JOURNAL OF SOLID STATE CHEMISTRY 9, 197–201 (1974)

The Reaction Between Solid Lead and Chlorine Gas

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Received May 7, 1973

When lead reacts with a chlorine atmosphere the reaction rate shows a logarithmic rate law followed by a parabolic one. Both reaction rates can be explained by assuming that electron holes in the reaction product are rate-determining. In the beginning, the reaction of holes with lead (I) ions on lead ion lattice sites in $PbCl_2$ is the rate-determining step; later, the transport of holes by diffusion through the growing $PbCl_2$ layer becomes rate-determining.

An oxide layer on the lead before chlorination retards the reaction, while, on the contrary, traces of oxygen in the chlorine gas accelerate the reaction. Both phenomena can be explained by assuming that a mixed compound $PbO_{1-x}Cl_{2x}$ is formed. It is concluded that the presence of impurities in the system may influence the reaction rate drastically.

Introduction

In our laboratory several investigations on lead halides are carried out. Especially the nonstoichiometry and related properties are studied (*1–5*). As Wagner (*6*) has pointed out, the oxidation of metals depends on the properties of the reaction product. We therefore started an investigation on the reaction rate between solid lead and chlorine gas.

Experimental Procedures

The reaction was carried out with polycrystalline lead which was evaporated on a quartz crystal microbalance (*7*). After admittance of chlorine gas, the formation of lead chloride can be followed since the frequency of the quartz crystal changes proportionally.

In preliminary experiments the evaporation was carried out in an Edwards coating unit 6E2 and the quartz crystal was brought through the atmosphere into a reaction chamber into which chlorine gas was admitted.

Later on we constructed a reaction vessel in which the evaporation of the lead as well as the reaction with chlorine gas could be carried out. Both instruments and the auxiliary apparatus have been described in full detail elsewhere (*8*).

Results

The following experiments have been carried out:

(a) The reaction between pure lead and pure chlorine gas is investigated at 373 K and at 448 K. In both cases first a logarithmic rate law and later a parabolic one has been observed for the growth of the reaction product (Figs. 1 and 2).

(b) In the preliminary experiments the lead was oxidized by the atmosphere before the reaction with chlorine gas started. In these cases we observed a retardation of the reaction. The rate of this retarded reaction resembles the rate of the reaction of pure lead monoxide, PbO, with chlorine gas (Figs. 1 and 2).

(c) In some experiments the chlorine atmosphere contains an increasing amount of traces of oxygen due to a leak in the reaction vessel. After several hours we observed a "breakthrough" of the reaction product resulting in a sudden increase of the reaction rate (Figs. 1 and 2).

(d) Water vapour in the chlorine atmosphere retards the reaction rate in the logarithmic and the parabolic stage of the reaction (Figs. 1 and 2).

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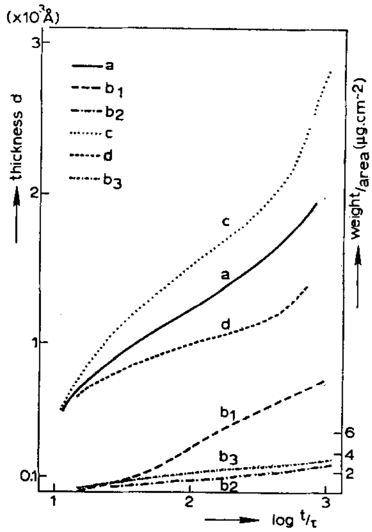

FIG. 1. Typical d vs t curves for the reaction Pb + Cl_2 at 373 K. First stage of the reactions; t plotted as $\log t/\tau$; t in seconds; $\tau = 1$ sec; (a) pure lead and pure chlorine gas; (b) (b_1) pure lead, after approx. 1 min exposure to the atmosphere, and chlorine gas; (b_2) pure lead, after approx. 1 hr exposure to the atmosphere, and chlorine gas; (b_3) lead monoxide, PbO, and chlorine gas (weight increment vs t plotted); (c) lead and chlorine gas, containing some traces of oxygen (see text); (d) lead and chlorine gas containing water vapour.

(e) Water vapour attacks a freshly prepared lead chloride layer when it is admitted into the reaction vessel after removal of the chlorine gas. First a fast decrease of the probe weight is observed, but later on a slow increase (Fig. 3).

Discussion

The five experiments mentioned above will now be discussed in the same sequence.

(a) We will first show that the observed logarithmic and parabolic growth must be expected from the reaction between solid lead and gaseous chlorine.

The reaction kinetics depends on the properties of lead chloride. $PbCl_2$ is an anionic conductor; the dominant defects are of the Schottky type (*1*):

$$\mathrm{O} \rightleftharpoons V_{\mathrm{Pb}}'' + 2V_{\mathrm{Cl}}^{\bullet}, \qquad (1)$$

where Kröger's notation is used (*9*).

According to Tubandt (*10*) and De Vries (*1*), the electrical conduction is due to the migration of the chloride ion vacancies.

In principle the formation of free electrons and holes is also possible:

$$\mathrm{O} \rightleftharpoons e' + h^{\bullet} \qquad (2)$$

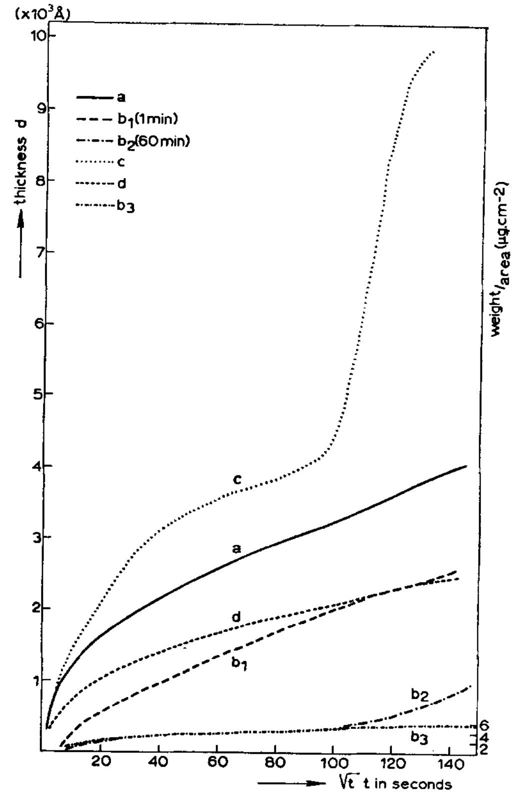

FIG. 2. Typical d vs t curves for the same reactions as mentioned in Fig. 1 at 373 K. Letter stage of the reactions; t plotted as $\sqrt{t}$; t in seconds.

Since lead chloride is an anionic conductor and the mobilities of the electronic defects exceed the mobilities of the ionic defects, we can assume that the concentrations of the ionic defects exceed the concentrations of the electronic defects largely. Verwey and Schoonman (*2*, *3*, *11*) concluded that in lead halides holes are more mobile than electrons.

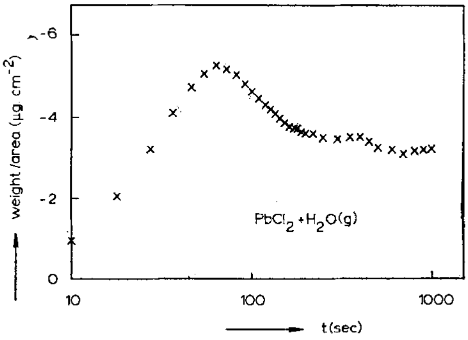

FIG. 3. Typical curve for the decrease of weight per area vs time for the reaction between freshly prepared lead chloride and water vapour at 308 K.

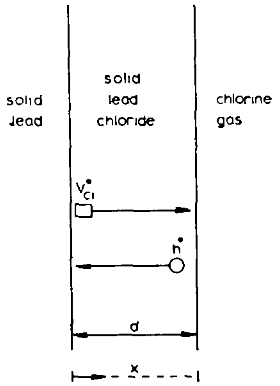

FIG. 4. Schematic survey of the lead chloride layer between solid lead and chlorine gas; (+ −) direction of the electric field across the layer; $V_{\mathrm{Cl}}^{\cdot}$ and h$^{\cdot}$ are the moving particles; x direction of growth perpendicular to the interfaces; d thickness of the layer.

When lead reacts with chlorine a coherent layer of lead chloride is formed and diffusion of certain particles must occur through the layer formed. On behalf of the arguments mentioned above, these particles are chloride ion vacancies and holes, while the contribution of cation vacancies and electrons can be ignored (Fig. 4).

In the earliest stage of the reaction the diffusion of anion vacancies exceeds that of the holes. Consequently an electric field is built up across the layer which accelerates the holes and slows down the anion vacancies. In the steady state this field equalizes the two flows.

At the chlorine/lead chloride interface several reaction steps occur; chlorine molecules are adsorbed, chlorine atoms are formed, chloride ion vacancies are consumed and holes are formed, leaving excess chloride ions on normal lattice sites.

At the lead/lead chloride interface lead atoms are adsorbed, chloride ion vacancies are formed and electron holes are consumed by the formation of substitutional lead ions.

Since Verwey (*2*, *11*) and De Gruijter and Kerssen (*12*) have observed lead(I) ions on a regular lead site, $\mathrm{Pb}'_{\mathrm{Pb}}$, we believe that $\mathrm{Pb}'_{\mathrm{Pb}}$ centres are present in the reaction layer near the $\mathrm{Pb/PbCl_2}$ interface, when electron holes are consumed by lead atoms built into the layer.

We distinguish two reaction steps:

$$h^{\cdot} + \mathrm{Pb}''_{\mathrm{Pb}} \rightarrow \mathrm{Pb}'_{\mathrm{Pb}} \tag{3}$$

and

$$h^{\cdot} + \mathrm{Pb}'_{\mathrm{Pb}} \rightarrow \mathrm{Pb}^{x}_{\mathrm{Pb}} \tag{4}$$

As discussed elsewhere all other possible reaction steps at the two interfaces tend to linear rate laws (*8*).

The hole concentration p in these reaction steps (3, 4) cannot be taken constant, since this concentration depends on the transport of holes, which is influenced by the electric field across the layer.

In view of the different Coulomb interaction between the $\mathrm{Pb}''_{\mathrm{Pb}}$ and $\mathrm{Pb}'_{\mathrm{Pb}}$ centres and the holes, it can be expected that a hole reacts faster with a $\mathrm{Pb}''_{\mathrm{Pb}}$ centre than with $\mathrm{Pb}'_{\mathrm{Pb}}$. We conclude that (4) is slower than (3) and that $\mathrm{Pb}'_{\mathrm{Pb}}$ centres are present near the interface $\mathrm{Pb/PbCl_2}$.

Following Ritchie (*13*, *14*) we can explain now the logarithmic rate law observed in the first stage of the reaction. In the literature many models giving a logarithmic rate law have been proposed. The greater part of these models, however, cannot be checked for lack of measurable parameters. The explanation presented hereby is in qualitative agreement with the properties of lead chloride.

The reaction rate of the rate-determining reaction (4) is:

$$dd/dt = k_4[\mathrm{Pb}'_{\mathrm{Pb}}]p \tag{5}$$

in which d is the layer thickness and k_4 the forward rate constant. The concentration $[\mathrm{Pb}'_{\mathrm{Pb}}]$ depends on reaction step (3). The following equilibrium constant K_3 can be written:

$$K_3 = \frac{[\mathrm{Pb}'_{\mathrm{Pb}}]}{[\mathrm{Pb}''_{\mathrm{Pb}}]p} \tag{6}$$

$[\mathrm{Pb}''_{\mathrm{Pb}}]$ is a constant since it depends on other reaction steps which are assumed to be in equilibrium. Introducing (6) into (5) yields:

$$dd/dt = \Gamma p^2 \tag{7}$$

in which Γ is a temperature-dependent constant.

The hole concentration p at the $\mathrm{Pb/PbCl_2}$ depends on the electric field across the layer and the hole concentration at the $\mathrm{Cl_2/PbCl_2}$ interface. This electric field depends on the various (effectively) charged particles at the two interfaces which differ from those in the "bulk" of the layer. These concentrations and the hole concentration at the $\mathrm{Cl_2/PbCl_2}$ interface depend on reaction steps in equilibrium and can therefore be taken constant. The excess number of charged particles N is thus a constant.

The electric field across the layer can be treated as a thin plane-parallel capacitor with plate separation d and dielectric constant ε. The potential across the layer is then:

$$V = eNd/\varepsilon \tag{8}$$

In the steady state the hole concentration is assumed to be given by the Boltzmann distribution law:

$$p = p_0 \exp(-eV/kT) \tag{9}$$

From (7–9) we obtain after integration the direct logarithmic rate law:

$$d(t) = k_d \ln t + A \tag{10}$$

in which k_d is the rate constant and A is a constant.

In the latter stage of the reaction, when the thickness of the lead chloride layer increases, the diffusion process within the layer becomes rate-determining. According to a.o. Wagner (*6*, *15*) and Fromhold (*16*) this leads to a parabolic rate law:

$$d(t)^2 = k_p \cdot t \tag{11}$$

in which k_p is the rate constant, depending on the diffusion of the holes through the layer. For more details we refer to the extended publication elsewhere (*8*).

(b) If the lead layer is first oxidized in the atmosphere, lead monoxide, PbO, is formed. In the beginning this oxide layer must be converted into a lead chloride layer. In general this reaction can be given by the over-all equation:

$$PbO(s) + Cl_2(g) \rightarrow PbCl_2(s) + 1/2O_2(g) \tag{12}$$

It is not excluded that a mixed compound $PbO_{1-x}Cl_{2x}$ is formed. Stable compounds like Pb_2OCl_2 and $Pb_3O_2Cl_2$ are known (*17*, *18*). After this reaction step the metallic lead is attacked and the reaction rate changes. The mixed compound must have higher diffusion constants than the PbO or pure $PbCl_2$ layer. When the lead oxide layer is not completely converted, the reaction rate resembles that of pure lead monoxide with gaseous chlorine. This supports the picture that an oxide layer is responsible for the retardation.

(c) When oxygen leaks into the chlorine atmosphere, oxygen is incorporated into the lead chloride lattice to some extent. Since the oxygen atoms form O^{2-} ions on Cl^- lattice sites, O'_{Cl}, a higher hole production can be expected, together with an increase of $[V^{\cdot}_{Cl}]$. Both particle flows are enhanced resulting in a higher reaction rate.

During the reaction time the amount of oxygen in the chlorine atmosphere increases slowly. The $[O'_{Cl}]$ rises slowly too, and, by diffusion, it is possible that these O'_{Cl} migrate through the whole layer to increase the O'_{Cl} and $V^{\cdot}_{Cl}$ concentrations. The reaction rate increases considerably resulting in a breakthrough when the whole layer is converted.

Although oxygen is held to be much less corrosive than chlorine, the reaction of lead with a mixture of the two gases is faster than that of lead with pure chlorine or pure oxygen.

(d) Water vapour in the chlorine atmosphere leads to the formation of OH^- ions on Cl^- lattice sites. Since both the logarithmic and the parabolic rate are retarded, the hole creation has presumably been slowed down.

(e) When water vapour attacks a freshly prepared lead chloride layer, chlorine is partly replaced:

$$H_2O(g) + Cl^x_{Cl} \rightarrow OH^x_{Cl} + HCl(g) \tag{13}$$

Hydrogen chloride was in fact detected by Willemsen (*19*) when water vapour was led over lead chloride at 400°C. During this replacement the weight of the solid sample decreases. After some time this reaction comes to an end and water vapour is adsorbed at the partly rearranged surface, so that the weight of the probe increases again (Fig. 3).

In conclusion we have found that mixing of the oxidizing gas (chlorine) with another oxidizing agent must be prevented, even if it is considered to be less corrosive than the gas atmosphere applied. An oxide layer, present on the metal under study, influences the reaction rate strongly. The same is true for water vapour. As a consequence all measurements in which no attempt is made to avoid these influences are suspect.

Acknowledgments

The author thanks Prof. Dr. J. H. van Santen for drawing his attention to the problem and many stimulating discussions. The valuable criticism of Prof. Dr. G. Blasse during the final stage of the experiments and the preparation of the manuscript is thankfully acknowledged. The helpful advice of Drs. A. F. Corsmit during the investigation have considerably contributed to the results.

This work was performed as part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)" and was made possible by financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO)."

References

1. K. J. de Vries and J. H. van Santen, *Physica* **29**, 482 (1963).

2. J. F. Verwey, *J. Phys. Chem. Solids* **31**, 163 (1970).

3. J. Schoonman, *J. Solid State Chem.* **4**, 466 (1972); **5**, 62 (1972).

4. B. Willemsen, *Phys. Status Solidi* (a) **11**, K 157 (1972); **14**, 565 (1972).

5. W. C. de Gruijter, *J. Solid State Chem.* **6**, 151 (1937).

6. C. Wagner, *Z. Phys. Chem.* **B21**, 25 (1932); **B32**, 447 (1936); **B40**, 455 (1938).

7. G. Sauerbrey, *Z. Physik.* **155**, 206 (1959).

8. J. M. L. Kerbusch, thesis, University of Utrecht, 1972.

9. F. A. Kröger, "The Chemistry of Imperfect Crystals," North Holland Publ. Comp., Amsterdam, 1964.

10. C. Tubandt and S. Eggert, *Z. Anorg. Chemie* **110**, 96 (1920).

11. J. F. Verwey, thesis, University of Utrecht, 1967.

12. W. C. de Gruijter and J. Kerssen, *J. Solid State Chem.* **5**, 467 (1972).

13. J. M. Ritchie, *Phil. Mag.* **19**, 421 (1969).

14. J. M. Ritchie and A. L. Hunt, *Surface Sci.* **15**, 524 (1969).

15. See e.g. P. Kofstad, "High Temperature Oxidation of Metals," Wiley, 1966.

16. A. T. Fromhold jr., *J. Phys. Chem. Solids* **33**, 95 (1972).

17. M. Renaud, E. Poidatz, and J. E. Chaix, *Can. J. Chem.* **48**, 2061 (1970).

18. G. Perrault, H. Vincent, and M. Renaud, *Bull. Soc. Fr. Minéral. Cristallogr.* **94**, 108 (1971).

19. B. Willemsen, *J. Solid State Chem.* **3**, 567 (1971).