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A thermochemical approach to the gas-phase reduction of metal sulphates

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The reduction of different metal sulphates by hydrogen occurs at different temperatures and can lead to a variety of products. It has been shown that the starting temperatures for the reduction of several sulphates are directly related to the magnitude of their (exothermic) heats of formation per equivalent. The thermochemical data also provide a basis for the interpretation of the relative thermal stabilities (under nitrogen atmosphere) of several metal sulphates. A consideration of the appropriate heat of formation values can also be useful in understanding the different reduction products obtained for different metal sulphates. Finally, the reduction behaviour of some binary metal sulphates is also consistent with the thermochemical data.

1. Introduction

The gas-phase reduction of $CuSO_4$ by H_2 to yield metallic copper can take place at moderately low temperatures (350 to 400° C), thus making this process of potential technical importance. Also, it is of some interest to explore in this connection the gas-phase reduction behaviour of other sulphates, not only with a view to their possible technical exploitation but also to elucidate the basic factors that may be related to the ease of reduction of different sulphates. A possible application of the gas-phase reduction of sulphates (or mixed sulphates) is the case in which a high area substrate such as silica gel is soaked with the aqueous solutions of appropriate sulphates which are subsequently reduced by H_2 in order to obtain finely dispersed metallic (or polymetallic) clusters as efficient catalytic sites on the substrate.

Until recently, little systematic information was available in the literature on the reduction of sulphates. However, recent extensive investigations of Habashi and co-workers [1, 2] have provided excellent systematic data on the reduction behaviour of sulphates under carefully controlled experimental conditions. Although several significant interpretative insights were also brought out in this work [1, 2], some aspects of the data need further analysis in order to attempt plausible answers to questions such as the following:

(1) What properties of sulphates are responsible for their different initial reduction temperatures?

(2) Can the product distribution in the reduction of metal sulphates be related to any of their properties?

(3) Why do some metal sulphates influence the reduction temperature of $CuSO_4$ whereas many others do not, when binary mixtures of $CuSO_4$ with other sulphates are subjected to reduction by H_2?

In the present paper, an attempt is made to present some theoretical considerations, based on a thermochemical approach, which appear to bear on the above questions and some other related matters.

2. Factors affecting the ease of reduction of sulphates

The relative ease of various sulphates for reduction by H_2 is indicated by their starting temperature of reduction, under otherwise comparable conditions. In a typical reduction of a metal sulphate, reactions such as the following may occur:

$$2MSO_4 + 5H_2 \longrightarrow MO + MS + SO_2 + 5H_2O \quad (1)$$

$$MO + H_2 \longrightarrow M + H_2O \quad (2)$$

Here MSO_4 is a binary sulphate which may undergo reduction to yield, besides SO_2 and H_2O, the corresponding metal oxide, metal sulphide or the metal, or, a mixture of these solid products. The *principal* point in this reduction is that the bonds holding the lattice of the solid metal sulphate are ruptured to various extents in order to yield the products. Since metal sulphates are predominantly ionic compounds, the strength of their bonding in the solid state, that is their solid state cohesion, will be determined by their lattice energy, U, values. For metallic sulphates with the same valency of the cation, e.g. divalent metal sulphates, the lattice energy is inversely related to the cation radius as through, for example the Kapustinskii equation [3] which may be written in its approximate form as follows:

$$U = \frac{-287.2 n_i Z_c Z_a}{(r_c + r_a)} \tag{3}$$

where U is the lattice energy; n_i is the number of ions per formula weight, i.e., 2 for a divalent metal sulphate, MSO_4; Z_c and Z_a are the valences of the cation and the anion, respectively; r_c is the cation radius and r_a is the anion radius. In Equation 3, some terms of secondary importance have been ignored [3]. From Equation 3, it is clear that divalent metal sulphates with low r_c values will have high lattice energies and vice versa so that the solid state cohesion of these sulphates should depend *inversely* on the r_c values of their metal ions. Since solid state cohesion depends inversely on the r_c of the metal ions (for sulphates containing cations of the same valency), the initial temperature of reduction should be inversely related to the r_c values for a given valent class, e.g., sulphates of divalent metals: no such correlation is observed, however (Table I). The initial reduction temperatures of sulphates are thus not related to the solid state cohesion of their ionic lattices. It may be added that the initial reduction temperatures have a kinetic significance since they were derived from the plots of thermogravimetric analysis [1].

A consideration of some relevant thermochemcial data provides a fruitful approach to the problem, however. It is observed that the initial reduction temperatures of sulphates are related to

TABLE I Starting temperatures of reduction of different sulphates by H_2 and some related quantities

Sulphate	r_c (Å)	Starting temperature of reduction (° C)	Heat of formation per equivalent, $-\Delta H_e$(kcal)			Predominant initial reduction products
			Sulphate	Oxide	Sulphide	
Cu_2SO_4	–	120	89.60	19.92	9.8	Cu
$CuSO_4$	0.69	230	92.00	18.80	6.05	Cu_2SO_4
$HgSO_4$	1.10	240	84.15	10.80	6.95	Hg_2SO_4
Ag_2SO_4	–	260	85.25	3.66	3.80	Ag
$NiSO_4$	0.72	340	106.50	29.20	10.0	Ni_3S_2
$CdSO_4$	0.97	340	110.68	30.43	17.25	CdS
$CoSO_4$	0.74	400	103.75	28.60	10.10	Co_9S_8
$ZnSO_4$	0.74	400	116.94	41.59	24.10	ZnO + ZnS
$Fe_2(SO_4)_3$	–	400	110.00	32.10	–	$FeSO_4$
$PbSO_4$	1.20	420	109.75	26.10	11.25	Pb + PbS (at 650° C)
$Al_2(SO_4)_3$	–	430	136.83	65.30	28.80	Al_2O_3
$FeSO_4$	0.76	440	110.00	31.90	11.40	Fe_3O_4 + FeS
$MnSO_4$	0.80	540	127.12	46.00	24.5	MnO + MnS
$MgSO_4$	0.65	670	152.75	71.92	41.5	MgO
Na_2SO_4	–	700	165.45	62.10	44.6	Na_2S

(1) The starting temperatures of reduction of sulphates are taken from the Table I of Habashi [1].

(2) The predominant *initial* products of reduction are as in the text of [1].

(3) The heats of formation per *equivalent* values are taken either from the Handbook [5] or Sanderson [6]; the $-\Delta H_e$ value for $FeSO_4$ was *estimated* from Fig. 3 of K. Tanaka and K. Tamaru, *J. Catal.* 2 (1963) 366, and is hence approximate; no accurate values of $-\Delta H_e$ for $FeSO_4$, $Fe_2(SO_4)_3$ and Fe_2S_3 could be found in the usual sources [5, 6].

(4) Although the initial reduction product (at 420° C), of $PbSO_4$ is PbO + PbS, a rather easy formation of Pb on reduction of $PbSO_4$ at a somewhat higher temperature (650° C) has been noted in Table I of [1]; in Fig. 2 and the related discussion here, Pb + PbS appear to be the initial reduction products consistent with the general considerations developed here.

(5) The cation radii given here are for divalent metals only since these are the ones needed for the discussion of arguments built around the Kapustinskii equation, i.e., Equation 3 in the text; the r_c values are from [7].

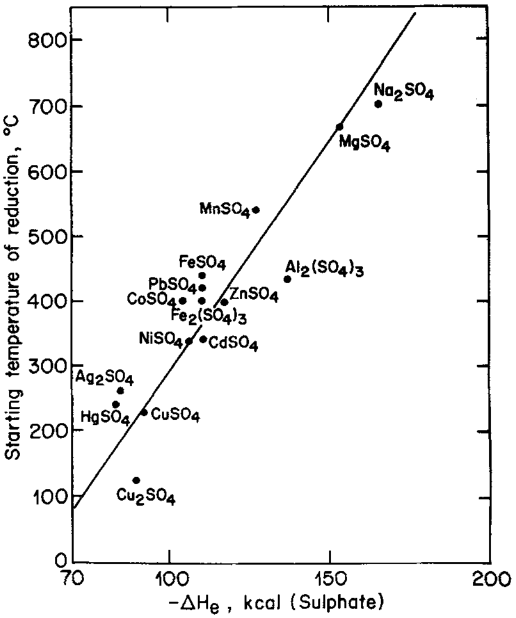


Figure 1 A plot of starting temperatures for reduction (by H_2) of metal sulphates against their heats of formation per equivalent values; see Table I for the data and the source references.

their thermochemical stability, as expressed by their (exothermic) heats of formation per *equivalent* values, i.e., $-\Delta H_e$ (Fig. 1).

It should be stated here that although sulphates are in general ionic compounds, they are not completely ionic as, for example, are the alkali halides, especially the fluoride of alkali metals. This is perhaps the reason why the stability of sulphates is not accurately reflected in the values of their lattice energies. Heats of formation, which are an index of the general thermodynamic stability of the compound irrespective of the nature of the bonding, are perhaps a better indicator of the stability of sulphates. It would, therefore, follow from Fig. 1 that sulphates possessing higher stability in the solid state are more difficult to reduce by hydrogen, i.e., they exhibit higher starting temperatures of reduction.

A consideration of thermochemical data also provides an explanation of the different products of initial reduction for different sulphates as in the next section.

3. Thermochemical explanation of the reduction product spectrum of sulphates

Although Habashi *et al.* [1, 2] provided excellent interpretations of the reduction mechanisms of many individual sulphates, they did not address themselves to the question of which property, if any, of the sulphates tends to determine the nature of the products obtained on the commencement of their reduction.

First of all, it is obvious that sulphates capable of being easily reduced to a lower valent state of initial reduction would do so because the process would involve minimum of structural changes and bond breaking/making events; this is indeed observed for $CuSO_4$, $HgSO_4$ and $Fe_2(SO_4)_3$ (Table I). As to the rest of the sulphates, the relative tendencies of their metals to form *oxides* appears to provide a useful empirical classification (Fig. 2) in which very low $-\Delta H_e$ values for oxides are associated with a complete reduction of the sulphate to the metal, namely, Ag_2SO_4 and Cu_2SO_4. With increasing $-\Delta H_e$ values for oxides, incomplete reduction gives sulphides; at much higher $-\Delta H_e$ values for oxide, a clear-cut tendency to gives oxides is observed, as would be expected. Only for the case of Na_2SO4, the reduction product is Na_2S even though $-\Delta H_e$ value of its oxide is extremely high (Fig. 2).

As regards the possible significance of Fig. 2, one may look at the process of the reduction by hydrogen of a metal sulphate, MSO_4 in the following way:

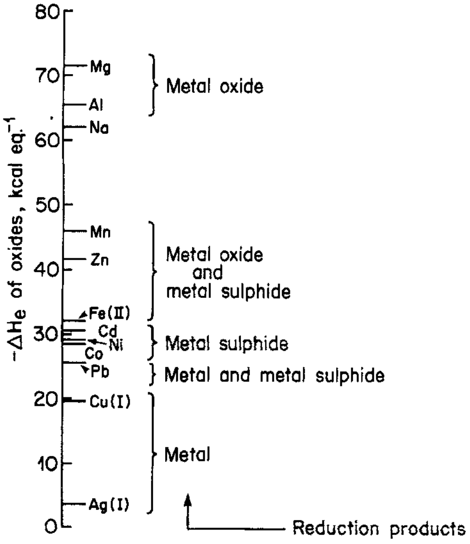
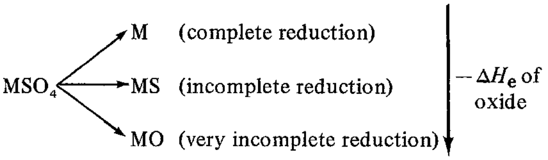


Figure 2 Metals arranged in the increasing order of their (exothermic) heats of formation per equivalent values for the oxides and indicating the predominant products obtained on the initial reduction of the corresponding metal sulphates; see Table I for the data and the source references.



The degree of incompleteness of reduction of the metal sulphate tends to increase with the ease of oxidation of the corresponding metal, the latter being reflected in the magnitude of its $-\Delta H_e$ value for the oxide.

It may be added that Fig. 2 can perhaps be of some use in predicting the probable reduction products of those sulphates for which the experimental data have not yet been reported in the literature.

4. Thermochemical interpretation of stability of sulphates

A matter somewhat related to the reduction behaviour of sulphates is the thermal decomposition (under a nitrogen atmosphere) of eleven sulphates under carefully controlled *identical* conditions, as reported by Ostroff and Sanderson [4], who interpreted these data in terms of the influence of the electronegativity of the cation on the stability of its sulphate. The decomposition of these sulphates (Table II) was carried out under a nitrogen atmosphere and referred to the reaction.

$$MSO_4 \longrightarrow MO + \text{volatile products} \quad (4)$$

TABLE II Thermal decomposition temperatures of some sulphates to give oxides and the appropriate heat of reaction per equivalent values.

Sulphate	Decomposition temperature (° C)	$-\Delta[(\Delta H_e)_{SO_4} - (\Delta H_e)_O]$ (kcal)
$FeSO_4$	537	–
$CuSO_4$	598	73.2
$ZnSO_4$	646	75.35
$NiSO_4$	675	77.30
$CoSO_4$	708	75.15
$MnSO_4$	755	81.12
$PbSO_4$	803	83.65
$CdSO_4$	816	80.25
$MgSO_4$	895	80.83
$CaSO_4$	1149	95.31
S_rSO_4	1374	102.05

(1) The thermal decomposition temperatures were obtained from [4] and were determined under a nitrogen atmosphere.

(2) The heats of reaction are the differences in the heats of formation of metal sulphates and the corresponding oxides, all taken as per equivalent [5,6].

The decomposition temperatures for these sulphates (Table II) have been plotted against the heats of reaction per *equivalent* of the above reaction in Fig. 3 here; the heat of reaction, of course, is the difference in the heats of formation of the metal sulphate and the metal oxide. A good correlation between the thermal stability and the thermochemical stability of the metal sulphates is indeed obtained (Fig. 3).

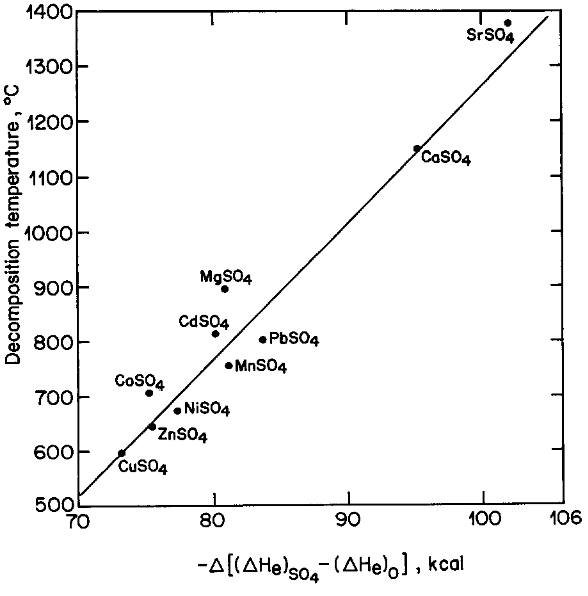
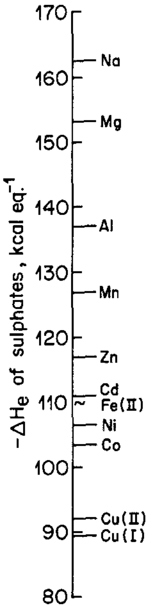


Figure 3 Temperatures for the thermal decomposition of metal sulphates to the corresponding oxides (under a nitrogen atmosphere) plotted againt the appropriate heat of reaction per equivalent values; Table I contains these data and their sources.

5. Some aspects of the reduction of binary sulphates

In the reduction of $CuSO_4$ mixed with another sulphate, it has been observed [2] that Na_2SO_4, $MgSO_4$, $Al_2(SO_4)_3$, $ZnSO_4$ and $CdSO_4$ do not influence the reduction of $CuSO_4$. However, $CoSO_4$, $NiSO_4$ and $FeSO_4$ are reduced at a lower temperature, whereas $MnSO_4$ is reduced at a higher temperature than that for their respective reductions in the absence of $CuSO_4$. It may be speculated that the reduction of $CuSO_4$ is influenced by those sulphates whose cations are quite similar to Cu^{2+} in that they are cations of transition metals or near-transition metals possessing some d-character; also the cations of these sulphates can display a multiple valency. On the other hand sulphates of sp metals, which do not exhibit a d-character, multi-valence or other characteristics of transition metals, do not affect the reduction of $CuSO_4$ namely, Na_2SO_4, $MgSO_4$, $Al_2(SO_4)_3$, $ZnSO_4$ and $CdSO_4$·



Figue 4 Metals arranged in the increasing order of the (exothermic) heats of formation values of their metal sulphates; this representation is used in the text to discuss the reduction behaviour of binary metal sulphates.

The behaviour of binary sulphates is also consistent with the general thermochemcial considerations. Sulphates whose heats of formation per equivalent are nearer to that for $CuSO_4$ tend to influence its reduction whereas sulphates having $-\Delta H_e$ values much higher than that for $CuSO_4$ tend not to affect its reduction (Fig. 4); the exception of Mn to this general trend may be noted and is believed to arise from the fact that $MnSO_4$ and $CuSO_4$ form a stable solid solution.

In conclusion, it may be stated that a thermochemical approach appears to provide a plausible basis for explaining the main tendencies observed in either the reduction of sulphates or their thermal decomposition.

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