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THERMOCHEMICAL STUDY ON THE SOLID STATE INTERACTION OF GRAPHITE WITH CUPRIC AND FERRIC SULPHATES

MAHMOOD M. BARBOOTI

Petroleum Research Centre, Council of Scientific Research, Jadiriyah P.O. Box 10039, Baghdad (Iraq)

TALIB H. EL-SHARIFI

Department of Chemical Engineering, College of Engineering, University of Baghdad, Jadiriyah, Baghdad (Iraq)

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ABSTRACT

Cupric sulphate and ferric sulphate are reduced directly into cuprous oxide and ferrous oxide, respectively, by solid state interaction with graphite on heating. The plots of free energy change vs. temperature demonstrate that reduction is more by carbon monoxide than by carbon when the heating atmosphere is carbon dioxide. In practice reduction by the C–CO_2 system is a minor contribution to the overall process, because the in situ production of CO becomes appreciable at temperature ranges where the decomposition of the salts and their reduction are near completion.

INTRODUCTION

Solid state interactions of carbon with inorganic materials have been the subject of several papers. Papers have studied the catalytic activity of different materials on carbon oxidation [1] or the reduction of the materials by carbon [2]. In all cases the temperature and atmosphere of heating are important factors in the progress of the reactions. Another mode of interaction between carbon and copper(II) sulphate was recently reported by Barbooti [3]. The sulphate decomposed directly into copper(I) oxide as a result of the immediate reduction of copper(II) oxide by carbon [3].

The present work is a thermochemical study on the action of carbon on copper(II) sulphate and iron(III) sulphate under different atmospheres.

Experimental

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded with a Stanton Redcroft model TG 760 thermobal-

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ance. In all experiments the sample size was 3–5 mg, the heating rate was 20 °C min^{-1}, and the working gas flow rate was 25 ml min^{-1}. Heating was carried out under nitrogen gas or carbon dioxide.

$Fe_2(SO_4)_3 \cdot 10H_2O$ and graphite were supplied by BDH. $CuSO_4 \cdot 5H_2O$ was supplied by Hopkin Williams. Weighed amounts of the sulphates and graphite were ground and mixed in an agate mortar for 20 min to give a graphite content of 10% by weight.

RESULTS AND DISCUSSION

$CuSO_4$: graphite system

Thermal treatment of the copper(II) sulphate–graphite mixture can initiate the following reactions

$$2CuSO_4 \rightarrow CuSO_4 \cdot CuO + SO_3 \rightarrow 2CuO + SO_3 \qquad (1)$$

$$2CuSO_4 + C \rightarrow Cu_2O + CO + 2SO_3 \quad [3] \qquad (2)$$

$$2CuSO_4 + CO_2 + C \rightarrow 2CuSO_4 + 2CO \rightarrow Cu_2O + CO_2 + CO + 2SO_3 \qquad (3)$$

Reactions (1) and (2) occur under air and nitrogen atmospheres with appreciable effect of atmosphere on the temperature interval [3,4]. Reaction (3) could occur under carbon dioxide flow only as a result of the well established interaction of graphite with CO_2 to form carbon monoxide [5], which is known to have good reducing ability. The possibility of these reactions was derived from the thermodynamic calculations to estimate the change of the accompanying free energy change ΔG with temperature, with the aid of value of enthalpy and entropy of formation of reactants and products quoted from Kubaschewski and Alcock [6] The plots of ΔG vs. temperature for reactions (1)–(3) are shown in Fig. 1.

Below 830 K, the simple decomposition of sulphate, reaction (1), is characterized by lower ΔG values than those of reaction (2), which means that the decomposition is thermodynamically assisted below this temperature. However, the rate of ΔG change for reaction (2) is greater than that of reaction (1), which makes reaction (2) more favourable at temperatures higher than 830 K. Several authors agree on a decomposition temperature of not less than 880 K for copper(II) sulphate [4,7]. Such a temperature reveals the occurrence of reduction reaction (2) at the expense of the decomposition reaction.

The TG curves shown in Fig. 2 support the above results and a noticeable difference can be seen in their shape, as well as in the characteristic temperatures of the change. Copper(II) sulphate in the presence of graphite starts decomposition at 875 K, and the maximum rate of weight loss (DTG peak maximum) was attained at 900 K compared with 910 and 1010 K, respectively, for sulphate on its own.

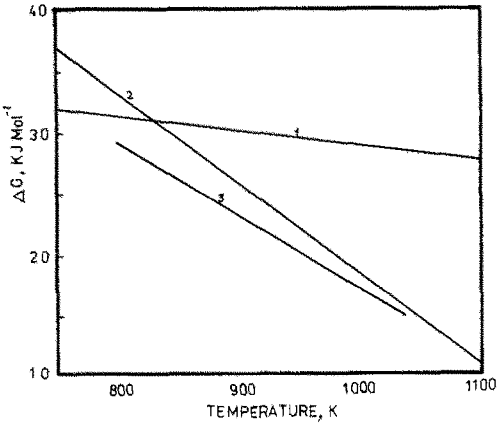

Fig. 1. Plots of free energy change for reactions (1)–(3).

However, the two-step nature of $CuSO_4$ decomposition (1) is retained in the presence of graphite, although the overlapping is greater in the latter case (Fig. 2). The essential step in the reaction is the decomposition into $CuO \cdot CuSO_4$ and further into CuO accompanied by immediate reduction by carbon. The reduction, which removes CuO as it is formed, may contribute to the increase of the decomposition rate.

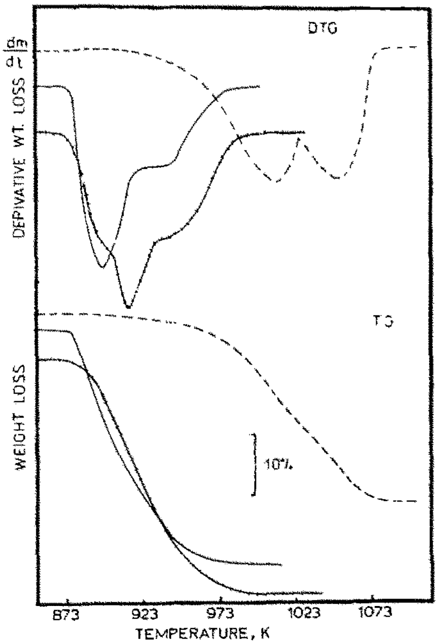

Fig. 2. TG and DTG curves of copper(II) sulphate (1), and copper(II) sulphate + graphite (2).

Under carbon dioxide flow conditions reaction (3) is likely to occur, especially when the reaction is thermodynamically assisted (Fig. 1), and the characteristic free energy changes have far lower values than reactions (1) and (2) over the temperature range involved. It is important to note that reaction (3) must be aided by the formation of carbon monoxide by the interaction of carbon with CO_2, and this was appreciable only beyond 902 K under our experimental conditions (Fig. 2): the rate gets faster as temperature increases further. By reference to the above mentioned temperatures, it can be seen that the reaction of copper(II) sulphate with carbon has already passed its maximum rate at this temperature. The effect of the second, freshly prepared, in situ reducing agent CO becomes less important in the main weight loss process. In the last stages, CO_2 could influence the reaction through its interaction with carbon, forming adsorbed CO on the carbon surface. These adsorbed CO molecules could then act as active sites for the adsorption of sulphate [2]. The TG curves indicated a faster rate of weight loss in the last stages under CO_2 flow than under nitrogen (Fig. 2).

$Fe_2(SO_4)_3$: graphite system

Heating of ferric sulphate in the presence of graphite can result in the following chemical changes

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3 \quad (4)$$

$$Fe_2(SO_4)_3 + C \xrightarrow{N_2} 2FeO + CO + 3SO_3 \quad (5)$$

$$Fe_2(SO_4)_3 + C + CO_2 \rightarrow Fe_2(SO_4)_3 + 2CO \xrightarrow{CO_2} 2FeO + CO + 3SO_3 \quad (6)$$

Several reports agree that reaction (4) occurs between 850 and 1020 K, with a maximum rate at 980 K [4,7]. The free energy changes for reactions (4)–(6)

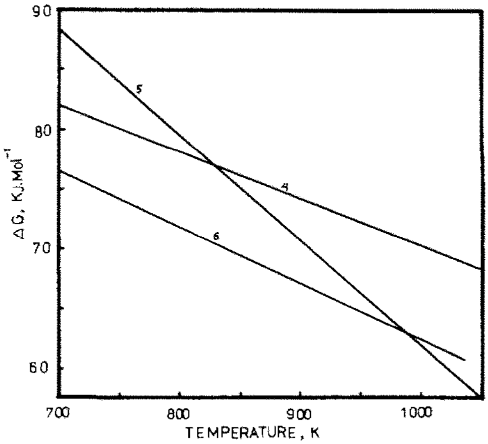

Fig. 3. Plots of free energy change for reactions (4)–(6).

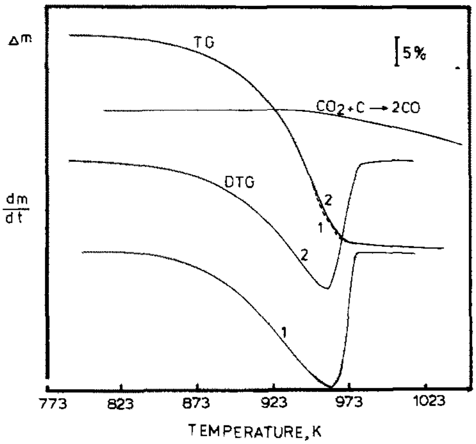

Fig. 4. TG and DTG curves of iron(III) sulphate (1) and iron(III) sulphate + graphite.

were calculated over the temperature range 700–1100 K using the enthalpy and entropy of formation of the species involved as reactants and products as given by Kubascheweski and Alcock [6], and plotted vs. temperature in Fig. 3. Reaction (4) appears endothermic and favoured at high temperatures, as ΔG decreases with the increase of temperature. The free energy change plot of reaction (5) is characterized by a greater slope than that of reaction (4), and the corresponding ΔG values are less than those of reaction (4) above 830 K. However, this may support the occurrence of appreciable weight loss beyond 815 K as can be seen at the TG curves of the ferric sulphate–graphite mixture (Fig. 4). The figure indicates a slow decomposition between 740 and 815 K and a main decomposition step between 815 and 948 K with a maximum rate at 925 K. Reaction (5), therefore, is the predominant chemical change within the system at the expense of reaction (4), as the main decomposition process occurs at a temperature range that is almost 70 K lower than that encountered for the decomposition of pure ferric sulphate.

Again CO_2 flow could initiate reaction (6), but at the temperature range where the interaction between graphite and carbon dioxide becomes appreciable, reaction (5) and to a less extent reaction (4) are approaching completion, i.e. reaction (6) could only contribute to the last stage of the main weight loss process.

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