THERMODYNAMICS OF THE OXIDATION OF ELEMENTS BY ALUMINIUM SULPHATE

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ABSTRACT

A thermochemical analysis using the Ellingham technique shows that the sulphate ion in solid aluminium sulphate can act as an oxidising agent towards a wide range of elements including pre-transition metals, transition metals, post-transition metals, and non-metals. The thermochemical predictions are correlated with experimental observations.

INTRODUCTION

We recently demonstrated [1] that alum, $KAl(SO_4)_2$, or more simply aluminium sulphate, can oxidise metallic tin to a mixture of SnO_2 and SnS_2 under mild conditions. The production of SnS_2 (mosaic gold) under these conditions was probably first described in a Chinese alchemical text of ca. 300 A.D., the *Bao-pu zi* (Master-of-Solidarity Manual) of Ko Hung, a translation of which has been published [2]. Having confirmed experimentally the action of the sulphate ion as an oxidant in the formation of SnS_2, where the sulphur is reduced from S(VI) to S($-$II), we employed known thermochemical data to analyse [1] the reaction, and found that oxidation of tin (eqn. 1) is thermodynamically feasible at all temperatures below 1000 K.

$$\tfrac{1}{3}Al_2(SO_4)_3 + 2Sn \rightarrow \tfrac{1}{3}Al_2O_3 + \tfrac{3}{2}SnO_2 + \tfrac{1}{2}SnS_2 \qquad (1)$$
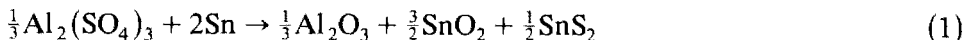
Not only is the reaction thermodynamically feasible, but the mixture requires only very modest heating to initiate a complex solid-phase process: DTA indicated an irreversible exothermic reaction, forming the SnS_2, at only 218°C. Similar thermochemical calculations suggested that the sulphates of many other metals should likewise be able to oxidise metallic tin to a mixture of SnO_2 and SnS_2: only the sulphates of Na, K, Rb, and Cs could be excluded.
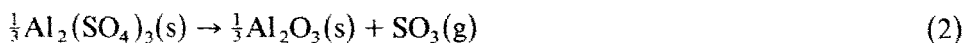
Alum appears in a number of other early Chinese procedures, apart from the mosaic gold recipe [1,2]. Thus, it is mentioned in the 6th century A.D. text *San-shi-liu Shui Fa* (Thirty-six methods for bringing minerals into aqueous solutions) [3], in connection both with the solubilisation of orpi-

ment As_2S_3, and, more importantly, with the production of metallic copper by precipitation from its aqueous solution.

We have now developed further the use of thermochemical analysis to encompass an investigation of the oxidising action of the sulphate ion in aluminium sulphate towards elements other than tin.

METHOD

It is convenient to consider each reaction as occurring in two steps (eqns. 2–4), and to base all stoichiometries upon one mole of SO_3: two possible oxidation processes were considered, one involving oxidation of the element to give both oxide and sulphide (eqns. 2 and 3), and the other involving formation of element oxide only, with reduction of SO_3 to SO_2 (eqns. 2 and 4).

$$\tfrac{1}{3}Al_2(SO_4)_3(s) \rightarrow \tfrac{1}{3}Al_2O_3(s) + SO_3(g) \tag{2}$$

$$SO_3(g) + \frac{4}{y}M \rightarrow \frac{3}{y}MO_y + \frac{1}{y}MS_y \tag{3}$$

$$SO_3(g) + \frac{1}{y}M \rightarrow \frac{1}{y}MO_y + SO_2(g) \tag{4}$$

The thermodynamic feasibility of redox reactions involving $Al_2(SO_4)_3$ as an oxidant was investigated using the Ellingham diagram technique [4]. Free energies for each component were computed using eqn. (5).

$$\Delta G_T^\ominus = \Delta H_{298}^\ominus - T\Delta S_{298}^\ominus + \int_{298}^{T} \Delta C_p \, dT - T\int_{298}^{T} (\Delta C_p / T) \, dT \tag{5}$$

with C_p in parametric form (eqn. 6):

$$C_p = a + bT + cT^{-2} \tag{6}$$

Values of $\Delta H_{298}^\ominus$ and $\Delta S_{298}^\ominus$, and of the parameters a, b, and c were taken from literature sources [5]: for systems involving phase changes, separate calculations were made for either side of each transition temperature. The range of systems studied was constrained only by the availability of appropriate thermodynamic data.

RESULTS AND DISCUSSION

Table 1 summarises the results for the oxidation of elements by aluminium sulphate to yield a $3:1$ mixture of metal oxide and metal sulphide (eqns. 2 and 3) as observed [1] initially for tin. For the vast majority of elements for which appropriate data are available, this oxidation is feasible, including in

TABLE 1

Results for the process $\frac{1}{3}Al_2(SO_4)_3 + \frac{4}{y}M \rightarrow \frac{1}{3}Al_2O_3 + \frac{3}{y}MO_y + \frac{1}{y}MS_y$

(i) M for which reaction is thermodynamically feasible at all temperatures in the range 300–1000 K

$\frac{1}{2}H_2$	B	C(IV)	Ti(IV)	Zn(II)
Li	Al	Si(IV)	Cr(III)	Cd(II)
Na[a]	Ga(III)	Sn(IV)	Mn(III)	Mo(IV)
K[a]	In(III)	Sn(II)	Mn(IV)	W(IV)
Be		Pb(II)	Fe(II)	W[d]
Mg		As(III)	Co[c]	Re(IV)
Ca[b]		Sb(III)	Ni(II)	Re(VII)
Sr[b]		Bi(III)	Cu(I)	U(IV)
Ba[b]				

(ii) M for which reaction is not feasible at any temperature in the range 300–1000 K

Cu(II)	Ag(I)	Hg(II)	Ru(IV)

(iii) M for which reaction is feasible over part only of the range 300–1000 K

Ge(II), feasible only if $T > 670$ K
Tl(I), feasible only if $T < 580$ K

[a] M_2O and M_2S. [b] MO and MS. [c] Feasible for both CoO/CoS_2 and Co_3O_4/CoS_2: CoO/CoS_2 most favoured. [d] WO_3 and WS_2.

the case of rhenium oxidation to the highest oxidation state, Re(VII). Of the elements considered in Table 1, only the noblest metals silver and mercury resist oxidation by aluminium sulphate: in addition gold may be expected likewise to resist oxidation, but both the likely products Au_2O and Au_2S are poorly characterised [6]. Despite the wide range of molecular compounds formed in low oxidation states by ruthenium, the lowest oxidation state for which ruthenium forms a well-characterised [7] oxide and sulphide is IV: oxidation of ruthenium metal to Ru(IV) oxide and sulphate by aluminium sulphate is not possible, a conclusion scarcely surprising in view of the generally noble character of the platinum metals (Ru, Os; Rh, Ir; Pd, Pt). It may be expected that the other platinum metals similarly resist such oxidation by aluminium sulphate.

In Table 2, the results are summarised for the oxidation of elements by aluminium sulphate to yield, in addition to aluminium oxide, a mixture of metal oxide and sulphur dioxide (eqns. 2 and 4). Rather more elements are considered in this table, construction of which required the availability of data only for the elements and their oxides, but not (as for Table 1) for their sulphides. Overall the patterns in Tables 1 and 2 are similar, but with a number of post-transition elements requiring a minimum temperature (often around 400 K) for onset of oxidation, and with detail differences for some of the transition elements, such as copper, ruthenium and rhenium.

TABLE 2

Results for the process $\frac{1}{3}Al_2(SO_4)_3 + \frac{1}{y}M \to \frac{1}{3}Al_2O_3 + \frac{1}{y}MO_y + SO_2$

(i) M for which reaction is thermodynamically feasible at all temperatures in the range 300–1000 K

$\frac{1}{2}H_2$	B	Si(IV)	T(IV)	Zn(II)
Li	Al	Ge(IV)	V(IV)	Cd(II)
Na[a]	Ga(III)		Cr(III)	Mo(IV)
K[a]	In(III)	Sn(IV)	Cr(VI)	Mo(VI)
Be		Sn(II)	Mn(II)	W(VI)
Mg			Mn(IV)	U(IV)
Ca[b]		P(V)	Fe(III)	
Sr[b]		Sb(III)	Fe[d]	
Ba[c]			Co(II)	
			Ni(II)	

(ii) M for which reaction is not feasible at any temperature in the range 300–1000 K

$\frac{1}{2}N_2$[e]	Ag(I)	Re(VII)	Au(III)	Hg(I)

(iii) M for which reaction is feasible over part only of the range 300–1000 K

Tl(I)	$T > 640$ K		
C(II)	$T > 490$ K	Cu(I)	$T > 580$ K
C(IV)	$T > 330$ K		
Ge(II)	$T > 700$ K		
Pb(II)	$T > 390$ K	Cu(II)	$T > 710$ K
As(III)	$T > 370$ K		
Bi(III)	$T > 530$ K	Ru(IV)	$T > 710$ K
S_8	$T > 480$ K	Re(IV)	$T > 390$ K

[a] M_2O. [b] MO. [c] MO or MO_2. [d] Fe_3O_4. [e] N_2O, NO or NO_2.

The results of Tables 1 and 2 may be used to connect and integrate a wide range of observations from chemical literature both ancient and modern. The oxidation of metallic tin, yielding SnO_2 and SnS_2, which was first observed [2] almost two thousand years ago, has already been discussed [1]. The oxidation of elemental hydrogen to give a mixture of water and hydrogen sulphide was reported [8] by Wöhler in 1845 (cf. Table 1), whereas formation of a mixture of water and sulphur dioxide (cf. Table 2) has also been reported in the hydrogen reduction of sulphates [9]. Several recent studies have demonstrated [10,11] that the sole solid product from the reduction of aluminium sulphate by hydrogen is aluminium oxide, but no analysis of the volatile products was reported, although it was assumed [10] that sulphur dioxide, rather than hydrogen sulphide, was produced. Of these two processes, the present calculations show that the first (yielding H_2O rather than SO_2) is substantially the more favourable at all temperatures in the range $200 \leqslant T/K \leqslant 1200$.

There are many diverse reports of the reactions of sulphur trioxide with elements which are relevant to the present discussion: thus elemental phosphorus yields [12] phosphoric oxide and sulphur dioxide, while carbon yields [13] carbon monoxide and sulphur dioxide in a reaction which gives [14] 100% conversion of carbon to CO at ca. 350°C. Sulphur is similarly oxidised to sulphur dioxide [15]. Amongst the metallic elements, zinc [16], iron [16], and magnesium [17] are all reported to be oxidised yielding mixtures of metal oxide and metal sulphide (cf. Table 1). Magnesium metal will reduce not only aluminium sulphate in this manner, but also the sulphates of a wide range of other metals, including Na, K, Mg, Ca, Ba, Mn, Fe, Co, Ni, and Cu [17]. On the other hand, Oddo reported [18] that wholly dry sulphur trioxide did not react at all with metals, even as reactive as potassium: this report is extremely surprising.

The reduction of alums, of aluminium sulphate, and of basic aluminium sulphates such as $H_2[Al_6(SO_4)_4(OH)_{12}]$ [19] has been widely studied [19–21] using hydrogen or sulphur, as well as mixtures of hydrogen and sulphur vapour as reductant, always with the objective of freeing these widely occurring minerals from all traces of sulphur, so that the resulting aluminium oxide can be used as a raw material for aluminium extraction. While the present calculations predict an onset temperature for reduction of aluminium sulphate by elemental sulphur of ca. 200°C (Table 2), efficient desulphurisation of aluminium sulphate by hydrogen/sulphur mixtures was most speedily effected at temperatures around 500°C.

The available experimental data are in broad agreement with our calculations, showing effective oxidation of a range of elements by aluminium sulphate, at modest temperatures. This agreement gives us confidence in the validity of our results for those systems where no experimental data are yet available. The sulphate ion in aluminium sulphate appears to have the ability to oxidise a wide range of elements, an ability which, until the present work, has not generally been recognised. It is possible that, for certain processes, aluminium sulphate could provide a cheap and effective oxidant for commercial application .

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