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Application of Inert Radioactive Gases in the Study of Solids

Part 2 *Thermal Decomposition of Various Iron Salts and Preparation of α-Fe_2O_3 in its Active State*

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The behaviour of different iron salts ($FeSO_4.7\ H_2O$, $FeC_2O_4.2\ H_2O$, Mohr's salt, and basic iron carbonate) was studied by means of the emanation method, DTA and dilatometry. The salts were heated within the temperature range of 20 to 1100° C, under identical conditions. The results obtained are compared and the process of thermal decomposition of the different salts is discussed.

The "activity" of ferric oxide obtained by decomposition of various iron salts is estimated, and it is suggested that the low "activity" of the sulphate-derived ferric oxides is related to a low thermal annealing rate, while the higher "activities" of the other two resultant ferric oxides are similarly related to higher thermal annealing rates.

1. Introduction

Many inorganic substances may be prepared in the active state by thermal decomposition of other substances, accompanied by the liberation of a gaseous product. For example, metallic oxides used as catalysts or absorbents, are prepared by thermal decomposition of their salts or hydroxides. There is an optimum temperature for preparing these oxides with the required properties (specific surface, catalytic activity, etc). This temperature is frequently determined by empirical means only, and a knowledge of the detailed decomposition mechanism of the initial substances would make these results more exact.

Therefore the behaviour of different iron salts was studied by means of the emanation method, differential thermal analysis and dilatometry, in the temperature interval of 20 to 1100° C. The results obtained by various methods under absolutely identical experimental conditions were compared.

2. Experimental

2.1. The Preparation of the Initial Iron Salts

The following iron salts were prepared for analysis: ferrous sulphate; Mohr's salt; ferrous oxalate; basic iron carbonates.

An oversaturated ferrous sulphate solution was obtained by dissolving carbonyl iron (transistor grade purity) in pure dilute sulphuric acid with a small excess at 50° C. Oversaturated ammonium sulphate (transistor grade purity), acetate and carbonate solutions were prepared by dissolving the respective salts in bi-distilled water at 50° C. Ferrous sulphate heptahydrate was obtained after crystallisation from a hot solution, acetone (AR Grade) being used for salting out. Mohr's salt was obtained by pouring together hot ferrous sulphate and ammonium sulphate solutions in the stoichiometric ratio. Ferrous oxalate was obtained by combining hot ferrous sulphate and ammonium oxalate (AR Grade) solutions; the carbonate was prepared as a precipitate by adding ammonium oxalate solution to ferrous sulphate solution. The white colour of the ferrous sulphate precipitate changed to green when exposed to the air after pressure-filtration, and finally changed to brown as a consequence of oxidation.

The radioactive inert gas was introduced into the samples in the course of their preparation: such amounts of radiothorium (Th^{228}) were added to ferrous sulphate solutions as to make the final activity 0.01 microcuries per g Fe_2O_3, to an order of magnitude.

2.2. Apparatus and Experimental Technique

The apparatus used for emanation measurements, differential thermal analysis (DTA) and dilatometric measurements is described in [1]. X-ray analyses were made with a Type URS 50 IM diffractometer of USSR manufacture, using an Fe Kα anticathode. The activity of samples is expressed in relative emanation power (REP) calculated for every temperature from the relation:

$$\text{REP}\ (\%) = \frac{I_{\text{solid}}\, M_{\text{liq}}}{I_{\text{liq}}\, M_{\text{solid}}}\ 100 \qquad (1)$$

where $I_{\text{solid}}/M_{\text{solid}}$ is the activity of emanation above the resultant Fe_2O_3 powder, and $I_{\text{liq}}/M_{\text{liq}}$ is the activity of an amount of the initial salts dissolved in 5% HCl, which when decomposed will give M_{solid} grammes of Fe_2O_3. The absolute magnitude of the activity (A) may be calculated from these REP values from equations 2 and 3

$$A_{\text{solid}} = I_{\text{solid}}\, K_1 \qquad (2)$$

$$A_{\text{liq}} = I_{\text{liq}}\, K_2 \qquad (3)$$

where K_1 and K_2 are efficiency coefficients of measurement of solid and liquid samples in the respective apparatus. For the present purpose, however, it is sufficient to express the emanation capacity in REP units.

3. Results and Discussion

The temperature relationship of the emanation power (curve 1) DTA curves (curve 3) and dilatometric curves (curve 4) for the four salts of iron are shown in figs. 1 to 4. These curves were obtained by heating the salts in the temperature range of 20 to 1100° C at a rate of 8 to 10° C per min. The emanation curves of the resultant Fe_2O_3, heated from 20 to 1100° C are also included in figs. 1 to 4 (curves 2).

3.1. Ferrous Sulphate ($FeSO_4.7\,H_2O$)

A three-stage dehydration of ferrous sulphate was observed to take place in the temperature interval of 60 to 320° C as indicated by three peaks on the emanation curve at 60, 120 and 310° C and by the corresponding endothermic effects on the thermographic curve (fig. 1). This is confirmed by data obtained on the basis of thermogravimetric [2] and differential thermogravimetric measurements [3], as well as by means of differential thermal analysis [4]. It is suggested that incongruent fusion of the salt, in its own hydrate water, takes place in this temperature range and that the process is accompanied by the partial oxidation of bivalent iron and the formation of an intermediate product, basic ferric sulphate. This intermediate product loses water at temperatures of 510 to 530° C corresponding to peaks on the emanation and DTA curves. The ferric sulphate formed by means of oxidation of ferrous sulphate and of the basic ferric sulphate was still present in the sample at 690° C and, began to thermally decompose at this temperature. This process was indicated, on the emanation and DTA curves by a peak at 700° C, a sudden change being observed on the dilatometric curve. Moreover, a second peak on the emanation curve (at 720° C) may be ascribed to the conversion of the initially formed amorphous phase to crystalline ferric oxide. X-ray analysis confirmed this assumption. The existence of such amorphous intermediates in the process of decomposition of inorganic salts has been reported for a number of cases [1, 5, 6]. X-ray diagrams of samples heated to 1100° C confirmed that only the alpha modification of ferric oxide was present. The emanation curve of the resultant ferric oxide is shown in curve 2 of fig. 1. The curve shows that on repeated heating of the sample, no chemical or physical changes take place.

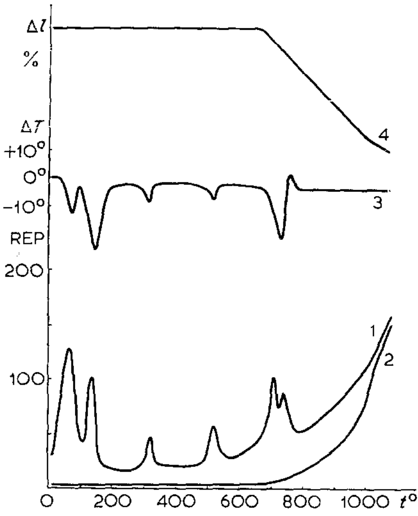

Figure 1 Thermal analysis of ferrous sulphate ($FeSO_4.7H_2O$): 1, emanation curve; 2, emanation curve of ferric oxide prepared by heating the sulphate to 1100° C; 3, DTA curve of the sulphate; 4, dilatometric curve of the sulphate. (REP = relative emanation power.)

3.2. Mohr's Salt ($Fe(NH_4)_2(SO_4)_2.6H_2O$)

The dehydration and thermal decomposition of Mohr's salt was similar in character to that of ferrous sulphate heptahydrate (see curves 2, 3,

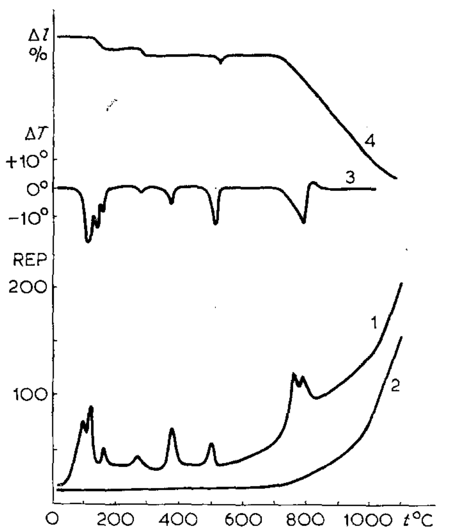

Figure 2 Thermal analysis of Mohr's salt ($Fe(NH_4)_2(SO_4)_2.6H_2O$): 1, emanation curve of Mohr's salt; 2, emanation curve of ferric oxide prepared by heating of Mohr's salt to 1100° C; 3, DTA curve of Mohr's salt; 4, dilatometric curve of Mohr's salt. (REP = relative emanation power.)

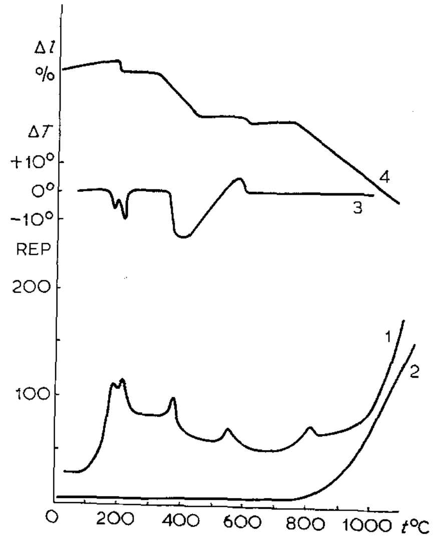

Figure 3 Thermal analysis of ferrous oxalate ($FeC_2O_4.2H_2O$): 1, emanation curve of the oxalate; 2, emanation curve of ferric oxide prepared by heating of the oxalate to 1100° C; 3, DTA curve of the oxalate; 4, dilatometric curve of the oxalate. (REP = relative emanation power.)

fig. 2). The only difference was, that during the incongruent fusion of the salt, some ammonia was lost, together with partial oxidation of ferrous iron [3, 7]. In addition, the decomposition of ammonium sulphate, corresponding to the peaks on the emanation and DTA curves, was completed at 390° C. The peaks observed at 760° C on both curves are ascribed to decomposition of ferrous sulphate [8]. The peak on the emanation curve at 780° C and the corresponding exothermic effect on the DTA curve indicate the existence of an intermediate amorphous phase of ferric oxide in the temperature interval of 760 to 780° C. X-ray analysis confirmed that the resulting product corresponds to the structure of the alpha modification of Fe_2O_3.

3.3. Ferrous Oxalate ($FeC_2O_4.2H_2O$)

The double peak on the emanation curve (curve 1, fig. 3), and the endothermic effects on the DTA curve (curve 3, fig. 3) at 180 and 220° C correspond to dehydration of the sample. The dissociation of the anhydrous oxalate started at 350° C and was accompanied by a peak on the emanation curve, an endothermic effect and decreasing sample volume, as shown in fig. 3. FeO and Fe, that were formed by the dissociation of the oxalate, are immediately oxidised to Fe_3O_4, and apparently the peak on the emanation curve at 550° C and the exothermal effect on the DTA curve correspond to this process. X-ray analysis of the samples confirmed this interpretation. Samples heated to 450° C contained mainly Fe_3O_4 and exhibited the characteristic line 2.53 Å, although the peaks were diffuse due to the high degree of dispersity; samples taken at 500° C also contain only Fe_3O_4, however the characteristic lines were more intensive. Samples heated to 670° C showed the presence of α-Fe_2O_3. The peak on the emanation curve at 760 to 830° C may be ascribed to the sintering of ferric oxide. This conclusion is confirmed by the dilatometric measurement (curve 4, fig. 3). The process of decomposition of hydrated ferrous oxalate is similarly described by other authors [8-13].

3.4. Basic Carbonate of Iron (II, III)

A rise of emanation power may be observed on the emanation curve up to 120° C (curve 1, fig. 4), connected with the release of adsorbed water from the sample. A similar phenomenon takes place when ferric hydroxide or ferrous carbonate is heated [4, 14, 15]. On further heating, above 300° C, the sample decomposed. The decrease of the emanation power above this temperature indicates a decrease of the specific surface area. The decomposition of the carbonate was most rapid at temperatures of 490 to 520° C, which was

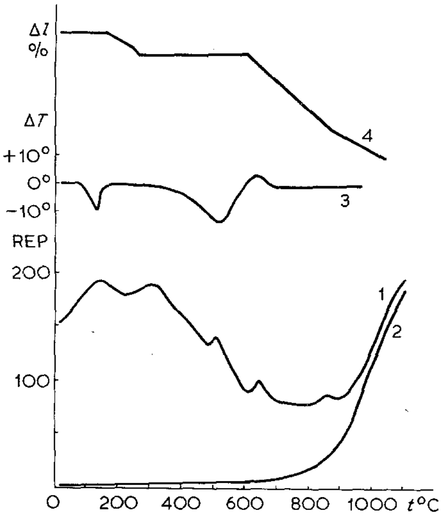

Figure 4 Thermal analysis of iron basic carbonate: 1, emanation curve of the carbonate, 2, emanation curve of ferric oxide prepared by heating of the carbonate to 1100° C; 3, DTA curve of the carbonate; 4, dilatometric curve of the carbonate. REP = relative emanation power.)

also reflected by peaks on the emanation and DTA curves (curves 1 and 3, fig. 4). The specific surface area continued to decrease above this temperature, as shown by the emanation curve.

The X-ray diffraction pattern of the sample taken at 500° C showed a number of lines, including one with $d = 2.53$ Å, which corresponds to Fe_3O_4 and the remaining two, close to each other, may be identified as $FeCO_3$ (2.76 Å) and α-Fe_2O_3 (2.59 Å).

On further heating, exothermic oxidation of the carbonate decomposition products began to prevail; the maximum rate of this process is reached at a temperature of roughly 640° C (the exothermic peak on the DTA curve). The X-ray diffraction pattern of a sample heated to 650° C was distinguished by peaks which are sharper than those observed on the pattern of a sample heated to 500° C. Moreover, the peak corresponding to $FeCO_3$ was missing and the peaks corresponding to Fe_3O_4 and α-Fe_2O_3 were clearer. A sample heated to 850° C had a diffraction pattern and included lines corresponding to α-Fe_2O_3. Therefore, the small peak on the emanation curve at temperatures of 830° C to 870° C may be explained by intensive growth of sample grains. The increased intensity of characteristic α-Fe_2O_3 lines on the diffraction pattern of a sample heated to 1100° C confirmed this view. This interpretation is also confirmed by the work of other authors [16, 17].

3.5. The "Activity" of the Resultant Ferric Oxides

Let us attempt to estimate the "activity" of the ferric oxide obtained by thermal decomposition of various iron salts, starting from the temperature relationship of the emanation power. According to Hüttig [20] the measure of the "activity" is the free energy of 1 g of material in the given state with regard to the normal state.

The decomposition temperature of iron salts can be denoted by T_d and the temperature at which the crystal lattice of the resulting product, α-Fe_2O_3, is formed by T_f. Values of T_d and T_f taken from curves 1 in figs. 1-4 are given in table I.

TABLE I Properties of the initial iron salts.

Initial iron salt	Decomposition temperature of the salt T_d, °C	Temperature of α-Fe_2O_3 formation T_f, °C
Oxalate	370	820
Basic carbonate	510	870
Sulphate	700	770
Mohr's salt	750	830

The temperature-dependence of the emanation power of the four iron salts can be expressed in the form:

$$\text{REP} = f(T - T_f). \qquad (4)$$

This relationship is plotted in fig. 5 for the four iron salts. Assuming that the rise of emanation power in the temperature interval $T > T_f$ is caused by diffusion of the inert gas in α-Fe_2O_3 only, then the temperature-dependence of the emanation power offers information concerning the conditions of the emanation release from the solid; this may include information about the growth of grains and the annealing of non-equilibrium defects that have a substantial influence on the diffusion properties of the substance. The slope of the emanation curves of the resultant ferric oxide in the temperature region $T > T_f$ is dependent on the initial iron salt (see fig. 5). The sulphate-derived ferric oxides exhibit a lower slope of the emanation curve than the other two ferric oxide samples. This could indicate a smaller rate of grain growth and a lower rate of annealing of non-equilibrium defects. The difference in the behaviours of various ferric oxides arises from

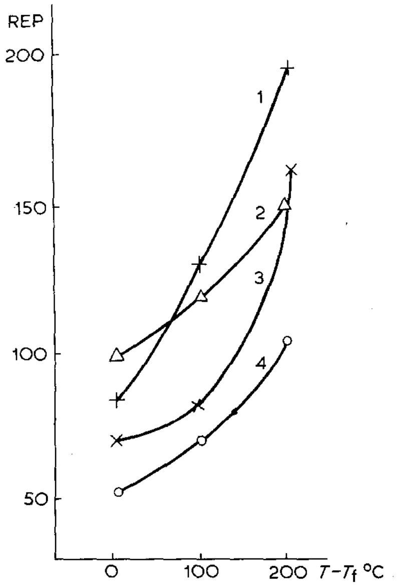

Figure 5 The temperature-dependence of the emanation power of ferric oxide prepared by heating of: 1, iron basic carbonate; 2, Mohr's salt; 3, oxalate and 4, sulphate of iron (II). (REP, = the relative emanation power; T_f = temperature of formation of α-Fe_2O_3 lattice.)

their derived structures [18, 19] based on the structure of their initial iron salts. Moreover, the oxalate and carbonate iron salts decompose at temperatures substantially below those of the iron sulphate types. Likewise the formation of α-Fe_2O_3 obtained by decomposition of oxalate or basic carbonate proceeds through intermediates, Fe_3O_4 or γ-Fe_2O_3, while ferrous sulphate and Mohr's salt decompose to form amorphous ferric oxide, which changes on further heating to crystalline α-Fe_2O_3.

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