The precipitates were removed and washed five times by centrifuging with diluted hydrochloric acid containing sodium nitrate to prevent peptization. After being dried, the precipitates were counted, using a thin-wall beta counting tube. Inasmuch as activities in the precipitates (*ca.* 0–100 counts per minute) were negligible in comparison with the activity of the standards (4500–4600 counts per minute per milliliter) the absence of exchange is indicated. Extreme washing reduced activities in the precipitates still further, showing that observed activities were probably due only to adsorption and occlusion. Neither alteration of *p*H nor of temperature gave any evidences of exchange.

Attempted Pyrophosphate–Hypophosphate Exchange.—Radiophosphoric acid was converted to pyrophosphate by evaporating with disodium hydrogen orthophosphate solution and igniting the residue for 2 hr. at 600°. The active pyrophosphate was dissolved in water and diluted appropriately with tetrasodium pyrophosphate solution. The exchange procedure was identical with that described above except that concentrations were reduced to 0.01 *M* to avoid precipitation of thorium pyrophosphate.[8] Results exactly comparable with those mentioned above are again interpreted as indicating no exchange. Again some adsorption and occlusion effects were noted.

It should be pointed out that the counting rates noted for the solids were not absolutely correct because the weights of the precipitates used were not determined and because the layers counted were not of uniform thickness, but the values obtained were of the correct orders of magnitude and the interpretations logical.

Acknowledgment.—Support received from the Office of Naval Research is gratefully acknowledged.

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[8] T. Moeller and G. K. Schweitzer, *Anal. Chem.*, **20**, 1201 (1948).

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Radiometric Determination of the Solubilities of Thorium and Certain Rare Earth Metal Hypophosphates

BY THERALD MOELLER AND GLADYS H. QUINTY

RECEIVED JUNE 20, 1952

Although the extremely small acid solubility of thorium hypophosphate has been used to advantage for the efficient removal of thorium from its admixtures with the rare earth elements,[1-6] no quantitative comparisons of hypophosphate solubilities which might lend support to the method have appeared. The availability of radiohypophosphate[7] provided a tool for solubility determinations. Neodymium and yttrium were selected as representative members of the cerium and yttrium sub-groups, respectively, for comparison with thorium.

Data summarized in Table I indicate that thorium hypophosphate remains essentially quantitatively insoluble in at least 4 *N* hydrochloric acid, whereas under comparable conditions the rare earth metal hypophosphates are sufficiently soluble to permit separations. Thorium hypophosphate is markedly less soluble than the pyrophosphate.[8]

TABLE I

SOLUBILITIES OF HYPOPHOSPHATES IN HYDROCHLORIC ACID SOLUTIONS

Sample	Hydrochloric acid concentration, *N*	Solubility, mole/liter × 10^4
ThP_2O_6	1.00	0.25
	2.00	.47
	4.00	1.65
	6.00	2.10
$Nd_4(P_2O_6)_3$	0.05	0.11
	.10	.48
	.20	1.60
	.30	2.00
	1.00	14.46
	2.00	34.70
$Y_4(P_2O_6)_3$	0.20	3.02
	0.30	5.52
	1.00	26.90

Experimental

Solubilities were determined by essentially the same procedure previously described for pyrophosphates.[8] Thorium, neodymium and yttrium hypophosphates were precipitated by adding suitable volumes of a standard sodium hypophosphate solution (26.4 mg. $P_2O_6^{-4}$ per ml.) of known radioactivity (*ca.* 4500 counts per minute per milliliter)[7] to excesses of the metal salt solutions. The precipitates were washed thoroughly, air-dried, and suspended in 50-ml. volumes of hydrochloric acid solutions of varying normalities. These suspensions were equilibrated for 5 days in a thermostat at 25 ± 0.1°, studies having shown that longer periods produced no significant changes. The suspensions were then filtered and the activities of the filtrates measured using an annular volume tube.[8] Comparisons of these activities with that of the standard indicated the solubilities. These are expressed in terms of anhydrous hypophosphates in Table I, the compositions of the precipitates having been determined by independent means.[9]

Although statistical errors at some of the low counting rates encountered and the probable presence of low activities of thorium decay products render these results not absolutely quantitative, the values are of the correct orders of magnitude and especially useful on comparative bases. The rare earth metal hypophosphates are too soluble at acidities above 1–2 *N* to permit accurate evaluations by this procedure.

Acknowledgment.—Support received from the Office of Naval Research is gratefully acknowledged.

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[1] F. Wirth, *Z. angew. Chem.*, **25**, 1678 (1912).

[2] F. Wirth, *Chem. Ztg.*, **37**, 773 (1913).

[3] M. Koss, *ibid.*, **36**, 686 (1912).

[4] A. Rosenheim, *ibid.*, **36**, 821 (1912).

[5] F. Hecht, *Z. anal. Chem.*, **75**, 28 (1928).

[6] T. Moeller, G. K. Schweitzer and D. D. Starr, *Chem. Revs.*, **42**, 63 (1948).

[7] T. Moeller and G. H. Quinty, THIS JOURNAL, **74**, 6122 (1952).

[8] T. Moeller and G. K. Schweitzer, *Anal. Chem.*, **20**, 1201 (1948).

[9] G. H. Quinty, Doctoral Dissertation, University of Illinois, 1951.

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The Solid State Reaction between Magnesium and Chromium Oxides

BY G. PARRAVANO

RECEIVED JUNE 30, 1952

Chemical reactivity of inorganic materials is known to be structure-sensitive, being dependent on a variety of variables which are involved in the history and preparation of the reacting substances. Thus, ill-defined phase boundary effects are responsible for the empirical relations often deduced for the kinetics of solid state changes. These relations cannot be used for the direct establishment of a reaction mechanism.

It has been realized that in order to minimize the conditions under which phase boundary processes will affect the kinetics of the reaction it is necessary to work with well sintered specimens, showing a distribution of particle size and shape over a narrower range than powders obtained at low temperatures. Under these conditions it is possible to find a kinetic behavior of the reacting system conforming more closely to theoretical expectations.

The present note shows how this agreement can be approached quite well in the study of the solid state reaction between magnesium and chromium oxides. The same reaction was previously investigated by Huttig and co-workers.[1] Their results obtained on powder mixtures do not lend themselves to any kinetic treatment.

Experimental

Chromium oxide (Mallinckrodt) and magnesium oxide (reagent, sulfate-free) powders were heated separately at 750° for six hours, cooled to room temperature, pressed into pellets under 5000 lb./sq. inch pressure and sintered at 1100°. The resulting specimens had a cross section of 98.5 sq. mm.

The formation of the spinel, $MgCr_2O_4$, was followed using a technique similar to that of Bengtson and Jagitsch.[2] A chromium oxide and magnesium oxide pellet were gently pressed together; and at different time intervals the change in weight of both pellets was recorded. In order to avoid material transport between the two pellets other than through the contact layer, a flow of air was maintained around the reacting specimens.

Results and Discussion

It was soon realized that at the temperatures investigated some evaporation of chromium oxide took place. The rate of this process was therefore determined on separate pellets of chromium oxide, by recording the loss of weight of the pellets at different time intervals and at constant temperature. The decrease in weight was found to be a linear function of the time of heat treatment. From the plots of weight decrease *vs.* time the following rate constants, k_e, were evaluated (Table I).

TABLE I

EVAPORATION OF CHROMIUM OXIDE

Temp., °C.	$k_e \times 10^6$ g. cm.$^{-2}$ hr.$^{-1}$
890	0.63
1000	15
1100	28
1200	105

From these data an activation energy of 36 kcal./mole was derived for the evaporation process.

It was found that during the reaction between magnesium and chromium oxides, the magnesium oxide specimen showed a continuous increase, while the chromium oxide specimen a continuous decrease in weight. The decrease in weight of the latter, after due allowance was made for the evaporation, was found to agree closely with the increase in weight of the magnesium oxide pellet.

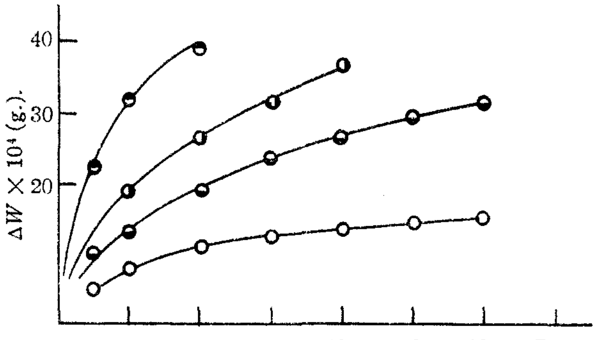

Fig. 1.—Weight increase of MgO pellet during reaction with Cr_2O_3: O, t = 1000°; ◒, t = 1100°; ◑, t = 1200°; ◓, t = 1250°.

Furthermore the area of this pellet which had reacted with chromium oxide became gray-brown in color. At the end of one run the gray-brown substance was collected and examined by X-rays. The resulting pattern was that of the spinel $MgCr_2O_4$.[3]

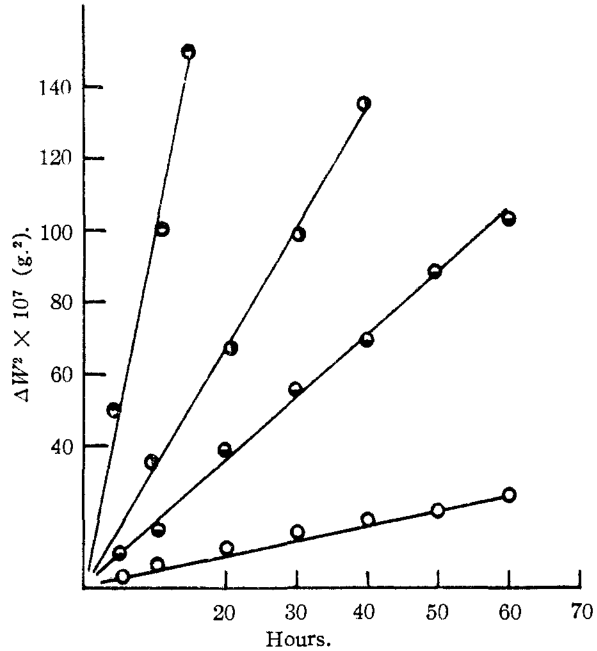

Fig. 2.—Weight increase of MgO pellet during reaction with Cr_2O_3, parabolic plot: O, t = 1000°; ◒, t = 1100°; ◑, t = 1200°; ◓, t = 1250°.

In Fig. 1 are presented the data for the weight increase of magnesium oxide specimens during the reaction with chromium oxide. These data can be fitted fairly well to a quadratic type of equation (Fig. 2)

$$d\Delta W/dt = k/\Delta W$$

where W is the weight increase and k is a constant. The values for the rate constant, $k_r = \Delta W^2/q \times$

TABLE II

REACTION BETWEEN MAGNESIUM AND CHROMIUM OXIDES

Temp., °C.	$k_r \times 10^7$, g.^{2} cm.$^{-4}$ hr.$^{-1}$
1000	0.226
1100	1.81
1200	3.54
1250	10.4

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[1] H. Kittel and G. F. Hüttig, *Z. anorg. Chem.*, **217**, 194 (1934); G. F. Hüttig, D. Zinker and H. Kittel, *Z. Elektrochem.*, **40**, 306 (1934); Th. Meyer and G. F. Hüttig, *ibid.*, **41**, 429 (1935).

[2] B. Bengtson and R. Jagitsch, *Arkiv. Kemi, Mineral. Geol.*, **24**, No. 18 (1947).

[3] M. Hamelin (*Rev. Met.*, **47**, 324 (1950)) has shown that the only compound formed by heating mixtures of magnesium and chromium oxides at temperatures between 1000 and 1400° is magnesium chromite,

$1/t$ (q = reacting area) at different temperatures are collected in Table II.

These data could be plotted according to the Arrhenius equation, from which an activation energy of 50 kcal./mole was derived.

On the basis of these results it can be concluded that in the present case the solid state reaction between magnesium and chromium oxides occurred only at the contact area between the two specimens and not by means of material transport through the gas phase and that the rate of the process is determined by *the diffusion of chromium oxide particles through the spinel layer.* The nature of the diffusing particles however cannot be ascertained from the present data.

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The System Water-Dioxane-Hydrogen Chloride

BY R. A. ROBINSON

RECEIVED JULY 7, 1952

In a recent note Grubb and Osthoff[1] published a study of the separation of water-dioxane mixtures at 25° into two layers on the addition of hydrogen chloride. They stated that this behavior had not been reported previously. It was, however, given brief mention in a review article 14 years ago[2] and has since[3] been studied quantitatively.

Figure 1a shows the tie-lines and the area corresponding to two-phase systems as determined by direct analysis of the conjugate solutions.[3] The points correspond to the data of Grubb and Osthoff.[1] (A few points on the lower right-hand side have been omitted to avoid over-crowding the graph.) In general the agreement between the two determinations is good; Grubb and Osthoff find that the region of partial miscibility is somewhat more extensive in the region of the water-rich mixtures but, considering the analytical difficulties inherent in this investigation, I think the agreement is satisfactory.

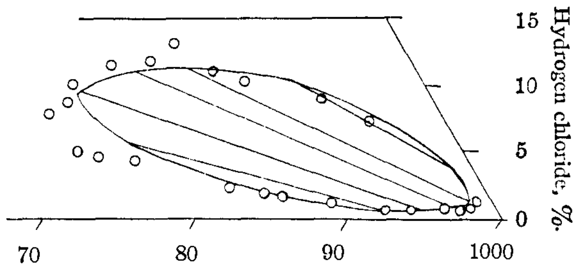

Fig. 1a.—Isotherm of the system water-dioxane-hydrogen chloride at 25°: O, data of Grubb and Osthoff; tie-lines from data of Robinson and Selkirk.

Some time ago, I made a few measurements on this system at 10° by the method I had used earlier at 25° and obtained the results given in Table I and Fig. 1b.

TABLE I

Upper layer			Lower layer		
HCl, %	H_2O, %	$C_4H_8O_2$, %	HCl, %	H_2O, %	$C_4H_8O_2$, %
4.68	3.8	91.5	9.56	9.6	80.8
2.84	2.5	94.7	10.02	14.5	75.5
1.49	1.4	97.1	9.50	18.0	72.5
0.76	2.0	97.2	8.33	21.8	69.9
.51	4.2	95.3	6.98	23.5	69.5
.57	5.6	93.8	5.03	23.8	71.2
.96	10.9	88.1	3.16	19.6	77.2

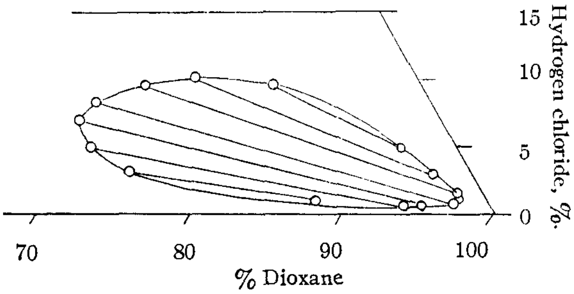

Fig. 1b.—Isotherm of the system water-dioxane-hydrogen chloride at 10°: O—O, tie-lines and composition of conjugate solution; present work.

Lowering the temperature by 15° causes the major axis of the (very approximately) elliptical curve to swing slightly in a counter-clockwise direction with, however, little change in composition of the conjugate solutions.

I have to thank Mr. Andrew Yeo Boon Hin and Mr. Oh Bak Kim for making some preliminary measurements on this system.

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[1] W. T. Grubb and R. C. Osthoff, THIS JOURNAL, **74**, 2108 (1952).

[2] H. S. Harned, *J. Franklin Institute*, **225**, 623 (1938).

[3] R. A. Robinson and R. C. Selkirk, *J. Chem. Soc.*, 1460 (1948).

Potential Antivirals. I. Simple Analogs of Chloramphenicol (Chloromycetin)

BY ARTHUR P. PHILLIPS

RECEIVED AUGUST 8, 1952

The simple chemical structure[1] and broad antibiotic spectrum[2] of chloramphenicol have made it an interesting model for other possible chemotherapeutic agents. While a variety of new synthetic and biologically produced drugs have become available in recent years for combating effectively many of the more common diseases of bacterial or protozoal origin, few if any of these are useful in the treatment of the important diseases attributed to a virus cause. Since chloramphenicol is somewhat effective against certain organisms believed to be viruses it seemed worthwhile to seek additional chemotherapeutic substances against important virus infections among various analogs of this useful antibiotic.

Two chemical units, the aromatic nitro and the dichloroacetyl, had been identified[1] as part of the chloramphenicol structure although these groupings had not been previously recognized in natural products, nor had they been thought desirable for incorporation into synthetic drugs. These two

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[1] M. C. Rebstock, *et al.*, THIS JOURNAL, **71**, 2458 (1949).

[2] I. W. McLean, Jr., *et al.*, *J. Clin. Investigation*, **28**, 953 (1949).