a straight line was obtained which had a slope of two-thirds. The added fact that we obtained consistent values for the temperature coefficient of the reaction (see Fig. 5) confirmed the relation that at high temperatures the rate of decomposition was proportional to  $p^{1/3}$ . We therefore attempted to make sufficient and reasonable assumptions to adapt these results to the general theory developed by Langmuir.

So far as we are aware this is the first case in which it has been necessary to assume a three-point contact for an adsorbed reacting molecule. However, on the basis of our knowledge of the structure of germane and crystalline germanium, such an assumption seems to us to be the most reasonable one. Like methane, the structure of germane is to be considered as tetrahedral. Metallic germanium has been shown<sup>11</sup> to have a diamond-type structure with octahedral cleavage. All surfaces of germanium crystals therefore have a triangular structure; that is, lines drawn between three adjacent atoms (points) on the surface form an equilateral triangle. These facts make the assumption of three contact points a reasonable one.

To develop equation (8) it has been necessary to assume that three points must be independently activated to cause evaporation of the germane molecule from the surface. Since we have no other evidence to support this assumption, it hardly seems advisable to give too detailed a picture of this mechanism, yet we can see no reason why such an assumption would not be a valid one.

We have also assumed that only one point is highly activated when dissociation takes place. We have no way at present of determining how and when the hydrogen molecule is subsequently formed.

The further assumption we have made, that only a small fraction of the condensing molecules dissociate and that equilibrium is essentially maintained between the condensing and the evaporating molecules, is a common one in chemical kinetics. A similar assumption regarding equilibrium between activated and non-activated molecules is made in developing some

<sup>11</sup> See Ewald and Hermann, "Strukturbericht," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931, p. 54.



of the theories of homogeneous reaction rates, which theories have been applied with a moderate degree of success.

Run III (Fig. 2) was started with a glass surface rather than with one on which germanium had already been deposited. As may be seen from the figure, the initial rate in this run was greater for the glass than for the germanium surface. A simple calculation, assuming a plane contact surface, shows that the deposit of a layer of germanium several thousand molecules thick was necessary before the rate became the same as that for the usual germanium surface. The catalytic activity of the first layers deposited on the glass is greater than that for the ordinary germanium crystal surface. The effect may be ascribed to the porosity of the glass but it also may be ascribed to the irregular crystal surface which is probably first formed. There can be no question that the catalytic activity is greatly influenced by the spacing and the geometry of the atoms at the surface.

Several runs, not described here, were made to demonstrate that the reaction is a heterogeneous one. Reaction cells were filled with glass wool and under these conditions the reaction at  $340^{\circ}$  was immeasurably faster than with the smaller surface.

The decomposition of antimony hydride has been studied by Stock and his co-workers.<sup>5,12</sup> These authors show that the rate of decomposition is proportional to  $p^m$  where  $m$  varies from 0.4 at  $0^{\circ}$  to 0.7 at  $75^{\circ}$ . At  $25^{\circ}$  the rate is proportional to  $p^{0.5}$ . According to their results the hydrogen produced in the decomposition of the hydride does not have an inhibiting effect. Applying the Langmuir theory in this case, the term in the denominator of the rate equation, similar to our equation (8), very probably cannot be neglected. The neglecting of this term is equivalent to assuming that only a very small fraction of the surface is covered by the reaction molecules. In the experiments with stibine, the conditions of lower temperature and higher molecular weight of the stibine would undoubtedly result in a greater amount of surface covered and the denominator term might therefore be of significance. A closer analysis of these results with a view to their extension are now being undertaken. In the case of the decomposition of arsine<sup>12,13</sup> there are not sufficient data for analysis.

### Summary

1. Experiments are described in which the catalytic rates of decomposition of germane,  $\text{GeH}_4$ , on a germanium surface are determined.
2. The rates of decomposition at higher temperatures are found to be proportional to the one-third power of the undissociated germane pressure.
3. At lower temperatures the hydrogen formed in the reaction displays an inhibiting effect.

<sup>12</sup> Stock and Guthmann, *Ber.*, **37**, 885 (1904); Echeandia, Thesis, Berlin, 1909; Stock, *Z. physik. Chem.*, **50**, 111 (1905).

<sup>13</sup> Stock, Echeandia and Voigt, *Ber.*, **41**, 1319 (1908).

4. By making assumptions applicable in this case an equation, based on Langmuir's adsorption theory, is developed; this equation is in agreement with the experimental results. The essential assumption made is that of three-point contact between the germane molecule and the germanium surface.

5. The temperature coefficient and the heat of activation have been determined. The significance of this energy term has been discussed in the light of the proposed theory.

6. A discussion of the validity of the assumptions made and of similar work in this field concludes the article.

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## A STUDY OF VAN DER WAALS FORCES BETWEEN TETRAHALIDE MOLECULES

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The theoretical and experimental investigations of the general problem of solubility conducted by the senior author and collaborators during a period of years have made evident the importance of a more accurate knowledge than we now possess of intermolecular forces between like and unlike molecules in the simplest possible cases, where the molecules are non-polar and where the molecular field, as shown by recent applications of wave mechanics, is spherical. While the noble gases are theoretically satisfactory for such an investigation, we selected the tetrahalides as practically far more suitable. They are not only available in large quantities, but their molecular volumes and intermolecular forces represent a wide range of variation. We are making a systematic study of certain properties of six tetrahalides and their solutions. The properties thus far measured are the expansion on mixing and the thermal pressure coefficient,  $(\partial p/\partial T)_V$ , from which can be calculated the important quantity,  $(\partial E/\partial V)_T$ . There is now under way, as a further part of the general program, a study of the activities of the same substances in their binary solutions.

**Preparation and Purification of Materials.**—Stock U. S. P. carbon tetrachloride, about 1500 cc., was shaken with c. p. sodium hydroxide sticks, and a small quantity of distilled water for two days. The liquid was then decanted, filtered, and the process repeated. After standing in contact with phosphorus pentoxide overnight, it was distilled from fresh phosphorus pentoxide. The distilling apparatus was of Pyrex glass, with all connections fused, except the connection to the receiving flask, which was a cork covered with tin foil, and the cork holding the thermometer, inserted in the distilling flask, which was also covered with tin foil. The first and last portions of the distillate were discarded, although the boiling point rose only  $0.08^\circ$  during the entire run. The fraction retained boiled at  $76.37$  to  $76.43^\circ$  (754 mm.). The purified material was kept in the dark, in a Pyrex flask, with a tin foil-covered stopper.