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THE KINETICS OF THE HIGH-TEMPERATURE HYDROLYSIS OF MAGNESIUM FLUORIDE.
PART II: INFLUENCE OF CHANGING SPECIMEN GEOMETRY, SPECIMEN TYPE, AND RESISTANCE OF THICK PRODUCT LAYERS ON THE REACTION RATE

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ABSTRACT

The kinetics of the reaction between magnesium fluoride and water vapor were gravimetrically determined on three specimen types—single crystal, sintered polycrystalline disk, and powder—in the temperature range from 950 to 1100°C at a water-vapor partial pressure of 55.3-mm Hg.

It was found that the rate-influencing effects of changing sample geometry and the formation of thick MgO product layers on samples reacted to large extents complicated the evaluation of the rate measurements. Apparent activation enthalpies of 42, 57, and 23 kcal/mole were obtained for the single-crystal, polycrystalline, and powder specimens, respectively. The deviations of these values from the activation enthalpy of 46.4 kcal/mole reported in Part I of this series are discussed with respect to possible rate-influencing factors.

I. INTRODUCTION

In the early stages of this investigation,* it was found that the results of reaction rate measurements were considerably influenced by carrying out the reactions until thick MgO product layers were formed. In addition, different rates and activation enthalpies were obtained from measurements on different sample types--single crystal, polycrystalline, and powder.

The objective of most kinetic measurements is the determination of a reaction mechanism. For high-temperature hydrolysis of magnesium fluoride, which is essentially an interface-controlled reaction, the mechanism determination requires the characterization and/or elimination of the effects of the above-mentioned rate-influencing factors. The purpose of this paper is to illustrate some of the complications that may arise in the evaluation of a reaction mechanism when the rate is influenced by several processes occurring simultaneously.

II. EXPERIMENTAL PROCEDURE

A. Apparatus

The apparatus used for the weight-loss measurements was a modified version of that described in Part I.[1] Weight loss was measured to within ± 1 mg with a fused-silica helix. The use of heated input tubing and immersion of the saturator bottles in a thermostat allowed the attainment of water-vapor pressures up to about 60-mm Hg. Single-crystal and polycrystalline-disk specimens were reacted in a platinum gauze basket, and the powder specimens were reacted in a platinum crucible.

B. Specimen Preparation

The same MgF_2 powder was used for making both sintered disk and powder specimens.** That this material showed no detectable weight loss

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**Supplied by K. K. Kelley, U. S. Bureau of Mines Experiment Station, Berkeley, California.

upon being heated to 600°C indicated that its water content was negligible.

The sintered polycrystalline disks were made by pressing the MgF_2 powder in air, then sintering in a dry argon atmosphere for 3 hours at 1100°C. The fired disks were about 1.0 cm diam by 0.2 cm thick, weighed about 0.5 g, and had an average density of 91% of the theoretical value, 3.17 g/cc. They were reacted without further preparation.

The single-crystal specimens were fabricated from material supplied by two sources.* Specimens of known crystallographic orientation were made from pieces of material whose orientations had been previously determined from back-reflection Laue x-ray patterns. The final specimens, which were either cubes or square slabs weighing approximately 0.5 g each, were cut with a diamond saw and polished down with 3/0 paper. External dimensions of each single-crystal and polycrystalline-disk specimen were determined within to ±0.001 cm with a micrometer.

C. Rate-Measurement Procedure

Rate determinations were made at 50°C intervals from 950 to 1100°C. All runs were made with a water-vapor pressure of 55.3 mm Hg. The procedure for carrying out reaction runs was the same as that described in Part I. However, the runs were carried out to a much greater extent, and involved as much as 70% total reaction at 1100°C.

D. Rate Calculations

The interface nature of the hydrolysis reaction requires that the rate expression take into account the change of interfacial area with time. In the work reported in Part I, area-change corrections were avoided by using a more sensitive helix and carrying out reactions only until about 2% of the total reaction was completed. Under such conditions the surface area could be assumed to have remained constant.

For certain geometric shapes, such as spheres, a 2/3 order rate equation may be used to express interfacial area as a function of time.[2] In this study, it was found that a modified 2/3 order rate equation compensated reasonably well for area changes in the polycrystalline cylindrical

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disks and square slabs, but that it applied exactly for cubes. The modified equation was developed with the assumption that the relative dimensions of the unreacted portion of the sample remained constant. For a disk of thickness h and diameter d, then, $h/d = C_D$, where C_D is constant for a given disk; and for a square slab of edge length ℓ and thickness h, $h/\ell = C_S$, where C_S is constant for a given slab. Thus, for a disk specimen, the area A_D may be expressed in terms of the volume V_D as

$$A_D = 1.85\left(\frac{2\,C_D + 1}{C_D^{2/3}}\right) V_D^{2/3},$$

and for a square slab

$$A_S = 2\left(\frac{2\,C_S + 1}{C_S^{2/3}}\right) V_S^{2/3}.$$

For a perfect cube, $C_S = 1$ and the relationship holds for any extent of reaction.

If the rate of reaction is expressed in terms of weight change of the reactant per unit time, and if it is assumed that the reaction rate is proportional to the surface area of the remaining reactant A, we have $dw/dt = k' A$, where w is the weight of unreacted material. If the area is expressed in terms of $V^{2/3}$ which is equal to $(w/\rho)^{2/3}$, where V is the volume of unreacted material and ρ is the density of the reactant, the final integrated rate expression for both specimen types becomes

$$\left(\frac{w}{w_0}\right)^{1/3} = 1 - \frac{k\,B\,t}{w_0^{1/3}},$$

where $B = (2C+1)/C^{2/3}$, k = a constant, t = total reaction time, and w_0 = initial sample weight. This integrated form of the 2/3 order expression shows that a plot of $(w/w_0)^{1/3}$ vs time should yield a straight line from whose slope a rate constant may be obtained.

B. Sintering of Powder Specimens

The low-activation enthalpy value for the powder specimens was believed to be principally a result of surface-area changes due to sintering of the reactant powder. To test this belief, MgF_2 powder was sintered by heating it in dry argon at rates similar to those used in the reaction runs. The specimen was heated until it reached the desired temperature, then the furnace power was immediately shut off and the specimen was allowed to cool in the furnace. Specimens heated to 950 and 1100°C had final bulk densities of 1.68 and 2.34 g/cc, respectively.

C. Microstructures of Reacted Specimens

Figure 4 shows the structures of fracture sections of reacted specimens of the three types. On all specimens a clearly defined interface can be seen between the MgF_2 reactant and MgO product layer.

In the powder specimen, the reaction apparently occurred at the outside of the sintered MgF_2 mass rather than on the surface of individual grains throughout the specimen. The extent of reaction is greatest on the top of the specimen, so evidently the sides and bottom received some protection from the crucible.

The product layers on the disk and powder specimens appear unoriented and amorphous. However, the single-crystal product layer seems to consist of a system of plates and channels oriented perpendicular to the MgF_2 surface. Because the specific volume ratio of MgO to MgF_2 is 0.57, the unchanged external dimensions of the disk and single-crystal specimens after reaction indicated that the product layers were highly porous.

IV. DISCUSSION OF RESULTS

The following sections will discuss the effects of several rate-influencing factors and indicate how they may lead to uncertainties in the apparent activation enthalpy values and their interpretation.

A. Rate-Influencing Factors

1. Reaction Mechanism

From the study of the reaction rate as a function of temperature and water-vapor pressure reported in Part I, a three-step interface-controlled-reaction mechanism was proposed. The rate expression developed

involved assumptions of an absence of product-layer effects, constant interfacial area, negligible HF pressure, chemisorption equilibrium, and steady-state conditions. The reaction rate was expressed as

$$R = k_3 \sigma = \frac{k_3 K_a \sigma_0 p}{\underline{k} T + K_a p},$$

where R, k_3, σ_0, and T have the same meaning as before, K_a is the equilibrium constant for chemisorption, σ is the concentration of chemisorbed water vapor in molecules per cm^2, p is the water-vapor partial pressure, and $\underline{k}$ is Boltzmann's constant. The development of this rate indicates that a number of requirements must be satisfied in order to obtain values of k_3, and from these, an activation enthalpy value that is significant in the interpretation of the reaction mechanism. One of these requirements is that, for a given set of experimental conditions, the assumptions used in deriving the rate expression must be valid. In addition, the rate dependence upon water-vapor pressure must be taken into consideration.

2. Surface Effects

The reaction rate of an interface reaction on a given specimen depends upon its true microscopic surface area. Therefore, in order to compare rates on specimens whose surface areas have been determined from their external dimensions, it is necessary to prepare their surfaces in a similar manner.

In addition, surface differences must be considered in comparing rates on different sample types. Although these differences are difficult to assess quantitatively, one would expect that, due to the presence of grain boundaries and pores, reaction rates would be higher on polycrystalline specimens than on single-crystal specimens of the same geometrically determined surface area. However, the experimental data do not indicate significant differences in reaction rates obtained for single-crystal and polycrystalline disk specimens. This behavior may be a consequence of the thick-product-layer effects discussed in Section IV. A.3.

In spite of the approximations involved, the 2/3 order rate expression fits the data reasonably well for all three specimen types. For the

polycrystalline-disk specimens, the assumption of a constant thickness-to-diameter ratio did not hold for large extents of reaction. However, the use of an empirical function that more accurately expressed the surface area as a function of sample weight gave similar rate constants and the same activation enthalpy. Therefore, the simpler 2/3 order equation was used for rate calculations.

The data for the powder specimens fit the 2/3 order equation quite well, despite the circumstance that the specimens did not have simple geometric shapes and that the reaction occurred unevenly on the powder mass as a whole. Barret et al. discussed analogous cases concerning thermal decompositions for which the 2/3 order expression may hold approximately, even though the reaction takes place at an interface in the powder mass rather than on individual grains.[5,6] These examples demonstrate that a fit to a 2/3 order rate law does not necessarily confirm the assumption of a mechanism involving the formation of a reaction interface on individual, approximately spherical grains.

3. Thick-Product-Layer Effects

The corrected weight-loss curves shown in Fig. 2 all have initial portions of decreasing rate followed by linear parts. The most likely causes for this behavior are associated with the formation of a thick product layer. Although there is some tendency for the amount of reaction up to the transition point to increase with temperature, no definite trend is evident. In addition, there appear to be no significant differences between the results on single-crystal and polycrystalline disk specimens. Although the product-layer effect is difficult to characterize quantitatively, several possible reasons can be advanced for its presence.

It is probable that the grain size of the MgO that forms upon reaction is small. For example, the electron photomicrograph (presented in Part I) of material from the product layer of a specimen reacted at 835°C indicated grain diameters in the range of 0.2 to 0.3 μ. At reaction temperatures in the range from 950 to 1100°C, it is likely that some sintering of the product-layer particles took place.[7] Although no shrinkage occurred in the product layer, it was coherent and possessed considerable strength. Even a mechanism involving welding of the particles without shrinkage could conceivably play a role in blocking some of the existing open pores, providing a certain amount of protection for the

reactant surface. The formation of protective scales from initially porous ones through sintering has been observed in other cases, particularly in the oxidation of refractory metals.[8] Although product-layer sintering may have affected the rate measurements reported here, a precise knowledge of the time and temperature dependence of sintering under the experimental conditions used would be necessary to correct the data for its effects.

Resistance to the effusion of reactant and product gases through the pore structure of the product layer could also contribute to a reaction-rate decrease with an increase in product-layer thickness. Although effusion under the reaction conditions is difficult to deal with quantitatively, its general features might be discussed qualitatively by means of the idealized model represented by Darcy's law,[9] which states $v = B_1(\Delta p/L)$, where v is the velocity of effusion, B_1 is a constant, Δp is the pressure gradient, and L the length of the effusion path.

From Darcy's law, it is evident that, if an effusion process were rate controlling and Δp remained constant, a parabolic rate law would result. Analysis of the experimental data showed that this law did not hold. On the other hand, it is possible that the pressure gradient as well as the product-layer thickness increased with time. This situation could result in behavior intermediate between that prescribed by a parabolic and a linear law as observed in the beginning stages of the reaction. Eventually steady-state conditions, which correspond to the linear parts of the reaction-rate curves might be obtained at a point when the pressure gradient increases proportionally with further increases in product-layer thickness.

If the HF pressure in the reaction chamber were constant, and the rate-controlling step were effusion of HF away from the interface, an increasing pressure gradient implies an increase in HF pressure at the interface. This condition could increase the back-reaction rate, resulting in a decreased net-reaction rate. Here again, such an effect would be difficult to evaluate, especially in view of the mechanism discussed in Part I, in which it was shown that the reaction rate probably has a complicated HF-pressure dependence.

The microstructures of sections of reacted specimens, as illustrated in Fig. 4, indicate different product-layer morphologies on the single-crystal and polycrystalline-disk specimens. Because effusion is influenced by such parameters as pore size, shape, interconnection, and

tortuosity, these structure differences could cause differences in the characteristics and temperature dependencies of effusion through the two product layers.

B. Effects of Rate-Influencing Factors on Apparent Activation Enthalpy

In Part I, an activation enthalpy of 46.4 kcal/mole was obtained from the temperature dependence of k_3. In this section the deviations from this value obtained from measurements on the three types of specimens are discussed with regard to the differences in experimental conditions.

The calculations of activation enthalpy values for the three specimen types were based upon the assumption that the water-vapor pressure was high enough to ensure that the surface concentration of water vapor was at its saturation value. Calculations made by extrapolating the data from Part I to the temperature range from 950 to 1100°C indicated that the experimental water-vapor pressure of 55.3 mm Hg was high enough to give nearly full surface coverage. If surface coverage only were considered, and if σ were not equal to σ_0, σ should decrease with increase of temperature at a given pressure. The rate-temperature dependence and activation enthalpy would thus be reduced. The value of 57 kcal/mole obtained for the polycrystalline disk specimens is actually higher than the "true" activation enthalpy of 46.4 kcal/mole. Although the single-crystal value of 42 kcal/mole is low, the experimental data are not precise enough to make a definite conclusion concerning the lack of full surface coverage.

The activation enthalpy of 23 kcal/mole calculated for the powder specimens is in agreement with that obtained by Deadmore et al. for similar specimens.[3] The most reasonable explanation for this result is that the implicit assumption of constant surface area for a given sample weight did not hold. The sintering experiments showed that a sample heated to 1100°C had a greater bulk density, and consequently a smaller external-surface area, than one heated to 950°C. Because the reaction took place at an interface on the powder mass as a whole, a disproportionately low rate was obtained for the specimen reacted at 1100°C, and a low activation enthalpy value was obtained.

The difference in activation enthalpies obtained from measurements on single-crystal and polycrystalline-disk specimens could have resulted from the difference in the morphologies of the product layers on the two specimen types. It is possible that effusion through the more complex product layer on the polycrystalline disks had a greater temperature dependence than effusion through the single-crystal product layer. If the effusion process were rate controlling, this difference in temperature dependence would result in a higher apparent activation enthalpy for the polycrystalline specimens.

V. CONCLUSIONS

The results of this study have shown that the reaction rate of an apparently simple solid-gas reaction may be dependent upon a complex combination of factors, which in themselves may be temperature dependent. Even if these factors are not taken into account, one still may obtain a reasonably good Arrhenius plot from which an apparent activation-energy value may be calculated. However, this value may not be significant in terms of a reaction mechanism, and at best gives a rough estimate of the temperature dependence of the reaction rate under specific experimental conditions.

FOOTNOTES AND REFERENCES

*Work done under the auspices of the U. S. Atomic Energy Commission.

†At the time this work was done the writers were, respectively, graduate research assistant and professor of ceramic engineering, Department of Mineral Technology, University of California. D. R. Messier is now at Argonne National Laboratories, Argonne, Illinois.

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Table I. Table of collected rate data.

T (°K)	$1/T \times 10^4$ (°K^{-1})	Single crystal			Polycrystalline disk			Powder	
		Run No.	B	k_3 (sec^{-1})	Run No.	B	k_3 (sec^{-1})	Run No.	k arbitrary units
1223	8.17	S-1	3.00	44.0	D-1	4.13	22.8	P-1	225
					D-2	4.17	34.8		
					D-3	4.24	30.6		
1273	7.85	S-2	3.00	73.2	D-4	4.24	61.4		
		S-3	3.04	86.7					
1323	7.55	S-4	3.03	157	D-5	4.09	175		
		S-5	3.03	161	D-6	4.14	163		
1373	7.28	S-6	3.00	260	D-7	4.17	374	P-2	620
		S-7	3.02	279	D-8	4.12	370		

FIGURE LEGENDS

Fig. 1. Typical experimental plots of unreacted fraction vs reaction time for the three specimen types (D is polycrystalline disk, P is powder, and S is single crystal).

Fig. 2. $(w/w_0)^{1/3}$ vs reaction time. (a) polycrystalline disks; (b) single crystal specimens; (c) powder specimens.

Fig. 3. Arrhenius Plot of log k_r vs $1/T$ for the three specimen types (□ single crystal; O, polycrystalline disk; and Δ, powder).

Fig. 4. Microstructure of sections of reacted specimens (X13). Top, powder; center polycrystalline disk; bottom, single crystal.

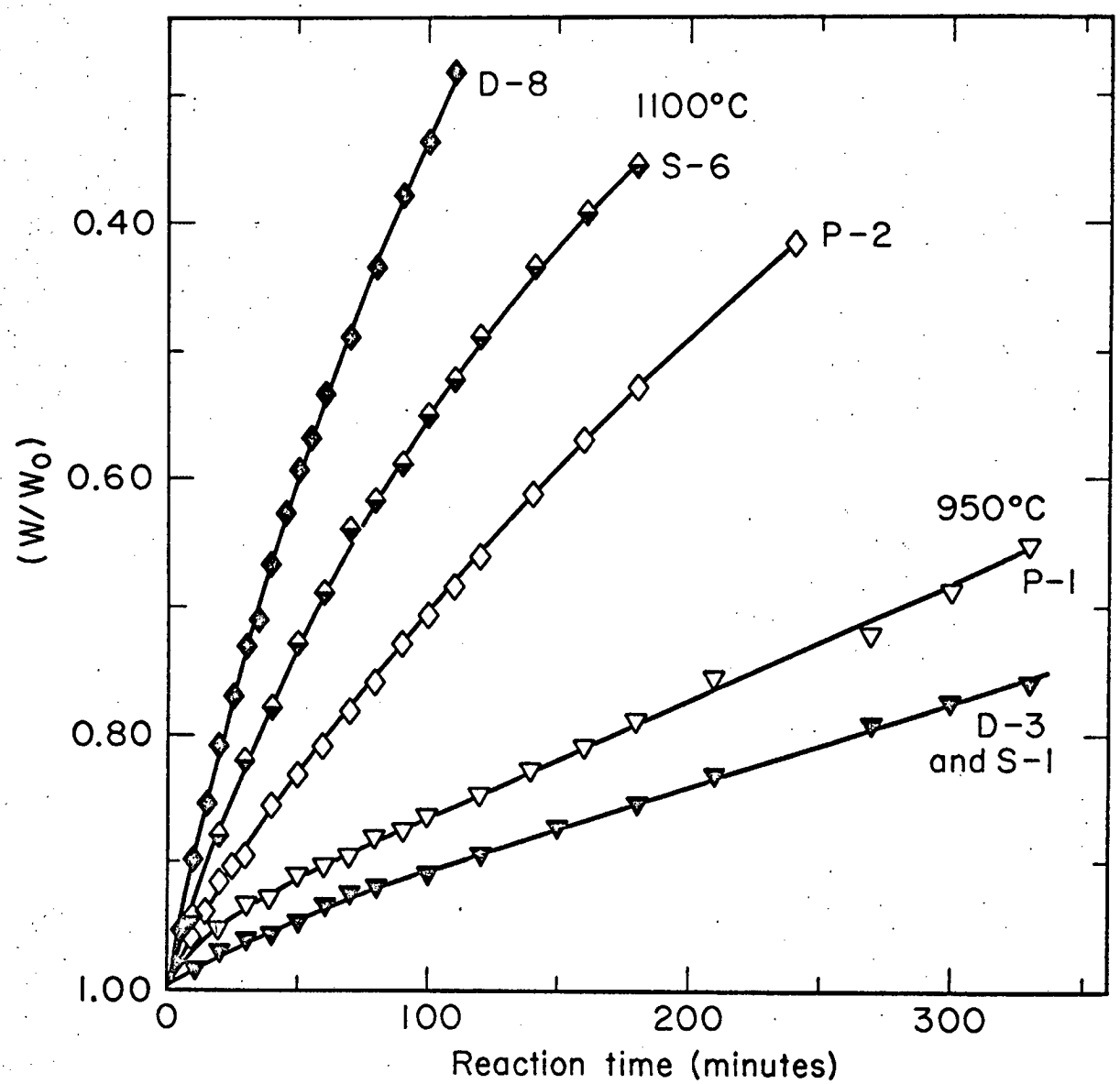

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Fig. 1

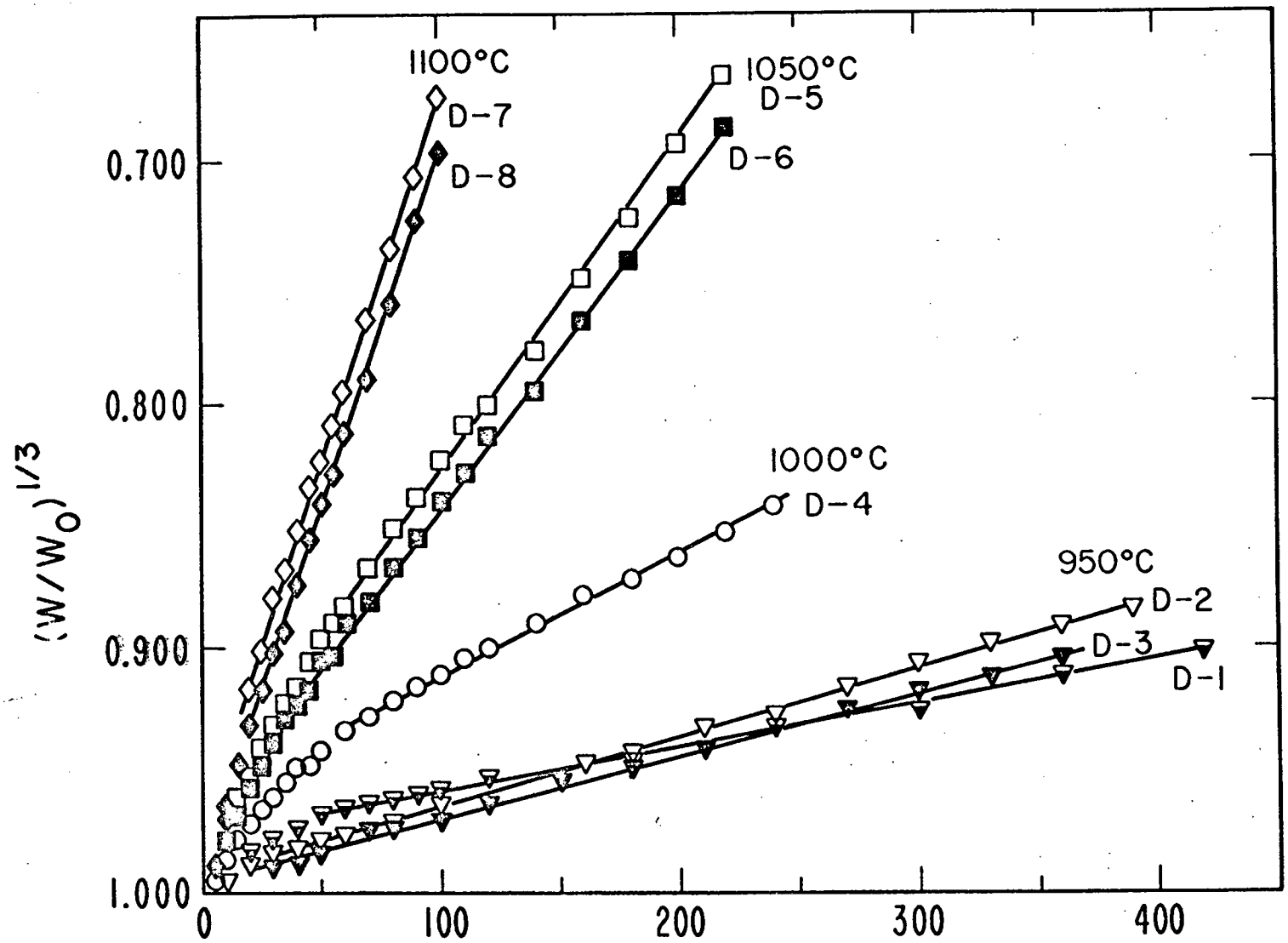

Fig. 2a

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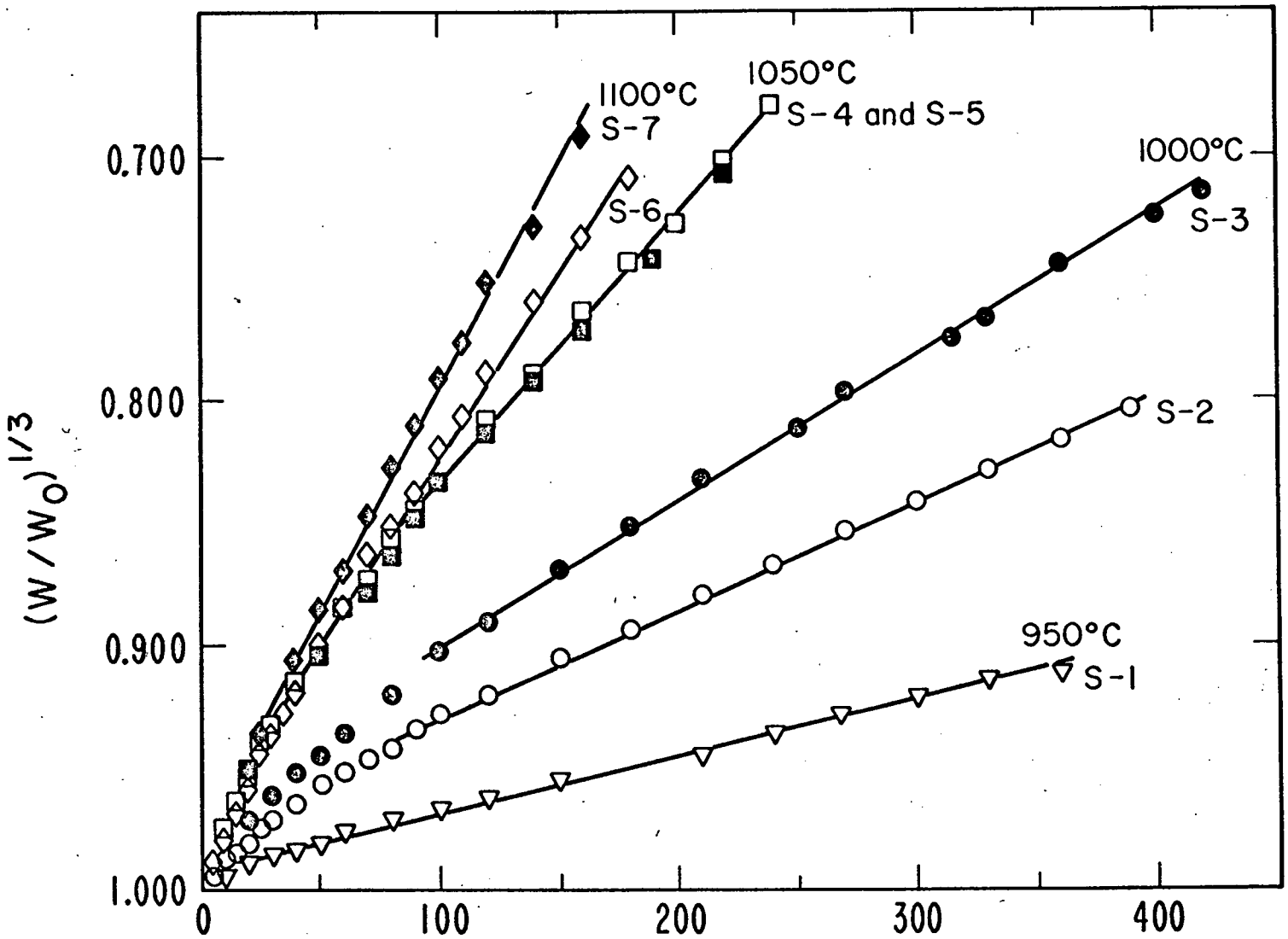

Fig. 2b

MU-33600

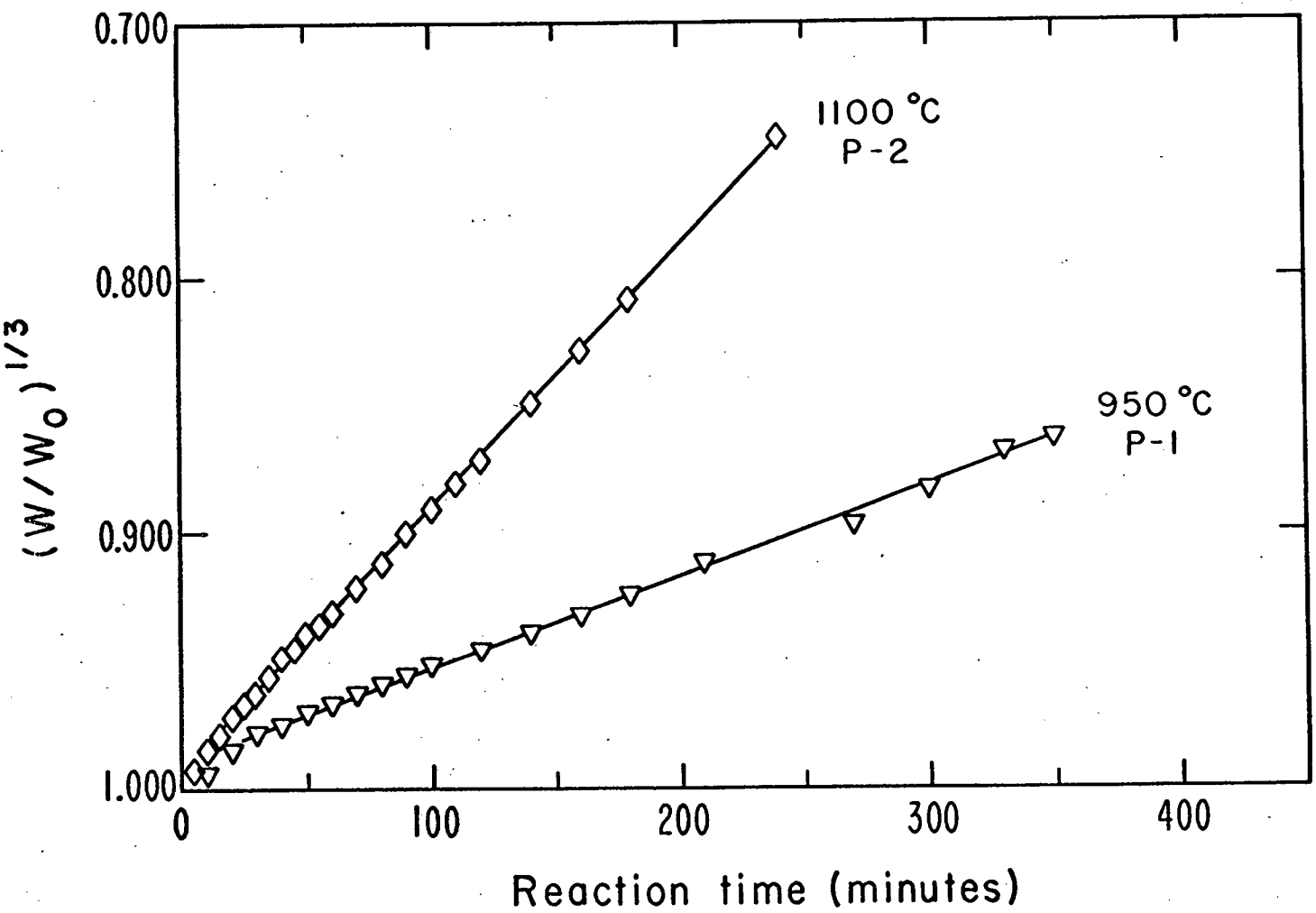

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Fig. 2c

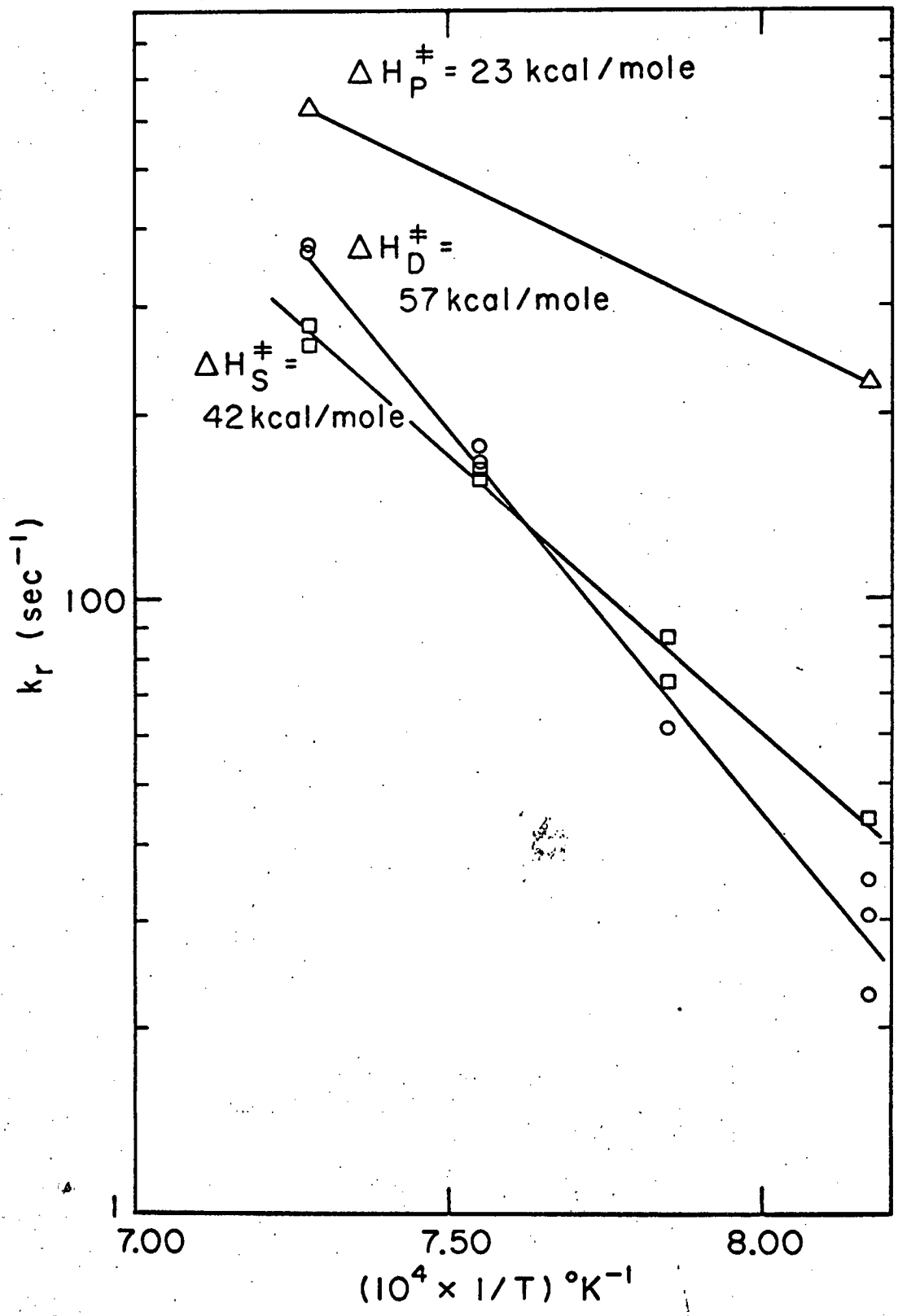

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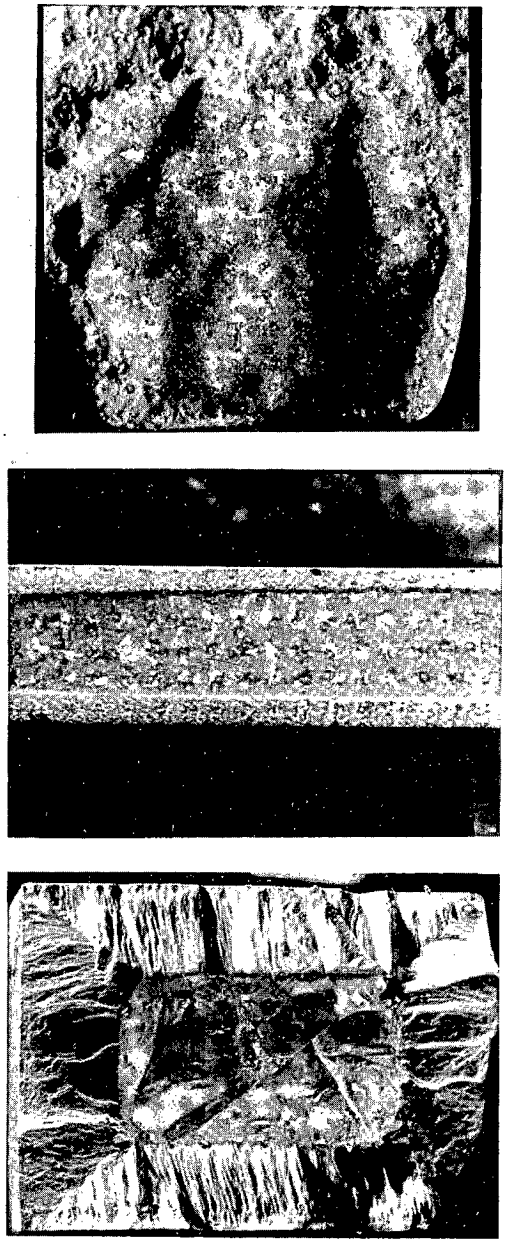
Fig. 3



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