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The Deposition Rate of Arsenic by the Hydrogen Reduction of Arsenic(III) Chloride*

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Synopsis

The hydrogen reduction of arsenic(III) chloride has been examined under different conditions. The reduction was carried out in gas phase, and the manometric measurement showed that the reaction in gas phase did not proceed below 450°C. Arsenic was deposited on a substrate heated in the flow of the mixed gas composed of arsenic(III) chloride and a large excess of hydrogen, and its deposition rate was measured. The activation energy of arsenic deposition was found to be 22.3 kcal/mol (298~370°C), when the rate-determining step was the chemical reaction proceeding on the surface of previously deposited arsenic.

I. Introduction

Mond⁽¹⁾, in 1890, prepared a high purity-nickel by the thermal decomposition of nickel carbonyl. At the same time, some trials to obtain metals or nonmetals from a gas phase had been carried out, and in 1925 van Arkel⁽²⁾ succeeded in depositing a high-purity titanium on a tungsten filament heated in gaseous titanium(IV) iodide. The similar process was applied to other refractory metals as zirconium, hafnium, thorium and so on. As these, the process to obtain metals or nonmetals from their volatile compounds by the thermal decomposition in a gas phase or by the deposition on a substrate heated at higher temperatures than those of the gas is called CVD process (Chemical Vapor Deposition), and which has been widely applied in various fields such as refining, coating and jointing of metals, preparation of electronic films or semiconductors and so on. The recent works on CVD are compiled in books by the investigators⁽³⁾ of the Battelle Memorial Institute.

In this study, the deposition of arsenic by the hydrogen reduction of arsenic(III) chloride was selected as one of fundamental investigations on CVD, because

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(2) A.E. van Arkel and J.H. de Boer, *Z. Anorg. Allgem. Chem.*, **148** (1925), 345.

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C.F. Powell, J.H. Oxley and J.M. Blocher, Jr., *Vapor Deposition*, John Wiley & Sons, New York (1966).

arsenic(III) chloride is volatile even at room temperature, though toxic, and its deposition temperature is lower than that of refractory metals.

Several investigations on the hydrogen reduction of arsenic(III) chloride were already reported. Meyer⁽⁴⁾ studied the chemical reaction of chlorine, arsenic(III) chloride and hydrogen, and he found that arsenic(III) chloride was reduced qualitatively to arsenic. Besson⁽⁵⁾ obtained the compound, $As_{11}Cl$, by electrodischarging in the mixed gas composed of arsenic(III) chloride and hydrogen. Miyake *et al.*⁽⁶⁾ investigated, from the standpoint for preparing a high-purity arsenic, the effect of the reaction temperature on the yield of arsenic formed by the hydrogen reduction of arsenic(III) chloride, and they reported that the suitable temperature range for the deposition lay between 800°C and 850°C. These studies treated the reaction occurring in gas phases.

The main purpose of this study is to measure the deposition rate of arsenic formed on the surface of a substrate covered with arsenic film, and the reduction reaction in a gas phase is also investigated in order to obtain some informations on the deposition mechanism of arsenic from the gas phase.

II. Experimental

1. Purification of arsenic(III) chloride

From the measurement of a mass spectrometer, hydrogen chloride and water were detected in the gas phase of crude arsenic(III) chloride. The purification was as follows; a vacuum line was set up, where two Kjeldahl flasks were connected with phosphorus(V) oxide trap. Crude arsenic(III) chloride was placed in one of Kjeldahl flasks, all the line was evacuated for a while and the other flask was cooled with liquid nitrogen. Arsenic(III) chloride was vaporized and condensed into the cooled flask through phosphorus(V) oxide trap. This operation was repeated several times.

2. The reaction temperature in gas phase and some kinetic investigations

The heterogeneous reaction proceeding on the surface of a substrate takes great parts in the deposition of metal in CVD process. It⁽⁷⁾, however, is possible that the metal having been formed by the homogeneous chemical reaction in the gas phase near the surface of a heated substrate co-deposits on the substrate. This possibility was checked by a manometric measurement.

Fig. 1 shows the instruments used for this purpose. The Bourdon gauge and the trap (9) was kept at a constant temperature, and all the system was evacuated ($10^{-4} \sim 10^{-5}$ mmHg). Arsenic(III) chloride was introduced into the reaction vessel, the cock(7) was closed, and the pressure of arsenic(III) chloride was measured

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(5) A. Besson and L. Fournier, Compt. Rend., **159** (1910), 872.

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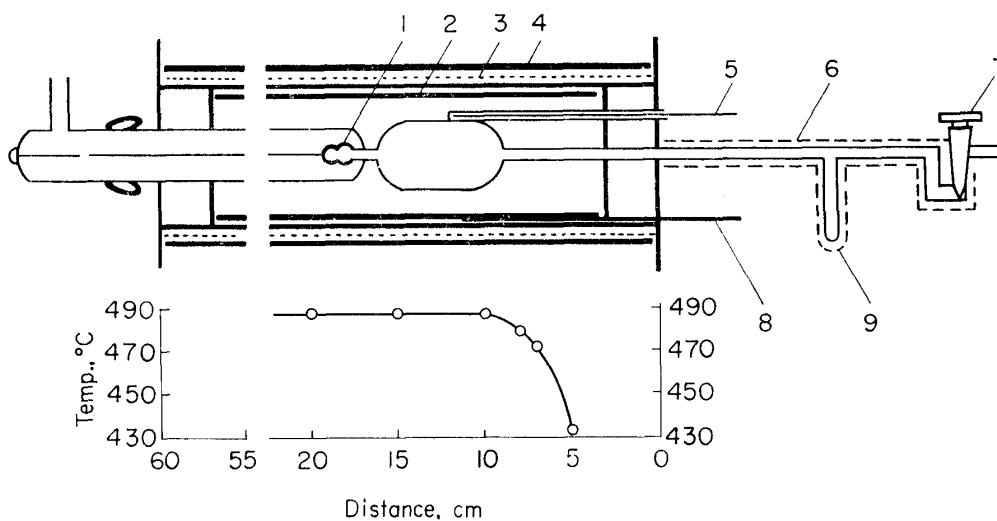


Fig. 1. Cross section of the reaction vessel and the temperature distribution in the electric furnace.

(1) Bourdon gauge, (2) stainless steel tube, (3) heater, (4) copper plate, (5) thermocouple for measuring the temperature of the reaction vessel, (6) band heater, (7) teflon cock, (8) thermocouple for controlling the temperature of the electric furnace and (9) trap.

with the Bourdon gauge. The trap was cooled with liquid nitrogen and arsenic(III) chloride was solidified. Then the cock (7) was opened, hydrogen was admitted as its pressure was measured and the cock (7) was closed again. The trap was heated with the band heater, and arsenic(III) chloride was evaporated quickly. As the heat resistance temperature of cock (7) was about 150°C, the external part of the furnace was kept at 80°C with the band heater. Time zero was defined when the quick vaporization of arsenic(III) chloride was finished, and the increasing pressure due to the reaction was followed with the Bourdon gauge.

3. The measurement of arsenic deposition

Fig. 2 shows the flowsheet. Hydrogen was passed into a heated titanium sponge (800~900°C), where nitrogen and oxygen are removed. Water was also removed with potassium hydroxide, active alumina, silica gel and Molecular Sieves, which prevent powdery titanium hydride formed at the furnace of the titanium sponge from being carried into the system after the rotor meter. The purified hydrogen was led into the vaporizer of arsenic(III) chloride and next into the vertical reactor. Unreacted arsenic(III) chloride and hydrogen chloride formed at the reactor were removed with the cooled traps and the washing bottle, and finally only hydrogen was exhausted in air.

The vaporizer was kept at several constant temperatures (-20°C, 0°C, 15.5°C and 25°C) with the thermostat, and the partial pressure of arsenic(III) chloride was kept constant during an arsenic deposition. The partial pressure of arsenic(III) chloride was measured with a Bourdon gauge after sampling the mixed gas, because the higher flow rate of hydrogen through the vaporizer might cause the lower partial pressure even when the temperature of the vaporizer was kept

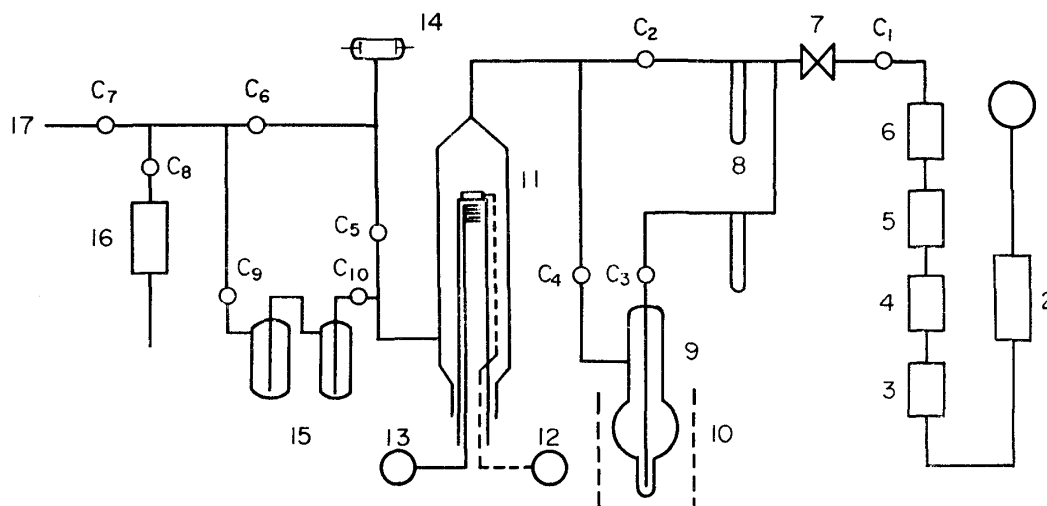


Fig. 2. Flowsheet for arsenic deposition by hydrogen reduction of arsenic(III) chloride. (1) hydrogen bomb, (2) heated titanium sponge, (3) potassium hydroxide, (4) active alumina, (5) silica gel, (6) Molecular Sieves, (7) rotor meter, (8) flow meter, (9) vaporizer of arsenic(III) chloride, (10) thermostat, (11) vertical reactor, (12) recorder, (13) transformer, (14) Geissler's tube, (15) liq.- N_2 trap, (16) washing bottle containing potassium hydroxide solution, (17) to vacuum pump and C_i ($i=1\sim 10$), vacuum cock.

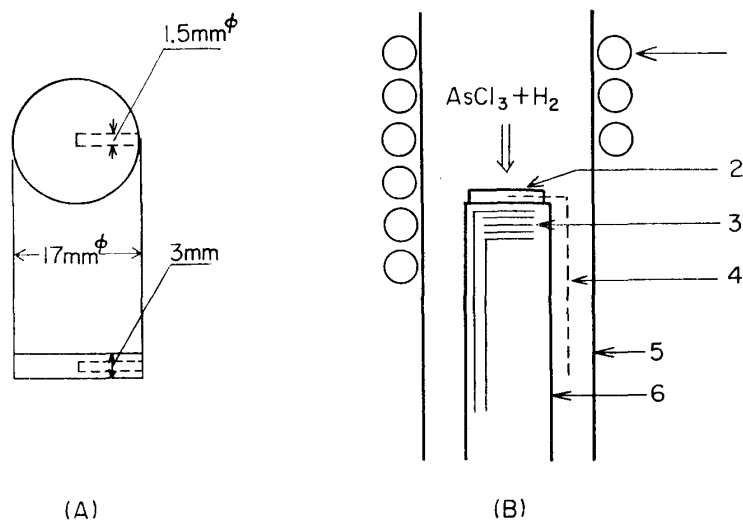


Fig. 3. Iron substrate (A) and vertical reactor (B)
 (1) water cooling tube, (2) iron substrate, (3) heater, (4) thermocouple, (5) 40 mm ϕ quartz tube and (6) 20 mm ϕ quartz tube.

constant.

Fig. 3 shows the reactor. An iron substrate was heated externally with a winding of sheath type nichrome heater, the temperature of which being controlled manually by regulating a heater current. The back of the substrate was covered with aluminium foil to prevent arsenic from depositing on the back. The iron substrate had a 1.5 mm ϕ hole into which the calibrated sheath type thermocouple was inserted for measuring the temperature of the substrate. Another thermocouple having been soldered on the surface of the substrate showed no temperature

difference between the surface and the hole.

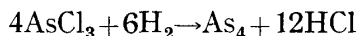
An iron substrate was made of electrolytic iron by means of a vacuum metallurgy. It was polished with No. 800 emery paper and was washed with benzene. It was weighed just before an arsenic deposition.

After a substrate was heated at a constant temperature in a pure hydrogen flow, the path of the pure hydrogen was changed to the vaporizer. This time was defined as time zero, and arsenic was deposited. The deposition was finished when the pure hydrogen was led into the reactor again. The substrate with deposited arsenic on its surface was weighed as soon as it was set off from the reactor.

III. Results and discussion

1. The reaction temperature and some kinetic investigations in gas phase

The reduction reaction is expressed by the following equation.



If As_4 was gaseous, the increase of the total pressure corresponding to 3 moles should be observed. In this study, however, arsenic was deposited on the part of the vessel heated at 80°C . The reaction proceeded so slowly, and at the same time, arsenic transferred so fast from the reaction vessel to the part heated at 80°C , that the partial pressure of arsenic in the system should be equal to the saturated pressure at 80°C , which is negligibly small. Consequently, the increase of the total pressure should correspond to 2 moles as long as the reaction rate was slow.

Fig. 4 and Fig. 5 show the pressure-time curves obtained under various initial pressures, where a and b mean those of arsenic(III) chloride and hydrogen, respectively. The reaction was found to have a measurable rate above 450°C .

As these curves were seemed to have a regularity, some kinetic investigations were tried. After t minutes, the pressure of arsenic(III) chloride is $a-x$. The reaction rate law is

$$-\frac{d(a-x)}{dt} = k(a-x)^\alpha \left(b - \frac{3}{2}x\right)^\beta \quad (1)$$

α, β ; order of reaction

a, b ; initial pressure of arsenic(III) chloride and hydrogen, respectively

The total pressure, p , is
$$p = a + b + \frac{1}{2}x \quad (2)$$

hence,
$$\frac{dp}{dt} = \frac{1}{2} \frac{dx}{dt} \quad (3)$$

from (1) and (3)
$$\frac{dp}{dt} = \frac{k}{2} (a-x)^\alpha \left(b - \frac{3}{2}x\right)^\beta \quad (4)$$

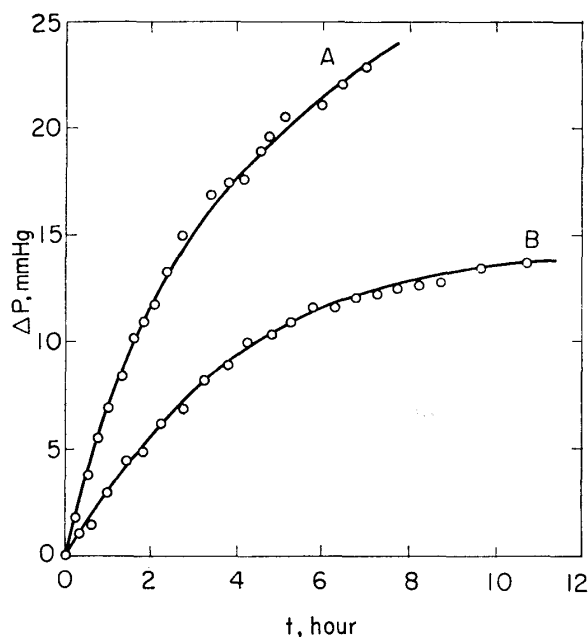


Fig. 4. Pressure-time curves obtained at 470°C under various initial pressures. (A); $a=7.74$ cm Hg, $b=10.05$ cmHg, (B); $a=7.73$ cmHg, $b=6.10$ cmHg.

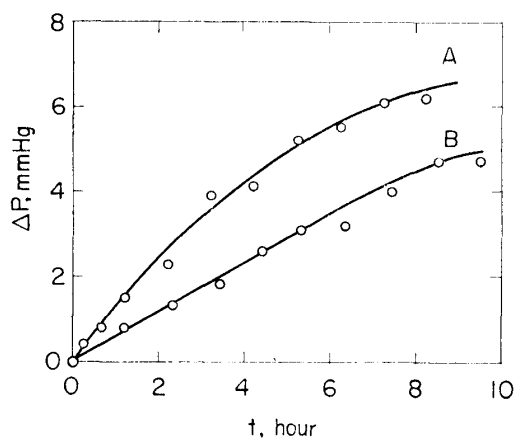


Fig. 5. Pressure-time curves obtained at 470°C under various initial pressures. (A); $a=4.06$ cmHg, $b=9.54$ cmHg (B); $a=4.02$ cmHg, $b=6.08$ cmHg

$$\text{at } t=0 \quad \left(\frac{d\dot{p}}{dt}\right)_{t=0} = \frac{k}{2} a^\alpha b^\beta \quad (5)$$

The logarithm of (5) is

$$\log\left(\frac{d\dot{p}}{dt}\right)_{t=0} = \log\left(\frac{k}{2}\right) + \alpha\log(a) + \beta\log(b) \quad (6)$$

Equation (6) shows $\log\left(\frac{d\dot{p}}{dt}\right)_{t=0}$ vs. $\log(a)$ (or $\log(b)$) should have the linearity if $\log(b)$ (or $\log(a)$) is constant.

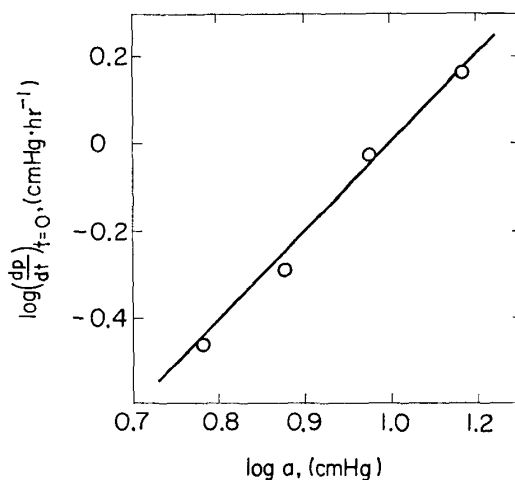


Fig. 6. Linear relationship between the logarithm of the initial rate, $(dp/dt)_{t=0}$, and the logarithm of the initial pressure of arsenic(III) chloride, a , under the constant initial pressure of hydrogen, 11.58 cmHg.

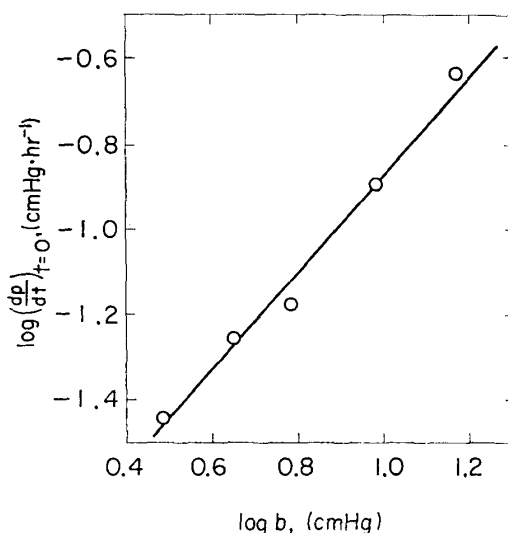


Fig. 7. Linear relationship between the logarithm of the initial rate, $(dp/dt)_{t=0}$, and the logarithm of the initial pressure of hydrogen, b , under the constant initial pressure of arsenic(III) chloride, 4.02 cmHg.

Fig. 6 and Fig. 7 show the linear relationship between $\log\left(\frac{dp}{dt}\right)_{t=0}$ and $\log(a)$ (or $\log(b)$). From the inclination, the values of α and β were obtained, and k could be calculated when $\log(a)$ or $\log(b)$ was extrapolated to zero.

The kinetic parameters thus obtained are given in Table 1. These orders of reaction are explained well, by the assumption that the activated complexes such as $\text{AsCl}_3 \cdot \text{H}_2$ or $(\text{AsCl}_3)_2$ might be formed at the rate-determining step. The reaction mechanism, however, was not known, because it could not be estimated how the impurities, the surface or the temperature distribution of the reaction vessel contributed to the main reaction path.

Table 1. Kinetic parameters for the hydrogen reduction of arsenic(III) chloride at 470°C .

AsCl ₃ cmHg	H ₂ cmHg	Order of reaction		log <i>k</i> (cmHg ⁻² hr ⁻¹)
		AsCl ₃	H ₂	
4.02	3.05-14.73		1.10	-2.93
7.71	6.10-12.13		0.92	-2.99
5.86-12.08	9.98	2.02		-2.72
6.08-12.15	11.58	2.05		-2.92

2. The measurement of the deposition rate of arsenic

Fig. 8 shows the relationship between the weight increase of deposited arsenic and the time of deposition. Deposited arsenic was black, amorphous powder and homogeneously coated the surface of the substrate. The weight increased fast at the beginning of deposition, and after 1 mg of deposition, it increased linearly. By the calculation from the density of amorphous arsenic, 1 mg of deposited arsenic was found to correspond to 10,000 Å of arsenic film thickness. The reason why the deposition proceeded fast at the beginning is thought due to the catalytic hydrogen reduction occurring on the surface of iron. When the surface of the iron substrate was completely covered with arsenic, the weight increased linearly, because the reaction proceeded on the surface of the previously deposited arsenic. In this study, considering this experimental result, the deposition rate was measured, after the surface of a substrate had been covered with arsenic completely.

Arsenic was deposited only by the heterogeneous reaction under this experimental temperature, because the reduction reaction in gas phase was not recognized to proceed below 450°C .

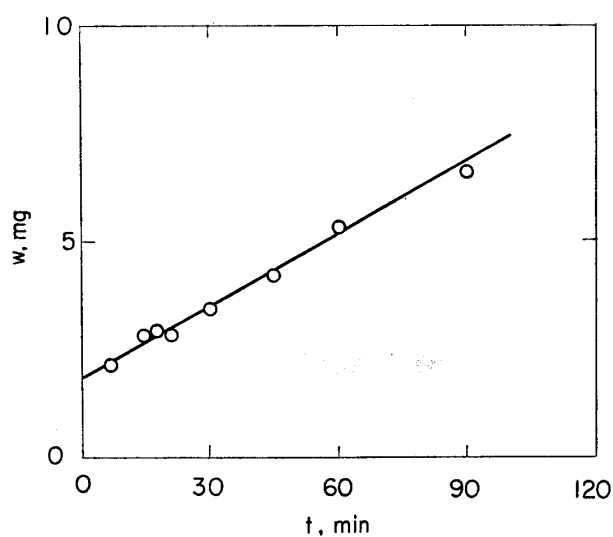


Fig. 8. Weight of deposited arsenic *vs.* time. Temperature of substrate, 370°C , temperature of vaporizer, 0°C and flow rate of hydrogen, 850 ml/min.

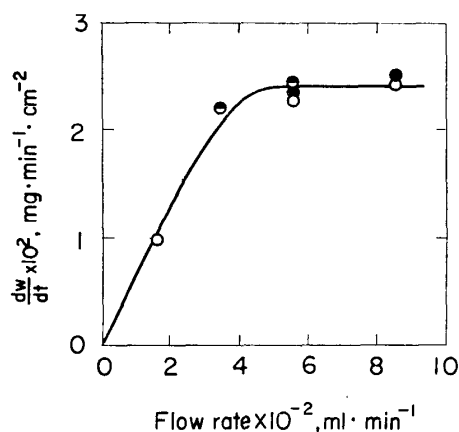


Fig. 9

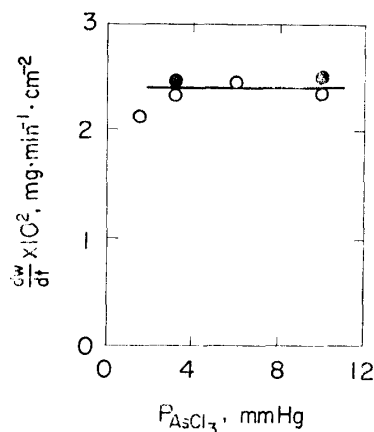


Fig. 10

Fig. 9. Dependence of the deposition rate of arsenic on the flow rate of hydrogen at 370°C. Partial pressure of arsenic(III) chloride; ○ 3.2 mmHg, ◐ 6.0 mmHg, ● 10.0 mmHg.

Fig. 10. Dependence of the deposition rate of arsenic on the partial pressure of arsenic(III) chloride at 370°C. Flow rate of hydrogen; ○ 550 ml/min, ● 850 ml/min.

The formation of arsin by the reaction between arsenic and hydrogen must be considered as the cause to decrease the weight of a substrate. This reaction⁽⁸⁾, however, does not take place below 1100°C. It is also necessary to consider the re-evaporation of deposited arsenic. Arsenic has a definite vapor pressure, 0.123 mmHg even at 300°C, and its rate of vaporization is thought rather large. Consequently the measured deposition rate may include the evaporation rate of previously deposited arsenic.

Fig. 9 shows the dependence of the deposition rate of arsenic on the flow rate of hydrogen. The deposition rate increased parabolically with increasing the flow rate and attained to a constant value above 500 ml/min.

The process of the metal deposition may be considered to consist of the following steps:

- (1) The diffusion of reactants to the surface of a substrate.
- (2) The chemical reaction on the surface, which has the process of adsorption and desorption of reactants and gaseous products, respectively.
- (3) The diffusion of gaseous products to the gas phase.

In this study, under dynamic flow, the boundary condition could not be estimated in detail. Qualitatively, however, the rate-determining step transfers from (1) to (2) with increasing the flow rate, and finally the deposition rate becomes independent of the flow rate. In consequence, in the region above 500 ml/min, the chemical reaction may be the rate-determining step.

Fig. 10 shows the dependence of the deposition rate of arsenic on the partial pressure of arsenic(III) chloride. The partial pressure had no great effect on the deposition rate. The latter, however, became slightly low at 2 mmHg.

Fig. 11 shows the Arrhenius plots in the range from 298°C to 370°C. The

(8) A.J.J. Vandeveldel, Bl. Acad. Belg., **30** (1895), 78.

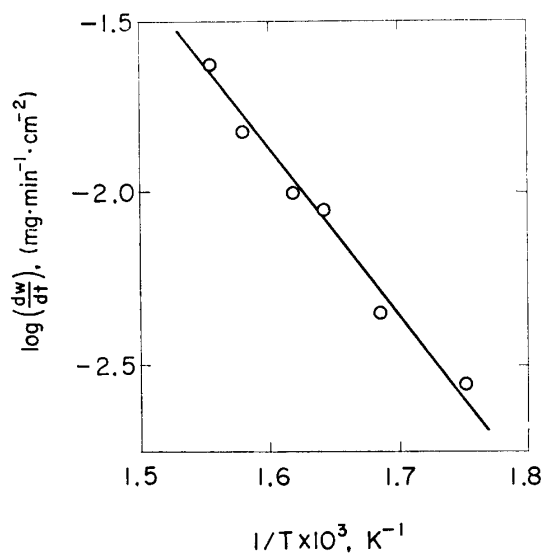


Fig. 11. Arrhenius plots of the deposition rates of arsenic at the flow rate of hydrogen, 550 ml/min, and the partial pressure of arsenic(III) chloride, 3.2 mmHg.

activation energy was found to be 22.3 kcal/mol, which was that of the process where the reaction proceeding on the surface of arsenic was the rate-determining step.

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