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CHLORINATION KINETICS OF RHENIUM, RHODIUM AND IRIDIUM

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Summary

The rates of reaction between flowing chlorine and rhodium, rhenium and iridium were measured by the rates of mass change of samples of the reacting metal and correlated as functions of temperature and chlorine pressure. Attempts were made to correlate the reaction rates with the vapor pressures and decomposition pressures of the chloride products.

1. Introduction

All metals combine with chlorine to form the respective chlorides with reaction rates that are dependent upon the metal, the chloride product, the temperature, the chlorine pressure and, in some instances, the crystallographic orientation of the metal. The kinetics of these reactions are of interest for several reasons. First of all, they indicate the conditions under which a particular material can be used in contact with chlorine without being attacked. Second, they delineate the conditions necessary to prepare specific chlorides. Finally, the nature of the reactions is of academic interest.

Several metal chlorination reactions have been studied within the Bureau of Mines by measuring the mass change of a metal sample held at constant temperature in a stream of gas containing a fixed concentration of chlorine. The experimental conditions necessary to obtain reliable and consistent data have been well developed [1-5]. In conjunction with the study of chlorides, vapor pressure measurements have also been conducted. The Knudsen effusion method, as used in this current study, has been developed to handle sensitive chlorides [6].

Rhenium, rhodium, and iridium were chosen to be studied because of their refractory nature and because vapor pressure and decomposition pressure measurements had previously been conducted on their chlorides. Figure 1 shows, by way of an Arrhenius plot, the relative ease of chlorination of the metals studied to date at the Albany Research Center.

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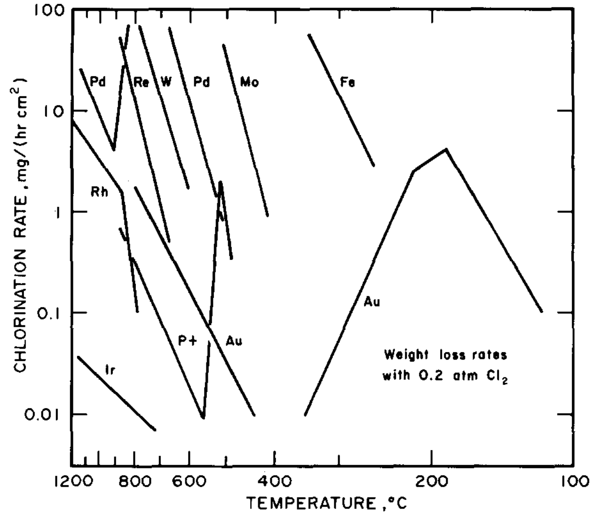

Fig. 1. An Arrhenius plot for the chlorination of several metals (chlorine pressure, 0.20 atm).

2. Rhenium

A complete description of the anhydrous Re–Cl system does not appear in the literature even though a number of the chlorides are described. At the temperatures and chlorine pressures which produce measurable reaction rates between chlorine and rhenium, three chlorides appear to be of significance: $ReCl_3$, $ReCl_5$ and $ReCl_6$. Buchler *et al.* [7] described and Rinke *et al.* [8] confirmed the vaporization of rhenium trichloride as Re_3Cl_9. The latter's equation for the vapor pressure of this trimer was printed in error and should read

$$\log P = -\frac{10870}{T} + 12.83$$

Geilmann *et al.* [9, 10] described the less stable pentachloride. The vapor pressure of the pentachloride and the equilibrium chlorine pressure for its decomposition to the trichloride and chlorine were given by Baryshnikov and Kelikman [11]. Controversy over the formation of the hexachloride was addressed by Colton [12] and the chlorination conditions that produce it were described by Brown and Colton [13]. Considering all this earlier work, it was assumed for this study that the chlorination product from the reactions conducted was the trichloride and that it vaporized immediately upon formation. The pentachloride is not a stable volatile species at the temperatures and chlorine pressures necessary for measurable chlorination of bulk rhenium.

In this work the masses of spectrographically pure rhenium samples approximately 1 cm × 2 cm × 0.3 cm were measured continuously during exposure to a stream of chlorine-containing gas. From 270 to 860 °C, and with chlorine pressures of 0.05–0.80 atm, measurable reaction rates were obtained only at 690 °C

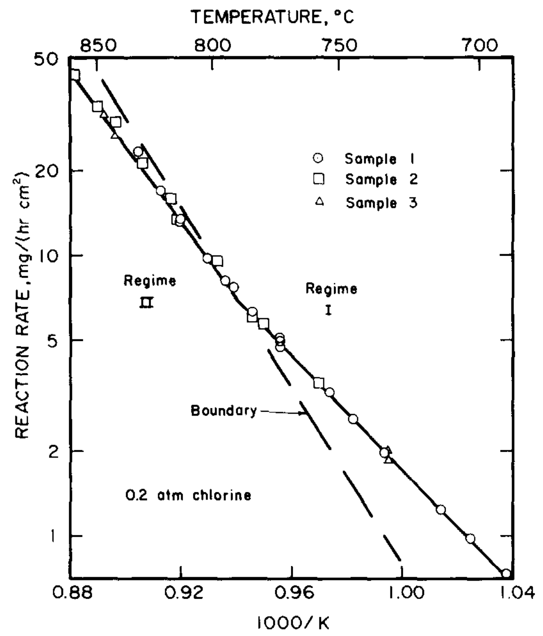

Fig. 2. The Arrhenius plot for the chlorination of rhenium with 0.20 atm of chlorine: ○, sample 1; □, sample 2; △, sample 3.

and above. Figures 2–4 present the data obtained. The Arrhenius plot in Fig. 2 shows two reaction regimes. The data in Fig. 3 show that the boundary between the regimes is also a function of chlorine concentration. All the data collected are correlated in Fig. 4. Mathematical expressions for the reaction rates in the two regimes, along with an equation of the boundary that were derived from the data, are given in terms of reaction rate R (mg h^{-1} cm^{-2}), chlorine pressure P (atm) and temperature T (K). These rate equations are represented in Figs. 2–4 by full lines and the boundary is shown by a broken line.

Of significance is the change in reaction rate dependence upon chlorine pressure. In regime I the reaction rate dependence on the 0.5 power of the chlorine pressure is indicative of a reaction-controlling equilibrium between diatomic chlorine molecules and chlorine atoms on the metallic surface [14]. In regime II the reaction rate dependence on a much lower order of the chlorine pressure is attributed to the reaction of chlorine with a non-volatile subchloride to give a volatile product.

Two small crystals of rhenium were partially chlorinated in 0.20 atm of chlorine at 773 and 842 °C, regime I and regime II respectively. The crystal chlorinated in regime I developed surfaces that appeared to have a higher degree of crystallographic oriented features. Similar crystallographic specific reactivity was reported by Glaski [15] who noted the inactivity of crystalline, chemically vapor deposited rhenium compared with reactive pelletized powder. This phenomenon was not considered in the present kinetic work, although the smooth fine-grained

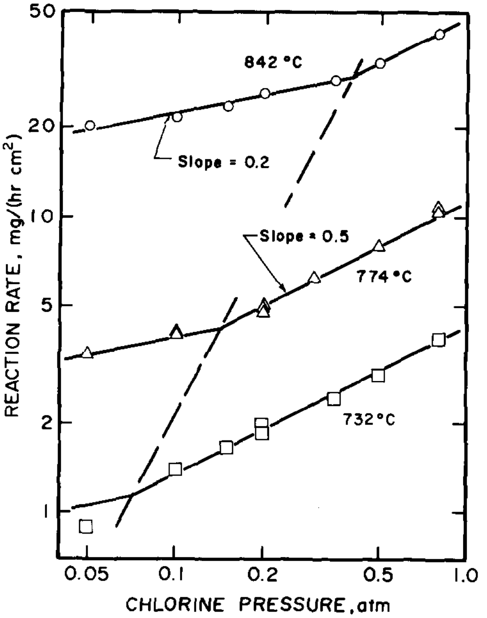

Fig. 3. The effect of chlorine pressure on the chlorination rate of rhenium.

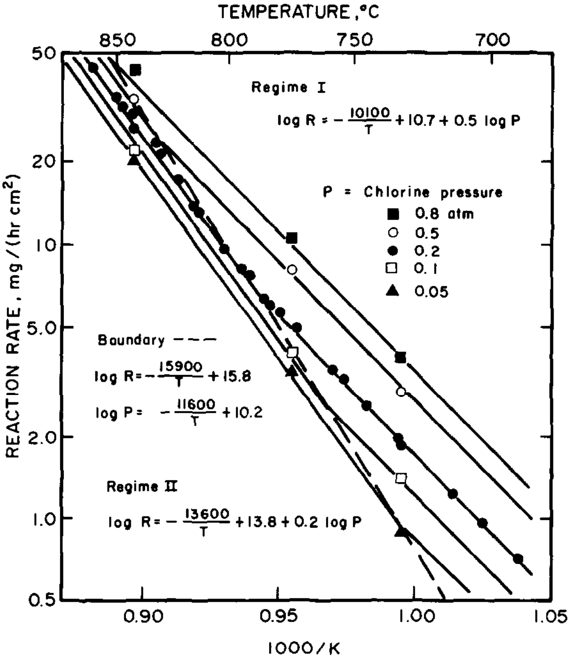

Fig. 4. Complete Arrhenius plot for rhenium chlorination at various chlorine pressures P: ■, $P = 0.80$ atm; ○, $P = 0.50$ atm; ●, $P = 0.20$ atm; □, $P = 0.10$ atm; ▲, $P = 0.05$ atm; – – –, boundary.

specimens rapidly acquired dull surfaces when chlorinated, indicating uneven attack on a microscopic scale.

In addition to determining the rate of rhenium chlorination, the vapor pressure over a rhenium chlorination product was measured by the Knudsen effusion method [6]. This chloride was made by passing chlorine over rhenium at 700 °C, or above, and condensing the product from the stream of excess chlorine. The handling of the unanalyzed chloride was done in a dry box. As others have reported [7], the observed vapor pressure changed with depletion of the sample. The data from four loadings of the effusion cell using three orifice sizes are shown in Fig. 5. Also shown are the reported vapor pressures of the trichloride and pentachloride, and the decomposition chloride pressure over the latter. Instead of assigning molecular species to the data, a necessity in the effusion method calculations, the ordinate axis is given as the product of pressure and the molecular weight of the effusing vapor. This allows comparison of data without assuming the identity of the vapor. Data collected with the first three samples, A, B and C, were confined to a limited range of experiments. With experience, a greater range of data was obtained with sample D, and it was allowed to become completely depleted. Data from this last sample show three distinct lines: D1, D2 and D3.

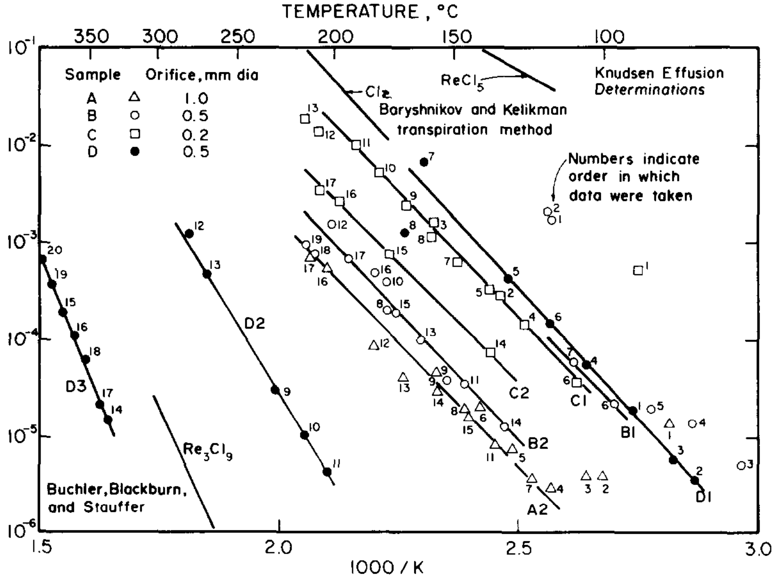

Fig. 5. Chlorine and chloride pressures in the Re–Cl system. The numbers indicate the order in which the data were taken.

Symbol	*Sample*	*Orifice diameter* (mm)
△	A	1.0
○	B	0.5
□	C	0.2
●	D	0.5

Note worthy in the vapor pressure measurements is the relative position of all the data points. Smaller orifices generally show higher vapor pressure measurements because the escape of vapor is more restricted and the pressure within a cell more nearly approaches equilibrium. Lines C2, B2 and A2 are typical. Lines B1, C1 and D1 are nearly equivalent; however, line C1, obtained with the smallest orifice, indicates the lowest pressure. At best, these data indicate a need for further investigation of the anhydrous Re–Cl system.

3. Rhodium

Although the literature does not specifically describe the conditions necessary for the chlorination of rhodium, Bell *et al.* [16] have measured equilibria for the Rh–Cl system between 700 and 1500 °C. They determined that $RhCl_3$ is the only condensed phase and has a chlorine dissociation pressure reaching 1 atm at 970 °C. Their data describe the vapor pressure of the trichloride and indicate that $RhCl_2$ is also a significant gaseous species (Fig. 6).

In this work, samples of spectrographically pure rhodium, approximately 1 cm × 2.5 cm × 0.02 cm, were exposed to chlorine pressures of 0.05–0.80 atm at 300–1150 °C. The kinetic data are displayed in the Arrhenius portion of Fig. 6(b). No measurable mass change was observed below 775 °C. At higher temperatures, two reaction regimes were encountered: one in which the reaction was independent of chlorine pressure, and the other in which the rate of reaction appeared to be proportional to the 1.25 power of the chlorine pressure as shown in Fig. 7. In regime I a mass loss of 0.5–3 mg occurred after chlorine was eliminated from the Cl–Ar gas mixture flowing past the continuously weighted sample. Electron micrographs showed rough grain surfaces with wide irregular grain boundaries resulting from reaction in regime I. Reaction in regime II produced microscopically smooth grain surfaces separated by sharp grain boundaries.

In addition to kinetic data, the chlorination product was collected and Knudsen effusion vapor pressure measurements were made using an effusion cell with a 1.0 mm orifice. These data are given in Fig. 6(a). When interpreted as the decomposition chlorine pressure over $RhCl_3$ there is reasonable agreement with the data of Bell *et al.* [16] labeled as line A in this same figure. Combining the equation for chlorine pressure from the effusion data with the equation correlating the kinetic data of regime II gives the equation for the kinetic data in regime I. This latter equation well represents the measured reaction rates (compare the data points and line for regime I in the Arrhenius portion of Fig. 6(b)). Reaction rates in regime I are evidently controlled by vaporization of the product chloride from the reacting surface.

The reaction-controlling mechanism in regime II is not obvious. The equation relating reaction rate and the 1.25 power of the chlorine pressure describes the experimental data well; however, it does not indicate the reaction sequence. A reaction scheme such as

$$2Rh + Cl_2(g) \overset{K_1}{\longleftrightarrow} 2RhCl$$

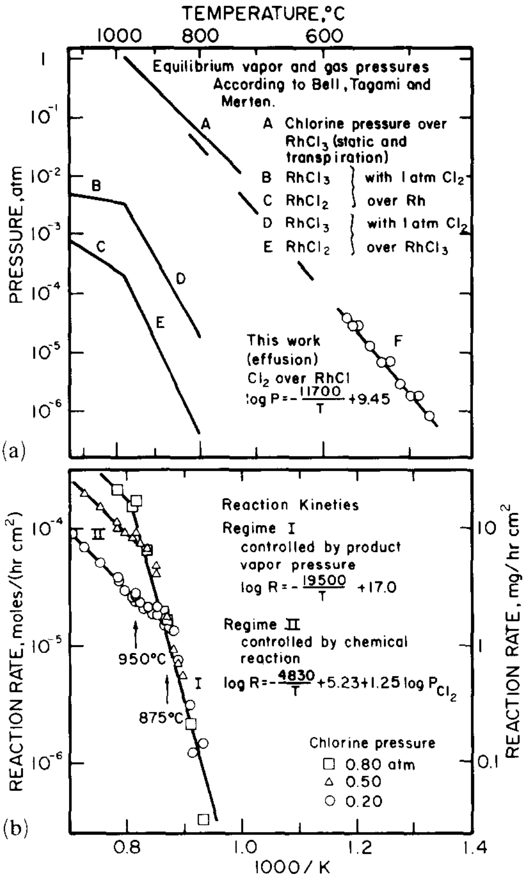

Fig. 6. (a) Vapor and gas pressures (line A, chlorine pressure over $RhCl_3$ (static and transpiration); line B, $RhCl_3$ with chlorine at 1 atm over rhodium; line C, $RhCl_2$ with chlorine at 1 atm over rhodium; line D, $RhCl_3$ with chlorine at 1 atm over $RhCl_3$; line E, $RhCl_2$ with chlorine at 1 atm over $RhCl_3$; line F, this work (effusion), chlorine over RhCl, equation in figure) and (b) reaction rates (□, $P = 0.80$ atm; △, $P = 0.50$ atm; ○, $P = 0.20$ atm) in the Rh–Cl system.

$$2RhCl + Cl_2(g) \overset{K_2}{\longleftrightarrow} 2RhCl_2$$

$$2RhCl_2 \xrightarrow{K_3} RhCl + RhCl_3(g)$$

is but one of several that could be suggested. In this scheme the intermediates RhCl and $RhCl_2$ are assumed to be at equilibrium on the reacting surface with the possibility that $RhCl_2$ becomes a vaporized product as suggested by Bell *et al.* The rate equation derived from this sequence of reactions has the form

$$\text{rate} = K(P^2 + P)$$

where K is a constant and P is the chlorine pressure. For comparison, this relationship is indicated in Fig. 7 by broken lines.

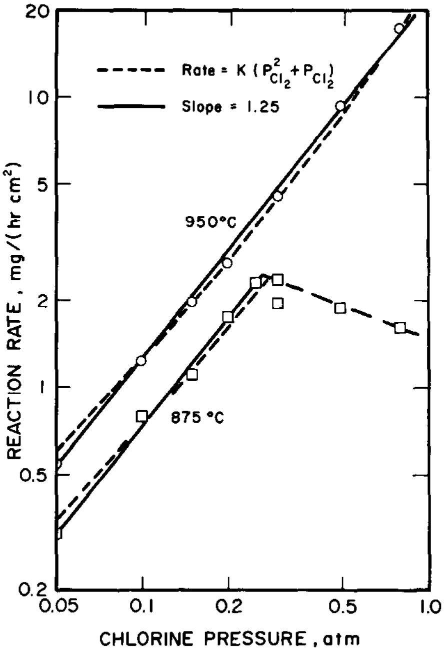

Fig. 7. The effect of chlorine pressures on the chlorination rate of rhodium: - - -, rate = $K(P_{Cl_2}^2 + P_{Cl_2})$; ——, slope of 1.25.

4. Iridium

Iridium chlorinates with difficulty as demonstrated by Stepin and Chrenyak [17]. They were unsuccessful in attempting to increase the rate of this reaction significantly by adding sulfur or carbon monoxide, by using radiation and by applying an electrical discharge. They observed that in the temperature range 400–700 °C a layer of chloride product forms over the iridium powder being chlorinated. Bell and Tagami [18, 19] identified the chlorination product as the trichloride, $IrCl_3$, and quantified the vapor pressure resulting from its decomposition. These latter measurements are in good agreement with those of Kolbin and Samoilou [20], who also confirmed the trichloride as the only chloride product.

As shown in Fig. 1, iridium is one of the more difficult-to-chlorinate metals; that is, measurable mass change upon exposure to chlorine occurs only at higher temperatures. Because of the low reaction rates, thin samples having up to 95 cm^2 of surface area and reaction times of at least 1 h were needed to obtain valid data points. These data are presented in the Arrhenius portion of Fig. 8. It consists of both mass gains and losses. For the mass gains, the data are assumed to represent the initial portion of a parabolic mass gain curves. Despite the effort to obtain accurate measurements but, because of the change from linear to parabolic mass changes, clear interpretation of the reaction mechanisms is not possible. Suffice it to say that (1) below 725 °C a chloride product is formed on iridium metal, (2) a

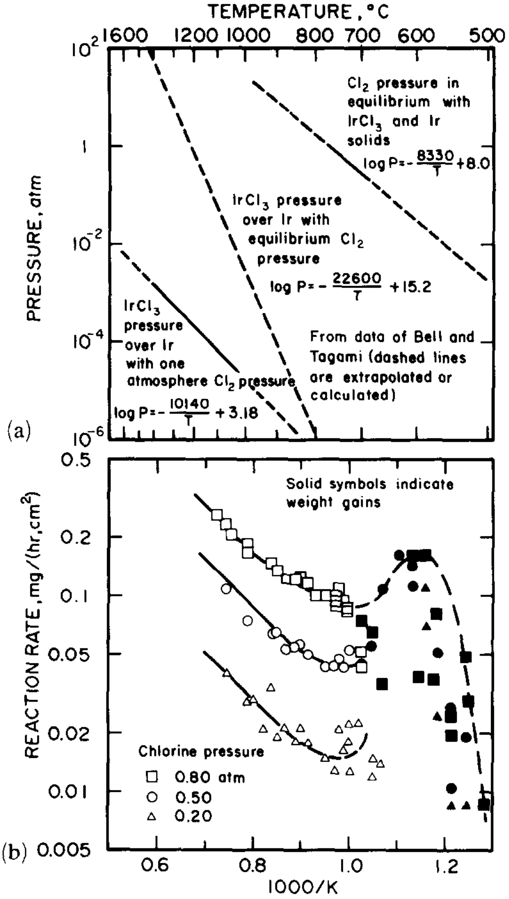

Fig. 8. (a) Vapor and gas pressures (———, from data of Bell and Tagmi [18, 19]; ---, extrapolated or calculated) and (b) reaction rates (□, $P=0.80$ atm; ○, $P=0.50$ atm; △, $P=0.20$ atm; ■, ●, ▲, mass gains) in the Ir-Cl system.

minimum reaction rate occurs at approximately 775 °C and (3) above this temperature the metal surface remains clean with a reaction that is proportional in rate to the 1.5 power of chlorine pressure.

5. Conclusions

Refractory and precious metals generally form chlorides at significant rates in the temperature range that allows the chloride products to evaporate as they are formed. Transitions from one stable chloride product to another and transitions that are dependent upon both the temperature and the chlorine pressure add to the complexity of the reaction kinetics. However, when these transitions are related to the vapor pressures and decomposition pressures of the chloride products, understanding of the chlorination process usually emerges. In many cases, this allows the sequence of steps making up a complex mechanism to be elucidated.

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