THE REACTION OF OXYGEN WITH MAGNESIUM CHLORIDE

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ABSTRACT

The kinetics and mechanisms of the reaction between magnesium chloride and oxygen have been studied over a range of oxygen partial pressures. At low temperatures the reaction is controlled by a phase-boundary process having an activation energy of 74.0 kJ, which changes to one of diffusion of chlorine at higher temperatures. The activation energy for the diffusion process is 41.2 kJ and there is a considerable loss of entropy in the formation of the transition state.

INTRODUCTION

There is sporadic interest in the recovery of metal ions from mixtures by differential precipitation, usually from acid solutions. It is however also possible to form oxides from chlorides by heating the latter in air and extracting the unreacted chlorides. Such methods are usually considered from a thermodynamic view point; the present paper briefly considers the kinetics of conversion of magnesium chloride to the oxide:

$$MgCl_2(s) + \tfrac{1}{2}O_2(g) = MgO(s) + Cl_2(g)$$
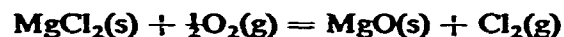
The thermodynamics of this reaction have been discussed by Kelley and an enthalpy change of 39.2 kJ mol^{-1} derived[1]. The reaction should go appreciably to the right at temperatures above 500K; at 700K and one atmosphere pressure the ratio $P_{O_2}/P_{Cl_2} = 1.0$.

Allen and Clark[2] in a study of Deacon process catalysts, obtained preliminary kinetic data for the reaction at low oxygen pressures. They suggested that a diffusion process was rate-controlling, with an activation energy of 135 kJ mol^{-1}.

EXPERIMENTAL

Sample preparation

Anhydrous magnesium chloride was prepared by the thermal decomposition of recrystallised A.R. ammonium magnesium chloride hexahydrate at 600K in a

stream of nitrogen[3]. The nitrogen was dried over molecular sieve and the heating was continued for six hours until constant weight was obtained. The overall weight loss obtained was 63.1% (theory 62.93%). The resulting magnesium chloride was analysed for chloride by standard methods[4] (experimental = 73.0% Cl, theory for $MgCl_2$ = 74.47% Cl). An infrared spectrum obtained using a Perkin-Elmer 457 and Nujol mull showed a small band at 3400 cm^{-1} when the mull was produced in the open laboratory but which was not present when the mull was prepared in a dry box. This peak was therefore assumed to be due to sorbed water. Attempts to obtain an X-ray diffraction spectrum were unsuccessful because of the rapid rate at which the compound absorbed water vapour from the atmosphere. All spectra showed peaks associated with the hexahydrate[5]. Microscopic estimation of the particle size indicated uniform, approximately spherical particles some 30 μm in diameter which appeared macroporous on S.E.M. examination.

Decomposition techniques

The decomposition reactions were carried out using a Stanton Redcroft TG750 thermobalance and recorder (10 mg f.s.d.). 10-mg samples were used throughout; these were weighed into aluminium pans in a dry box and stored over silica gel until required. The required gas mixtures were obtained by passing metered flows of dry oxygen and nitrogen through a manifold and then into the furnace at a total flow of 30 dm^3 min^{-1}.

Some preliminary TG runs were carried out at each partial pressure of oxygen so that the general thermal behaviour could be assessed. For the isothermal work the furnace temperature was preset with purge gas flowing.

RESULTS

Products

The preliminary TG runs indicated complete conversion of the magnesium chloride into oxide in a single stage with weight losses very close to theory (observed loss 57.5%, theoretical loss 57.67%). X-ray examination showed only MgO present in the residue.

Kinetics and mechanisms

The weight-loss vs. time curves (41 in all) were all deceleratory. The experimental curves were tested by the method of reduced time plots and were compared with models based on nucleation control, phase-boundary control or diffusion control of the rate determining step[6]. Experimental reduced-time curves based on the time for 50% reaction (α vs. $t/t_{0.5}$) were constructed and compared with the various model systems. This comparison usually decided the likely rate-controlling mechanism easily. The best fit between experimental data and calculated reduced-time curves varied with temperature but not with partial pressure of oxygen. At low temperatures
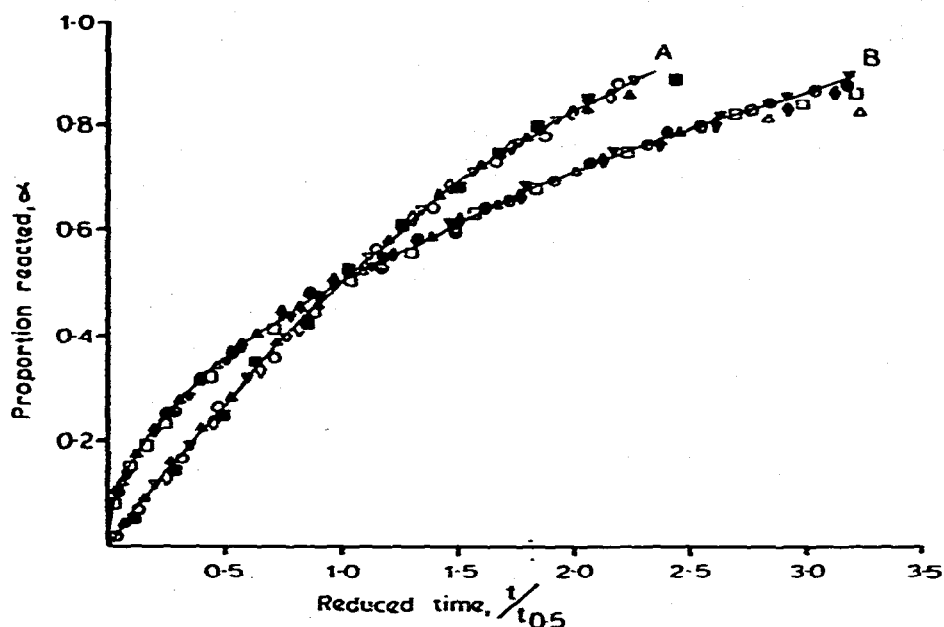
Fig. 1. Comparison of experimental and calculated reduced-time plots for the high and low temperature mechanisms.

Curve A: contracting disc equation, $1 - (1 - \alpha)^{\frac{1}{3}} = kt$. ▽, 618K/0.2 atm; ▲, 628K/0.5 atm; ◇, 638K/0.75 atm; ○, 658K/0.50 atm; ■, 693K/1.0 atm.

Curve B: parabolic law, $\alpha^2 = kt$. ▼, 753K/1.0 atm; ◆, 735K/0.2 atm; ●, 713K/0.5 atm; ⊖, 753K/0.75 atm; △, 713K/0.2 atm.

TABLE 1

ARRHENIUS PARAMETERS FOR THE REACTION $MgCl_2 + \frac{1}{2}O_2 = MgO + Cl_2$

$PO_2(atm.)$	Phase boundary process		Diffusion process	
	$E(kJ\ mol^{-1})$	$log\ A(sec^{-1})$	$E(kJ\ mol^{-1})$	$log\ A(sec^{-1})$
0.20	80.1	3.8	41.9	14.0
0.50	76.3	3.6	40.4	13.2
0.75	72.4	4.0	44.3	13.7
1.00	74.8	3.9	39.9	13.2

(618–693K) the best fit was in terms of the contracting disc equation:

$$1-(1-\alpha)^{\frac{1}{3}} = kt$$

where α = proportion decomposed and t = time.

At temperatures above 693K (713–760K) the best fit obtainable was in terms of the parabolic law:
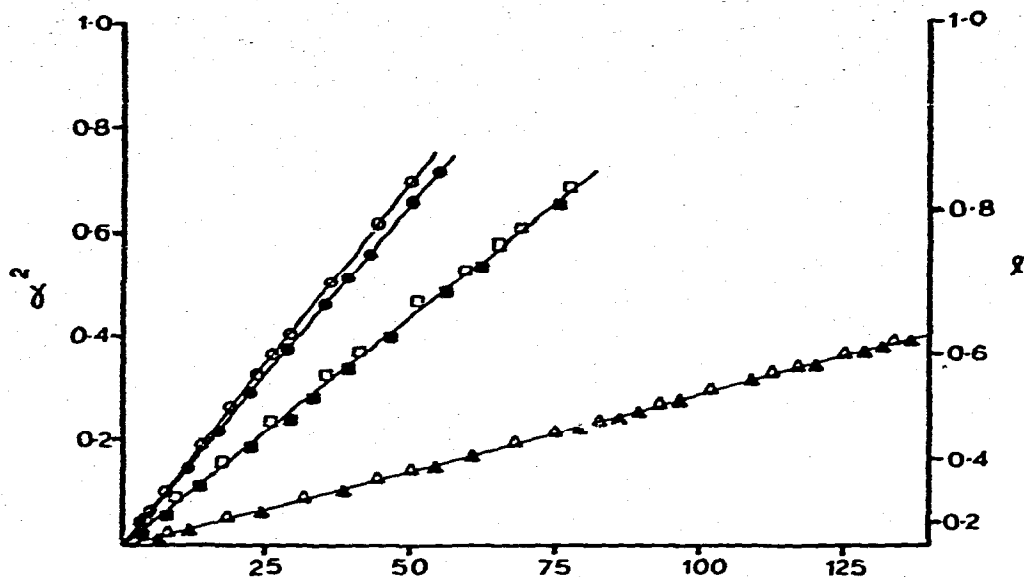
$$\alpha^2 = kt$$

Fig. 2. Test of the contracting disc equation for typical data. o, 693K/1.0 atm; ●, 693K/0.75 atm; □, 673K/1.0 atm; ▣, 658K/0.5 atm; △, 638K/0.75 atm; ▲, 628K/0.2 atm; ◇, 618K/1.0 atm; ◆, 618K/0.2 atm.
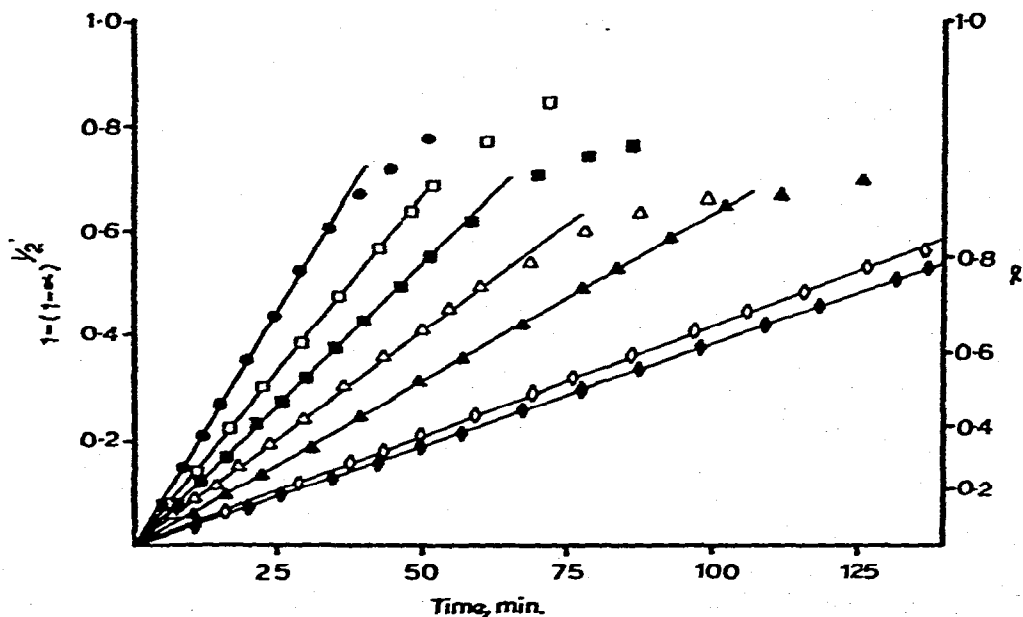
Fig. 3. Test of parabolic law for typical data. o, 753K/1.0 atm; ●, 753K/0.2 atm; □, 735K/0.75 atm; ▣, 735K/1.0 atm; △, 713K/1.0 atm; ▲, 713K/0.5 atm.

A few runs carried out at 700K did not show clear-cut behaviour, but tended to follow the contracting disc equation at low values of α and the parabolic law at high α values.
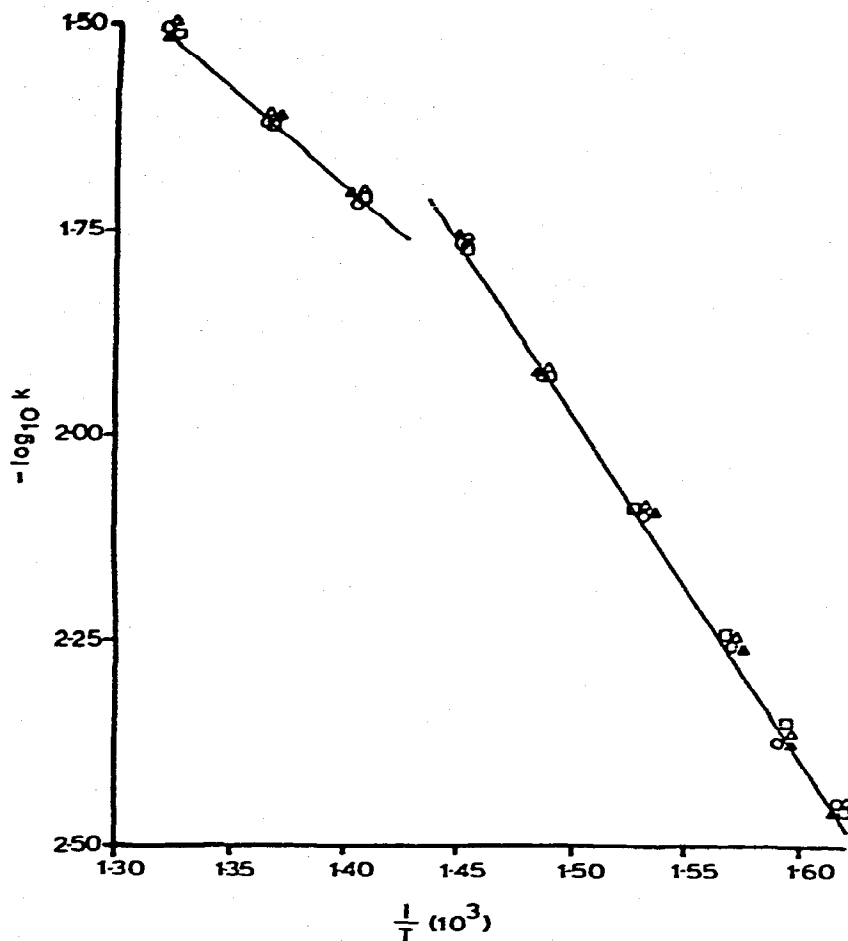
Fig. 4. Arrhenius plot, showing change in slope. o, $PO_2 = 0.2$ atm; □, $PO_2 = 0.5$ atm; △, $PO_2 = 0.75$ atm; ▲, $PO_2 = 1.0$ atm.

A comparison of experimental and calculated reduced-time plots is shown in Fig. 1. Rate constants were calculated from the slopes of the $f(\alpha)$–t plots and the values used to derive Arrhenius parameters (Table 1). Typical linear plots of the two functions are shown in Figs. 2 and 3. Arrhenius plots are shown in Fig. 4.

DISCUSSION

Kinetics and mechanisms

The results in the table indicate that increasing temperature causes a change in mechanism from phase boundary to diffusion control. These processes have activation energies of 74.0 and 41.2 kJ, respectively. Such a change from a high temperature coefficient process to a low one is to be expected. It is therefore not surprising that some runs showed mixed behaviour.

The numerical values of the activation energies are not comparable with the only other determination. Allen and Clark[2] obtained a value of 135 kJ using initial rates, and suggested that diffusion might be rate controlling. These initial rates would almost certainly be measured over very low values of α and it is not surprising that a different value was obtained.

The phase-boundary process

The activation energy derived for this process is greater than the enthalpy change (39.2 kJ) which suggests that the process is a simple one. The low frequency factor suggests a considerable loss of entropy in the formation of the transition state. The overall entropy change for the reaction is 58.8 J K^{-1} mol^{-1} and the frequency factors given in the Table 1 correspond to a loss of entropy in the formation of the transition state of about $- 160$ J K^{-1} mol^{-1}. This is considerably more than the loss of entropy on solidification of oxygen[7] ($- 84$ J K^{-1} mol^{-1}), and it therefore seems likely that the transition state will involve both molecular oxygen and molecular chlorine, e.g.,
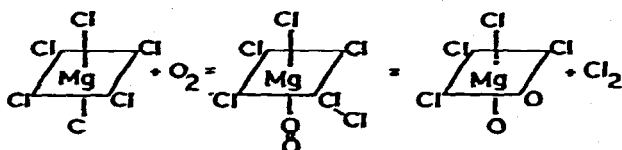
The diffusion process

In a diffusion-controlled reaction it is at first surprising that variation in the external partial pressure of reactant gas should have such a small effect on the Arrhenius parameters. This must mean that the rate-controlling step is diffusion of the product gas, chlorine, rather than the reactant gas, oxygen. This effect is in line with the observations of Allen and Clark who noted that variation in oxygen pressure between 5 and 20 cm Hg made no difference to the reaction rate. Such effects are also those expected from a simple diffusion process in which the diffusion rates of oxygen and chlorine vary as $1/p^{\frac{1}{2}}$ (Grahams Law).

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