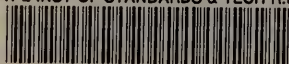


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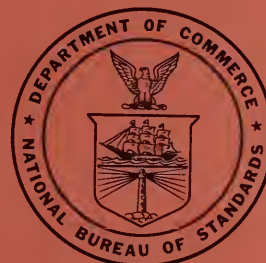
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Part 1. Sulfates

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High Temperature Properties and Decomposition of Inorganic Salts

Part 1. Sulfates

K. H. Stern and E. L. Weise

Institute for Basic Standards
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Foreword

The National Standard Reference Data System is a government-wide effort to give to the technical community of the United States optimum access to the quantitative data of physical science, critically evaluated and compiled for convenience. This program was established in 1963 by the President's Office of Science and Technology, acting upon the recommendation of the Federal Council for Science and Technology. The National Bureau of Standards has been assigned responsibility for administering the effort. The general objective of the System is to coordinate and integrate existing data evaluation and compilation activities into a systematic, comprehensive program, supplementing and expanding technical coverage when necessary, establishing and maintaining standards for the output of the participating groups, and providing mechanisms for the dissemination of the output as required.

The NSRDS is conducted as a decentralized operation of nation-wide scope with central coordination by NBS. It comprises a complex of data centers and other activities, carried on in government agencies, academic institutions, and nongovernmental laboratories. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data.

For operational purposes, NSRDS compilation activities are organized into seven categories as listed below. The data publications of the NSRDS, which may consist of monographs, loose-leaf sheets, computer tapes, or any other useful product, will be classified as belonging to one or another of these categories. An additional "General" category of NSRDS publications will include reports on detailed classification schemes, lists of compilations considered to be Standard Reference Data, status reports, and similar material. Thus, NSRDS publications will appear in the following eight categories:

<i>Category</i>	<i>Title</i>
1	General
2	Nuclear Properties
3	Atomic and Molecular Properties
4	Solid State Properties
5	Thermodynamic and Transport Properties
6	Chemical Kinetics
7	Colloid and Surface Properties
8	Mechanical Properties of Materials

The present compilation is in category 5 of the above list. It constitutes the seventh publication in the new NBS series known as the National Standard Reference Data Series.

A. V. ASTIN, *Director.*

Preface

During the past decade or two, inorganic salts, particularly in the liquid state, have assumed increasing importance in a variety of applications. They are useful as reaction media, in metallurgical processes, and in electrochemical power sources such as fuel cells and thermal batteries.

Experimentalists and theoreticians have found molten salts an interesting subject for study since these ionic fluids offer an unusual opportunity for the study of short-range ionic interactions in the liquid state.

So far, attention in this field has largely been focused on the halides since their stability at high temperatures is well known. The only decomposition which they can undergo is dissociation to the elements. The extent of this dissociation can be easily calculated from existing thermodynamic compilations.

For most inorganic salts the situation is more complicated. In many cases the decomposition reactions are not well defined and high-temperature thermodynamic and kinetic data are either lacking or scattered through the literature. Thus, although the study of many salts would undoubtedly prove interesting and useful, they have received little attention because in many cases not even the range of thermal stability is known.

The purpose of the present publication is to alleviate this situation by publishing in concise form thermodynamic and kinetic data relevant to the high-temperature behavior of important classes of inorganic salts. For the present, data in this work are restricted to anhydrous compounds with monatomic cations and oxyanions containing one element besides oxygen. Each volume in this series will deal with compounds of one anion, sulfates in the present volume.

Thermodynamic information has been heavily stressed because it is most important for dealing with the stability problem, and because it constitutes the bulk of what is available. Whenever possible we have used in our calculations data already critically evaluated by others—references are given in the appropriate places—but we have also included qualitative and semiquantitative information on the assumption that some knowledge is better than none. However, in these cases we have tried to warn the reader by posting appropriate “Beware!” signs.

Thermodynamic variables which have been included are

- (a) Phase transition temperatures above 298.15 °K, except those at high pressure, together with the corresponding enthalpies and entropies.
- (b) Equilibrium constants and decomposition pressures, as well as relevant free-energy functions from 298.15 °K to as high a temperature as data exist. ΔH_f and S^0 values of reactants and products at 298.15 °K from which the above functions are calculated are also given.
- (c) Densities at 298.15 °K and above.

Kinetic data which have been included are

- (a) Qualitative and quantitative information on the kinetics of thermal decomposition.

For the convenience of the user a number of special tables are also included; for example, a listing of compounds in the order of increasing melting points and decomposition pressures which may prove useful is given.

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High Temperature Properties and Decomposition of Inorganic Salts

Part 1. Sulfates

K. H. Stern and E. L. Weise

The literature dealing with the high-temperature behavior of inorganic sulfates has been critically reviewed. Free energy functions of reactants and products of the decomposition reactions were calculated and have been tabulated from 298 °K up to as high a temperature as possible. Free energy functions, equilibrium constants of reactions, and partial pressures of gaseous components were tabulated. Auxiliary data on phase transitions, densities, and kinetics of chemical decomposition have also been included.

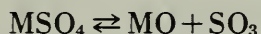
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The Sulfates

A. Introduction

In this section the general features of sulfate decomposition are summarized. In all metallic sulfates the SO_4^- ion is a well defined entity in which the oxygen atoms are arranged tetrahedrally about the sulfur atom with an S—O bond length of 1.51 Å, 0.19 Å less than the sum of the single-bond covalent radii of the atoms. Pauling [96c]¹ has listed the various resonance structures which give these bonds some double-bond character. The tetrahedral structure of the sulfate ion is distorted to some extent by cations, the distortion increasing with the polarizing power of the cation. Since the polarizing power increases with increasing electronegativity and decreasing ionic radius, salts with small, highly charged cations would be expected to be least stable. For example, Ostroff and Sander-son [90] found that the decomposition temperature for eleven anhydrous sulfates of divalent cations is a linear function of $(r/S)^{1/2}$, where r is the crystal (Goldschmidt) radius and S is the electronegativity. Similar observations have been made for the alkali metal sulfates [125].

Few metal sulfates are sufficiently stable at high temperatures to have a measurable melting point. All decompose eventually with evolution of SO_3 . The latter in turn dissociates to SO_2 and O_2 . Thus in a closed system there are always two simultaneous equilibria:



Equilibrium data for the second reaction are given in separate tables for calculation of partial pressures of the 3 gases, and of the total decomposition pressure. The first reaction is only schematically repre-

sented above. Although many sulfates do decompose directly to the oxide containing the metallic element with unchanged valence, some show oxidation, e.g., $\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3$, $\text{SnSO}_4 \rightarrow \text{SnO}_2$, $\text{MnSO}_4 \rightarrow \text{Mn}_3\text{O}_4$ or reduction, e.g., $\text{Ag}_2\text{SO}_4 \rightarrow \text{Ag}^\circ$. Some decompose through an intermediate oxysulfate or basic salt such as $\text{CuO} \cdot \text{CuSO}_4$, or even a sequence of intermediates. It is primarily because of these complications that a brief but critical review has been included at the beginning of each section, describing the high-temperature behavior of each sulfate.

The literature has been searched through mid-1964, and some later references have been included.

The bibliography, beginning with reference 11, is arranged alphabetically by author. The references preceding [11] are those critical compilations that have been used here most frequently. Original publications, the data of which have been reworked, presented, and referenced in the first ten compilations are not usually listed separately in the bibliography.

B. Phase Transitions

1. *Solid Transitions.* The literature on solid transitions is confusing. Several systems of naming them exist and differences in the reported values of the transition temperatures frequently differ so much that it is not clear whether the same or a different transition is being described.

A number of well-defined transitions have been listed in NBS Circular 500 [1]. The data on these and others have been collected and are listed.

2. *Melting Points.* Melting points have been reported for several of the more common sulfates. We have selected what appear to be reliable values. It should be noted, however, that the decomposition which occurs below the melting point makes a measurement of the pure compound difficult and that the solid phase may contain some oxide.

¹Figures in brackets indicate the literature references at the end of this paper.

Melting points are usually obtained by rapid heating of the salt to minimize decomposition, but it cannot always be avoided. The listed values should therefore be regarded as lower limits.

3. *Boiling Points.* The dissociation pressures of sulfates rise so rapidly above the melting point that measurement of the boiling point is impossible. We have listed only those values calculated for the alkali metal salts from the law of corresponding states by Lorentz and Hertz [70].

C. Density

The total literature of high-temperature density measurements on inorganic sulfates is very small. There exists only one set of reliable values for the liquid salts, those of Jaeger [59] on the alkali metal sulfates. We have reproduced his original values without attempting to fit them to an equation. One reason for the lack of data is that most sulfates decompose considerably below the melting point so that a measurement of any physical property of the pure liquid is inherently impossible.

Most density values of solid sulfates have been reported for ambient temperatures. Except for a very limited study of PbSO_4 [80] there appears to have been no study of the temperature dependence for any solid sulfate.

The densities of solid salts are generally determined either directly by pycnometry, or are calculated from crystallographic (x-ray diffraction) data. In the latter method the atomic packing must be assumed. Since no allowance is made for crystal imperfections, calculated densities are generally higher than experimental values by as much as 10 percent. Since most crystallographers do not indicate the temperature for which the density is calculated, we have preferentially listed experimental values when these were available. However, in some cases experimental values seem to depend on the method of preparation, for some unknown reason. Thus, although the density of a given sample can certainly be determined to four or five significant figures, we would caution against attributing too much significance to figures beyond the third. This is particularly true because the units of the reported density values are frequently in doubt. In many cases they are not stated at all; in others it is not clear whether the unit is g/cm^3 or g/ml ; in still others they are specific gravity values and may be referred to water at 4 °C or at some other temperature. The difference between milliliters and cubic centimeters is so small (the ratio is 1.000028) as to be negligible. However, the difference in the density of water between 4 and 20 °C is in the third significant figure (1.00000 and 0.99823 g/ml , respectively) and no longer negligible for the better measurements.

We have indicated the units as reported by the original authors. When no units are given it can generally be assumed that g/ml is meant.

D. Decomposition Equilibria

As a measure of the stability of each sulfate, we have calculated wherever possible, thermodynamically, the partial pressures, and total pressure, of the SO_3 , SO_2 , and O_2 decomposition products that would be expected at equilibrium at various temperatures in a closed system containing initially only the sulfate. This is the type of system in which decomposition pressure measurements are made by the static method.

For these calculations, four items of information are needed:

(1) Knowledge of the course of the decomposition. This is described under each sulfate. Where specific references are not given, the description is an abstract from such sources as the handbooks of inorganic chemistry of Gmelin, Pascal, and Mellor.

(2) High-temperature thermal data such as those tabulated in reference [2] in the form of enthalpy and entropy increments above 298.15 °K, for each compound.

(3) Heats of formation at 298.15 °K.

(4) Entropies at 298.15 °K.

These data are required for the decomposition products as well as for the sulfates themselves. Items (3) and (4) are tabulated as "Thermodynamic Data" under each sulfate to show the data used and to point out the gaps in existing data.

It has usually been most convenient to perform the calculations through the medium of "free energy functions" (fef) as discussed in reference [4], pp. 166–9. Where the high-temperature thermal data are available in the form of enthalpy and entropy increments ($H_T - H_{298}$ and $S_T - S_{298}$), these are combined with 298.15 °K entropies to get the free energy functions:

$$\text{fef} = \frac{G_T^\circ - H_{298}^\circ}{T} = \frac{H_T^\circ - H_{298}^\circ}{T} - (S_T^\circ - S_{298}^\circ) - S_{298}^\circ$$

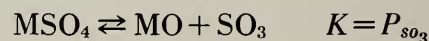
where T is the temperature of interest in °K. Then for a given T °K, the fef 's for decomposition products and sulfate are added and subtracted, in the same manner as heats of formation in a thermochemical equation, to yield a Δfef for the decomposition reaction. The heat of reaction at 298.15 °K is obtained from the heats of formation. Then the Gibbs free energy change attending the reaction is

$$\Delta G_T^\circ = T\Delta\text{fef} + \Delta H_{298}^\circ$$

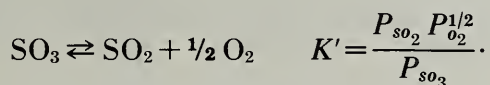
from which the equilibrium constant for the reaction is obtained through the relation:

$$\Delta G_T^\circ = -RT \ln K.$$

For the case of simplest stoichiometry:



the activity, here taken as equal to partial pressure, of SO_3 in atm is equal to K . SO_2 and O_2 appear by decomposition of SO_3 :



When both equilibria are attained simultaneously:

$$P_{\text{SO}_2} + P_{\text{O}_2} = (3/2)(2)^{1/3} (KK')^{2/3}$$

and

$$P_{\text{SO}_2} = 2/3(P_{\text{SO}_2} + P_{\text{O}_2})$$

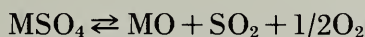
and

$$P_{\text{O}_2} = 1/3(P_{\text{SO}_2} + P_{\text{O}_2})$$

since

$$P_{\text{SO}_2} = 2P_{\text{O}_2}$$

This is true only in an initially evacuated system where all the gases originate from the MSO_4 . When P_{SO_3} is very much less than P_{SO_2} , the reaction is often written in the literature as:



for which the equilibrium constant is KK' .

If the metallic element undergoes oxidation during the decomposition, equilibrium constants are obtained through free energy functions as before, but calculation of partial pressures from them is more complicated because the relation, $P_{\text{SO}_2} = 2P_{\text{O}_2}$, no longer holds. The general method is shown for the case of $\text{MnSO}_4 \rightarrow \text{Mn}_3\text{O}_4$ in the section on MnSO_4 .

In the tables, these functions, constants, and pressures are given at 100 degree intervals. For other temperatures interpolation will be most accurate with *fef*'s, calculating pressures from them.

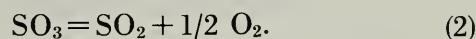
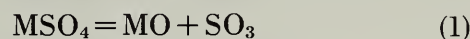
For the three gases, the high-temperature thermal data are derived from spectroscopic observations, and are available to higher temperatures than needed here. But for the solids, the data are obtained from calorimetric measurements which must be discontinued either at the limit of the apparatus or at the temperature at which decomposition becomes noticeable during the time of the experiment. Thus the calculated pressures would not exceed about 10^{-3} atm, or less. We have therefore extrapolated, at the *fef* level, for several hundred degrees or to about 1 atm total decomposition pressure. To go beyond 1 atm would involve fugacities; calculation of these would involve uncertain extrapolations and is therefore not justified. Extrapolating more than a few hundred degrees becomes increasingly dangerous, particularly because unreported phase transitions might change the slope of a *fef* versus T plot.

E. Kinetics of Thermal Decomposition

By far the largest number of sulfate decomposition studies are concerned with practical applications, usually with the liberation of SO_3 and SO_2 from naturally occurring sulfates, e.g., CaSO_4 and Na_2SO_4 , at the lowest possible temperature. Since certain metal oxides are catalysts for the decomposition, experiments are commonly carried out with these as additives, i.e., with impure materials; moreover, the experimental conditions are rarely described adequately. This latter problem also afflicts several of the studies on pure materials.

Kinetic studies of sulfate decomposition can be conveniently divided into isothermal and nonisothermal ones. Chief among the latter are thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA is particularly useful for determining the stability ranges of compounds whose knowledge is necessary for analytical purposes, but gives relatively little information concerning the kinetics of the decomposition. DTA is useful in determining phase transition temperatures and can be used to determine enthalpies and activation energies. The accuracy with which these quantities can be obtained is still rather poor, however [83].

Since the rate of sulfate decomposition under isothermal conditions depends on a rather large number of experimental conditions, these must be carefully controlled. Thus, for the specific case of a metal sulfate having only a single stable valence state which decomposes directly to the oxide—the simplest possible case—the following two reactions must be considered:



Assuming that the oxide formed in (1) is not a catalyst for the decomposition the following variables affect the reaction rate: (a) temperature, (b) gas phase composition; this may be variable if, for example, the system is initially pumped out and the rate followed by measuring the pressure change, or it may be kept constant by passing a gas over the decomposing sample. In the latter case the reaction rate may depend on (c) gas composition—inert, or some mixture involving the components of the system, and (d) flow rate; (e) since the reaction occurs at a solid-solid interface, sample size and shape may be significant. However, most studies indicate that the oxide formed in (1) is sufficiently porous to the gases that the rate calculated for a unit area of interface is independent of depth of penetration.

In the description of the decomposition kinetics of the individual sulfates we discuss only those studies, rather few in number, which meet at least

some of the criteria outlined above. In any case, however, these discussions are to be regarded only as guides to the behavior to be expected from a given compound. Any numerical values given are to be used in this sense and certainly do not have the validity attached to thermodynamic parameters.

To illustrate the present state of knowledge in this field, we have summarized in a separate table all the activation energies for decomposition which are discussed under the individual compounds. It is clear that the variety of results obtained, including the great differences in E_a obtained by different investigators for the same reaction, makes any discussion of these results premature. They are included only to stimulate further work in this field.

Units, Symbols, and Abbreviations

J = joule
 cal = thermochemical calorie = 4.1840 J
 P = pressure; 1 atm = 101325 N m⁻² = 1013250 dyn cm⁻²
 $T(^{\circ}\text{K})$ = temperature in degrees Kelvin, defined in the thermodynamic scale by assigning 273.16 $^{\circ}\text{K}$ to the triple point of water (freezing point, 273.15 $^{\circ}\text{K}$ = 0 $^{\circ}\text{C}$)
 R = gas constant = 8.3143 J mol⁻¹ deg⁻¹ = 1.98717 cal mol⁻¹ deg⁻¹
 H° = standard enthalpy
 ΔH_f° = standard heat of formation
 S° = standard entropy
 G° = standard Gibbs (free) energy
 $\text{fef} = \text{free energy function} = \frac{G_T^{\circ} - H_{298.15}^{\circ}}{T}$
 TGA = thermogravimetric analysis
 DTA = differential thermal analysis.

SO₃, SO₂, and O₂

The SO₃ produced on decomposition of a sulfate dissociates partially to SO₂ and O₂. Data for this secondary equilibrium are presented in tables A, B, and C.

The free energy functions (fef) for SO₃, SO₂, and O₂ (table A) are calculated from data in reference [6] using entropies from [6]. The entropies for these gases tabulated in [6] and [9] supersede those in [1] and [3].

The heats of formation for these gases in [6] are based on those in [1], differing by only 0.01 kcal/mol for SO₂ and 0.02 for SO₃. They are part of a set of enthalpies consistent with those of the sulfates and oxides in [1]. The equilibrium constants of table B, calculated from these enthalpies of the gases, are used later with metal sulfate data wherever the latter are taken from [1].

Reference [9], the first part of a revision of [1], has a small, but significant change in the heat of formation of SO₃. Otherwise the data there for these gases differ only slightly from the data of [6]

as shown in the table immediately below. Table C presents a new set of equilibrium values incorporating the effect of these changes. In the future table C should be used for calculations with the forthcoming revised data for sulfates. Table C should also be used instead of table B for any independent purpose.

Thermodynamic Data (298.15 $^{\circ}\text{K}$)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	Refer- ences
SO ₃	256.6671 256.65	61.3449 61.34	6 9
SO ₂	248.097 ₄ 248.1 ₁	59.2967 59.30	6 9, 10
O ₂	205.05 205.00	49.0070 48.996	6 9

ΔH_f°			
	kJ mol ⁻¹	kcal mol ⁻¹	Refer- ences
SO ₃	-395.2 ₆ -395.72	-94.47 -94.58	6 9
SO ₂	-296.8 ₃ -296.83	-70.947 -70.944	6, 10 9
O ₂	0	0	

Dissociation of SO₃

SO₃(g) \rightleftharpoons SO₂(g) + 1/2 O₂(g)
 $\Delta H_{298.15}^{\circ} = 98.40_8$ kJ, 23.52 kcal, reference [6] data
 98.89₃ kJ, 23.63₆ kcal, reference [9] data.

A. Free energies, reference [6] data

T	SO ₃	SO ₂	O ₂	Reaction	
	fef	fef	fef	Δfef	ΔG_T°
$^{\circ}\text{K}$	J	J	J	J	kJ
298.15	-256.67	-248.10	-205.05	-93.956	+70.37
400	-258.75	-249.71	-206.20	-94.065	60.79
500	-262.89	-252.86	-208.42	-94.182	51.30
600	-267.76	-256.52	-210.94	-94.232	41.88
700	-272.84	-260.31	-213.51	-94.219	32.47
800	-277.91	-264.06	-216.02	-94.157	23.10
900	-282.87	-267.70	-218.45	-94.056	13.77
1000	-287.67	-271.22	-220.77	-93.935	+4.48
1100	-292.28	-274.58	-222.99	-93.801	-4.77
1200	-296.71	-277.81	-225.11	-93.650	-13.97
1300	-300.96	-280.90	-227.13	-93.504	-23.14
1400	-305.03	-283.86	-229.06	-93.353	-32.30
1500	-308.94	-286.69	-230.90	-93.199	-41.38
1600	-312.69	-289.40	-232.67	-93.048	-50.46
1700	-316.30	-292.01	-234.36	-92.893	-59.50
1800	-319.77	-294.51	-235.99	-92.743	-68.53
1900	-323.11	-296.93	-237.55	-92.600	-77.53
2000	-326.32	-299.25	-239.07	-92.458	-86.53

B. Equilibrium constants, reference [6] data

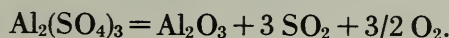
<i>T</i>	log <i>K</i>	<i>K</i>
°K		
298.15	−12.329	4.69×10^{-13}
400	−7.938	$1.15_4 \times 10^{-8}$
500	−5.358	4.39×10^{-6}
600	−3.646	2.26×10^{-4}
700	−2.423	3.78×10^{-3}
800	−1.508	3.11×10^{-2}
900	−0.798	0.159 ₂
1000	−.234	.583
1100	+ .226	1.68 ₃
1200	.608	4.06
1300	.930	8.51
1400	1.205	16.0 ₃
1500	1.441	27.6
1600	1.647	44.4
1700	1.828	67.3
1800	1.989	97.5
1900	2.131	135.2
2000	2.260	182

C. Free energies and equilibrium constants, reference [9] data

<i>T</i>	Δ <i>f</i> <i>e</i>	Δ <i>G</i> _{<i>T</i>} ^o	log <i>K</i>	<i>K</i>
°K	<i>J</i>	<i>kJ</i>		
298.15	−93.964	+ 70.88	−12.417	3.83×10^{-13}
400	−94.073	61.26	−7.999	1.00×10^{-8}
500	−94.190	51.80	−5.411	3.88×10^{-6}
600	−94.240	42.35	−3.687	2.06×10^{-4}
700	−94.228	32.93	−2.457	3.49×10^{-3}
800	−94.165	23.56	−1.538	2.90×10^{-2}
900	−94.065	14.23	−0.826	1.49×10^{-1}
1000	−93.943	+ 4.95	−.259	5.51×10^{-1}
1100	−93.809	−4.30	+ .204	1.60
1200	−93.659	−13.50	.587 ₅	3.87
1300	−93.512	−22.67	.911	8.15
1400	−93.362	−31.82	1.187	15.4
1500	−93.207	−40.92	1.425	26.6
1600	−93.056	−50.00	1.632	42.9
1700	−92.902	−59.04	1.814	65.2
1800	−92.751	−68.06	1.975	94.4
1900	−92.609	−77.07	2.119	131.5
2000	−92.466	−86.04	2.247	177

Aluminum

The kinetics of the decomposition have been studied by Pechkovsky and Ketov [102] and Warner and Ingraham [138]. No intermediate oxysulfate has been reported, the decomposition proceeding directly to the oxide



Between 650 and 950 °C the rate of decomposition, as measured by weight loss, is independent of flow rate of an inert gas, indicating that the product layer is porous to the flow of gases. Under these conditions $k = 1.14 \times 10^{10} \text{ g cm}^{-2} \text{ min}^{-1} \exp(-268,000/RT)$. With increasing oxygen content of the flow gas the reaction rate decreases somewhat, but the effect is not very great. Between 21 and 100 percent O₂ the rate is virtually independent of oxygen content.

Decomposition pressures reported in the literature do not represent true equilibria. Kelley [1946] and Warner and Ingraham [137] noted that $\gamma\text{-Al}_2\text{O}_3$ is formed initially, which changes slowly to the stable $\alpha\text{-Al}_2\text{O}_3$.

Free energy functions for $\alpha\text{-Al}_2\text{O}_3$ and Al₂(SO₄)₃ are calculated from data in [2]. Those calculated from data in [6] are only slightly different.

Density of Al₂(SO₄)₃

Phase	<i>T</i> °K	<i>d</i>	Refer- ences
c	ambient	2.71	89

Transitions of Al₂(SO₄)₃

Phase change		
c → c	None known,	298–1100 °K
c → l.	Decomposes	

Thermodynamic Data (298.15 °K)

	<i>S</i> ^o		
	J mol ^{−1} deg ^{−1}	cal mol ^{−1} deg ^{−1}	Refer- ences
Al ₂ (SO ₄) ₃	239	57.2	1, 3, 8
α-Al ₂ O ₃	50.9 ₆	12.18	3, 4, 6, 8

Δ*H**f*^o

	kJ mol ^{−1}		Refer- ences
	kJ mol ^{−1}	kcal mol ^{−1}	
Al ₂ (SO ₄) ₃	−3435	−821.0	1, 8
α-Al ₂ O ₃	−1669.8	−399.09	1

Decomposition of $Al_2(SO_4)_3$

- (1) $Al_2(SO_4)_3(c) \rightleftharpoons Al_2O_3(\alpha) + 3 SO_3(g)$ $\Delta H_{298.15}^\circ = 579.6_5$ kJ, 138.5 kcal
 (2) $Al_2(SO_4)_3(c) \rightleftharpoons Al_2O_3(\alpha) + 3 SO_2(g) + 3/2 O_2(g)$ $\Delta H_{298.15}^\circ = 874.8_7$ kJ, 209.1 kcal.

A. Free energies

T	Al_2O_3	$Al_2(SO_4)_3$	Reaction (1)	
	fef	fef	Δfef	ΔG_T°
$^\circ K$	J	J	J	kJ
298.15	-50.96	-239.32	-581.64	+406.22
400	-54.29	-250.54	-579.99	347.65
500	-61.13	-273.26	-576.54	291.37
600	-69.20	-300.12	-572.36	236.23
700	-77.65 ₅	-328.15	-568.03	182.05
800	-86.15	-356.31	-563.58	128.78
900	-94.35	-383.71	-559.25	76.32
1000	-102.34	-410.20	-555.14	+24.51
1100	-110.00	-435.60	-551.25	-26.72

B. Equilibrium constants

T	$\log K_1$	K_1	$\log K_2$	K_2
$^\circ K$				
298.15	-71.165	6.84×10^{-72}	-108.152	7.05×10^{-109}
400	-45.394	4.04×10^{-46}	-69.208	6.19×10^{-70}
500	-30.437	3.66×10^{-31}	-46.511	3.08×10^{-47}
600	-20.564	2.73×10^{-21}	-31.502	3.15×10^{-32}
700	-13.583	2.61×10^{-14}	-20.852	1.41×10^{-21}
800	-8.408	3.91×10^{-9}	-12.932	1.17×10^{-13}
900	-4.429	3.72×10^{-5}	-6.826	1.49×10^{-7}
1000	-1.280	5.25×10^{-2}	-1.982	1.04×10^{-2}
1100	+1.269	18.6	+1.947	88.5

c. Equilibrium pressures (atm)

T	SO_2	O_2	SO_3	Total
$^\circ K$				
298.15	1.17×10^{-24}	5.83×10^{-25}	1.90×10^{-24}	3.65×10^{-24}
400	5.26×10^{-16}	2.63×10^{-16}	7.39×10^{-16}	1.53×10^{-15}
500	5.82×10^{-11}	2.91×10^{-11}	7.15×10^{-11}	1.59×10^{-10}
600	1.26×10^{-7}	6.29×10^{-8}	1.40×10^{-7}	3.29×10^{-7}
700	2.93×10^{-5}	1.46×10^{-5}	2.97×10^{-5}	7.36×10^{-5}
800	1.69×10^{-3}	8.42×10^{-4}	1.58×10^{-3}	4.10×10^{-3}
900	5.50×10^{-2}	2.75×10^{-2}	5.74×10^{-2}	1.40×10^{-1}
1000	4.57×10^{-1}	2.29×10^{-1}	3.74×10^{-1}	1.06
1100	3.41	1.71	2.65	7.77

Americium

Am(III): $Am_2(SO_4)_3$ does not melt, but decomposes with oxidation to AmO_2 . A TGA curve [50a] showed a plateau for the anhydrous salt extending to 990 $^\circ K$. Conversion to AmO_2 was complete by 1070 $^\circ K$.

Antimony

On heating, $Sb_2(SO_4)_3$ decomposes with partial oxidation: oxysulfates exist, about which little is known.

There are no thermodynamic data above 298 $^\circ K$.

Thermodynamic data (298.15 $^\circ K$)

S°			
	$J mol^{-1} deg^{-1}$	$cal mol^{-1} deg^{-1}$	References
$Sb_2(SO_4)_3$			
Sb_2O_4	127. ₂	30.4	9, 3, 8
Sb_2O_5	125.	29.9	9, 3, 8
Sb_4O_6 (II, cubic)	220. ₉	52.8	9
Sb_4O_6 (I, orthorhombic)	246. ₀	58.8	9, 3, 8

$\Delta H f^\circ$

	$kJ mol^{-1}$	$kcal mol^{-1}$	References
$Sb_2(SO_4)_3$	-2402. ₅	-574.2	9
Sb_2O_4	-907.5	-216.9	9
Sb_2O_5	-971.9	-232.3	9
Sb_4O_6 (II, cubic)	-1440.5	-344.3	9
Sb_4O_6 (I, orthorhombic)	-1417.1	-338.7	9

Barium

$BaSO_4$ melts without obvious decomposition. Free energy functions for $BaSO_4$ and BaO are calculated from data in [2].

Density of $BaSO_4$

Phase	T	d	References
c, II	$^\circ K$ 288	4.499	7

Transitions of $BaSO_4$

Phase change	T	ΔH	ΔS	References
	$^\circ K$	$kJ mol^{-1}$	$J mol^{-1} deg^{-1}$	
c, II \rightarrow c, I	1422			1, 5
c, I \rightarrow l.	1620	40.6	25	5

S°			
	$J\ mol^{-1}\ deg^{-1}$	$cal\ mol^{-1}\ deg^{-1}$	References
BaSO ₄	132.2	31.6	1, 3, 8
BaO	70.3	16.8	1, 3, 4, 8

ΔH_f°			
	$kJ\ mol^{-1}$	$kcal\ mol^{-1}$	References
BaSO ₄	-1465.2	-350.2	1, 8
BaO	-558.1	-133.4	1

Decomposition of BaSO₄

- (1) $BaSO_4(c) \rightleftharpoons BaO(c) + SO_3(g)$
 $\Delta H_{298.15}^\circ = 511.9\ kJ, 122.3\ kcal$
 (2) $BaSO_4(c) \rightleftharpoons BaO(c) + SO_2(g) + 1/2\ O_2(g)$
 $\Delta H_{298.15}^\circ = 610.3\ kJ, 145.8\ kcal$

A. Free Energies

T	BaO	BaSO ₄	Reaction (1)	
	fef	fef	Δfef	ΔG_T°
$^\circ K$	J	J	J	kJ
298.15	-70.29	-132.21	-194.74	+453.84
400	-72.11	-136.48	-194.38	434.17
500	-75.77	-145.02	-193.64	415.09
600	-79.91	-154.98	-192.70	396.31
700	-84.18	-165.23	-191.80	377.65
800	-88.39	-175.35	-190.95	359.15
900	-92.38	-185.06	-190.20	340.74
1000	-96.23	-194.35	-189.55	322.38
1100	-99.91	-203.13	-189.06	303.93
1200	-103.39	-211.58	-188.51	285.68
1300	-106.69	-219.62	-188.03	267.48

B. Equilibrium constants

T	$\log K_1$	K_1	$\log K_2$	K_2
$^\circ K$				
298.15	-79.506	3.12×10^{-80}	-91.835	1.46×10^{-92}
400	-56.693	2.03×10^{-57}	-64.631	2.34×10^{-65}
500	-43.361	4.36×10^{-44}	-48.719	1.91×10^{-49}
600	-34.499	3.17×10^{-35}	-38.145	7.16×10^{-39}
700	-28.178	6.64×10^{-29}	-30.601	2.51×10^{-31}
800	-23.448	3.57×10^{-24}	-24.956	1.11×10^{-25}
900	-19.775	1.68×10^{-20}	-20.574	2.67×10^{-21}
1000	-16.838	1.45×10^{-17}	-17.072	8.47×10^{-18}
1100	-14.430	3.72×10^{-15}	-14.204	6.25×10^{-15}
1200	-12.435	3.67×10^{-13}	-11.827	1.49×10^{-12}
1300	-10.746	1.80×10^{-11}	-9.816	1.53×10^{-10}

C. Equilibrium pressures (atm)

T	SO ₂	O ₂	SO ₃	Total
$^\circ K$				
298.15	7.53×10^{-62}	3.77×10^{-62}	3.12×10^{-80}	1.13×10^{-61}
400	1.03×10^{-43}	5.15×10^{-44}	2.03×10^{-57}	1.55×10^{-43}
500	4.18×10^{-33}	2.09×10^{-33}	4.36×10^{-44}	6.27×10^{-33}
600	4.68×10^{-26}	2.34×10^{-26}	3.17×10^{-35}	7.02×10^{-26}
700	5.01×10^{-21}	2.50×10^{-21}	6.64×10^{-29}	7.51×10^{-21}
800	2.90×10^{-17}	1.45×10^{-17}	3.57×10^{-24}	4.36×10^{-17}
900	2.42×10^{-14}	1.21×10^{-14}	1.68×10^{-20}	3.64×10^{-14}
1000	5.24×10^{-12}	2.62×10^{-12}	1.45×10^{-17}	7.85×10^{-12}
1100	4.28×10^{-10}	2.14×10^{-10}	3.72×10^{-15}	6.41×10^{-10}
1200	1.64×10^{-8}	8.22×10^{-9}	3.67×10^{-13}	2.47×10^{-8}
1300	3.60×10^{-7}	1.80×10^{-7}	1.80×10^{-11}	5.40×10^{-7}

Beryllium

The weight loss of BeSO₄ measured in a current of air has been studied by Marchal [75]. Decomposition rates below 883 °K were too slow to be measurable. At 973 °K the weight loss was a linear function of time up to a composition corresponding to the basic salt 5BeO · SO₃. Beyond this composition the rate was considerably higher. Marchal's directly measured equilibrium decomposition pressures, 863 to 1103 °K, are higher than those calculated here for decomposition to BeO. However, others have not been able to confirm the formation of an intermediate oxysulfate, noting rather that the last traces of SO₃ are retained tenaciously.

Free energy functions for BeSO₄ are calculated from data in [126], and for BeO from data in [134]. A better value for the heat of formation of BeO at 298.15 °K than that used in the calculations is -598.7 kJ, -143.1 kcal [4, 6, 8, 10], but the older value from (1) is used because the BeSO₄ value depends on it. The calculated decomposition pressures above 900 °K are based on an extrapolation of the free energy function (fef) of BeSO₄.

Density of BeSO₄

Phase	T	d	References
c	$^\circ K$		
c	ambient	$2.54\ g/cm^3$ (crystallographic)	49
	298	2.44 ₃	7

Transitions of BeSO₄

Phase		References
c → c	None observed, 298-900 °K	
c → l.	Decomposition	

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	Refer- ences
BeSO ₄	77.91	18.62	126
BeO	14.1	3.37	1, 3, 4, 8
ΔH_f°			
	kJ mol ⁻¹	kcal mol ⁻¹	Refer- ences
BeSO ₄	-1196.6	-286.0	1, 8
BeO	-610.9	-146.0	1 (see text)

Decomposition of BeSO₄

- (1) BeSO₄(c) \rightleftharpoons BeO(c) + SO₃(g)
 $\Delta H_{298.15}^\circ = 190.6$ kJ, 45.5₅ kcal
 (2) BeSO₄(c) \rightleftharpoons BeO(c) + SO₂(g) + 1/2 O₂(g)
 $\Delta H_{298.15}^\circ = 289.0$ kJ, 69.0₇ kcal.

A. Free energies

T	BeO	BeSO ₄	Reaction (1)	
	fef	fef	Δfef	ΔC_T°
$^\circ K$	J	J	J	kJ
298.15	-14.10	-77.91	-192.86	+133.08
400	-15.22	-92.59	-181.37	118.03
500	-17.56	-106.36	-174.10	103.03
600	-20.43	-119.45	-168.73	89.34
700	-23.48	-131.84	-164.49	75.44
800	-26.58	-143.64	-160.85	61.90
900	-29.63	-155.02	-157.49	48.84
(1000)	-32.61	-166.57	-153.71	36.87
(1100)	-35.49	-177.61	-150.16	25.40
(1200)	-38.28	-188.74	-146.25	15.08

B. Equilibrium constants

T	log K_1	K_1	log K_2	K_2
$^\circ K$				
298.15	-23.314	4.85×10^{-24}	-35.643	2.28×10^{-36}
400	-15.412	3.87×10^{-16}	-23.350	4.47×10^{-24}
500	-10.815	1.53×10^{-11}	-16.173	6.71×10^{-17}
600	-7.777	1.67×10^{-8}	-11.423	3.78×10^{-12}
700	-5.629	2.35×10^{-6}	-8.052	8.87×10^{-9}
800	-4.041	9.10×10^{-5}	-5.549	2.83×10^{-6}
900	-2.835	1.46×10^{-3}	-3.634	2.32×10^{-4}
(1000)	-1.926	1.19×10^{-2}	-2.160	6.92×10^{-3}
(1100)	-1.206	6.22×10^{-2}	-0.980	1.05×10^{-1}
(1200)	-0.656	2.21×10^{-1}	-0.048	8.95×10^{-1}

C. Equilibrium pressures (atm)

T	SO ₂	O ₂	SO ₃	Total
$^\circ K$				
298.15	2.18×10^{-24}	1.09×10^{-24}	4.85×10^{-24}	8.12×10^{-24}
400	3.42×10^{-16}	1.71×10^{-16}	3.87×10^{-16}	9.00×10^{-16}
500	2.08×10^{-11}	1.04×10^{-11}	1.53×10^{-11}	4.65×10^{-11}
600	3.06×10^{-8}	1.53×10^{-8}	1.67×10^{-8}	6.25×10^{-8}
700	5.40×10^{-6}	2.70×10^{-6}	2.35×10^{-6}	1.05×10^{-5}
800	2.52×10^{-4}	1.26×10^{-4}	9.10×10^{-5}	4.69×10^{-4}
900	4.76×10^{-3}	2.38×10^{-3}	1.46×10^{-3}	8.60×10^{-3}
(1000)	4.58×10^{-2}	2.29×10^{-2}	1.19×10^{-2}	8.05×10^{-2}
(1100)	2.80×10^{-1}	1.40×10^{-1}	6.22×10^{-2}	4.82×10^{-1}
(1200)	1.17	0.585	0.221	1.98

Bismuth

Bi₂(SO₄)₃ is sufficiently stable at 650 °K for ignition to constant weight. Noticeable decomposition begins about 25° above this temperature, yielding one or possibly a sequence of two oxysulfates. In open air the product Bi₂O₃ · SO₃ persists at least as high as 1250 °K. The final product is expected to be Bi₂O₃. A complication is the low melting point of this oxide, 1090 °K [5].

Density of Bi₂(SO₄)₃

Phase	T	d	Refer- ences
	$^\circ K$		
c	288	5.08	16

Transitions of Bi₂(SO₄)₃

Phase change	
c \rightarrow c c \rightarrow l.	No information. Decomposes.

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	Refer- ences
Bi ₂ (SO ₄) ₃ Bi ₂ O ₃	151.5	36.2	1, 3, 9, 8
ΔH_f°			
	kJ mol ⁻¹	kcal mol ⁻¹	Refer- ences
Bi ₂ (SO ₄) ₃ Bi ₂ O ₃	-2544.3 -573.88	-608.1 -137.16	9, 8 8

No calculation of decomposition pressures is possible. High-temperature data exists only for Bi_2O_3 [2].

Cadmium

Solid phase transitions and decomposition products of CdSO_4 have been studied recently by two groups of workers [57, 95], both of whom give reviews of the confused earlier literature. On heating, CdSO_4 undergoes at least one polymorphic transformation, probably two, but there is still disagreement on the transition temperatures. The highest temperature form melts near 1300 °K. However, slow decomposition to $2 \text{ CdO} \cdot \text{CdSO}_4$ is observed well below this temperature. The final product of decomposition is CdO . Marchal [76] measured decomposition pressures in the range 1053 to 1303 °K, but her experimental difficulties cast doubt on their value. They cannot be calculated thermodynamically because no high temperature data exist for any of these compounds.

Density of CdSO_4

Phase	<i>T</i>	<i>d</i>	References
	°K		
c	293	4.692 (20/4)	116
c	297	4.691	7

Transitions of CdSO_4

Phase change	<i>T</i>	References
c → c		
c → 1.	No information 1273	

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
CdSO_4	123.	29.4	3, 8
CdO	54.8	13.1	1, 3, 8

ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	References
CdSO_4	-928.8	-222.0 ± 0.3	11
	-926.17	-221.36	1, 8
CdO	-254.6	-60.86	1
	-256.1	-61.2 ± 0.2	11, 8

Calcium

CaSO_4 decomposes directly to CaO . The supposed existence of an intermediate oxysulfate and discrepant values for the melting point of CaSO_4 are explained [87] by a eutectic between CaO and CaSO_4 near 1638 °K, with less than 20 percent CaO .

The increase in pressure in a static system was studied by Briner, Pamm, and Paillard [21], but their data are not sufficiently precise to yield kinetic parameters.

Of the various equilibrium decomposition pressure measurements, those of Tschappat and Pièce [131] agree very closely with those calculated thermodynamically.

The free energy functions of CaSO_4 and CaO are calculated from data in [2]. The decomposition pressures in the range 1500 to 1800 °K depend on an extrapolation of the free energy function of CaSO_4 .

Density of CaSO_4

Phase	<i>T</i>	<i>d</i>	References
	°K		
c, II	298	2.960 ± 0.005	14-5

Transitions of CaSO_4

Phase change	<i>T</i>	ΔH	ΔS	References
	°K	kJ mol ⁻¹	J mol ⁻¹ deg ⁻¹	
c, II → c, I	1453	21	14.2	5
c, I → 1.	see text			

c, II (or α) is the mineral anhydrite. A metastable (β) form exists to a few hundred degrees above ambient temperature.

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
$\text{CaSO}_4(\text{II})$	106.7	25.5	1, 3, 4, 8
CaO	39.7	9.5	1, 3, 4, 8

ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	References
CaSO_4	-1432.7	-342.42	1, 8
CaO	-635.5	-151.9	1, 8

Decomposition of CaSO₄

- (1) $\text{CaSO}_4(\text{c}) \rightleftharpoons \text{CaO}(\text{c}) + \text{SO}_3(\text{g})$
 $\Delta H_{298.15}^\circ = 401.9_6 \text{ kJ}, 96.0_7 \text{ kcal}$
 (2) $\text{CaSO}_4(\text{c}) \rightleftharpoons \text{CaO}(\text{c}) + \text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$
 $\Delta H_{298.15}^\circ = 500.3_6 \text{ kJ}, 119.5_9 \text{ kcal}$

A. Free energies

<i>T</i>	CaO	CaSO ₄	Reaction (1)	
	fef	fef	Δfef	Δ <i>G</i> _{<i>T</i>} [°]
^{°K}	<i>J</i>	<i>J</i>	<i>J</i>	<i>kJ</i>
298.15	−39.75	−106.69	−189.72	+345.39
400	−41.51	−110.83	−189.42	326.18
500	−44.89	−118.74	−189.04	307.44
600	−48.74	−127.82	−188.68	288.74
700	−52.72	−137.36	−188.20	270.20
800	−56.61	−147.03	−187.50	251.96
900	−60.29	−156.73	−186.43	234.18
1000	−63.85	−166.36	−185.16	216.81
1100	−67.24	−175.85	−183.67	199.91
1200	−70.46	−185.06	−182.11	183.43
1300	−73.51	−194.01	−180.46	167.36
1400	−76.44	−202.76	−178.72	151.75
(1500)	−79.24	−211.25	−176.94	136.55
(1600)	−81.92	−219.45	−175.16	121.70
(1700)	−84.52	−227.32	−173.50	107.01
(1800)	−86.99	−234.81	−171.95	92.45

B. Equilibrium constants

<i>T</i>	log <i>K</i> ₁	<i>K</i> ₁	log <i>K</i> ₂	<i>K</i> ₂
^{°K}				
298.15	−60.507	3.11×10^{-61}	−72.836	1.46×10^{-73}
400	−42.592	2.56×10^{-43}	−50.530	2.95×10^{-51}
500	−32.115	7.67×10^{-33}	−37.473	3.37×10^{-38}
600	−25.135	7.33×10^{-26}	−28.781	1.66×10^{-29}
700	−20.161	6.90×10^{-21}	−22.584	2.61×10^{-23}
800	−16.450	3.55×10^{-17}	−17.958	1.10×10^{-18}
900	−13.590	2.57×10^{-14}	−14.389	4.08×10^{-15}
1000	−11.324	4.74×10^{-12}	−11.558	2.77×10^{-12}
1100	−9.491	3.23×10^{-10}	−9.265	5.43×10^{-10}
1200	−7.984	1.037×10^{-8}	−7.376	4.21×10^{-8}
1300	−6.724	1.888×10^{-7}	−5.794	1.61×10^{-6}
1400	−5.662	2.18×10^{-6}	−4.457	3.49×10^{-5}
(1500)	−4.755	1.76×10^{-5}	−3.314	4.85×10^{-4}
(1600)	−3.972	1.067×10^{-4}	−2.325	4.73×10^{-3}
(1700)	−3.288	5.15×10^{-4}	−1.460	3.47×10^{-2}
(1800)	−2.683	2.08×10^{-3}	−0.694	2.02×10^{-1}

C. Equilibrium pressures (atm)

<i>T</i>	SO ₂	O ₂	SO ₃	Total
^{°K}				
298.15	3.49×10^{-49}	1.75×10^{-49}	3.11×10^{-61}	5.24×10^{-49}
400	2.59×10^{-34}	1.30×10^{-34}	2.56×10^{-43}	3.89×10^{-34}
500	1.31×10^{-25}	6.57×10^{-26}	7.67×10^{-33}	1.97×10^{-25}
600	8.19×10^{-20}	4.09×10^{-20}	7.33×10^{-26}	1.23×10^{-19}
700	1.11×10^{-15}	5.54×10^{-16}	6.90×10^{-21}	1.66×10^{-15}
800	1.34×10^{-12}	6.72×10^{-13}	3.55×10^{-17}	2.02×10^{-12}
900	3.22×10^{-10}	1.61×10^{-10}	2.57×10^{-14}	4.83×10^{-10}
1000	2.48×10^{-8}	1.24×10^{-8}	4.74×10^{-12}	3.73×10^{-8}
1100	8.39×10^{-7}	4.19×10^{-7}	3.23×10^{-10}	1.26×10^{-6}
1200	1.52×10^{-5}	7.62×10^{-6}	1.04×10^{-8}	2.29×10^{-5}
1300	1.73×10^{-4}	8.64×10^{-5}	1.89×10^{-7}	2.60×10^{-4}
1400	1.35×10^{-3}	6.73×10^{-4}	2.18×10^{-6}	2.02×10^{-3}
(1500)	7.78×10^{-3}	3.89×10^{-3}	1.76×10^{-5}	1.17×10^{-2}
(1600)	3.55×10^{-2}	1.78×10^{-2}	1.07×10^{-4}	5.34×10^{-2}
(1700)	1.34×10^{-1}	6.70×10^{-2}	5.15×10^{-4}	2.02×10^{-1}
(1800)	4.34×10^{-1}	2.17×10^{-1}	2.08×10^{-3}	6.53×10^{-1}

Cerium

For high-temperature properties, see “Rare Earths.”

Density

Phase	<i>T</i>	<i>d</i>	Refer-ences
Ce ₂ (SO ₄) ₃ (c) Ce(SO ₄) ₂ (c)	^{°K} 294	3.912	17

Thermodynamic data (298.15 °K)

S[°]

	J mol ^{−1} deg	cal mol ^{−1} deg	Refer-ences
Ce ₂ (SO ₄) ₃ Ce(SO ₄) ₂ Ce ₂ O ₃ CeO ₂			

Δ*H*_{*f*}[°]

	kJ mol ^{−1}	kcal mol ^{−1}	Refer-ences
Ce ₂ (SO ₄) ₃ Ce(SO ₄) ₂ Ce ₂ O ₃ CeO ₂	1088.7	260.2	8

Cesium

Cs_2SO_4 is stable even beyond the melting point. According to Jaeger [59], vaporization is first noticeable at 1600 °K, and is very fast by 1710 °K. Spitsyn and Shostak [125], in maintaining Cs_2SO_4 for 2 hr at each of several temperatures, found no weight loss at 1073 °K, 0.2 percent loss at 1173 °K, and 0.87 percent loss at 1273 °K, 13.9 percent loss at 1473 °K, attributed entirely to vaporization.

No high-temperature thermal data are available for Cs_2SO_4 and Cs_2O from which equilibrium de-

Density of Cs_2SO_4

Phase	<i>T</i>	<i>d</i>	Refer- ences
	°K		
Solid	293	4.246	133
	298	4.243	7
	333	4.222	132
Liquid	1309	3.037	59
	1336	3.018	59
	1378	2.988	59
	1438	2.937	59
	1494	2.889	59
	1547	2.841	59
	1604	2.787	59
	1645	2.743	59
	1696	2.690	59
	1743	2.636	59
	1803	2.566	59

Transitions of Cs_2SO_4

Phase change	<i>T</i>	ΔH	ΔS	Refer- ences
	°K	<i>kJ mol</i> ⁻¹	<i>J mol</i> ⁻¹ deg ⁻¹	
c, II → c, I	933			5
c, I → l.	1277	40.2	31.4	5

Thermodynamic data (298.15 °K)

<i>S</i> ^o			
	<i>J mol</i> ⁻¹ deg ⁻¹	<i>cal mol</i> ⁻¹ deg ⁻¹	Refer- ences
$\text{Cs}_2\text{SO}_4(\text{II})$ Cs_2O			

$\Delta H f^\circ$

	<i>kJ mol</i> ⁻¹	<i>kcal mol</i> ⁻¹	Refer- ences
$\text{Cs}_2\text{SO}_4(\text{II})$	-1420.0	-339.38	1, 8
Cs_2O	-317.6	-75.9	1, 8

composition pressures could be calculated. Entropies have not been reported for either compound.

Chromium

Cr (II). CrSO_4 is known only in solution and as hydrates and double salts, all easily oxidized by air. The monohydrate on heating yields Cr_2O_3 .

Cr (III). $\text{Cr}_2(\text{SO}_4)_3$ is stable to 573 °K, but decomposes not far above that temperature, ultimately to Cr_2O_3 . The course of the decomposition is unknown. Oxysulfates have been prepared in ways other than by pyrolysis of the anhydrous sulfate.

Density of $\text{Cr}_2(\text{SO}_4)_3$

Phase	<i>T</i>	<i>d</i>	Refer- ences
	°K		
c	298	2.706	81

Transitions of $\text{Cr}_2(\text{SO}_4)_3$

Phase change	
c → c	No information.
c → l.	Decomposition.

Thermodynamic data (298.15 °K)

<i>S</i> ^o			
	<i>J mol</i> ⁻¹ deg ⁻¹	<i>cal mol</i> ⁻¹ deg ⁻¹	Refer- ences
$\text{Cr}_2(\text{SO}_4)_3$ Cr_2O_3	81.17	19.4	1, 3, 8

$\Delta H f^\circ$

	<i>kJ mol</i> ⁻¹	<i>kcal mol</i> ⁻¹	Refer- ences
$\text{Cr}_2(\text{SO}_4)_3$ Cr_2O_3	-1128.4	-269.7	1, 8

Cobalt

The decomposition of CoSO_4 has been studied by Pechkovsky [100, 103] in a dynamic system at a flow rate of 3 l/hr between 1023 and 1223 °K. Increase of SO_2 in the carrier gas inhibited the decomposition. The decomposition is linear in time with no evidence for an oxysulfate, i.e., $\alpha = kt$. In *k* is a linear function of 1/*T* between 1113 and 1133 °K, the slope yielding on activation energy of 319 kJ (76.2 kcal).

In an initially evacuated static system the product is CoO, though Co₃O₄ often appears in TGA runs in air. Decomposition pressures have been measured by Warner [136] over the range 950 to 1170 °K. The results are compared graphically with those in the earlier literature. The measured pressures are not tabulated, but equations derived from them are given for ΔG° and $\log P_{\text{SO}_3}$ as functions of temperature, valid only over the experimental range. From these we have calculated Δ_{fef} , extrapolating for 900 and 1200 °K. Equilibrium constants and decomposition pressures are calculated from these Δ_{fef} values.

The entropy of CoSO₄ listed by [1] on which Δ_{fef} at 298.15 °K depends, is quite uncertain, although close to what one would estimate. Later critical compilations [3, 8] do not list an entropy.

Density of CoSO₄

Phase	<i>T</i>	<i>d</i>	Refer- ences
α	°K		
	298	3.86 g/cm ³	25
β	298	3.770 g/cm ³	109

These densities are crystallographic. Pycnometric values are doubtful because the high-temperature β -form can be frozen in. Materials used may be mixtures.

Transitions of CoSO₄

Phase change	<i>T</i>	ΔH	ΔS	Refer- ences
	°K	<i>kJ mol</i> ⁻¹	<i>J mol</i> ⁻¹ <i>deg</i> ⁻¹	
$\alpha \rightarrow \beta$	705 ± 8	6.8 ± 0.6	9.6 ± 0.8	109

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	<i>J mol</i> ⁻¹ <i>deg</i> ⁻¹	<i>cal mol</i> ⁻¹ <i>deg</i> ⁻¹	Refer- ences
CoSO ₄	113.4	27.1	1
CoO	52.97	12.66	3, 8
Co ₃ O ₄	102.5	24.5	3, 8

ΔH_f°

	<i>kJ mol</i> ⁻¹	<i>kcal mol</i> ⁻¹	Refer- ences
CoSO ₄	-887.0	-212.0 ± 0.4	11
CoO	-238.9	-57.1	19, 8
	-878.	-210.	1
Co ₃ O ₄	-905.0	-216.3	8

Decomposition of CoSO₄

- (1) CoSO₄(c) \rightleftharpoons CoO(c) + SO₃(g)
 $\Delta H_{298.15}^\circ = 252.4 \text{ kJ, } 60.3_2 \text{ kcal}$
 (2) CoSO₄(c) \rightleftharpoons CoO(c) + SO₂(g) + 1/2 O₂
 $\Delta H_{298.15}^\circ = 351.3 \text{ kJ, } 83.9_6 \text{ kcal.}$

A. Free energies, reaction (1)

<i>T</i>	Δ_{fef}	ΔG_T°
°K	<i>J</i>	<i>kJ</i>
298.15	-196.2	193.8 ₉
(900)	-188.3	82.9 ₃
1000	-187.4	64.9 ₄
1100	-186.6	47.1 ₁
(1200)	-185.8	29.4 ₆

B. Equilibrium constants

<i>T</i>	$\log K_1$	<i>K</i> ₁	$\log K_2$	<i>K</i> ₂
°K				
298.15	-33.966	1.08×10^{-34}	-46.383	4.14×10^{-47}
(900)	-4.813	1.54×10^{-5}	-5.639	2.29×10^{-6}
1000	-3.392	4.06×10^{-4}	-3.651	2.23×10^{-4}
1100	-2.237	5.79×10^{-3}	-2.033	9.27×10^{-3}
(1200)	-1.282	5.22×10^{-2}	-0.694 ₅	2.02×10^{-1}

C. Equilibrium pressures (atm)

<i>T</i>	SO ₂	O ₂	SO ₃	Total
°K				
298.15	1.5×10^{-31}	7.5×10^{-32}	1.1×10^{-34}	2.3×10^{-31}
(900)	2.2×10^{-4}	1.1×10^{-4}	1.5×10^{-5}	3.4×10^{-4}
1000	4.6×10^{-3}	2.3×10^{-3}	4.1×10^{-4}	7.4×10^{-3}
1100	5.6×10^{-2}	2.8×10^{-2}	5.8×10^{-3}	8.9×10^{-2}
(1200)	4.3×10^{-1}	2.2×10^{-1}	5.2×10^{-2}	7.0×10^{-1}

Copper

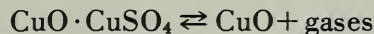
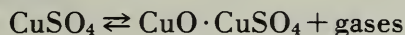
Cu (I). Cu₂SO₄ oxidizes in air.

Cu (II). There is general agreement that the first product of the decomposition of CuSO₄ is an oxysulfate, CuO·CuSO₄. In kinetic studies, the temperature range of this reaction has been reported as 1092 to 1133 °K [61] and 1053 to 1123 °K [128], possibly because of differences in the gas phase composition. The rate of decomposition decreases with increasing oxygen content of the flow gas and increases with increasing SO₃ content because these gases also displace the SO₃ = SO₂ + 1/2 O₂ equilibrium in opposite directions.

The decomposition of both sulfate and oxysulfate is zero-order. For the former an Arrhenius activation energy of 212 kJ (50.6 kcal) was obtained between 1053 and 1123 °K, and for the decomposition of the oxysulfate *E*_a = 346 kJ (82.8 kcal) between 1133 and 1193 °K [128]. However, somewhat different values of 238 kJ (56.8 kcal) and 269 kJ (64.3 kcal) for these reactions have also been reported

[103]. Although the values for the sulfate decomposition agree fairly well, those for the oxysulfates are quite different, possibly because the Russian workers ran this decomposition at a lower temperature, 1033 to 1073 °K.

Two sets of measurements [85, 117], in fair agreement, have been made of the equilibrium decomposition pressures, 948 to 1093 °K, in the systems



where the pressures in the first system are higher than in the second. For lack of data on the oxysulfate, it is not yet possible to calculate these pressures thermodynamically. We have, however, calculated pressures for the system



using high-temperature thermal data from [2] and extrapolating the free energy function of CuSO_4 above 900 °K. These pressures are, as they should be, intermediate between those for the two actual systems. Inasmuch as the latter pressures differ by less than an order of magnitude, the calculated pressures given in the tables that follow will serve as a rough approximation to the actual systems, particularly outside the narrow temperature range of the measurements.

The entropy of CuSO_4 is uncertain. [3] lists $25.3 \pm 1.0 \text{ cal mol}^{-1} \text{ deg}^{-1}$ as "suggested" in [60]. We estimate 26.9. The heat of formation of CuSO_4 has recently been redetermined [11] as $-183.4 \pm 0.6 \text{ kcal mol}^{-1}$ ($767.3 \text{ kJ mol}^{-1}$), but the value from [1] was retained in the calculations because it is part of a self-consistent set.

Density of CuSO_4

Phase	<i>T</i>	<i>d</i>	References
	°K		
?	298	3.542 (pycnometric)	81
α	298	4.113 g/cm ³ (crystallographic)	110
β	453	3.923 g/cm ³ (crystallographic)	110

Transitions of CuSO_4

Phase change	<i>T</i>	Δ <i>H</i>	Δ <i>S</i>	References
	°K			
α → β	?	No data	No data	
c → 1	decomposes			

Thermodynamic data (298.15 °K)

<i>S</i> ^o			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
CuSO ₄	113.4	27.1	1 (see text)
CuO	42.63	10.19	3, 4, 8
Cu ₂ O	93.7	22.4	3, 8

Δ <i>Hf</i> ^o			
	kJ mol ⁻¹	kcal mol ⁻¹	References
CuSO ₄	-769.86	-184.00	1, 8 (see text)
CuO	-155.4	-37.1	1, 8
Cu ₂ O	-1667.	-39.84	1, 8

Decomposition of CuSO_4

- (1) $\text{CuSO}_4(\text{c}) \rightleftharpoons \text{CuO}(\text{c}) + \text{SO}_3(\text{g})$
 $\Delta H_{298.15}^\circ = 219.4_5 \text{ kJ}, 52.4_5 \text{ kcal}$
 (2) $\text{CuSO}_4(\text{c}) \rightleftharpoons \text{CuO}(\text{c}) + \text{SO}_2(\text{g}) + 1/2 \text{ O}_2(\text{g})$
 $\Delta H_{298.15}^\circ = 317.8_6 \text{ kJ}, 75.9_7 \text{ kcal}.$

A. Free energies

<i>T</i>	CuO	CuSO ₄	Reaction (1)	
	fef	fef	Δfef	Δ <i>G</i> _{<i>T</i>} ^o
°K	<i>J</i>	<i>J</i>	<i>J</i>	<i>kJ</i>
298.15	-42.63	-113.39	-185.92	+164.02
400	-44.45 ₅	-117.47	-185.74	145.16
500	-47.82	-125.27	-185.44	126.73
600	-51.76	-134.26	-185.25	108.30
700	-55.81	-143.59	-185.06	89.91
800	-59.79	-152.88	-184.82	71.60
900	-63.64	-162.09	-184.42	53.47
(1000)	-67.32	-171.29	-183.69	35.76
(1100)	-70.92	-180.50	-182.70	18.48

B. Equilibrium constants

<i>T</i>	log <i>K</i> ₁	<i>K</i> ₁	log <i>K</i> ₂	<i>K</i> ₂
°K				
298.15	-28.734	1.85×10^{-29}	-41.063	8.65×10^{-42}
400	-18.954	1.11×10^{-19}	-26.892	1.28×10^{-27}
500	-13.238	5.78×10^{-14}	-18.596	2.54×10^{-19}
600	-9.427	3.74×10^{-10}	-13.073	8.45×10^{-14}
700	-6.708	1.96×10^{-7}	-9.131	7.40×10^{-10}
800	-4.674	2.12×10^{-5}	-6.182	6.58×10^{-7}
900	-3.103	7.89×10^{-4}	-3.902	1.25×10^{-4}
(1000)	-1.868	1.355×10^{-2}	-2.102	7.91×10^{-3}
(1100)	-0.877 ₂	1.325×10^{-1}	-0.651	2.23×10^{-1}

C. Equilibrium pressures (atm)

<i>T</i>	SO ₂	O ₂	SO ₃	Total
°K				
298.15	5.31×10^{-28}	2.66×10^{-28}	1.85×10^{-29}	8.15×10^{-28}
400	1.49×10^{-18}	7.44×10^{-19}	1.11×10^{-19}	2.34×10^{-18}
500	5.05×10^{-13}	2.52×10^{-13}	5.78×10^{-14}	8.15×10^{-13}
600	2.43×10^{-9}	1.21×10^{-9}	3.74×10^{-10}	4.01×10^{-9}
700	1.03×10^{-6}	5.15×10^{-7}	1.96×10^{-7}	1.74×10^{-6}
800	9.53×10^{-5}	4.76×10^{-5}	2.12×10^{-5}	1.64×10^{-4}
900	3.16×10^{-3}	1.58×10^{-3}	7.89×10^{-4}	5.52×10^{-3}
(1000)	5.00×10^{-2}	2.50×10^{-2}	1.36×10^{-2}	8.86×10^{-2}
(1100)	4.64×10^{-1}	2.32×10^{-1}	1.33×10^{-1}	8.28×10^{-1}

Dysprosium

For high-temperature properties, see "Rare Earths."

Density of Dy(SO₄)₃

Phase	<i>T</i>	<i>d</i>	References
c	°K 297	3.801	17

Erbium

For high-temperature properties, see "Rare Earths."

Density of Er₂(SO₄)₃

Phase	<i>T</i>	<i>d</i>	References
c	°K 297	3.851	17

Thermodynamic data (298.15 °K)

<i>S</i> °			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
Er ₂ (SO ₄) ₃ Er ₂ O ₃			

ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	References
Er ₂ (SO ₄) ₃ Er ₂ O ₃	-1897.9	-453.6	8

Europium

For high-temperature properties, see "Rare Earths."

Density

Phase	<i>T</i>	<i>d</i>	References
	°K		
EuSO ₄ (c)	293	4.989	79
EuSO ₄ (c)	298	4.981	79
Eu ₂ (SO ₄) ₃ (c)	297	3.997	17

Gadolinium

For high-temperature properties, see "Rare Earths."

Thermodynamic data (298.15 °K)

<i>S</i> °			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
Gd ₂ (SO ₄) ₃ Gd ₂ O ₃			
<i>ΔH_f</i> °			
	kJ mol ⁻¹	kcal mol ⁻¹	References
Gd ₂ (SO ₄) ₃ Gd ₂ O ₃	-1815.9	-434.0	8

Gallium

Ga₂(SO₄)₃ decomposes, without melting, to Ga₂O₃. Marchal [76] measured equilibrium decomposition pressures over the range 833 to 973 °K, from which it appears that this compound is less stable than Al₂(SO₄)₃. Pressures cannot yet be calculated thermodynamically.

Density of Ga₂(SO₄)₃

Phase	<i>T</i>	<i>d</i>	References
c	°K 296	3.239	17

Thermodynamic data (298.15 °K)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
$\text{Ga}_2(\text{SO}_4)_3$ $\text{Ga}_2\text{O}_3(\beta)$	84.9	20.3	3, 8

 ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
$\text{Ga}_2(\text{SO}_4)_3$ $\text{Ga}_2\text{O}_3(\beta)$	-1079.	-258	1, 8

Germanium

Density of $\text{Ge}(\text{SO}_4)_2$

Phase	T	d	References
c	$^\circ\text{K}$ 295	3.92	121

Thermodynamic Data (298.15 °K)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
$\text{Ge}(\text{SO}_4)_2$ $\text{GeO}_2(\text{c, soln.})$	55.27	13.21	3

 ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
$\text{Ge}(\text{SO}_4)_2$ $\text{GeO}_2(\text{c})$	-539.7	-129.0	5

Hafnium

Von Hevesy and Cremer [135] attempted to measure equilibrium decomposition pressures of $\text{Hf}(\text{SO}_4)_2$ in the range 823 to 923 °K, but were not sure of obtaining true equilibrium. Decomposition was direct to HfO_2 , not through an intermediate oxysulfate, and the sulfate appeared to be more stable than $\text{Zr}(\text{SO}_4)_2$.

Thermodynamic data (298.15 °K)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
$\text{Hf}(\text{SO}_4)_2$ HfO_2	59.33	14.18	3, 4, 8

 ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
$\text{Hf}(\text{SO}_4)_2$ HfO_2	-1113.1	-266.0	4, 8

Holmium

For high-temperature properties, see "Rare Earths."

Density of $\text{Ho}_2(\text{SO}_4)_3$

Phase	T	d	References
c	$^\circ\text{K}$ 297	3.830	17

Thermodynamic data (298.15 °K)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
$\text{Ho}_2(\text{SO}_4)_3$ Ho_2O_3			

 ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
$\text{Ho}_2(\text{SO}_4)_3$ Ho_2O_3	-1881.1	-449.6	8

Indium

Seward [122] measured equilibrium decomposition pressures of $\text{In}_2(\text{SO}_4)_3$ over the range 918 to 1093 °K, from which it appeared to be more stable than $\text{Al}_2(\text{SO}_4)_3$. The product was In_2O_3 without an oxysulfate intermediate, contrary to indications in the early literature.

A kinetic study [63] at temperatures above 1073 °K shows that the initial rate of decomposition is nearly

constant, but decreases with time [63]. The degree of decomposition is given by

$$\alpha = 1 - e^{-kt^n}$$

which can also be written in the logarithmic form

$$\ln[-\ln(1-\alpha)] = n \ln t + \ln k.$$

From the linear plot of the left-hand side versus $\ln t$ the constants n and k are obtained. n increases linearly from 1.0 at 1123 °K to 1.6 at 1273 °K while k increases logarithmically from 0.021 to 0.410 between these temperatures. The values of n indicate that decomposition proceeds from nuclei in two dimensions.

Density of $\text{In}_2(\text{SO}_4)_3$

Phase	T	d	References
c	°K 298	3.43 ₈	7

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
$\text{In}_2(\text{SO}_4)_3$ In_2O_3			

ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	References
$\text{In}_2(\text{SO}_4)_3$ In_2O_3	290 ₈ -930.9 -926.8	-695 -222.5 -221.5	1 1 8

Iridium

Ir (III). $\text{Ir}_2(\text{SO}_4)_3$ is known with certainty only as a hydrate, oxidizing in air.

Ir (IV). $\text{Ir}(\text{SO}_4)_2$ has been reported.

Iron

The sulfates of both Fe (II) and Fe (III) decompose without melting.

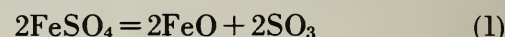
The decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 is reversible, without the formation of an intermediate oxy-sulfate. FeSO_4 decomposes irreversibly, with oxidation, to Fe_2O_3 , through intermediates that have not been identified with certainty, though FeO is often assumed.

Neumann and Heintke [84] measured decomposition pressures by the static method for both FeSO_4 (633–862 °K) and $\text{Fe}_2(\text{SO}_4)_3$ (793–973 °K). They include comparative tables of all the values from the earlier literature. At particular temperatures, pressures are higher for FeSO_4 than for $\text{Fe}_2(\text{SO}_4)_3$. With FeSO_4 , irreversibility prevented approaching pressures from two directions. Later, Warner and Ingraham [137] published values for $\text{Fe}_2(\text{SO}_4)_3$ (903–997 °K), but compared their results only with the erroneous data of Wöhler, Plüddemann, and Wöhler [144]. They agree better with Neumann and Heintke; plots of the two sets of pressures against temperature would cross near 960 °K. These pressures cannot be calculated thermodynamically because high-temperature thermal data exist only for the oxides [2].

Kinetics

FeSO_4

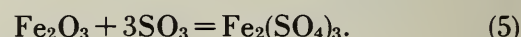
When FeSO_4 is heated above 823 °K, the FeO formed is immediately oxidized by the oxygen or SO_3 liberated in the reaction [84, 101, 115]. The reactions occurring are



corresponding to the net reaction



If the SO_3 remains in the system the following reaction may occur



However, this reaction is slow and may be suppressed by removing the SO_3 .

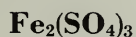
As expected, an increase of O_2 content in the sweep gas inhibits the decomposition.

When the weight loss was measured in air [104] between 953 and 1003 °K the decomposition followed the Roginsky equation

$$1 - (1 - \alpha)^{1/3} \approx \alpha = kt$$

when α is the degree of decomposition. From the linear temperature dependence of $\ln k$ on $1/T$ an Arrhenius activation energy of 253 kJ (60.4 kcal) was obtained. Since, at any temperature in the above range, the decomposition pressure of FeSO_4 is greater than that of $\text{Fe}_2(\text{SO}_4)_3$ the rate-determining step for the decomposition of the former is the decomposition of the ferric salt. The decomposition

appears to occur exclusively on the surface of the original material, rather than in the interior of the grains. Only in the final phases of the decomposition does the diffusion of gases through the oxide product appear to be rate-limiting.



The decomposition of $\text{Fe}_2(\text{SO}_4)_3$ is zero-order between 973 and 1073 °K. Activation energies of 83 kJ (19.9 kcal) [138] and 154 kJ (36.8 kcal) [127] for the reaction have been reported, the latter value for vacuum conditions, the former in a stream of dry N_2 .

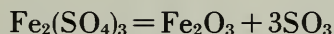
When the gas phase has a constant composition of SO_3 , SO_2 , and O_2 , the reaction rate is a linear function of $\frac{p_e(\text{SO}_2) - p(\text{SO}_2)}{p_e(\text{SO}_2)}$, i.e., the driving force is the difference between the actual and the equilibrium pressure of SO_2 .

In air between 953 and 1053° Roginsky's equation holds [104], i.e., the degree of decomposition is a linear function of time. This implies that the decomposition is not autocatalytic and that the new phase is instantaneously formed on the surface of the original material. The interphase then migrates into the material. During the later stages the rate is controlled by the diffusion of product gases through the solid oxide. The logarithm of the rate constant k in the Roginsky equation

$$1 - (1 - \alpha)^{1/3} \approx \alpha = kt$$

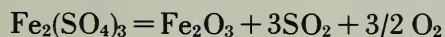
is a linear function of $1/T$. The Arrhenius activation energy calculated from the slope is 289 kJ (69.1 kcal), quite different from the other values reported.

No explanation is evident for the wide range of activation energies reported by different authors since one would not expect a radical change in mechanism to be produced by a change of experimental conditions. At 1000 °K, Warner and Ingraham give for the reaction



$$\Delta G = 526.510 - 501.03 T \text{ (in joules)}$$

and for the reaction



$$\Delta G = 194,165 - 184.55 T \text{ (in joules)}.$$

Since the equilibrium $\text{SO}_3 = \text{SO}_2 + 1/2 \text{ O}_2$ is established relatively slowly, the rate determining step is more likely to involve the expulsion of an SO_3 molecule from the crystal lattice. All of the reported activation energies are much less than $\Delta H = 526$ kJ (125.8 kcal), but ΔH per mole of SO_3 is $526/3 = 176$ kJ (42 kcal) which is at least in the right range.

Densities

Phase	<i>T</i>	<i>d</i>	References
$\text{FeSO}_4(\text{c})$	°K 288	3.346	130
$\text{Fe}_2(\text{SO}_4)_3(\text{c})$	ambient	3.10	89

Thermodynamic data (298.15 °K)

	<i>S</i> °		References
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	
FeSO_4	107.5	25.7	3, 8
$\text{Fe}_2(\text{SO}_4)_3$			
$\text{FeO}(\text{Fe}_{0.947}\text{O})$	563.6	13.74	3
Fe_3O_4	146.4	35.0	1, 3
Fe_2O_3	87.4	20.9	3

ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	References
FeSO_4	-922.6	-220.5	1, 8
$\text{Fe}_2(\text{SO}_4)_3$			
$\text{FeO}(\text{Fe}_{0.947}\text{O})$	-266.5	-63.7	1
	-264.4	-63.2	8
Fe_3O_4	-1117.	-267.0	1, 8
Fe_2O_3	-822.15	-196.5	1, 8

Lanthanum

For high-temperature properties, see "Rare Earths."

Density of $\text{La}_2(\text{SO}_4)_3$

Phase	<i>T</i>	<i>d</i>	References
c	°K 294	3.829	17

Transitions of $\text{La}_2(\text{SO}_4)_3$

Phase change	
c → 1.	Decomposition

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg	cal mol ⁻¹ deg ⁻¹	References
La ₂ (SO ₄) ₃ La ₂ O ₃			
ΔH_f°			
	kJ mol ⁻¹ deg	kcal mol ⁻¹	References
La ₂ (SO ₄) ₃ La ₂ O ₃	-1801.2	-430.5	8

Lead

Pb (II). Because PbSO₄ decomposes noticeably below the melting point, this value is difficult to determine reliably. The ultimate decomposition product is PbO. Various oxysulfates have been prepared in ways other than by pyrolysis of PbSO₄. Some have congruent melting points and form eutectics with PbO or PbSO₄; for a summary and references see [96b] and for thermodynamics, see [60]. [1] lists PbO · PbSO₄, mp 1243 °K, 2PbO · PbSO₄, mp 1223 °K. The former is the mineral lanarkite. Hoschek [57] found three intermediates before PbO in the pyrolysis of PbSO₄, the two oxysulfates above and 4PbO · PbSO₄. However, Terem and Akalan [127] in a kinetic study found no evidence for intermediates, and gave an Arrhenius activation energy of 384.9 kJ (92.0 kcal) for the zero-order reaction



No equilibrium decomposition-pressure measurements are available. Nichols and White [88] measured pressures by a dynamic method at four temperatures in the range 1035 to 1177 °K. From high-temperature thermal data in [2] we have calculated pressures for decomposition direct to PbO.

If decomposition is indirect, observed pressures will be somewhat higher.

Pb (IV). The compound Pb(SO₄)₂ has not been prepared free of H₂SO₄.

Density of PbSO₄

Phase	T	d	References
c, II	°K		
	288	6.2907	80
	298	6.2866	80
	308	6.2824	80
	318	6.2780	80

Transitions of PbSO₄

Phase change	T	ΔH	ΔS	References
	°K	kJ mol ⁻¹	J mol ⁻¹ deg ⁻¹	
c, II → c, I	1139	17.0	14.9	1, 5
c, I → l.	1360	40	29.7	1, 5

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
PbSO ₄ (II)	147.3	35.2	1, 3, 8
PbO (yellow)	67.4	16.1	3, 10
PbO (red)	65.3	15.6	3, 10

 ΔH_f°

	kJ mol ⁻¹ deg ⁻¹	kcal mol ⁻¹ deg ⁻¹	References
PbSO ₄ (II)	-918.39	-219.50	1, 8
PbO (yellow)	-217.8 ₆	-52.07	1, 10
PbO (red)	-219.2 ₄	-52.40	1, 8, 10

Decomposition of PbSO₄

(1) $\text{PbSO}_4(\text{c}) \rightleftharpoons \text{PbO}(\text{c}) + \text{SO}_3(\text{g})$
 to yellow PbO: $\Delta H_{298.15}^\circ = 305.35 \text{ kJ}$, 72.98 kcal
 to red PbO: $\Delta H_{298.15}^\circ = 303.97 \text{ kJ}$, 72.65 kcal
 (2) $\text{PbSO}_4(\text{c}) \rightleftharpoons \text{PbO}(\text{c}) + \text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$
 to yellow PbO: $\Delta H_{298.15}^\circ = 403.76 \text{ kJ}$, 96.50 kcal
 to red PbO: $\Delta H_{298.15}^\circ = 402.38 \text{ kJ}$, 96.17 kcal.

A. Free energies

<i>T</i>	PbO (yellow)	PbSO ₄	Reaction (1)	
	fef	fef	Δfef	Δ <i>G</i> _{<i>T</i>} ^o
°K	<i>J</i>	<i>J</i>	<i>J</i>	<i>kJ</i>
298.15	−67.36	−147.28	−176.75	+252.65
400	−69.25	−151.42	−176.57	234.72
500	−72.76	−159.41	−176.24	217.23
600	−76.82	−168.70	−175.88	199.82
700	−81.04	−178.32	−175.56	182.45
800	−85.19	−188.03	−175.07	165.29
900	−89.29	−197.74	−174.42	148.37
1000	−93.22	−207.36	−173.53	131.82
1100	−96.99	−216.81	−172.45	115.65
(1200)	−101.55	−226.02	−172.24	98.66
(1300)	−106.94	−234.89	−173.01	80.43
(1400)	−111.96	−243.34	−173.66	62.23
(1500)	−116.61	−251.29	−174.26	43.96

PbO (red)

298.15	−65.27	−174.66	+251.89
400	−67.24	−174.56	234.14
500	−71.06	−174.44	216.75
600	−75.27	−174.33	199.37
700	−79.58	−174.10	182.10
800	−83.83	−173.71	165.00
900	−87.95	−173.08	148.19

B. Equilibrium constants

To PbO (yellow)

<i>T</i>	log <i>K</i> ₁	<i>K</i> ₁	log <i>K</i> ₂	<i>K</i> ₂
°K				
298.15	−44.261	5.48×10^{-45}	−56.590	2.57×10^{-57}
400	−30.648	2.25×10^{-31}	−38.586	2.59×10^{-39}
500	−22.692	2.03×10^{-23}	−28.050	8.91×10^{-29}
600	−17.394	4.04×10^{-18}	−21.040	9.12×10^{-22}
700	−13.614	2.43×10^{-14}	−16.037	9.18×10^{-17}
800	−10.792	1.61×10^{-11}	−12.300	5.01×10^{-13}
900	−8.610	2.46×10^{-9}	−9.409	3.90×10^{-10}
1000	−6.885	1.30×10^{-7}	−7.119	7.60×10^{-8}
1100	−5.491	3.23×10^{-6}	−5.265	5.43×10^{-6}
(1200)	−4.294	5.08×10^{-5}	−3.686	2.06×10^{-4}
(1300)	−3.231	5.88×10^{-4}	−2.301	5.00×10^{-3}
(1400)	−2.322	4.76×10^{-3}	−1.117	7.64×10^{-2}
(1500)	−1.531	2.94×10^{-2}	−0.090	8.13×10^{-1}

To PbO (red)

298.15	−44.128	7.45×10^{-45}	−56.457	3.49×10^{-57}
400	−30.573	2.67×10^{-31}	−38.511	3.08×10^{-39}
500	−22.642	2.28×10^{-23}	−28.000	1.00×10^{-28}
600	−17.355	4.42×10^{-18}	−21.001	9.98×10^{-22}
700	−13.587	2.59×10^{-14}	−16.010	9.77×10^{-17}
800	−10.773	1.69×10^{-11}	−12.281	5.24×10^{-13}
900	−8.600	2.51×10^{-9}	−9.399	3.99×10^{-10}

C. Equilibrium pressures (atm)

To PbO (yellow)

<i>T</i>	SO ₂	O ₂	SO ₃	Total
°K				
298.15	2.36×10^{-38}	1.18×10^{-38}	5.48×10^{-45}	3.55×10^{-38}
400	2.38×10^{-26}	1.19×10^{-26}	2.25×10^{-31}	3.57×10^{-26}
500	2.51×10^{-19}	1.26×10^{-19}	2.03×10^{-23}	3.77×10^{-19}
600	1.19×10^{-14}	5.92×10^{-15}	4.04×10^{-18}	1.78×10^{-14}
700	2.57×10^{-11}	1.28×10^{-11}	2.43×10^{-14}	3.85×10^{-11}
800	7.95×10^{-9}	3.97×10^{-9}	1.61×10^{-11}	1.19×10^{-8}
900	6.73×10^{-7}	3.36×10^{-7}	2.46×10^{-9}	1.01×10^{-6}
1000	2.26×10^{-5}	1.13×10^{-5}	1.30×10^{-7}	3.41×10^{-5}
1100	3.89×10^{-4}	1.95×10^{-4}	3.23×10^{-6}	5.87×10^{-4}
(1200)	4.40×10^{-3}	2.20×10^{-3}	5.08×10^{-5}	6.64×10^{-3}
(1300)	3.68×10^{-2}	1.84×10^{-2}	5.88×10^{-4}	5.59×10^{-2}
(1400)	2.27×10^{-1}	1.13×10^{-1}	4.76×10^{-3}	3.45×10^{-1}
(1500)	1.097	0.549	2.94×10^{-2}	1.675

To PbO (red)

298.15	2.90×10^{-38}	1.45×10^{-38}	7.45×10^{-45}	4.35×10^{-38}
400	2.67×10^{-26}	1.33×10^{-26}	2.67×10^{-31}	4.00×10^{-26}
500	2.72×10^{-19}	1.36×10^{-19}	2.28×10^{-23}	4.07×10^{-19}
600	1.26×10^{-14}	6.29×10^{-15}	4.42×10^{-18}	1.89×10^{-14}
700	2.67×10^{-11}	1.34×10^{-11}	2.59×10^{-14}	4.01×10^{-11}
800	8.19×10^{-9}	4.10×10^{-9}	1.69×10^{-11}	1.23×10^{-8}
900	6.83×10^{-7}	3.41×10^{-7}	2.51×10^{-9}	1.03×10^{-6}

Lithium

Decomposition of Li₂SO₄ begins to be noticeable not far above its melting point [59, 125], the Li₂O product apparently dissolving in the Li₂SO₄, while some volatilization of the Li₂SO₄ occurs. No measurements of decomposition pressures have been made, nor can the pressures be calculated thermodynamically. High-temperature thermal data exist for Li₂O [2] but not for Li₂SO₄.

Density of Li₂SO₄

Phase	<i>T</i>	<i>d</i>	References
	°K		
c, II c, I	298	2.221	7
	883	2.07 g/cm ³ (crystallographic)	45
Liquid	1133	2.004	59
	1147	1.999	59
	1170	1.989	59
	1196	1.978	59
	1236	1.962	59
	1250	1.956	59
	1274.4	1.947	59
	1311	1.932	59
	1330	1.924	59
	1347	1.917	59
	1363	1.911	59
	1385	1.901	59
	1430	1.884	59
	1441	1.879	59
	1457	1.873	59
	1465.4	1.869	59
	1487	1.860	59

Transitions of Li₂SO₄

Phase changes	<i>T</i>	ΔH	ΔS	References
	$^{\circ}\text{K}$	kJ mol^{-1}	$\text{J mol}^{-1} \text{deg}^{-1}$	
Li ₂ SO ₄ , c II \rightarrow c I	859	27.2	31.8	5
c, I \rightarrow l.	1132	7.5	6.7	5

Thermodynamic data (298.15 $^{\circ}\text{K}$)

S°			
	$\text{J mol}^{-1} \text{deg}^{-1}$	$\text{cal mol}^{-1} \text{deg}^{-1}$	References
Li ₂ SO ₄ (II) Li ₂ O	37.89	9.056	10

ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
Li ₂ SO ₄ (II)	-1434.4	-342.83	1, 8
Li ₂ O	-595.8	-142.4	1, 8
	-598.7	-143.1 \pm 0.5	10

Lutetium

See "Rare Earths"

Magnesium

MgSO₄ begins to decompose below the melting point, directly to MgO without an oxysulfate intermediate. Literature melting points therefore vary widely.

Equilibrium decomposition pressures, by the static method, of Marchal [75] (1223–1463 $^{\circ}\text{K}$) are thought to be too high because of attack on the boat. Knopf and Staude [64] made measurements (1144–1313 $^{\circ}\text{K}$) by a dynamic method. Their data expressed as P_{SO_3} are somewhat lower than Marchal's, the difference increasing with temperature. It is not yet possible to calculate these pressures thermodynamically for lack of high-temperature thermal data for MgSO₄, though such data are available for its decomposition product, MgO [2, 134]. For a thermodynamic treatment of Marchal's data, see [60].

Kinetically the decomposition of MgSO₄ has been studied in a flow system in the range 1223 to 1323 $^{\circ}\text{K}$ [98]. When N₂ flows over the salt at 3 l/hr the decomposition is linear in time. Under these conditions the product gases are continuously removed and the equilibrium $\text{SO}_3 = \text{SO}_2 + 1/2 \text{O}_2$ is not established.

If these gases flow over the salt at 3 l/hr the reaction rate is nearly independent of oxygen con-

tent, but the proportion of SO₃ relative to SO₂ decreases with decreasing O₂ content. The activation energy in the range 1293 to 1333 $^{\circ}\text{K}$ is 661 kJ (158.0 kcal) [103].

Density of MgSO₄

Phase	<i>T</i>	<i>d</i>	References
	$^{\circ}\text{K}$		
c, II	288	2.71	130
c, II	298	2.66	7

Transitions of Mg MgSO₄

Phase change	<i>T</i>	ΔH	ΔS	References
	$^{\circ}\text{K}$	kJ mol^{-1}	$\text{J mol}^{-1} \text{deg}^{-1}$	
c, II \rightarrow c, I	1283	14.6	No data	5
c, I \rightarrow l.	1400			
			10.4	5, cf. 114

Thermodynamic data (298.15 $^{\circ}\text{K}$)

S°			
	$\text{J mol}^{-1} \text{deg}^{-1}$	$\text{cal mol}^{-1} \text{deg}^{-1}$	References
MgSO ₄	91.6 ₃	21.9	1, 3, 8, 10
MgO (powder)	27.8 ₇	6.66	1, 3
MgO (crystal)	26.8	6.4	1, 3

ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
MgSO ₄	-1278.	-305.5	1, 8, 10
MgO (powder)	-598.10	-142.95	1
MgO (crystal)	-601.83	-143.84	1
	-601.2	-143.7	8, 10

Manganese

Mn(II). The melting point of MnSO₄, 700 $^{\circ}\text{C}$, quoted in handbooks, is erroneous. Decomposition begins before melting. The product usually observed on pyrolysis in air is Mn₃O₄, as in TGA [28, 90], though Mn₂O₃ may appear mixed with it in the lower temperature range, complicating the kinetic picture [97]. Marchal [76] measured decomposition pressures in the range 1093 to 1383 $^{\circ}\text{K}$. We have calculated them thermodynamically, by the method described below, using high-temperature thermal data from [2] with an extrapolation of the free energy function of MnSO₄ to 1200 $^{\circ}\text{K}$. We also calculated the pressures for decomposition to Mn₂O₃. A comparison of these two sets of pressures with the calculated oxygen pressures for pairs of the four oxides of manganese show that Mn₃O₄ is the product expected thermodynamically

in an initially evacuated system containing only MnSO_4 originally, in agreement with Mah [71].

Marchal's measured decomposition pressures are substantially lower than those calculated here. Kelley [60] used them to calculate the heat and free energy of formation of MnSO_4 , but the thermodynamic constants available then (1936) have been mostly superseded, so that the near agreement of this heat of formation with those based on the work of Thomsen and of Berthelot is fortuitous. Mah [71] calculated partial pressures of SO_2 and O_2 expected for the decomposition of MnSO_4 to Mn_3O_4 , using some constants different from those used here, and a simplified method that ignores P_{SO_3} and assumes $P_{\text{SO}_2} = 3P_{\text{O}_2}$, obtaining pressures slightly lower than those tabulated here.

Mn (III). $\text{Mn}_2(\text{SO}_4)_3$ is said to be stable at 473 °K, decomposition beginning about 100° higher, to MnSO_4 , O_2 , and SO_3 .

Mn (IV). $\text{Mn}(\text{SO}_4)_2$ is somewhat unstable at room temperature.

Calculation of Partial Pressures

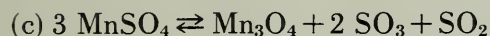
There are four equilibrium equations and corresponding equilibrium constants:



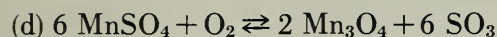
$$K_1 = \frac{(P_{\text{SO}_2})(P_{\text{O}_2})^{1/2}}{(P_{\text{SO}_3})}$$



$$K_2 = (P_{\text{SO}_2})^3(P_{\text{O}_2})$$



$$K_3 = (P_{\text{SO}_3})^2(P_{\text{SO}_2})$$



$$K_4 = \frac{(P_{\text{SO}_3})^6}{(P_{\text{O}_2})}$$

Three relations are needed to solve for the three pressures, but only two of these four equilibrium-constant expressions are independent; any two can be derived algebraically from the other two. For example: $K_2 = K_1^2 K_3$. The required third relation is obtained from:

SO_2	O_2	SO_3	
x	$\frac{x}{3}$	0	moles formed in reaction <i>b</i>
$-n$	$-\frac{n}{2}$	$+n$	moles formed in reaction <i>a</i>
$(x-n)$	$(\frac{x}{3} - \frac{n}{2})$	n	moles present at final equilibrium.

Reaction (b), rather than (c) or (d), is chosen for the

first step for mathematical convenience. K_3 and K_4 now become:

$$K_3 = n^2(x-n) \text{ or } x = \frac{K_3}{n^2} + n \quad (1)$$

$$K_4 = \frac{n^6}{(\frac{x}{3} - \frac{n}{2})} \text{ or } x = 3 \left(\frac{n^6}{K_4} + \frac{n}{2} \right) \quad (2)$$

Equating (1) and (2) to eliminate x :

$$6n^8 + K_4n^3 - 2K_3K_4 = 0. \quad (3)$$

K_3 and K_4 are first evaluated for each temperature of interest from thermodynamic data of the compounds involved. Equation (3) is then solved for n at each temperature.

Then:

$$P_{\text{SO}_3} = n$$

$$P_{\text{SO}_2} = \frac{K_3}{(P_{\text{SO}_3})^2}$$

$$P_{\text{O}_2} = \frac{P_{\text{SO}_2}}{3} - \frac{P_{\text{SO}_3}}{6}$$

Densities

Phase	<i>T</i>	<i>d</i>	References
$\text{MnSO}_4(\text{c})$	°K 298	3.181 (25/4)	81
$\text{Mn}_2(\text{SO}_4)_3(\text{c})$	288	3.24 (g/cm ³)	16

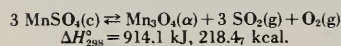
Thermodynamic data (298.15 °K)

<i>S</i> °			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
MnSO_4	112.	26.8	1, 3, 8
MnO	59.71	14.27	3, 8
$\text{Mn}_3\text{O}_4(\alpha)$	154.	36.8	91
Mn_2O_3	110.5	26.4	3, 8
$\text{MnO}_2(\text{I})$	53.05	12.68	1, 3, 8

ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	References
MnSO_4	-1063.74	-254.24	1, 4, 8
MnO	-385.1	-92.05	1, 4, 8
$\text{Mn}_3\text{O}_4(\alpha)$	-1386.6	-331.4	4, 8
Mn_2O_3	-956.9	-228.7	91
$\text{MnO}_2(\text{I})$	-520.9	-124.5	1, 8

Decomposition of MnSO₄



A. Free energies

<i>T</i>	Mn ₃ O ₄	MnSO ₄	Δ _{fef}	Δ <i>G</i> _{<i>T</i>} [°]
	fef	fef		
°K	<i>J</i>	<i>J</i>	<i>J</i>	<i>kJ</i>
298.15	−153.97	−112.13	−766.92	685.42
400	−159.93	−116.32	−766.32	607.55
500	−171.46	−124.77	−764.16	532.00
600	−184.64	−134.68	−761.10	457.42
700	−198.11	−145.10	−757.24	384.01
800	−211.40	−155.44	−753.28	311.45
900	−224.22	−165.56	−749.09	239.90
1000	−236.44	−175.35	−744.80	169.28
1100	−248.11	−184.77	−740.56	99.46
(1200)	−259.30	−194.18	−735.30	+31.72

B. Equilibrium constants

<i>T</i>	log <i>K</i>	<i>K</i>
°K		
298.15	−120.076	8.40 × 10 ^{−121}
400	−79.331	4.67 × 10 ^{−80}
500	−55.573	2.67 × 10 ^{−56}
600	−39.819	1.52 × 10 ^{−40}
700	−28.653	2.22 × 10 ^{−29}
800	−20.334	4.63 × 10 ^{−21}
900	−13.922	1.20 × 10 ^{−14}
1000	−8.841	1.44 × 10 ^{−9}
1100	−4.722	1.90 × 10 ^{−5}
(1200)	−1.381	4.16 × 10 ^{−2}

C. Equilibrium Pressures (atm)

<i>T</i>	SO ₂	O ₂	SO ₃	Total
°K				
298.15	1.26 × 10 ^{−30}	4.20 × 10 ^{−31}	1.74 × 10 ^{−33}	1.68 × 10 ^{−30}
400	1.94 × 10 ^{−20}	6.43 × 10 ^{−21}	1.35 × 10 ^{−22}	2.59 × 10 ^{−20}
500	1.69 × 10 ^{−14}	5.57 × 10 ^{−15}	2.87 × 10 ^{−16}	2.27 × 10 ^{−14}
600	1.47 × 10 ^{−10}	4.81 × 10 ^{−11}	4.50 × 10 ^{−12}	1.99 × 10 ^{−10}
700	9.09 × 10 ^{−8}	2.96 × 10 ^{−8}	4.14 × 10 ^{−9}	1.25 × 10 ^{−7}
800	1.09 × 10 ^{−5}	3.54 × 10 ^{−6}	6.63 × 10 ^{−7}	1.51 × 10 ^{−5}
900	4.39 × 10 ^{−4}	1.41 × 10 ^{−4}	3.29 × 10 ^{−5}	6.13 × 10 ^{−4}
1000	8.20 × 10 ^{−3}	2.61 × 10 ^{−3}	7.19 × 10 ^{−4}	1.15 × 10 ^{−2}
1100	8.80 × 10 ^{−2}	2.79 × 10 ^{−2}	8.73 × 10 ^{−3}	1.25 × 10 ^{−1}
(1200)	6.03 × 10 ^{−1}	1.90 × 10 ^{−1}	6.48 × 10 ^{−2}	8.57 × 10 ^{−1}

Mercury

Hg (I). Pascal [1958], using very old references, describes Hg₂SO₄ as unstable to light, disproportionating to Hg[°] and HgSO₄, and melting with decomposition to Hg[°], O₂, and SO₂.

Hg (II). According to a recent study by Hoschek [57], HgSO₄ is unchanged after 2 hr at 673 °K, but by 773 °K decomposition occurs to HgO · HgSO₄ and then 2HgO · HgSO₄, identified through their x-ray spectra. All three compounds are volatile at elevated temperatures. The supposed next product HgO was not observed because it is even more volatile. If HgSO₄ is heated rapidly to 973 °K, some Hg₂SO₄ appears along with the oxysulfates before volatilization is complete. No thermal data above 298 °K exist for any of these compounds.

Densities

Phase	<i>T</i>	<i>d</i>	References
HgSO ₄ (c)	°K		
	298	6.49 (pycnometric)	13
	298	6.50 (crystallographic)	13

Thermodynamic data (298.15 °K)

	<i>S</i> [°]		
	J mol ^{−1} deg ^{−1}	cal mol ^{−1} deg ^{−1}	References
HgSO ₄			
Hg ₂ SO ₄	201.	48.0	1, 3, 9, 8
Hg ₂ O			
HgO (red)	70.3	16.8	3, 8, 10
HgO (yellow)	72.4	17.3	3

Δ*H*_{*f*}[°]

	kJ mol ^{−1}	kcal mol ^{−1}	References
HgSO ₄	−704.2	−168.3	1, 8
Hg ₂ SO ₄	−743.1 ₂	−177.61	9
Hg ₂ O	−91.2	−21.8	1
HgO (red)	−90.7	−21.68	1, 8
HgO (yellow)	−90.21	−21.56	1

Neodymium

For high-temperature properties, see "Rare Earths."

Density of Nd₂(SO₄)₃

Phase	<i>T</i>	<i>d</i>	References
c	^{°K} 294	3.961	17

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
Nd ₂ (SO ₄) ₃ Nd ₂ O ₃			

ΔHf[°]

	kJ mol ⁻¹	kcal mol ⁻¹	References
Nd ₂ (SO ₄) ₃ Nd ₂ O ₃	-1782.4	-426.0	8

Nickel

NiSO₄ decomposes, without melting, to NiO. TGA curves have not shown evidence of an oxysulfate intermediate [22, 28, 73, 90]; some decomposition of the NiO may occur [22], especially if the thermobalance is continuously evacuated [28]. Equilibrium decomposition pressures have been measured by Marchal [76] (973–1218 °K) and by Wöhler and Flick [141] (1048–1119 °K) whose values are about twice as high as Marchal's. Neither found an oxysulfate intermediate. For a thermodynamic treatment of Marchal's data, see [60]. Both also worked with CoSO₄ and agree that NiSO₄ is the less stable in the sense that its decomposition pressures are higher in these temperature ranges. It is not yet possible to calculate those pressures thermodynamically for lack of high-temperature

thermal data on NiSO₄. Such data are available for NiO [2]. The necessary thermodynamic constants at 298 °K are known, as tabulated below, except the entropy of NiSO₄. [1] gives a value for it that seems much too low; [3] does not list one.

Density of NiSO₄

Phase	<i>T</i>	<i>d</i>	References
c	^{°K} 288	3.543(25/4)	81

Transitions of NiSO₄

Phase change	
c → c c → l.	No information Decomposition

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
NiSO ₄ NiO	38.0	9.08	3, 8

ΔHf[°]

	kJ mol ⁻¹	kcal mol ⁻¹	References
NiSO ₄ NiO	-870.7 -239.7	-208.1 ± 0.2 -57.3 ± 0.1	11 19

Palladium

Anhydrous PdSO₄ has not been prepared free of H₂O or H₂SO₄. The hydrate PdSO₄ · 2H₂O on heating loses H₂O, then SO₂, yielding ultimately the metal.

Density of PdSO₄

Phase	<i>T</i>	<i>d</i>	References
c	^{°K} 287	4.012	17

Plutonium

For the oxidation states Pu(III) and Pu(VI) (PuO_2^{2+}) only sulfates in solution or double salts are known. Pu(IV) forms a tetrahydrate but, contrary to earlier reports, attempts [32] to prepare a stoichiometric $\text{Pu}(\text{SO}_4)_2$ by heating materials initially containing H_2O and H_2SO_4 led to a product of composition varying with conditions. TGA showed a $\text{Pu}(\text{SO}_4)_2$ plateau that was not quite level, followed by a drop to the $\text{PuO}_{2.09}$ level.

Polonium

Like tellurium, Po forms a basic sulfate, $2\text{PoO}_2 \cdot \text{SO}_3$, but in contrast to Te it also forms a normal sulfate $\text{Po}(\text{SO}_4)_2$ anhydrous and hydrated. The anhydrous salt is stable to above 673 °K, decomposing to PoO_2 near 823 °K [14].

Potassium

In the short time of TGA runs [53, 73], K_2SO_4 appears stable to 1173 °K. A slight loss in weight by 1273 °K was attributed to sublimation [73].

Spitsyn and Shostak [125], in maintaining K_2SO_4 for 2 hr at each of various temperatures, found no loss in weight at 1073 and 1173 °K, a barely measurable loss at 1273 °K, and 3.6 percent loss at 1473 °K. Because the residue showed no alkaline reaction or change in percentage composition, even on repeating the heating in a stream of steam, they concluded that all the weight loss was due to volatilization and none to decomposition. They believed they had ruled out the possibility that K_2O , known to be volatile at high temperature, might have formed by decomposition but escaped as fast as SO_3 . On the other hand, Kröger and Stratmann [67], by an application of the Knudsen effusion method, reported both decomposition pressures (1114–1272 °K) and sublimation pressures (1085–1272 °K), the former being between one and two orders of magnitude higher than the latter. An isolated value [21] for the equilibrium decomposition pressure of K_2SO_4 at 1223 °K by the static method is two orders of magnitude higher than that of Kröger and Stratmann.

These discrepancies could be resolved if it were possible to calculate the decomposition pressures thermodynamically, but the necessary high-temperature thermal data are available only for K_2SO_4 [2], not K_2O . Further, the 298 °K entropy of K_2O is unknown.

Density of K_2SO_4

Phase	<i>T</i>	<i>d</i>	References
	°K		
c, II (α)	291	2.663	55
c, II	293.8 ₅	2.662	12
c, II	298	2.662	12
c, I (β)	298	2.621 ± 0.004	120
c, II (α)	313.6 ₅	2.655	12
Liquid	1343.4	1.888	59
	1376	1.870	59
	1418	1.848	59
	1472	1.818	59
	1520	1.792	59
	1579	1.760	59
	1670	1.737	59
	1645	1.724	59
	1673	1.709	59
	1713	1.687	59
	1736	1.674	59
	1763.6	1.660	59
	1803.5	1.637	59
	1859	1.607	59
	1929	1.569	59

Transitions of K_2SO_4

Phase change	<i>T</i>	Δ <i>H</i>	Δ <i>S</i>	References
	°K	<i>kJ mol</i> ⁻¹	<i>J mol</i> ⁻¹ <i>deg</i> ⁻¹	
c, II → c, I	856	8.12	9.50	1, 2, 5
c, I → l.	1342	36.6 ₅	27.3 ₂	1, 2, 5

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	<i>J mol</i> ⁻¹ <i>deg</i> ⁻¹	<i>cal mol</i> ⁻¹ <i>deg</i> ⁻¹	References
$\text{K}_2\text{SO}_4(\text{II})$	175.7	42.0	1, 3, 8
K_2O	116.7	27.9	3, 8
KO_2			
Δ <i>Hf</i> [°]			
	<i>kJ mol</i> ⁻¹	<i>kcal mol</i> ⁻¹	References
$\text{K}_2\text{SO}_4(\text{II})$	-1436.9	-342.66	1, 8
K_2O	-361.5	-86.4	1, 8
KO_2	-280.	-67.	1
	-283.	-67.7	8

Praseodymium

For high-temperature properties, see "Rare Earths."

Density of $\text{Pr}_2(\text{SO}_4)_3$

Phase	T	d	References
c	$^{\circ}\text{K}$ 297	3.797	17

Thermodynamic data (298.15 $^{\circ}\text{K}$)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
$\text{Pr}_2(\text{SO}_4)_3$ Pr_2O_3 $\text{PrO}_{1.72}$ $\text{PrO}_{1.833}$ PrO_2			
ΔH_f°			
	kJ mol^{-1}	kcal mol^{-1}	References
$\text{Pr}_2(\text{SO}_4)_3$ Pr_2O_3 $\text{PrO}_{1.72}$ $\text{PrO}_{1.833}$ PrO_2	 -1827.6 -937.2 -952.3 -1004.2	 -436.8 -224.0 -227.6 -240.0	 8 8 8 8

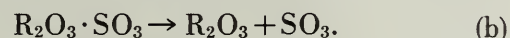
Radium

Thermodynamic data (298.15 $^{\circ}\text{K}$)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
RaSO_4 RaO	142.	34	1
ΔH_f°			
	kJ mol^{-1}	kcal mol^{-1}	References
RaSO_4 RaO	 -1473. -523.	 -352 -125	 1 1

Rare Earths

On heating, all of the anhydrous sulfates of the trivalent rare-earth elements and yttrium, type formula $\text{R}_2(\text{SO}_4)_3$, decompose, without first melting, to basic salts (oxysulfates) of the type $\text{R}_2\text{O}_3 \cdot \text{SO}_3$, then to an oxide. The oxide final product is R_2O_3 for all these elements except cerium, praseodymium, and terbium, which, in air, at 1 atm pressure, form CeO_2 , Pr_6O_{11} , and the somewhat variable oxide usually written Tb_4O_7 .



There have been three comprehensive studies which, taken together, reveal the trend in stability of the sulfates and oxysulfates within the rare-earth series. Wöhler and Grünzweig [142, Ce] [143, others] measured equilibrium decomposition pressures for reaction (a) for scandium, yttrium, and 8 of the rare-earth elements, in the range 973 to 1293 $^{\circ}\text{K}$. Nathans and Wenlandt [83] performed TGA and DTA, covering reactions (a) and (b) for yttrium and all the rare earths. Ivakin [58], by a weight-loss technique in a stream of dry N_2 , working with yttrium and 7 of the rare earths, investigated the kinetics of reaction (a) at 1223 and 1323 $^{\circ}\text{K}$ and of reaction (b) at 1573 $^{\circ}\text{K}$. From these three sources one may conclude that with the exception of Ce the stability of the sulfates in reaction (a) decreases from La to somewhere in the Sm Eu Gd group, and then increases to Lu, while the stability of the oxysulfates in reaction (b) decreases all the way from La to Lu. These conclusions hold for either kinetic or equilibrium definitions of "stability," and they ignore a few reversals of order which are probably attributable to experimental errors in view of the close similarity of adjacent members of the rare-earth series. Among the more stable sulfates the order of decreasing stability in reaction (a) is La-Y-Lu (or Yb) according to kinetics [58], equilibrium pressures [143], and DTA [83], but not by TGA [83]. In reaction (b) Y falls near Ho and Er [58,83] in accordance with the crystal radii of R^{+3} ions and the lanthanide contraction.

By the equilibrium decomposition pressure criterion, $\text{Sc}_2(\text{SO}_4)_3$ is less stable than any of the rare-earth sulfates except cerium. However, unlike the rare earths, it seems to decompose directly to Sc_2O_3 [143] rather than through reactions (a) and (b).

$\text{Ce}_2(\text{SO}_4)_3$ is much less stable than the sulfates of the other rare earths [83, 142, 143], and less stable than $\text{Sc}_2(\text{SO}_4)_3$ [143]. The product is CeO_2 rather than Ce_2O_3 , but the mechanism is unknown. Least stable by far is $\text{Ce}(\text{SO}_4)_2$ which also yields CeO_2 ultimately. Wöhler, Plüddemann, and

Wöhler [144] measured equilibrium decomposition pressures in the range 634 to 755 °K in what they believed to be the system $2\text{Ce}(\text{SO}_4)_2 \rightleftharpoons \text{Ce}_2(\text{SO}_4)_3 + \text{SO}_3 + 1/2 \text{O}_2$. Duval [34] by TGA found an intermediate $3\text{CeO}_2 \cdot 4\text{SO}_3$.

Ivakin's kinetic investigation [58] showed that the oxysulfates in reaction (b) decompose in accordance with a simple zero-order rate law, whereas reaction (a) is more complex kinetically. Thus a plot of the equation

$$1 - (1 - \alpha)^{1/3} = kt$$

is a line whose slope changes at one point from k_1 to k_2 . This would suggest a compound intermediate between $\text{R}_2(\text{SO}_4)_3$ and $\text{R}_2\text{O}_3 \cdot \text{SO}_3$, but x-ray diffraction patterns were interpreted as showing that the only possible intermediate was a solid solution of variable composition.

The relative stabilities of the sulfates of Sc, Y, and the rare earths may be represented in the following order of decreasing stability:



This refers to decomposition of the normal anhydrous sulfate to its first decomposition product, oxysulfate or oxide as the case may be for each element. The dashed line preceding Gd represents the other rare-earth elements. With increasing atomic number the stability first decreases in the order Pr-Nd-Sm-Eu and then increases in the order Tb-Dy-Ho-Er-Tm-Yb.

The high-temperature behavior of the bivalent sulfates SmSO_4 , EuSO_4 , and YbSO_4 has not been investigated. They are expected to undergo self-oxidation, like FeSO_4 , to yield ultimately R_2O_3 .

Rhodium

The compound $\text{Rh}_2(\text{SO}_4)_3$ is difficult to prepare in pure form. The reported density needs confirmation.

Density of $\text{Rh}_2(\text{SO}_4)_3$

Phase	<i>T</i>	<i>d</i>	Refer- ence
c	°K 291	3.44	17

Rubidium

In the short time of TGA runs [41, 73], Rb_2SO_4 appears stable to 1173 °K. A slight loss in weight by 1273 °K was attributed to sublimation [73].

Spitsyn and Shostak [125], in maintaining Rb_2SO_4 for 2 hr at each of various temperatures, found no

loss in weight at 1073 °K, a very slight loss at 1173 °K, 0.3 percent loss at 1273 °K, and 6.3 percent loss at 1473 °K (22.4% in 8 hr). They believed this was due entirely to volatilization, none to decomposition. But see the discussion under Potassium.

It is not yet possible to calculate decomposition pressures thermodynamically. Neither entropies nor high-temperature thermal data are available for Rb_2SO_4 or Rb_2O .

Density of Rb_2SO_4

Phase	<i>T</i>	<i>d</i>	Refer- ences
	°K		
c, II	293	3.614	132
c, II	298	3.613	7
c, II	333	3.594	133
Liquid	1359	2.538	59
	1385	2.521	59
	1418	2.499	59
	1468	2.466	59
	1508	2.440	59
	1562	2.403	59
	1617	2.367	59
	1670	2.331	59
	1688	2.319	59
	1755	2.275	59
	1818	2.233	59

Transitions of Rb_2SO_4

Phase change	<i>T</i>	Refer- ences
	°K	
c, II → c, I	923	1
c, I → 1.	1347	1

Thermodynamic data (298.15 °K)

<i>S</i> °			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	Refer- ences
Rb_2SO_4 Rb_2O			

*Δ*H*_f°*

	kJ mol ⁻¹	kcal mol ⁻¹	Refer- ences
Rb_2SO_4 Rb_2O	-1424.7 -330.	-340.5 -78.9	1, 8 1, 8

Ruthenium

No simple sulfates have been isolated. The compound RuOSO_4 has not been prepared in well-defined form.

Samarium

For high-temperature properties, see "Rare Earths."

Density

Phase	T	d	References
	$^{\circ}\text{K}$		
$\text{SmSO}_4(\text{c})$ $\text{Sm}_2(\text{SO}_4)_3(\text{c})$	297	4.059	17

Thermodynamic data (298.15 $^{\circ}\text{K}$)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
SmSO_4 $\text{Sm}_2(\text{SO}_4)_3$ Sm_2O_3			

ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
SmSO_4 $\text{Sm}_2(\text{SO}_4)_3$ Sm_2O_3	 -3884.8 -1815.4	 -928.5 -433.9	 82 8, 82

Scandium

For high-temperature properties, see "Rare Earths."

Density of $\text{Sc}_2(\text{SO}_4)_3$

Phase	T	d	References
	$^{\circ}\text{K}$		
c	297	2.605	17
c	298	2.57 ₉	7

Silver

Ag_2SO_4 decomposes above its melting point to Ag metal. In TGA [53] it has appeared stable to 1063 $^{\circ}\text{K}$. but not beyond. Marchal [76] measured decomposition pressures by the static method in the range 1090 to 1493 $^{\circ}\text{K}$. The Ag metal product

melts within this range. For a rough thermodynamic treatment of these data see [60]. These pressures cannot be calculated thermodynamically for lack of high-temperature thermal data for Ag_2SO_4 , though such data are available [2] for Ag (and for Ag_2O). The other data that would be required are tabulated below.

For the transition temperature, a higher value 703 ± 3 $^{\circ}\text{K}$ was obtained by [52].

Density of Ag_2SO_4

Phase	T	d	Reference
	$^{\circ}\text{K}$		
c, II	298	5.363	145

Transitions of Ag_2SO_4

Phase change	T	ΔH	ΔS	References
	$^{\circ}\text{K}$	kJ mol^{-1}	$\text{J mol}^{-1} \text{ deg}^{-1}$	
c, II \rightarrow c, I	685	8.0	11.7	1, 5;
c, I \rightarrow 1.	933	17.	17.	see text 1, 5

Thermodynamic data (298.15 $^{\circ}\text{K}$)

S°			
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
$\text{Ag}_2\text{SO}_4(\text{II})$	200.4	47.9	3, 8
Ag_2O	121.3	29.0	3, 9, 8
Ag	42.70	10.20	3, 9, 8

ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
$\text{Ag}_2\text{SO}_4(\text{II})$	-713.37	-170.50	1, 8
Ag_2O	-31.05	-7.42	9
Ag	0.000	0.000	

Sodium

In the short time of TGA runs, Na_2SO_4 appears stable to beyond 1173 $^{\circ}\text{K}$ [39, 53]. Spitsyn and Shostak [125], in maintaining Na_2SO_4 for 2 hr at each of various temperatures, observed no weight loss at 1073 and 1173 $^{\circ}\text{K}$. 0.04 percent at 1273 $^{\circ}\text{K}$ and 1.05 percent at 1473 $^{\circ}\text{K}$. The composition of the residue showed that both decomposition and

volatilization had occurred. Kröger and Strattmann [67], by the Knudsen effusion method, measured the low-vapor pressure of Na_2SO_4 in the range 1025 to 1124 °K, but not the decomposition pressure. For comparison with their own measurements on K_2SO_4 , they present a curve of the decomposition pressure of Na_2SO_4 based on fragmentary data of Marchal [1929] and Terres [1954] in the range 1473 to 1623 °K with extrapolation down to about 1140 °K. But these data must be in error; near 1100 °K, the decomposition pressure would be higher by a factor of 10^7 than that calculated thermodynamically.

The decomposition pressures in the tables below are based on high-temperature thermal data from [2] and thermodynamic data for 298.15 °K as tabulated. $\text{Na}_2\text{SO}_4(\text{V})$ is the mineral thenardite. The nomenclature for the crystal forms is that of Kracek [66]. The value for the heat of formation of Na_2SO_4 , $-330.90 \text{ kcal mol}^{-1}$, in [1] was calculated there from data of Pitzer and Coulter [113] who used $\text{Na}_2\text{SO}_4(\text{V})$. According to Coughlin [26] there is a constant $\Delta H = 0.74 \text{ kcal mol}^{-1}$ between types V and III from 298 to 450 °K, whence the heat of formation of $\text{Na}_2\text{SO}_4(\text{III})$ at 298.15 °K is taken to be

$$\begin{aligned} -330.90 + 0.74 &= -330.16 \text{ kcal mol}^{-1} \\ &= -1381.4 \text{ kJ mol}^{-1}. \end{aligned}$$

The entropy of Na_2O is uncertain. [3] has an estimated value:

$$18.2 \pm 1.0 \text{ cal mol}^{-1} \text{ deg}^{-1} (= 72.8 \text{ J mol}^{-1} \text{ deg}^{-1}).$$

Density of Na_2SO_4

Phase	<i>T</i>	<i>d</i>	References
	°K		
c, V	298	2.664 ± 0.001	66
c, III	298	2.697 ± 0.001	66
c, I	993	2.64 g/cm^3 (crystallographic)	123
Liquid	1173	2.061	59
	1218	2.039	59
	1263	2.017	59
	1305	1.997	59
	1350	1.971	59

Transitions, of Na_2SO_4

Phase change	<i>T</i>	ΔH	ΔS	References
	°K	kJ mol^{-1}	$\text{J mol}^{-1} \text{ deg}^{-1}$	
c, V \rightarrow c, III	450	3.1 ₀	6.9	5
c, III \rightarrow c, I	515	7.49	14.5 ₆	5
c, I \rightarrow l.	1157	23.8 ₅	20.6 ₃	5

Thermodynamic data (298.15 °K)

	S°		
	$\text{J mol}^{-1} \text{ deg}^{-1}$	$\text{cal mol}^{-1} \text{ deg}^{-1}$	References
$\text{Na}_2\text{SO}_4(\text{V})$	149.5	35.73	1, 3, 8
$\text{Na}_2\text{SO}_4(\text{III})$	156.5	37.4	3
Na_2O	72.8	17.4	1
	76.1 ± 4	18.2 ± 1.0	3
Na_2O_2	94.6	22.6	3, 8
NaO_2	116.	27.7	3, 8

ΔH_f°

	kJ mol^{-1}	kcal mol^{-1}	References
$\text{Na}_2\text{SO}_4(\text{V})$	-1384.5	-330.90	1
$\text{Na}_2\text{SO}_4(\text{III})$	-1381.4	-330.16	see text
Na_2O	-416.	-99.4	1, 10
Na_2O_2	-504.6	-120.6	1
NaO_2	-259.	-61.9	1

Decomposition of Na_2SO_4

(1) $\text{Na}_2\text{SO}_4(\text{c}) \rightleftharpoons \text{Na}_2\text{O}(\text{c}) + \text{SO}_3(\text{g})$
 from $\text{Na}_2\text{SO}_4(\text{III})$: $\Delta H_{298.15}^\circ = 570.3_2 \text{ kJ}$, 136.3_1 kcal
 from $\text{Na}_2\text{SO}_4(\text{V})$: $\Delta H_{298.15}^\circ = 573.4_2 \text{ kJ}$, 137.0_2 kcal
 (2) $\text{Na}_2\text{SO}_4(\text{c}) \rightleftharpoons \text{Na}_2\text{O}(\text{c}) + \text{SO}_2(\text{g}) + 1/2 \text{ O}_2(\text{g})$
 from $\text{Na}_2\text{SO}_4(\text{III})$: $\Delta H_{298.15}^\circ = 668.7_3 \text{ kJ}$, 159.8_3 kcal
 from $\text{Na}_2\text{SO}_4(\text{V})$: $\Delta H_{298.15}^\circ = 671.8_2 \text{ kJ}$, 160.5_2 kcal .

A. Free energies

<i>T</i>	Na_2O	Na_2SO_4	Reaction (1)	
	fef	fef	Δfef	ΔG_T°
	<i>J</i>	<i>J</i>	<i>J</i>	<i>kJ</i>
298.15 (III)	-72.80	-156.48	-172.99	+518.74
400	-75.65	-161.77	-172.62	501.27
500	-81.04	-172.51	-171.43	484.61
514 (III \rightarrow I)		-174.22	-170.90	482.48
600 (I)	-87.28	-187.36	-167.68	469.71
700	-93.68	-202.34	-164.18	455.39
800	-99.87	-216.81	-160.97	441.55
900	-105.90	-230.62	-158.15	427.99
1000	-111.63	-243.80	-155.49	414.83
1100	-117.19	-256.44	-153.04	401.98
298.15 (V)		-149.49	-179.97	+519.76
350		-151.13	-179.96	510.43
400		-154.77	-179.63	501.57
450		-159.70	-179.29	492.74

B. Equilibrium constants

<i>T</i>	log <i>K</i> ₁	<i>K</i> ₁	log <i>K</i> ₂	<i>K</i> ₂
°K				
298.15 (III)	−90.877	1.33×10^{-91}	−103.206	6.22×10^{-104}
400	−65.454	3.52×10^{-66}	−73.292	4.06×10^{-74}
500	−50.622	2.39×10^{-51}	−55.980	1.05×10^{-56}
514	−49.026	9.42×10^{-50}	−54.106	7.83×10^{-55}
600	−40.889	1.29×10^{-41}	−44.535	2.92×10^{-45}
700	−33.979	1.05×10^{-34}	−36.402	3.96×10^{-37}
800	−28.828	1.49×10^{-29}	−30.336	4.61×10^{-31}
900	−24.838	1.45×10^{-25}	−25.636	2.31×10^{-26}
1000	−21.667	2.15×10^{-22}	−21.901	1.26×10^{-22}
1100	−19.085	8.22×10^{-20}	−18.859	1.38×10^{-19}
298.15 (V)	−91.054	8.83×10^{-92}	−103.383	4.14×10^{-104}
350	−76.171	6.75×10^{-77}	−85.946	1.13×10^{-86}
400	−65.492	3.22×10^{-66}	−73.430	3.72×10^{-74}
450	−57.191	6.44×10^{-58}	−63.697	2.01×10^{-64}

C. Equilibrium pressures (atm)

<i>T</i>	SO ₂	O ₂	SO ₃	Total
°K				
298.15 (III)	1.98×10^{-69}	9.89×10^{-70}	1.33×10^{-91}	2.97×10^{-69}
400	1.49×10^{-49}	7.44×10^{-50}	3.52×10^{-66}	2.23×10^{-49}
500	6.03×10^{-38}	3.02×10^{-38}	2.39×10^{-51}	9.05×10^{-38}
514	1.07×10^{-36}	5.35×10^{-37}	9.42×10^{-50}	1.61×10^{-36}
600	2.57×10^{-30}	1.29×10^{-30}	1.29×10^{-41}	3.86×10^{-30}
700	6.80×10^{-25}	3.40×10^{-25}	1.05×10^{-34}	1.02×10^{-24}
800	7.52×10^{-21}	3.76×10^{-21}	1.49×10^{-29}	1.13×10^{-20}
900	1.02×10^{-17}	5.11×10^{-18}	1.45×10^{-25}	1.53×10^{-17}
1000	3.16×10^{-15}	1.58×10^{-15}	2.15×10^{-22}	4.74×10^{-15}
1100	3.37×10^{-13}	1.69×10^{-13}	8.22×10^{-20}	5.06×10^{-13}
298.15 (V)	1.51×10^{-69}	7.54×10^{-70}	8.83×10^{-92}	2.26×10^{-69}
350	6.35×10^{-58}	3.18×10^{-58}	6.75×10^{-77}	9.53×10^{-58}
400	1.40×10^{-49}	7.01×10^{-50}	3.22×10^{-66}	2.10×10^{-49}
450	4.32×10^{-43}	2.16×10^{-43}	6.44×10^{-58}	6.48×10^{-43}

Strontium

SrSO₄(II) is the mineral celestite (celestine). There has been some disagreement on the thermal stability of SrSO₄. Gmelin quotes Grahmann [1913] as finding a 4 percent loss in weight at 1273 °K, while [106] shows a TGA curve level only to 573 °K, then falling off gradually for a total weight loss of 1 percent by 1157 °K. On the other hand, [53] found no weight loss by TGA to beyond 1273 °K, and [90] by a special TGA technique found a "decomposition temperature" of 1647 °K (0.6% loss in 15 min after rapid heating to just below this temperature). Finally, two DTA curves [22, 50] on celestite to 1473 and 1573 °K respectively show notable deflections only for the transition II → I, but no sure sign of a thermal effect attending decomposition.

It is not yet possible to calculate decomposition pressures thermodynamically because high-temperature thermal data are lacking for SrSO₄, though available for the SrO product [2]. The other necessary data are listed below. The entropy of SrSO₄ is uncertain. [3] does not accept the value listed by [1], but has an estimated $28.2 \pm 1.0 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ($118.0 \pm 4 \text{ J mol}^{-1} \text{ deg}^{-1}$) taken from the earlier [60]. We would estimate $28.7 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ($120.1 \text{ J mol}^{-1} \text{ deg}^{-1}$).

Density of SrSO₄

Phase	<i>T</i>	<i>d</i>	Refer- ence
c, II	°K ambient	3.91	129

Transitions of SrSO₄

Phase changes	<i>T</i>	Refer- ences
c, II → c, I c, I → l.	°K 1425 1878	1, 5 1, 5

Thermodynamic data (298.15 °K)

<i>S</i> ^o			
	J mol ^{−1} deg ^{−1}	cal mol ^{−1} deg ^{−1}	Refer- ences
SrSO ₄	121.8	29.1	1
SrO	118.0 54.4	28.1 ± 1.0(2.0) 13.0	3, 8 1, 3, 8

Δ*H*^o

	kJ mol ^{−1}	kcal mol ^{−1}	Refer- ences
SrSO ₄	−1445.	−345.3	1, 8
SrO	−590.4	−141.1	1, 8

Terbium

For high-temperature properties, see "Rare Earths."

Density of Tb₂(SO₄)₃

Phase	<i>T</i> (°K)	<i>d</i>	Refer- ences
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Thermodynamic data (298 °K)

S°			
	J mol ⁻¹ deg	cal mol ⁻¹ deg	Refer- ences
Tb ₂ (SO ₄) ₃ Tb ₂ O ₃ TbO _{1.71} TbO _{1.8}			

 ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	Refer- ences
Tb ₂ (SO ₄) ₃ Tb ₂ O ₃ TbO _{1.71} TbO _{1.8}	 -1827.6 -934.3 -947.3	 -436.8 -223.3 -226.4	 8 8 8

Thallium

Tl(I). According to most of the older literature, as collected in the handbooks of Gmelin, etc., Tl₂SO₄ may be heated as far as the melting point without noticeable decomposition or volatilization, after which it is volatile without decomposition, although one author reported formation of Tl₂O₃. More recently two TGA curves have shown contradictory results. One [108] has a plateau as far as 628 °K, then loss of weight interpreted as formation of Tl₂O₃, not quite complete by 1153 °K. The other [53] shows a plateau to 1000 °K, then rapid volatilization.

Favorskaya and Ponomaryeva [44] measured by a dynamic method vapor pressure of Tl₂SO₄ in the range 973 to 1233 °K, finding no evidence of decomposition. Decomposition pressures cannot be calculated thermodynamically for lack of any high-temperature thermal data. Even the data at 298.15 °K are quite fragmentary. The entropy of Tl₂O listed by [1] is ignored by [3].

Tl(III). Little is known about Tl₂(SO₄)₃. It has been reported (see Gmelin, etc.) to decompose readily to Tl₂SO₄.

Densities

Phase	T	d	Refer- ences
	°K		
Tl ₂ SO ₄ (c)	298	6.77 ± 0.02	46
Tl ₂ SO ₄ (c)	303	6.768 ± 0.003	24
Tl ₂ (SO ₄) ₃ (c)	288	5.22	16

Transitions

Phase change	T	ΔH	ΔS	Refer- ences
	°K	kJ mol ⁻¹	J mol ⁻¹ deg ⁻¹	
Tl ₂ SO ₄ , II → I Tl ₂ SO ₄ , c → I.	765 905	23	25.3	46 1

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	Refer- ences
Tl ₂ SO ₄ Tl ₂ (SO ₄) ₃ Tl ₂ O Tl ₂ O ₃	99.0	23.8	1

 ΔH_f°

	kJ mol ⁻¹	kcal mol ⁻¹	Refer- ences
Tl ₂ SO ₄ Tl ₂ (SO ₄) ₃ Tl ₂ O Tl ₂ O ₃	 -927.6 -175.3	 -221.7 -41.9	 1 1

Thorium

Th(SO₄)₂ is stable to at least 673 °K, the temperature commonly used in preparing the anhydrous salt from the hydrates. At higher temperatures it decomposes before a melting point is reached, to ThO₂ without passing through an oxysulfate intermediate [144, 78]. The equilibrium decomposition pressure measurements (848–1058 °K) of Wöhler, Plüddemann, and Wöhler [144] have been superseded by the better values of Mayer et al. [78], (907–1057 °K). The latter combined their pressure data with their dropping-calorimeter heat-capacity measurements (623–897 °K) to obtain analytic expressions for ΔG° , ΔS° , ΔH° , and $\log K$ for the decomposition reaction. It is from these that we have calculated the pressures tabulated below. [2] has high-temperature thermal data for ThO₂ but not for Th(SO₄)₂.

Density of Th(SO₄)₂

Phase	T	d	References
	°K		
c	291	4.37	16

Transitions of Th(SO₄)₂

Phase change		References
c → c c → l.	None, 297–1057 °K Decomposes	78

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
Th(SO ₄) ₂ ThO ₂	148. 65.3	35.4 15.6	78 3, 8

ΔHf°

	kJ mol ⁻¹ deg ⁻¹	kcal mol ⁻¹ deg ⁻¹	References
Th(SO ₄) ₂ ThO ₂	−2541.4 −1226.7	−607.4 −293.2	78 8

Decomposition of Th(SO₄)₂

- (1) Th(SO₄)₂(c) ⇌ ThO₂(c) + 2SO₃(g)
 $\Delta H_{298.15}^\circ = 524.2 \text{ kJ, } 125.3 \text{ kcal}$
 (2) Th(SO₄)₂(c) ⇌ ThO₂(c) + 2SO₂(g) + O₂(g)
 $\Delta H_{298.15}^\circ = 720.9 \text{ kJ, } 172.3 \text{ kcal.}$

B. Equilibrium constants

T	log K ₁	K ₁	log K ₂	K ₂
°K				
298.15	−69.429	3.72 × 10 ^{−70}	−94.087	8.19 × 10 ^{−95}
400	−46.040	9.12 × 10 ^{−47}	−61.916	1.21 × 10 ^{−62}
500	−32.394	4.04 × 10 ^{−33}	−43.110	7.76 × 10 ^{−44}
600	−23.326	4.72 × 10 ^{−24}	−30.618	2.41 × 10 ^{−31}
700	−16.903	1.25 × 10 ^{−17}	−21.749	1.78 × 10 ^{−22}
800	−12.137	7.30 × 10 ^{−13}	−15.153	7.03 × 10 ^{−16}
900	−8.484	3.28 × 10 ^{−9}	−10.080	8.32 × 10 ^{−11}
1000	−5.612	2.44 × 10 ^{−6}	−6.080	8.32 × 10 ^{−7}
1100	−3.314	4.85 × 10 ^{−4}	−2.862	1.37 × 10 ^{−3}
1200	−1.450	3.55 × 10 ^{−2}	−0.234	5.83 × 10 ^{−1}

C. Equilibrium pressures (atm)

T	SO ₂	O ₂	SO ₃	Total
°K				
298.15	5.47 × 10 ^{−32}	2.74 × 10 ^{−32}	1.93 × 10 ^{−35}	8.21 × 10 ^{−32}
400	2.90 × 10 ^{−21}	1.45 × 10 ^{−21}	9.55 × 10 ^{−24}	4.35 × 10 ^{−21}
500	5.38 × 10 ^{−15}	2.69 × 10 ^{−15}	6.35 × 10 ^{−17}	8.13 × 10 ^{−15}
600	7.84 × 10 ^{−11}	3.92 × 10 ^{−11}	2.17 × 10 ^{−12}	1.20 × 10 ^{−10}
700	7.09 × 10 ^{−8}	3.55 × 10 ^{−8}	3.54 × 10 ^{−9}	1.10 × 10 ^{−7}
800	1.12 × 10 ^{−5}	5.60 × 10 ^{−6}	8.54 × 10 ^{−7}	1.77 × 10 ^{−5}
900	5.50 × 10 ^{−4}	2.75 × 10 ^{−4}	5.73 × 10 ^{−5}	8.82 × 10 ^{−4}
1000	1.19 × 10 ^{−2}	5.92 × 10 ^{−3}	1.56 × 10 ^{−3}	1.93 × 10 ^{−2}
1100	1.40 × 10 ^{−1}	7.00 × 10 ^{−2}	2.20 × 10 ^{−2}	2.32 × 10 ^{−1}
1200	1.05	5.26 × 10 ^{−1}	1.88 × 10 ^{−1}	1.77

Thulium

For high-temperature properties, see “Rare Earths.”

Density of Tm₂(SO₄)₃

Phase	T	d	References
c	°K 297	3.906	17

Tin

Sn (II). At room temperature SnSO₄ is stable for several months in air and much longer in the dark in vacuo, but on heating it undergoes self-oxidation to SnO₂ + SO₂. Thus above 633 °K in O₂-free N₂ complete conversion has been found at 651 °K, but little decomposition below this temperature [31]. Similarly, on heating in air for 2 hr at each of several temperatures, no change was observed at 573 °K, SnSO₄ + SnO₂ (but no oxysulfate) at 623 °K, and only SnO₂ remained at 673 °K; the reaction became fast between 623 °K and 673 °K [57]. In TGA with continuous evacuation, heating at 100°/hr, decomposition began at 593 °K and was complete to SnO₂ by about 870 °K [28].

Sn (IV). Anhydrous Sn(SO₄)₂, very hygroscopic, becomes thermally unstable not far above 373 °K [51]. However, in vacuum TGA, heating at 90°/hr to 573 °K, then at 150°/hr, decomposition first became noticeable near 573 °K with complete conversion to SnO₂ by about 860 °K [28].

No calculation of decomposition pressures is possible. High-temperature thermal data exist only for SnO₂ [2], and the 298.15 °K data are incomplete as shown below.

Densities

Phase	<i>T</i>	<i>d</i>	References
SnSO ₄ (c)	°K ambient	4.185 g/cm ³ (crystallographic)	118
Sn(SO ₄) ₂ (c)	291	3.45	16

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
SnSO ₄			
Sn(SO ₄) ₂			
SnO	56.5	13.5	1, 3, 8
SnO ₂	52.3	12.5	1, 3

ΔH_f°			
	kJ mol ⁻¹	kcal mol ⁻¹	References
SnSO ₄			
Sn(SO ₄) ₂			
SnO	−1646.	−393.4	1, 8
SnO ₂	−286.2	−68.4	1, 8
	−580.7	−138.8	1, 8

Titanium

Ti (II). TiSO₄, uncertain existence.

Ti (III). Ti₂(SO₄)₃ Thermal properties unknown except that it yields TiO₂ on ignition.

Ti (IV). Anhydrous Ti(SO₄)₂ has only recently been prepared [51, 23]. Hayek and Engelbrecht [51] found that it decomposed in 2 steps, beginning at 423 °K, ultimately yielding TiO₂. Chuklantsev [23], by a procedure resembling TGA, heating at 1.7°/min in dry argon, found decomposition beginning at 423 °K to produce TiOSO₄; then near 703 °K this began decomposing to TiO₂, complete by about 873 °K. The decomposition pressures reported by [144] for TiOSO₄ (741–853 °K) are not to be trusted. No pressures can be calculated thermodynamically because high-temperature thermal data are available only for TiO₂ [2].

Densities

Phase	<i>T</i>	<i>d</i>	References
	°K		
Ti(SO ₄) ₂ (c)	293	2.47 ± 0.16	23
TiOSO ₄ (c)	293	3.53 ± 0.21	23

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
Ti ₂ (SO ₄) ₃			
Ti(SO ₄) ₂			
TiOSO ₄			
TiO ₂ (rutile)	50.38	12.04	3, 4
TiO ₂ (anatase)	49.92	11.93	1, 3, 4, 10

ΔH_f°			
	kJ mol ⁻¹	kcal mol ⁻¹	References
Ti(SO ₄) ₃			
Ti(SO ₄) ₂			
TiOSO ₄			
TiO ₂ (rutile)	−943.5	−225.5	10
TiO ₂ (anatase)	−912.5	−218.1	10
TiO _{1.9–2.0}	−943.5	−225.5	8

Uranium

U (III). Difficult to isolate from solution; oxidized readily by H₂O.

U (IV). It is not certain that a pure anhydrous U(SO₄)₂ has been obtained, although hydrates are well known. The latter, on heating, are said to yield first the anhydrous salt (near 570 °K), then UO₂SO₄ even in the absence of air.

U (VI). Anhydrous UO₂SO₄ and several of its hydrates are known. The anhydrous salt is sufficiently stable at 773 °K to permit its preparation by slowly heating the hydrates to that temperature. At high temperatures it decomposes, without melting, to an oxide, the stoichiometry of which depends on conditions, varying between UO₃ and UO₂. Formulas such as U₃O₈ and U₄O₉ are approximated. Because of this nonstoichiometry, Owens and Mayer [92] chose not to attempt equilibrium decomposition-pressure measurements. They report values of *H_T* − *H*₂₉₈ for UO₂SO₄ in the range 373 to 820 °K. These high-temperature thermal data could be used along with those in [2] for UO₂ and UO₃ to calculate two sets of decomposition pressures between which observed values would usually lie, but this hardly seems worth while in view of the uncertainty in the UO₂SO₄ entropy at 298.15 °K upon which such calculations would strongly depend.

Densities

Phase	<i>T</i>	<i>d</i>	References
U(SO ₄) ₂ (c) UO ₂ SO ₄ (c)	°K 291	4.60	16

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
U(SO ₄) ₂ UO ₂ SO ₄	155 ± 25	37 ± 6	92
U ₃ O ₈	282.4	67.5	3, 116a
UO ₂	77.9 ₅	18.63	1, 3, 4, 116a, 8
UO ₃	98.6 ₆	23.58	1, 3, 4, 116a, 8
U ₄ O ₉	336	80.3	3, 116a, 8

Δ*H**f*[°]

	kJ mol ⁻¹	kcal mol ⁻¹	References
U(SO ₄) ₂	-2259	-540	116a
UO ₂ SO ₄	-1888 ± 6	-451.2 ± 1.5	92
U ₃ O ₈	-3574	-854.1	116a
UO ₂	-1084	-259.2	4, 116a, 8
UO ₃	-1226	-293	116a
U ₄ O ₉	-4510	-1078	116a

Vanadium

V (II). Only the hydrate VSO₄ · 7H₂O is known.

V (III). Rivenq [119] described the preparation and pyrolysis of anhydrous V₂(SO₄)₃. On heating in vacuo, the compound was stable 573 to 598 °K but decomposed above 653 °K. According to the author's interpretation of weight-loss curves, the decomposition is complicated, its course dependent on temperature. The final product below 673 °K was V₂O₅, while above 681 °K a mixture of V₂O₄ and V₂O₅ was formed. The results need confirmation by other methods.

V (IV). Anhydrous VOSO₄ decomposes, without melting, above about 673 °K, with oxidation to V₂O₅, SO₃, and SO₂. The reaction is reversible. Neumann and Sonntag [86] measured equilibrium decomposition pressures in the range 704 to 826 °K. For a thermodynamic treatment (sigma function) of these data see [60]. These pressures cannot yet be calculated thermodynamically because high-temperature thermal data are available only for V₂O₅ [2], and the entropy of VOSO₄ is unknown.

V (v). Anhydrous V₂O₅ · 2SO₃, V₂O₅ · 3SO₃, and V₂O₅ · 4SO₃ are known. The preparation of the last of these has been described by Hayek and Engelbrecht [51] who found it to be unstable 373 to 473 °K.

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
VOSO ₄ V ₂ O ₅	131	31.3	1, 3, 4, 8

Δ*H**f*[°]

	kJ mol ⁻¹	kcal mol ⁻¹	References
VOSO ₄ V ₂ O ₅	-1307.5 -1561	-312.5 -373	1 1, 4

Ytterbium

For high-temperature properties, see "Rare Earths."

Density

Phase	<i>T</i>	<i>d</i>	References
YbSO ₄ (c) Yb ₂ (SO ₄) ₃ (c)	°K 297	3.964	17

Yttrium

For high-temperature properties, see "Rare Earths."

Density of Y₂(SO₄)₃

Phase	<i>T</i>	<i>d</i>	References
c	°K 297	2.949	17

Thermodynamic data (298.15 °K)

<i>S</i> [°]			
	J mol ⁻¹ deg	cal mol ⁻¹ deg	References
Y ₂ (SO ₄) ₃ Y ₂ O ₃			

Δ*H**f*[°]

	kJ mol ⁻¹	kcal mol ⁻¹	References
Y ₂ (SO ₄) ₃ Y ₂ O ₃	-1905.4	-455.4	8

Zinc

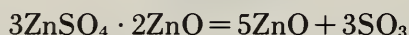
Hoschek [57] quotes Shargorodski [1949] as finding a transition $\alpha \rightarrow \beta$ at 1008 °K, and Gmelin references Friedrich [1911] as reporting one at 1013 °K. Gruver [50] published DTA curves of two samples of ZnSO_4 , one showing clearly a thermal effect beginning at 1013 °K, the other none. [1] and [5] do not list this transformation. Extrapolation of a binary phase diagram [62] yields a melting point at 1003 °K, seemingly impossible. A melting point has not been measured directly and probably cannot be because of decomposition.

Decomposition is through an oxysulfate intermediate, the formula of which has been variously reported. A review is given by Hoschek [57] whose own data yield the formula $2\text{ZnO} \cdot 3\text{ZnSO}_4$. In TGA curves the oxysulfate either does not appear definitely [22] or appears only as a nick, not a plateau [28, 53, 90, 127].

Terem and Akalan [127] report activation energies for the two steps in the decomposition of ZnSO_4 , using a thermogravimetric technique. Between 1113 and 1173 °K, E_a for the reaction



is 212 kJ (50.6 kcal). Between 1233 and 1293 °K E_a for the reaction



is 77.0 kJ (18.4 kcal).

Pechkovsky and coworkers [103], on heating ZnSO_4 under isothermal conditions between 1148 and 1163 °K, observed a change in slope for the degree of decomposition versus time. From the slopes the activation energy for the sulfate decomposition was found to be 271 kJ (64.7 kcal), and for the oxysulfate 385 kJ (92.0 kcal). The latter value differs markedly from that of Terem and Akalan but it is not clear whether both studies are dealing with the same oxysulfate.

Wöhler, Plüddemann, and Wöhler [144] measured decomposition pressures in the range 948 to 1073 °K, but these data are considered unreliable [60]. The pressures tabulated below are based on high-temperature thermal data in [2], and involve an extrapolation of the free-energy function of ZnSO_4 above 1000 °K. Being calculated for the decomposition $\text{ZnSO}_4 \rightarrow \text{ZnO}$, they are intermediate between the somewhat higher pressures expected for $\text{ZnSO}_4 \rightarrow$ oxysulfate and the lower pressures for Oxysulfate $\rightarrow \text{ZnO}$. The entropy of ZnSO_4 is uncertain. The value in [1] is too high. That of [3] used here is an estimate. The heats of formation of ZnSO_4 and ZnO in [1] are subject to revision, but had to be used because they are part of a self-consistent set.

Density of ZnSO_4

Phase	<i>T</i>	<i>d</i>	References
c	288	3.74 ₄	7
c	298	3.546	81

Transitions of ZnSO_4

Phase change	<i>T</i>	References
$\alpha \rightarrow \beta$	°K 1013	see text

Thermodynamic data (298.15 °K)

<i>S</i> °			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	References
ZnSO_4	113	27.0	3
ZnO	43.64	10.43	3, 4, 8

ΔH_f°			
	kJ mol ⁻¹	kcal mol ⁻¹	References
ZnSO_4	-975.3	-233.1 ± 0.2	11
	-978.55	-233.88	1, 8
ZnO	-348.0	-83.17	1, 8

Decomposition of ZnSO_4

- (1) $\text{ZnSO}_4(\text{c}) \rightleftharpoons \text{ZnO}(\text{c}) + \text{SO}_3(\text{g})$
 $\Delta H_{298.15}^\circ = 235.4 \text{ kJ, } 56.26 \text{ kcal}$
 (2) $\text{ZnSO}_4(\text{c}) \rightleftharpoons \text{ZnO}(\text{c}) + \text{SO}_2(\text{g}) + 1/2 \text{ O}_2(\text{g})$
 $\Delta H_{298.15}^\circ = 333.8_0 \text{ kJ, } 79.78 \text{ kcal.}$

A. Free energies

<i>T</i>	ZnO	ZnSO_4	Reaction (1)	
	fef	fef	Δfef	ΔG_T°
°K	<i>J</i>	<i>J</i>	<i>J</i>	<i>kJ</i>
298.15	-43.64	-112.97	-187.34	+179.54
400	-45.33	-116.98	-187.10	160.55
500	-48.66	-124.73	-186.82	141.98
600	-52.47	-133.65	-186.58	123.44
700	-56.36	-142.95	-186.28	105.00
800	-60.19	-152.23	-185.87	86.70
900	-63.85	-161.49	-185.23	68.68
1000	-67.36	-170.58	-184.45	50.94
(1100)	-70.71	-179.43	-183.56	33.47
(1200)	-73.93	-187.92	-182.72	16.129

B. Equilibrium constants

<i>T</i>	log <i>K</i> ₁	<i>K</i> ₁	log <i>K</i> ₂	<i>K</i> ₂
°K				
298.15	-31.452	3.53×10^{-32}	-43.781	1.66×10^{-44}
400	-20.964	1.09×10^{-21}	-28.902	1.25×10^{-29}
500	-14.831	1.48×10^{-15}	-20.189	6.47×10^{-21}
600	-10.746	1.80×10^{-11}	-14.392	4.06×10^{-15}
700	-7.834	1.47×10^{-8}	-10.257	5.53×10^{-11}
800	-5.661	2.18×10^{-6}	-7.169	6.78×10^{-8}
900	-3.986	1.03×10^{-4}	-4.784	1.64×10^{-5}
1000	-2.661	2.18×10^{-3}	-2.895	1.27×10^{-3}
(1100)	-1.589	2.58×10^{-2}	-1.363	4.34×10^{-2}
(1200)	-0.702	1.99×10^{-1}	-0.094	8.05×10^{-1}

C. Equilibrium pressures (atm)

<i>T</i>	SO ₂	O ₂	SO ₃	Total
°K				
298.15	8.19×10^{-30}	4.09×10^{-30}	3.53×10^{-32}	1.23×10^{-29}
400	6.80×10^{-20}	3.40×10^{-20}	1.09×10^{-21}	1.04×10^{-19}
500	4.38×10^{-14}	2.19×10^{-14}	1.48×10^{-15}	6.71×10^{-14}
600	3.20×10^{-10}	1.60×10^{-10}	1.80×10^{-11}	4.99×10^{-10}
700	1.82×10^{-7}	9.15×10^{-8}	1.47×10^{-8}	2.89×10^{-7}
800	2.09×10^{-5}	1.05×10^{-5}	2.18×10^{-6}	3.36×10^{-5}
900	8.15×10^{-4}	4.07×10^{-4}	1.03×10^{-4}	1.33×10^{-3}
1000	1.48×10^{-2}	7.40×10^{-3}	2.18×10^{-3}	2.44×10^{-2}
(1100)	1.56×10^{-1}	7.77×10^{-2}	2.58×10^{-2}	2.59×10^{-1}
(1200)	1.09	5.45×10^{-1}	1.99×10^{-1}	1.84

Transitions of Zr(SO₄)₂

Phase change		Refer-ences
c → c	None observed, 298–1050 °K	
c → l.	Decomposes	

Thermodynamic data (298.15 °K)

S°			
	J mol ⁻¹ deg ⁻¹	cal mol ⁻¹ deg ⁻¹	Refer-ences
Zr(SO ₄) ₂ ZrO ₂ (α)	133.1 50.71	31.8 12.12	estimated 3, 4, 8
Δ <i>H</i> _f °			
	kJ mol ⁻¹	kcal mol ⁻¹	Refer-ences
Zr(SO ₄) ₂ ZrO ₂ (α)	-2500. -1080. ₃ -1085. ₇ -1094.1	-597.4 -258.2 -259.5 -261.5	1 (see text) 1 8 4, 10

Zirconium

Von Hevesy and Cremer [135] attempted to measure equilibrium decomposition pressures of Zr(SO₄)₂ in the range 849 to 905 °K, but were not sure of obtaining true equilibrium. Decomposition was direct to ZrO₂, not through an intermediate oxysulfate, and the sulfate appeared to be less stable than Hf(SO₄)₂. A TGA curve [68] also shows no sign of an oxysulfate.

We calculated decomposition pressures using high-temperature thermal data for Zr(SO₄)₂ from [124] and for ZrO₂ from [2], estimating the entropy of Zr(SO₄)₂; but the pressures so obtained were too low by far more than could be attributed to the uncertainty in the entropy estimate. The difficulty lies rather in the reported [1] heat of formation of Zr(SO₄)₂.

Density of Zr(SO₄)₂

Phase	<i>T</i>	<i>d</i>	Refer-ence
c	°K 289	3.22	16

Relative Thermal Stability of Some Sulfates

In order of increasing stability; criterion: equilibrium partial pressure of SO₃ at 1000 °K. Note that the products are not always the first actually formed.

Sulfate	Product	<i>P</i> _{SO₃}
		<i>atm</i>
Al ₂ (SO ₄) ₃	Al ₂ O ₃	3.74×10^{-1}
CuSO ₄	CuO	1.36×10^{-2}
BeSO ₄	BeO	1.19×10^{-2}
ZnSO ₄	ZnO	2.18×10^{-3}
Th(SO ₄) ₂	ThO ₂	1.56×10^{-3}
MnSO ₄	Mn ₃ O ₄	7.19×10^{-4}
PbSO ₄	PbO (yellow)	1.30×10^{-7}
CaSO ₄	CaO	4.74×10^{-12}
BaSO ₄	BaO	1.45×10^{-17}
Na ₂ SO ₄	Na ₂ O	2.15×10^{-22}

Relative Thermal Stability of Some Sulfates

In order of increasing stability; criterion: equilibrium partial pressure of SO_3 at 298.15 °K. In all instances in this table, the immediate product is believed to be the metal oxide with no change in oxidation number.

Sulfate	P_{SO_3}
	<i>atm</i>
$\text{Sn}(\text{SO}_4)_2$	2×10^{-13}
$\text{Al}_2(\text{SO}_4)_3$	2×10^{-24}
NiSO_4	6×10^{-32}
CoSO_4	1×10^{-34}
$\text{Th}(\text{SO}_4)_2$	2×10^{-35}
MgSO_4	6×10^{-40}
CaSO_4	3×10^{-61}
Li_2SO_4	3×10^{-69}
SrSO_4	5×10^{-71}
BaSO_4	3×10^{-80}
Na_2SO_4	1×10^{-91}
K_2SO_4	7×10^{-110}
Rb_2SO_4	6×10^{-114}
Cs_2SO_4	3×10^{-115}

Arrhenius Activation Energies for the Thermal Dissociation of Some Inorganic Sulfates

Reactant	Product	E_a
		<i>kJ</i>
$\text{Fe}_2(\text{SO}_4)_3$	Fe_2O_3	83.3, 154.
FeSO_4	Fe_2O_3	253.
$\text{Al}_2(\text{SO}_4)_3$	Al_2O_3	268.
CoSO_4	CoO	319.
PbSO_4	PbO	385.
ZnSO_4	$2\text{ZnO} \cdot 3\text{ZnSO}_4$	212, 271.
CuSO_4	$\text{CuO} \cdot \text{CuSO}_4$	212, 238.
$2\text{ZnO} \cdot 3\text{ZnSO}_4$	ZnO	77, 385.
$\text{CuO} \cdot \text{CuSO}_4$	CuO	346, 269.

Melting Points in Increasing Order

Compound	MP	MP
	°K	°C
Ti_2SO_4	905	632
Ag_2SO_4	933	660
ZnSO_4	1003	730
Li_2SO_4	1132	859
Na_2SO_4	1157	884
CdSO_4	1273	1000
Cs_2SO_4	1277	1004
K_2SO_4	1342	1069
Rb_2SO_4	1347	1074
PbSO_4	1360	1087
MgSO_4	1400	1127
BaSO_4	1620	1347
SrSO_4	1878	1605

Boiling Points

None have been measured. The following are calculated from the Law of Corresponding States by Lorenz and Hertz [70].

Compound	BP
	°K
Na_2SO_4	1702
K_2SO_4	1971
Rb_2SO_4	1981
Cs_2SO_4	1900

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