A Theoretical Consideration of Simple Catalytic Reactions. Decomposition of Gaseous Hydrides

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The thermal decomposition of gaseous hydrides on their own constituent elements to produce hydrogen gas is one of the simplest catalytic reactions. During the reaction, the surfaces of the elements are always renewed by the continuous deposition of fresh elements and only two elements are involved including the catalyst. The kinetics of such reactions are summarized in Table I. A similar reaction, the decomposition of nickel carbonyl, was also listed in the Table. The reason why the kinetics of these similar reactions are so different is to be treated here in a semi a priori fashion.

TABLE I

Kind of reaction	Kinetics of decomp.	Apparent activation energy
AsH_3 on As1)	$v=kP_{AsH_3}$	23.2 kcal./mol·
SnH_4 on Sn2)	$v=kP_{SnH_4}$	9.1
H_2Se on Se3)	$v=kP_{H_2Se}$	
SbH_3 on Sb4,5)	$v=kP_{SbH_3}^{0.6\sim1.0}$	8.8 at $P_{SbH_3}=40$cm.
CH_4 on C6)	$v=\frac{kP_{CH_4}}{1+bP_{H_2}}$	53.4
$Ni(CO)_4$ on Ni7,8)	$v=\frac{kP_{Ni(CO)_4}}{1+bP_{CO}}$	10.3, 12.0
GeH_4 on Ge9)	$v=k$	41.2

As to the other gaseous hydrides, the decompositions of silane, $SiH_4$10), and diborane, $B_2H_6$11,12) have also been studied, but these decompositions were found to be homogeneous reactions. In the cases of methane6,13,14), germane9) and nickel carbonyl9), both heterogeneous and homogeneous reaction take place under ordinary circumstances at their decomposition temperatures, but the heterogeneous reaction only is taken into account in Table I.

In the case of germane decomposition it has been shown in previous papers9,15-17) that (1) the decomposition on germanium is a zero order reaction, and (2) during the decomposition the whole surface of the germanium is practically covered by chemisorbed hydrogen atoms the number of which is approximately equal to that of surface germanium atoms. (3) No hydrogen deuteride is formed by the decomposition of germane in the presence of an

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1) K. Tamaru, *J. Phys. Chem.*, **59**, 777 (1955).
2) K. Tamaru, ibid., **60**, 610 (1956).
3) M. Bodenstein, *Z. physik. Chem.*, **29**, 429 (1899).
4) A. Stock et al., *Ber.*, **37**, 901 (1904); **40**, 532 (1907); **41**, 1309 (1908)
5) K. Tamaru, *J. Phys. Chem.*, **59**, 1084 (1955).
6) R. M. Barrer, *Proc. Roy. Soc.*, **A149**, 253 (1935).
7) A. P. Garratt and W. H. Thompson, *J. Chem. Soc.*, **1934**, 1882.
8) C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 440 (1935).
9) K. Tamaru, M. Boudart and H. Taylor, *J. Phys. Chem.*, **59**, 801 (1955).
10) T. R. Hogness et al., *J. Am. Chem. Soc.*, **58**, 108 (1936).
11) R. P. Clarke and R. N. Pease, ibid., **73**, 2132 (1951).
12) J. K. Bragg et al., ibid., **73**, 2134 (1951).
13) L. S. Kassel, ibid., **54**, 3949 (1932).
14) H. H. Storch, ibid., **54**, 4188 (1932).
15) P. J. Fensham, K. Tamaru, M. Boudart and H. Taylor, *J. Phys. Chem.*, **59**, 806 (1955).
16) K. Tamaru and M. Boudart, "Advances in Catalysis", Vol. IX, Academic Press Inc., N. Y. (1957), p. 699.
17) K. Tamaru, *J. Phys. Chem.*, **61**, 647 (1957).

excess of deuterium. (4) When the mixture of germanium hydride and deuteride are decomposed together, abundant quantities of equilibrated deuteride are produced. (5) No exchange takes place between the two kinds of germane. (6) The desorption rate of the chemisorbed hydrogen on germanium at full coverage is equal to the decomposition rate of germanium hydride. (7) The ratio of the decomposition rates of germane and deuterogermane is 1.8 to 1.

The zero-order kinetics and the observation 2 exclude the Eley-Rideal mechanism, i. e., involving collisions of germane molecules in the gas phase, or those in the van der Waals' adsorption layer with the chemisorbed species on the surface. The observations 2 and 3 exclude the possibility of hydrogen molecules splitting off from the germanium hydrides on the surface, such as, for example, $\mathrm{GeH_4(a)} \rightarrow \mathrm{GeH_2(a)+H_2(g)}$, throughout the decomposition, because this process will not give so much hydrogen deuteride as has been found in the product, bearing in mind that no exchange reaction between hydrogen and deutrium molecules takes place while germane is being decomposed.

The following mechanism for the decomposition is consistent with all the data;

$$\mathrm{GeH_4(g)} \rightarrow \mathrm{GeH_3(a)+H(a)} \tag{A}$$

$$\mathrm{GeH_3(a)} \rightarrow \mathrm{GeH_2(a)+H(a)} \tag{B}$$

$$\mathrm{GeH_2(a)} \rightarrow \mathrm{GeH(a)+H(a)} \tag{C}$$

$$\mathrm{2H(a)\ or\ 2GeH(a)} \rightarrow \mathrm{H_2(g)} \tag{D}$$

and the last step, the desorption of hydrogen atoms to form hydrogen molecules, is a rate-determining step for the reaction. As the chemisorbed hydrogen covers the surface during the decomposition, the chemisorption of the germane, as will be shown later, is suppressed by the chemisorbed hydrogen and accordingly it appears most probable that as soon as the hydrogen desorbs, the step A takes place to keep the saturation of the surface, which results in the observation 5, no exchange between $\mathrm{GeH_4}$ and $\mathrm{GeD_4}$ being detected during the reaction.

For most of the other hydrides, the chemisorption step onto the surface could be considered as rate-determining from their kinetics. By making some assumptions we can expect to treat this kind of reaction with a statistical mechanical method to estimate the rate of each elementary step of the reaction and hence the order of reaction.

The rate of the heterogeneous elementary reaction V per unit surface area of catalyst surface is given by the following equation[18].

$$V=\frac{\boldsymbol{kT}}{\boldsymbol{h}}Gq^*\frac{N_a}{F_a^\circ}\mathrm{Q}_{\mathrm{C}^*(0)} \tag{1}$$

where G is the number of sites for the activated complex a^* per cm^2., q^* is the partition function of a^* and N_a is the concentration of initial reactant a in the gas phase, F_a° is the partition function of a per unit volume and $\mathrm{Q}_{\mathrm{C}^*(0)}$ is the probability that the sites for the activated complexes are vacant.

The following assumptions are used for the calculation of the rate of each elementary step of the decompositions.

(1) The bond energies between a hydrogenated element and the hydrogen atoms are the same for all the hydrogen atoms in the hydride molecule and are independent of the number of hydrogen atoms remaining within the hydride fragment.

(2) The translational, rotational and vibrational partition functions of the activated complexes of each elementary reaction and those of the chemisorbed radicals or molecules are taken as unity.

(3) All the elementary reactions other than the rate-determining step are rapid enough to be considered in equilibrium in the stationary state of the reaction.

(4) Each hydrogen atom of hydrides is assumed to split off one by one, as has been shown in the case of germane decomposition, and as each successive removal of a hydrogen atom accompanies an M-H bond cutting to form a M-M bond and an adjacent H(a), it is assumed that the true activation energy in each step is almost the same except the last step.

N_a in the Eqation 1 can be replaced by $\boldsymbol{P_a/kT}$ and T by $T_m\mathrm{e}^{1-\frac{T_m}{T}}$, where T_m is the median of the reaction temperature range[18,19]. Thus

$$V=\frac{\boldsymbol{kT_m eG}}{\boldsymbol{h}}\frac{P_a}{F_a}\mathrm{Q}_{\mathrm{C}^*(0)}\exp\left(-\frac{\Delta^*E}{\boldsymbol{RT}}\right) \tag{2}$$

where $F_a=\frac{\boldsymbol{kT_m}}{\boldsymbol{B}}F_a^\circ(T_m)\ e^{n+1}$ and n is the sum of the exponents of T in the translational and rotational partition functions, $\boldsymbol{B}$, conversion factor from mmHg into

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[18] J. Horiuti, *Catalyst*, Inst. Catalyst Res., Hokkaido Univ., Sapporo, **2**, 1 (1947); **7**, 107 (1951).

[19] T. Kwan, "Advances in Catalysis", Vol. VI Academic Press Inc., N. Y. (1954), p. 67.

c.g.s. unit, P_a, the pressure of a in mmHg, $F_a^\circ(T_m)$, translational, rotational and vibrasional partition functions of a at T_m, and Δ^*E is the difference of potential energy between the initial reactant a and the activated complex a^*. The values of F_a are listed in Table II.

TABLE II

T	a	F_a(mm.$^{-1}$)	a	F_a(mm.$^{-1}$)
551°K	AsH_3	3.2×10^{15}	H_2	4.2×10^{10}
350	SnH_4	1.1×10^{15}	H_2	8.6×10^{9}
573	H_2Se	2.8×10^{15}	H_2	4.8×10^{10}
308	SbH_3	0.9×10^{15}	H_2	5.5×10^{9}
1000	CH_4	5.0×10^{14}	H_2	3.4×10^{11}
381	$Ni(CO)_4$	6.5×10^{17}	CO	3.4×10^{13}
551	GeH_4	2.4×10^{15}	H_2	4.2×10^{10}

When a part of the catalyst surface is covered by the adsorption of a^*, etc., $Q_{C^*(0)}$ is expressed as follows;

$$Q_{C^*(0)}=\{Q_{C(a)}F_a\exp(-\Delta E(a)/RT)/P_a\}^{\alpha} \tag{3}$$

where $Q_{C(a)}$ is the probability that the sites for the adsorption are occupied by a, $\Delta E(a)$, the heat of adsorption of a, and α, the ratio of the number of lattice points for the activated complex over that for a, which is usually assumed to be unity.

Decomposition of Stibine on Antimony Surface.—The heat of the reaction is 34.8 kcal./mol.[20] and hydrogen does not chemisorb on an antimony surface[21]. The rate of each elementary reaction at 35° can be expressed as follows,

$$V_A=S(P_{SbH_3}/F_{SbH_3})Q_{C^*(0)}\exp(-\Delta^*E_A/RT)$$
$$=1.1\times10^{-15}SP_{SbH_3}\exp(-\Delta^*E_A/RT) \tag{4}$$

$$V_B=S(P_{SbH_3}/F_{SbH_3})(F_{H_2}/P_{H_2})^{\frac{1}{2}}\times\exp(-\Delta^*E_B/RT)Q_{C^*(0)}$$
$$=1.4\times10^{-2}S\frac{P_{SbH_3}}{\sqrt{P_{H_2}}}\times\frac{\exp(-\Delta^*E_A/RT)}{(1+1.4\times10^{-2}P_{SbH_3}/P_{H_2}^{\frac{1}{2}})} \tag{5}$$

$$V_C=\frac{2}{3}S\left(\frac{P_{SbH_3}}{F_{SbH_3}}\right)^{\frac{2}{3}}\exp(-\Delta^*E_C/RT)Q_{C^*(0)}$$
$$=0.6\times10^{-10}S(P_{SbH_3})^{\frac{2}{3}}\exp(-\Delta^*E_C/RT) \tag{6}$$

where V_A, V_B and V_C are the rates of the following elementary reactions, respectively,

$$SbH_3(g)\rightarrow SbH_2(a)+H(a) \tag{A}$$
$$SbH_2(a)\rightarrow SbH(a)+H(a) \tag{B}$$
$$2SbH(a)\text{ or }2H(a)\rightarrow H_2(g) \tag{C}$$

and S is $kTGe/h$ and Δ^*E_A, Δ^*E_B and Δ^*E_C are the activation energies for the steps, A, B and C, respectively.

The temperature, T_e, at which V_A and V_C are equal can be obtained by putting $V_A=V_C$.

$$T_e=\frac{\Delta^*E_C-\Delta^*E_A}{2.30R[(1/3)\log(F_{SbH_3}/P_{SbH_3})+\log(2/3)]}$$
$$=(\Delta^*E_C-\Delta^*E_A)/(21.6-1.52\log P_{SbH_3}) \tag{7}$$

Above this temperature V_A controls the overall rate and below this temperature V_C controls the rate, provided Δ^*E_C is larger than Δ^*E_A. In other words, at higher temperatures the decomposition is of first order, while at lower temperatures it is proportional to 2/3 power of the stibine pressure, being independent of hydrogen pressure. In the transition region of the two, at higher stibine pressures the activation energy becomes larger, as V_C controls the rate more predominantly, and at lower pressures vise versa from the Equation 7.

As shown in a previous paper[5] the observed activation energy for this reaction is dependent upon the partial pressure of stibine and decreases as the pressure decreases, and the order of the reaction increases as the reaction temperature becomes higher from a fractional order to a first order. Hence the experimental results seem to support those theoretical conclusions, if it is tentatively assumed that the difference between Δ^*E_C and Δ^*E_A is around 6 kcal./mol. provided that all the other assumptions are valid.

Another explanation of the experimental results is the interpretation of the fractional order on the basis of the Langmuir concept, assuming that the adsorption of $SbH_3(a)$ is appreciable. As has been discussed in the previous paper[5], however, this explanation seems to have little physical meaning according to Boudart[22].

Decomposition of Arsine on an Arsenic Surface at 278C°.—The heat of the reaction at 551°K is 38.6 kcal./mol. from the value at standard temperature and the

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[20] "Handbook of Chemistry and Physics", 35th Edition, by C. D. Hodgman et al., Chemical Rubber Publishing Co., Ohio. (1953).

[21] B. M. W. Trapnell, "Advances in Catalysis," Vol. IX., Academic Press Inc., N. Y., (1957), p. 238.

[22] M. Boudart, "Structure and Properties of Solid Surfaces", edited by G. R. Gomer and C. S. Smith, University of Chicago Press Chicago, Illinois, (1953) p. 400.

heat capacities of the gases[23], the followings are the results of a similar calculation for the decomposition.

$$V_A=3.1\times10^{-16}SP\exp(-\Delta^*E_A/\boldsymbol{RT}) \tag{8}$$

$$V_B=8.3\times10^{-6}S(P_{\mathrm{AsH_3}}/P_{\mathrm{H_2}}^{\frac{1}{2}})\times\exp(-\Delta^*E_A/\boldsymbol{RT}) \tag{9}$$

$$V_C=3.1\times10^{-11}SP_{\mathrm{AsH_3}}^{\frac{2}{3}}\exp(-\Delta^*E_C/\boldsymbol{RT}) \tag{10}$$

where Δ^*E_C in the Equation 10 is the true activation energy for the step C. The overall reaction is first order as is shown by the experiments, step A being rate-determining, provided that $\Delta^*E_C-\Delta^*E_A<$ 10 kcal. If this is the case and all the other assumptions are valid, $\boldsymbol{T_e}$, where V_A equals to V_C, becomes lower than 200°C at 100 mm. of arsine pressure from the similar calculations and above this temperature the decomposition will be first order, which is the case in the experiments.

Decomposition of Methane on Carbon Surface.—The decomposition of methane on a carbon surface at 1000°K can be treated in the same way. The change of the heat content in this decomposition, ΔH, is 21.6 kcal. per mole at this temperature, as ΔH at 25°C is 17.89 kcal./mol.[23] and $\Delta C_p=9.18-5.96\times10^{-3}T-0.051\times10^5T^{-2}$[24].

According to Barrer[6], the heat of adsorption of hydrogen on carbon is about 50 kcal./mol. being independent of its coverage. The results of the calculation are as follows, if we use the same suffixes for V_A, V_B, V_C and V_D as in the germane decomposition.

$$V_A=S(P_{\mathrm{CH_4}}/F_{\mathrm{CH_4}})\exp(-\Delta^*E_A/\boldsymbol{RT})\mathrm{Q}_{\mathrm{C^*(0)}}$$
$$=2.0\times10^{-15}S\frac{P_{\mathrm{CH_4}}\exp(-\Delta^*E_A/\boldsymbol{RT})}{1+0.24\,P_{\mathrm{H_2}}} \tag{11}$$

if it is noted that the step A takes place on the unsaturated carbon bonds on the surface and hence

$$\mathrm{Q}_{\mathrm{C^*(0)}}=\frac{1}{1+(P_{\mathrm{H_2}}/F_{\mathrm{H_2}})\exp(50{,}000/\boldsymbol{RT})}$$

and

$$V_B=S\frac{P_{\mathrm{CH_4}}}{F_{\mathrm{CH_4}}}\left(\frac{F_{\mathrm{H_2}}}{P_{\mathrm{H_2}}}\right)^{\frac{1}{2}}\mathrm{Q}_{\mathrm{C^*(0)}}\exp(-\Delta^*E_B/\boldsymbol{RT})$$
$$=2.1\times10^{-9}S\frac{P_{\mathrm{CH_4}}}{P_{\mathrm{H_2}}^{\frac{1}{2}}}\,\frac{\exp(-\Delta^*E_A/\boldsymbol{RT})}{1+0.23\,P_{\mathrm{H_2}}} \tag{12}$$

$$V_C=S\frac{P_{\mathrm{CH_4}}}{F_{\mathrm{CH_4}}}\,\frac{F_{\mathrm{H_2}}}{P_{\mathrm{H_2}}}\mathrm{Q}_{\mathrm{C^*(0)}}\exp(-\Delta^*E_C/\boldsymbol{RT})$$
$$=2.1\times10^{-2}S\frac{P_{\mathrm{CH_4}}}{P_{\mathrm{H_2}}}\,\frac{\exp(-\Delta^*E_A/\boldsymbol{RT})}{1+0.23\,P_{\mathrm{H_2}}} \tag{13}$$

as Δ^*E_B and Δ^*E_C are equal to $\Delta^*E_A-\frac{1}{3}(25{,}000-21{,}600)$ and $\Delta^*E_A-\frac{2}{3}(25{,}000-21{,}600)$, respectively and the coverage of CH(a), $\mathrm{Q}_{\mathrm{C^*(CH(\alpha))}}$, of $\mathrm{H_2(g)}\rightleftarrows\mathrm{2H(a)}$, are appreciable according to the calculation. On the other hand,

$$V_D=8.0\,S\frac{P_{\mathrm{CH_4}}^{\frac{1}{2}}\exp(-\Delta^*E_{0D}/\boldsymbol{RT})}{(1+4.0\,P_{\mathrm{CH_4}}^{\frac{1}{4}})^2}$$
$$\fallingdotseq\frac{S}{2}\exp(-\Delta^*E_{0D}/\boldsymbol{RT}) \tag{14}$$

which is obtained from the following equations,

$$V_D=\frac{S}{2}\left(\frac{P_{\mathrm{CH_4}}}{F_{\mathrm{CH_4}}}\right)^{\frac{1}{2}}\mathrm{Q}_{\mathrm{C^*(0)}}\exp(-\Delta^*E_D/\boldsymbol{RT})$$

$$\theta_H/(1-\theta_H)=(P_{\mathrm{CH_4}}/F_{\mathrm{CH_4}})^{\frac{1}{4}}\times\exp\left(\frac{-25{,}000\times4+21{,}600}{4\boldsymbol{RT}}\right)$$
$$=4.0\times P_{\mathrm{CH_4}}^{\frac{1}{4}}$$

$$\mathrm{Q}_{\mathrm{C^*(0)}}=(1-\theta_H)^2$$

$$\Delta^*E_D=\Delta^*E_{0D}-\frac{1}{2}(25{,}000\times4-21{,}600)$$

where $\Delta^*{}_0E_D$ is the true activation energy for the step D.

The observed activation energy for this reaction is 53.4 kcal. and $\exp(70{,}000/\boldsymbol{RT})$ is equal to 2.0×10^{15}. Hence the step A is rate-determining, if Δ^*E_{0D} is less than 120 kcal./mol., which is most probably the case.

Barrer found that a kinetic expression,

$$V=\frac{\boldsymbol{k}P_{\mathrm{CH_4}}}{1+0.022\,P_{\mathrm{H_2}}}$$

is applicable to this reaction, which is in fair agreement with the theoretical equation 11, if the ambiguity of the heat of adsorption of hydrogen on carbon is taken into account. As $\exp(30{,}000/\boldsymbol{RT})$ is equal to 3.6×10^6, the assumption 4 of the equal activation energies can be adjusted to nearly 30 kcal. for the step B, if all the other assumptions are valid.

Decomposition of Germane on a Germanium Surface at 302°C.—The results of a similar calculation are as follows, as the heat of adsorption of hydrogen on

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[23] F. D. Rossini and D. D. Wagman, "The Selected Values of Chemical Thermodynamic Properties," U. S. Government Printing Office (1952).

[24] Kelley, Bull. of Bur. of Mines, No. 407 (1937).

germanium is 23.5 kcal./mol. at low coverages[17].

$$V_A=S\frac{P_{\mathrm{GeH_4}}}{2.4\times10^{15}}\left(\frac{1}{1+0.23\sqrt{P_{\mathrm{H_2}}}}\right)^2 \times\exp\left(-\varDelta^*E_A/RT\right) \tag{15}$$

$$V_B=S\frac{P_{\mathrm{GeH_4}}}{F_{\mathrm{GeH_4}}}\left(\frac{F_{\mathrm{H_2}}}{P_{\mathrm{H_2}}}\right)^{\frac{1}{2}}\times\exp\left[-\left(\varDelta^*E_A-\frac{1}{3}(q+11{,}800)\right)\Big/RT\right]Q_{\mathrm{C^*(0)}} =\frac{3.1\times10^{-10}SP_{\mathrm{GeH_4}}\exp[-(\varDelta^*E_A-q/3)/RT]}{(1+0.23P_{\mathrm{H_2}}^{\frac{1}{2}})^2P_{\mathrm{H_2}}^{\frac{1}{2}}} \tag{16}$$

$$V_C=\frac{2.3\times10^{-2}SP_{\mathrm{GeH_4}}\exp[-(\varDelta^*E_A-2q/3)/RT]}{P\left[1+0.23P_{\mathrm{H_2}}^{\frac{1}{2}}+0.023\frac{P_{\mathrm{GeH_4}}}{P_{\mathrm{H_2}}}\exp\left(\frac{2q}{3RT}\right)\right]^2} \tag{17}$$

$$V_D=\frac{S}{2}\exp\left(-\varDelta^*E_{0D}/RT\right) \tag{18}$$

where q is the heat of the reaction and $\varDelta^*E_{0D}$ is the true activation energy for the step D. As the decomposition is probably exothermic, either V_A or V_D is the rate-determining step.

The experimental results show that the step D is the rate-determining step and the observed activation energy is 41.2kcal./mol. As $\exp(41{,}200/RT)$ is equal to 2.2×10^{16} at 302°C, V_D can be slower than V_A by 10^2 at the slowest at 10 cm. pressure of germane if $\varDelta^*E_A$ is small enough. As will be shown later the observed reaction rate agrees satisfactorily with the calculated V_D. In the cases of the decompositions of tin hydride, arsine, etc., on the other hand, in which the step A is rate-determining, the partition functions of the activated complexes of V_A are usually not unity, but have fairly large values, which is probably the case in V_A of the Equation 15. This is probably one of the reasons why the step D is rate-determining, and, consequently, at much higher temperatures it can be expected that the reaction becomes first order in respect to germane, V_A being rate-determining, as the apparent activation enenrgy of V_A is smaller than $\varDelta^*E_{0D}$.

The fact that no exchange between GeD_4 and GeH_4 to form GeH_xD_y is observed during the reaction is explained by the slow rate of chemisorption of germane on the germanium surface, as the rate of chemisorption is retarded by the chemisorbed hydrogen atoms which cover the surface. If the desorption of hydrogen is assumed to be the only rate-determining step, the adsorption rate of germane onto the surface is so retarded by the chemisorbed hydrogen that it turns out slower than the desorption rate from the calculation. This implies that the adsorption rate is so retarded by the chemisorbed hydrogen atoms that another potential energy cascade appears at this adsorption step besides the desorption step, while the germanium surface is still almost saturated in this case.

Decomposition of Other Hydrides and Nickel Carbonyl.—The decomposition of tin hydride on tin surfaces can be treated in the similar way. It can be shown that the step A is rate-determining and the reaction is first order as in Table I, provided that the heat of the reaction is between 40 and −40 kcal./mol. and $\varDelta^*E_{0D}$ is not larger than 20 kcal./mol.

In the case of the decomposition of hydrogen selenide, a similar calculation shows that it should be of first order in respect to hydrogen selenide.

The decomposition of nickel carbonyl on nickel surface can be treated in a similar way, though the nature of the chemical bonds between CO and nickel atom are different from those in the hydrides. The heat of the decomposition was given by Fischer et al.[25] The results of the calculation showed that the chemisorption of nickel carbonyl on nickel surface is rate-determining, having the kinetic expression of $v=kP_{\mathrm{Ni(CO)_4}}/(1+bP_{\mathrm{CO}})$ as Bawn has observed. The value of b in the expression was also computed with a reasonable agreement.

The observed and the calculated reaction rates are shown in Table III, where the unit of pressure, P, is mmHg. and the activation energy at 10 cm. stibine pressure is used for stibine decomposition; the tin and germanium surface are considered to be smooth. In these calculations the number of the sites for the reactions per cm.^{2}, G, is taken as 10^{15}. The discrepancies between the observed and

TABLE III

	Temp.	Observed rate	Calculated rate
GeH_4	302°C	5.2×10^{13}	0.5×10^{13} mol./sec. cm.^{3}
AsH_3	278	7.9×10^{9} P	6.0×10^{3} P
SbH_3	35	8.2×10^{10} P	3.6×10^{8} P
SnH_4	77	2.3×10^{13} P	3.7×10^{7} P

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[25] A.K. Fischer et al., *J. Am. Chem. Soc.*, **79**, 2044 (1957).

the calculated values are probably due to the large values of the partition functions of the activated complexes, not being unity.

The number of collisions of gas molecules on unit surface area per second (n_c) and that of reacted molecules (n_r) are shown in Table IV, where $\varDelta^*E$ is the observed activation energy for the reaction. In the case of germane decomposition it is shown that $n_c \exp(-\varDelta^*E/RT)$ is much smaller than n_r, which suggests that the rate-determining step is not the chemisorption step on bare surface.

TABLE IV

	Temp.	n_c	$n_c \exp\left(\frac{-\varDelta^*E}{RT}\right)$	n_r
GeH_4	302°C	1.7×10^{20} P	3.7×10^{4} P	5.2×10^{13}
AsH_3	278	1.7×10^{20} P	1.1×10^{11} P	0.8×10^{10} P
SbH_3	35	1.8×10^{20} P	3.3×10^{15} P	0.8×10^{11} P
SnH_4	77	1.7×10^{20} P	3.5×10^{14} P	2.3×10^{13} P

A tin surface, for instance, does not chemisorb hydrogen[26], nevertheless it chemisorbs tin hydride to decompose it to tin and hydrogen. This chemisorption depends upon the bond strength between the chemisorbed species and the element, and if the total strength of the dissociative adsorption is strong enough to chemisorb, the chemisorption takes place to decompose the hydride. Thus hydrogen from hydride might be chemisorbed on the elements on which hydrogen gas is not chemisorbed. The fact that arsine can be decomposed on antimony more rapidly than on an arsenic surface[1], or that ammonia can be decomposed on germanium[27] might be explained on this basis.

Summary

The decomposition of arsine, stibine, tin hydride, methane, germane, hydrogen selenide and nickel carbonyl on the surface of the corresponding elements have been discussed from the statistical mechanical view-point. As these decompositions are catalytic reactions of the simplest type, several reasonable assumptions enable us to calculate the rates of each elementary step of each reaction and hence to decide the rate-determining step in a semi a priori fashion. It is shown that the calculations impose definite limitations to the possible mode of decompositions of this kind.

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[26] B. M. W. Trapnell, *Proc. Roy. Soc.*, **A218**, 566 (1953).

[27] K. Tamaru, *J. Phys. Chem.*, **60**, 612 (1956).