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High Temperature Properties and Decomposition of Inorganic Salts

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
National Bureau of Standards
Washington, D.C.

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Foreword

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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, looseleaf 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:

Category	*Title*
1	General
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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. ΔHf 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.

Contents

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.

Key words: Sulfates, thermodynamic functions, decomposition pressures

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 Sanderson [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:

$$MSO_4 \rightleftarrows MO + SO_3$$

$$SO_3 \rightleftarrows SO_2 + 1/2O_2$$

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 presented above. Although many sulfates do decompose directly to the oxide containing the metallic element with unchanged valence, some show oxidation, e.g., $FeSO_4 \rightarrow Fe_2O_3$, $SnSO_4 \rightarrow SnO_2$, $MnSO_4 \rightarrow Mn_3O_4$ or reduction, e.g., $Ag_2SO_4 \rightarrow Ag^\circ$. Some decompose through an intermediate oxysulfate or basic salt such as $CuO \cdot CuSO_4$, 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.

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[1] Figures 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:

$$MSO_4 \rightleftarrows MO+SO_3 \qquad K=P_{so_3}$$

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:

$$SO_3 \rightleftarrows SO_2 + \tfrac{1}{2} O_2 \qquad K' = \frac{P_{so_2} P_{o_2}^{1/2}}{P_{so_3}}.$$

When both equilibria are attained simultaneously:

$$P_{SO_2} + P_{O_2} = (3/2)(2)^{1/3} (KK')^{2/3}$$

and

$$P_{SO_2} = 2/3(P_{SO_2} + P_{O_2})$$

and

$$P_{O_2} = 1/3(P_{SO_2} + P_{O_2})$$

since

$$P_{SO_2} = 2P_{O_2}.$$

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:

$$MSO_4 \rightleftarrows MO + SO_2 + 1/2O_2$$

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, $P_{SO_2} = 2P_{O_2}$, no longer holds. The general method is shown for the case of $MnSO_4 \rightarrow Mn_3O_4$ 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:

$$MSO_4 = MO + SO_3 \tag{1}$$

$$SO_3 = SO_2 + 1/2\ O_2. \tag{2}$$

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(°K) = temperature in degrees Kelvin, defined in the thermodynamic scale by assigning 273.16 °K to the triple point of water (freezing point, 273.15 °K = 0 °C)
R = gas constant = 8.3143 J mol^{-1} deg^{-1} = 1.98717 cal mol^{-1} deg^{-1}
H° = standard enthalpy
ΔHf° = standard heat of formation
S° = standard entropy
G° = standard Gibbs (free) energy
fef = free energy function $= \dfrac{G^\circ_T - H^\circ_{298.15}}{T}$
TGA = thermogravimetric analysis
DTA = differential thermal analysis.

SO_3, SO_2, and O_2

The SO_3 produced on decomposition of a sulfate dissociates partially to SO_2 and O_2. Data for this secondary equilibrium are presented in tables A, B, and C.

The free energy functions (fef) for SO_3, SO_2, and O_2 (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 SO_2 and 0.02 for SO_3. 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 SO_3. 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 °K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
SO_3	256.6671	61.3449	6
	256.65	61.34	9
SO_2	248.097_4	59.2967	6
	248.1_1	59.30	9, 10
O_2	205.05	49.0070	6
	205.00	48.996	9

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	References
SO_3	-395.2_6	−94.47	6
	−395.72	−94.58	9
SO_2	-296.8_5	−70.947	6, 10
	−296.83	−70.944	9
O_2	0	0	

Dissociation of SO_3

$SO_3(g) \rightleftarrows SO_2(g) + 1/2\ O_2\ (g)$
$\Delta H^\circ_{298.15} = 98.40_8$ kJ, 23.52 kcal, reference [6] data
98.89_3 kJ, 23.63_6 kcal, reference [9] data.

A. Free energies, reference [6] data

T	SO_3	SO_2	O_2	Reaction	
	fef	fef	fef	Δfef	ΔG°_T
°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

T	log K	K
°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

T	Δfef	ΔG°_T	log K	K
°K	J	kJ		
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

$$Al_2(SO_4)_3 = Al_2O_3 + 3\ SO_2 + 3/2\ O_2.$$

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 $k = 1.14 \times 10^{10}$ g cm^{-2} 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 O_2 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 $\gamma - Al_2O_3$ is formed initially, which changes slowly to the stable $\alpha - Al_2O_3$.

Free energy functions for $\alpha - Al_2O_3$ and $Al_2(SO_4)_3$ are calculated from data in [2]. Those calculated from data in [6] are only slightly different.

Density of $Al_2(SO_4)_3$

Phase	T°K	d	References
c	ambient	2.71	89

Transitions of $Al_2(SO_4)_3$

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

Thermodynamic Data (298.15 °K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Al_2(SO_4)_3$	239	57.2	1, 3, 8
$\alpha - Al_2O_3$	50.9_6	12.18	3, 4, 6, 8

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	References
$Al_2(SO_4)_3$	−3435	−821.0	1, 8
$\alpha - Al_2O_3$	−1669.8	−399.09	1

Decomposition of $Al_2(SO_4)_3$

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

A. Free energies

T	Al_2O_3	$Al_2(SO_4)_3$	Reaction (1)	
	fef	fef	Δfef	ΔG°_T
°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
°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
°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 °K. Conversion to AmO_2 was complete by 1070 °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 °K.

Thermodynamic data (298.15 °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

ΔHf°

	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
	°K		
c, II	288	4.499	7

Transitions of $BaSO_4$

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

Thermodynamic data (298.15 °K)

	$S°$		
	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

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	References
$BaSO_4$	−1465.$_2$	−350.2	1, 8
BaO	−558.1	−133.4	1

Decomposition of $BaSO_4$

(1) $BaSO_4(c) \rightleftarrows BaO(c) + SO_3(g)$
$\Delta H^\circ_{298.15} = 511.9_1$ kJ, 122.3_5 kcal
(2) $BaSO_4(c) \rightleftarrows BaO(c) + SO_2(g) + 1/2\ O_2(g)$
$\Delta H^\circ_{298.15} = 610.3_2$ kJ, 145.8_7 kcal.

A. Free Energies

T	BaO	$BaSO_4$	Reaction (1)	
	fef	fef	Δfef	ΔG°_T
°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
°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
°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 $BeSO_4$ 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 $5BeO \cdot SO_3$. 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 SO_3 are retained tenaciously.

Free energy functions for $BeSO_4$ 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 $BeSO_4$ value depends on it. The calculated decomposition pressures above 900 °K are based on an extrapolation of the free energy function (fef) of $BeSO_4$.

Density of $BeSO_4$

Phase	T	*d*	References
	°K		
c	ambient	2.54 *g/cm*^{3}(crystallographic)	49
c	298	2.44$_3$	7

Transitions of $BeSO_4$

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

Thermodynamic data (298.15 °K)

S^0	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$BeSO_4$	77.91	18.62	126
BeO	14.1	3.37	1, 3, 4, 8

$\Delta Hf°$	kJ mol^{-1}	kcal mol^{-1}	References
$BeSO_4$	$-1196._6$	-286.0	1, 8
BeO	-610.9	-146.0	1 (see text)

Decomposition of $BeSO_4$

(1) $BeSO_4(c) \rightleftarrows BeO(c) + SO_3(g)$
$\Delta H°_{298.15} = 190.6$ kJ, 45.5_5 kcal
(2) $BeSO_4(c) \rightleftarrows BeO(c) + SO_2(g) + 1/2\ O_2(g)$
$\Delta H°_{298.15} = 289._0$ kJ, 69.0_7 kcal.

A. Free energies

T	BeO	$BeSO_4$	Reaction (1)	
	fef	fef	Δfef	$\Delta G°_T$
°*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
°*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
°*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

$Bi_2(SO_4)_3$ 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 $Bi_2O_3 \cdot SO_3$ persists at least as high as 1250 °K. The final product is expected to be Bi_2O_3. A complication is the low melting point of this oxide, 1090 °K [5].

Density of $Bi_2(SO_4)_3$

Phase	T	d	References
	°*K*		
c	288	5.08	16

Transitions of $Bi_2(SO_4)_3$

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

Thermodynamic data (298.15 °K)

$S°$	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Bi_2(SO_4)_3$			
Bi_2O_3	$151._5$	36.2	1, 3, 9, 8

$\Delta Hf°$	kJ mol^{-1}	kcal mol^{-1}	References
$Bi_2(SO_4)_3$	-2544.3	-608.1	9, 8
Bi_2O_3	-573.88	-137.16	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 literautre. 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 $2\ CdO \cdot CdSO_4$ 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	*T*	*d*	References
	°K		
c	293	4.692 (20/4)	116
c	297	4.691	7

Transitions of $CdSO_4$

Phase change	*T*	References
c → c	No information	
c → l.	1273	

Thermodynamic data (298.15 °K)

$S°$

	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

$\Delta Hf°$

	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	*T*	*d*	References
	°K		
c, II	298	2.960±0.005	14–5

Transitions of $CaSO_4$

Phase change	*T*	ΔH	ΔS	References
	°K	*kJ mol⁻¹*	*J mol⁻¹ deg⁻¹*	
c, II → c, I	1453	21	$14._2$	5
c, I → l.	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)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$CaSO_4$(II)	$106._7$	25.5	1, 3, 4, 8
CaO	$39._7$	9.5	1, 3, 4, 8

$\Delta Hf°$

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

Decomposition of $CaSO_4$

(1) $CaSO_4(c) \rightleftarrows CaO(c) + SO_3(g)$
$\Delta H^\circ_{298.15} = 401.9_6$ kJ, 96.0_7 kcal
(2) $CaSO_4(c) \rightleftarrows CaO(c) + SO_2(g) + 1/2\ O_2(g)$
$\Delta H^\circ_{298.15} = 500.3_6$ kJ, 119.5_9 kcal.

A. Free energies

T	CaO	$CaSO_4$	Reaction (1)	
	fef	fef	Δfef	ΔG°_T
°K	*J*	*J*	*J*	*kJ*
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

T	$\log K_1$	K_1	$\log K_2$	K_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)

T	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	T	d	References
	°K		
$Ce_2(SO_4)_3$ (c)	294	3.912	17
$Ce(SO_4)_2$ (c)			

Thermodynamic data (298.15 °K)

S°

	J mol^{-1} deg	cal mol^{-1} deg	References
$Ce_2(SO_4)_3$			
$Ce(SO_4)_2$			
Ce_2O_3			
CeO_2			

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	References
$Ce_2(SO_4)_3$			
$Ce(SO_4)_2$			
Ce_2O_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 decomposition pressures could be calculated. Entropies have not been reported for either compound.

Density of Cs_2SO_4

Phase	T	d	References
	°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	T	ΔH	ΔS	References
	°K	*kJ mol⁻¹*	*J mol⁻¹ deg⁻¹*	
c, II → c, I	933			5
c, I → l.	1277	$40._2$	$31._4$	5

Thermodynamic data (298.15 °K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
Cs_2SO_4(II)			
Cs_2O			

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	References
Cs_2SO_4(II)	−1420.0	−339.38	1, 8
Cs_2O	$-317._6$	−75.9	1, 8

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). $Cr_2(SO_4)_3$ 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 $Cr_2(SO_4)_3$

Phase	T	d	References
	°K		
c	298	2.706	81

Transitions of $Cr_2(SO_4)_3$

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

Thermodynamic data (298.15 °K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$Cr_2(SO_4)_3$			
Cr_2O_3	81.1_7	19.4	1, 3, 8

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	References
$Cr_2(SO_4)_3$			
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., $\alpha = kt$. ln 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 Co_3O_4 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 $\log P_{SO_3}$ as functions of temperature, valid only over the experimental range. From these we have calculated Δfef, extrapolating for 900 and 1200 °K. Equilibrium constants and decomposition pressures are calculated from these Δfef values.

The entropy of $CoSO_4$ listed by [1] on which Δfef at 298.15 °K depends, is quite incertain, although close to what one would estimate. Later critical compilations [3, 8] do not list an entropy.

Density of $CoSO_4$

Phase	T	d	References
	°K		
α	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 $CoSO_4$

Phase change	T	ΔH	ΔS	References
	°K	*kJ mol^{-1}*	*J mol^{-1} deg^{-1}*	
$\alpha \rightarrow \beta$	705±8	6.8±0.6	9.6±0.8	109

Thermodynamic data (298.15 °K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$CoSO_4$	$113._4$	27.1	1
CoO	52.97	12.66	3, 8
Co_3O_4	$102._5$	24.5	3, 8

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	References
$CoSO_4$	$-887._0$	-212.0 ± 0.4	11
CoO	$-238._9$	-57.1	19, 8
	$-878.$	$-210.$	1
Co_3O_4	-905.0	-216.3	8

Decomposition of $CoSO_4$

(1) $CoSO_4(c) \rightleftarrows CoO(c) + SO_3(g)$
$\Delta H^\circ_{298.15} = 252.4$ kJ, 60.3_2 kcal
(2) $CoSO_4(c) \rightleftarrows CoO(c) + SO_2(g) + 1/2\ O_2$
$\Delta H^\circ_{298.15} = 351.3$ kJ, 83.9_6 kcal.

A. Free energies, reaction (1)

T	Δfef	ΔG°_T
°K	*J*	*kJ*
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

T	$\log K_1$	K_1	$\log K_2$	K_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)

T	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). Cu_2SO_4 oxidizes in air.

Cu (II). There is general agreement that the first product of the decomposition of $CuSO_4$ is an oxysulfate, $CuO \cdot CuSO_4$. 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 SO_3 content because these gases also displace the $SO_3 = SO_2 + 1/2\ O_2$ 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

$$CuSO_4 \rightleftarrows CuO \cdot CuSO_4 + \text{gases}$$

$$CuO \cdot CuSO_4 \rightleftarrows CuO + \text{gases}$$

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

$$CuSO_4 \rightleftarrows CuO + \text{gases}$$

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 ± 1.0 cal mol^{-1} 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 ± 0.6 kcal mol^{-1} (767.3 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	T	d	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	T	ΔH	ΔS	References
	°K			
α → β	?	No data	No data	
c → l	decomposes			

Thermodynamic data (298.15 °K)

$S°$

	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_2O	93.7	22.4	3, 8

$\Delta Hf°$

	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_2O	−1667.	−39.84	1, 8

Decomposition of $CuSO_4$

$$(1)\ CuSO_4(c) \rightleftarrows CuO(c) + SO_3(g)$$
$$\Delta H^\circ_{298.15} = 219.4_5\ \text{kJ},\ 52.4_5\ \text{kcal}$$
$$(2)\ CuSO_4(c) \rightleftarrows CuO(c) + SO_2(g) + 1/2\ O_2(g)$$
$$\Delta H^\circ_{298.15} = 317.8_6\ \text{kJ},\ 75.9_7\ \text{kcal.}$$

A. Free energies

T	CuO	$CuSO_4$	Reaction (1)	
	fef	fef	Δfef	ΔG°_T
°K	*J*	*J*	*J*	*kJ*
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

T	log K_1	K_1	log K_2	K_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)

T	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 $Dy(SO_4)_3$

Phase	T	d	References
	°K		
c	297	3.801	17

Erbium

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

Density of $Er_2(SO_4)_3$

Phase	T	d	References
	°K		
c	297	3.851	17

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Er_2(SO_4)_3$			
Er_2O_3			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Er_2(SO_4)_3$			
Er_2O_3	$-1897._9$	-453.6	8

Europium

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

Density

Phase	T	d	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)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Gd_2(SO_4)_3$			
Gd_2O_3			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Gd_2(SO_4)_3$			
Gd_2O_3	$-1815._9$	-434.0	8

Gallium

$Ga_2(SO_4)_3$ decomposes, without melting, to Ga_2O_3. Marchal [76] measured equilibrium decomposition pressures over the range 833 to 973 °K, from which it appears that this compound is less stable than $Al_2(SO_4)_3$. Pressures cannot yet be calculated thermodynamically.

Density of $Ga_2(SO_4)_3$

Phase	T	d	References
	°K		
c	296	3.239	17

Thermodynamic data (298.15 °K)

S°

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$Ga_2(SO_4)_3$ $Ga_2O_3(\beta)$	84.9	20.3	3, 8

Δ*Hf*°

	kJ mol⁻¹	kcal mol⁻¹	References
$Ga_2(SO_4)_3$ $Ga_2O_3(\beta)$	−1079.	−258	1, 8

Germanium

Density of $Ge(SO_4)_2$

Phase	*T*	*d*	References
c	°*K* 295	3.92	121

Thermodynamic Data (298.15 °K)

S°

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$Ge(SO_4)_2$ GeO_2(c, soln.)	55.2_7	13.21	3

Δ*Hf*°

	kJ mol⁻¹	kcal mol⁻¹	References
$Ge(SO_4)_2$ GeO_2(c)	−539.7	−129.0	5

Hafnium

Von Hevesy and Cremer [135] attempted to measure equilibrium decomposition pressures of $Hf(SO_4)_2$ 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 $Zr(SO_4)_2$.

Thermodynamic data (298.15 °K)

S°

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$Hf(SO_4)_2$ HfO_2	59.33	14.18	3, 4, 8

Δ*Hf*°

	kJ mol⁻¹	kcal mol⁻¹	References
$Hf(SO_4)_2$ HfO_2	−1113.1	−266.0	4, 8

Holmium

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

Density of $Ho_2(SO_4)_3$

Phase	*T*	*d*	References
c	°*K* 297	3.830	17

Thermodynamic data (298.15 °K)

S°

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$Ho_2(SO_4)_3$ Ho_2O_3			

Δ*Hf*°

	kJ mol⁻¹	kcal mol⁻¹	References
$Ho_2(SO_4)_3$ Ho_2O_3	−1881.1	−449.6	8

Indium

Seward [122] measured equilibrium decomposition pressures of $In_2(SO_4)_3$ over the range 918 to 1093 °K, from which it appeared to be more stable than $Al_2(SO_4)_3$. 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 $In_2(SO_4)_3$

Phase	T	d	References
	°K		
c	298	3.43_8	7

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$In_2(SO_4)_3$			
In_2O_3			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$In_2(SO_4)_3$	$290_8.$	−695	1
In_2O_3	−930.9	−222.5	1
	−926.8	−221.5	8

Iridium

Ir (III). $Ir_2(SO_4)_3$ is known with certainty only as a hydrate, oxidizing in air.

Ir (IV). $Ir(SO_4)_2$ has been reported.

Iron

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

The decomposition of $Fe_2(SO_4)_3$ to Fe_2O_3 is reversible, without the formation of an intermediate oxysulfate. $FeSO_4$ 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 $Fe_2(SO_4)_3$ (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 $Fe_2(SO_4)_3$. With $FeSO_4$, irreversibility prevented approaching pressures from two directions. Later, Warner and Ingraham [137] published values for $Fe_2(SO_4)_3$ (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

$$2FeSO_4 = 2FeO + 2SO_3 \quad (1)$$

$$SO_3 = SO_2 + 1/2O_2 \quad (2)$$

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3 \quad (3)$$

corresponding to the net reaction

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3. \quad (4)$$

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

$$Fe_2O_3 + 3SO_3 = Fe_2(SO_4)_3. \quad (5)$$

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 $Fe_2(SO_4)_3$ 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.

$Fe_2(SO_4)_3$

The decomposition of $Fe_2(SO_4)_3$ 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 $\frac{p_e(SO_2)-p(SO_2)}{p_e(SO_2)}$, 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

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

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

and for the reaction

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_2 + 3/2\ O_2$$

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

Since the equilibrium $SO_3 = SO_2 + 1/2\ O_2$ 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	*T*	*d*	References
	°*K*		
$FeSO_4$(c)	288	3.346	130
$Fe_2(SO_4)_3$(c)	ambient	3.10	89

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$FeSO_4$	107.$_5$	25.7	3, 8
$Fe_2(SO_4)_3$			
$FeO(Fe_{0.947}O)$	563.6	13.74	3
Fe_3O_4	146.$_4$	35.0	1, 3
Fe_2O_3	87.4	20.9	3

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$FeSO_4$	−922.6	−220.5	1, 8
$Fe_2(SO_4)_3$			
$FeO(Fe_{0.947}O)$	−266.$_5$	−63.7	1
	−264.$_4$	−63.2	8
Fe_3O_4	−1117.	−267.0	1, 8
Fe_2O_3	−822.1$_5$	−196.5	1, 8

Lanthanum

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

Density of $La_2(SO_4)_3$

Phase	*T*	d	References
	°*K*		
c	294	3.829	17

Transitions of $La_2(SO_4)_3$

Phase change	
c → l.	Decomposition

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg	cal mol^{-1} deg^{-1}	References
$La_2(SO_4)_3$			
La_2O_3			

$\Delta Hf°$

	kJ mol^{-1} deg	kcal mol^{-1}	References
$La_2(SO_4)_3$			
La_2O_3	-1801.2	-430.5	8

Lead

Pb (II). Because $PbSO_4$ 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 $PbSO_4$. Some have congruent melting points and form eutectics with PbO or $PbSO_4$; for a summary and references see [96b] and for thermodynamics, see [60]. [1] lists $PbO \cdot PbSO_4$, mp 1243 °K, $2PbO \cdot PbSO_4$, mp 1223 °K. The former is the mineral lanarkite. Hoschek [57] found three intermediates before PbO in the pyrolysis of $PbSO_4$, the two oxysulfates above and $4PbO \cdot PbSO_4$. 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

$$PbSO_4 \rightleftarrows PbO + SO_3.$$

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 $Pb(SO_4)_2$ has not been prepared free of H_2SO_4.

Density of $PbSO_4$

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

Transitions of $PbSO_4$

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

$\Delta Hf°$

	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 $PbSO_4$

(1) $PbSO_4(c) \rightleftarrows PbO(c) + SO_3(g)$
to yellow PbO: $\Delta H^\circ_{298.15} = 305.3_5$ kJ, 72.98 kcal
to red PbO: $\Delta H^\circ_{298.15} = 303.9_7$ kJ, 72.65 kcal
(2) $PbSO_4(c) \rightleftarrows PbO(c) + SO_2(g) + 1/2\ O_2(g)$
to yellow PbO: $\Delta H^\circ_{298.15} = 403.7_6$ kJ, 96.50 kcal
to red PbO: $\Delta H^\circ_{298.15} = 402.3_8$ kJ, 96.17 kcal.

A. Free energies

T	PbO (yellow)	$PbSO_4$	Reaction (1)	
	fef	fef	Δfef	ΔG°_T
°K	*J*	*J*	*J*	*kJ*
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)

T	log K_1	K_1	log K_2	K_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)

T	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 Li_2SO_4 begins to be noticeable not far above its melting point [59, 125], the Li_2O product apparently dissolving in the Li_2SO_4, while some volatilization of the Li_2SO_4 occurs. No measurements of decomposition pressures have been made, nor can the pressures be calculated thermodynamically. High-temperature thermal data exist for Li_2O [2] but not for Li_2SO_4.

Density of Li_2SO_4

Phase	T	d	References
	°K		
c, II	298	2.221	7
c, I	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 Li_2SO_4

Phase changes	T	ΔH	ΔS	References
	°K	*kJ mol⁻¹*	*J mol⁻¹ deg⁻¹*	
Li_2SO_4, c II → c I	859	$27._2$	$31._8$	5
c, I → l.	1132	7.5	6.7	5

Thermodynamic data (298.15 °K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
Li_2SO_4(II)			
Li_2O	37.89	9.056	10

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	References
Li_2SO_4(II)	−1434.4	−342.83	1, 8
Li_2O	−595.8	−142.4	1, 8
	−598.7	−143.1 ± 0.5	10

Lutetium

See "Rare Earths"

Magnesium

$MgSO_4$ 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 °K) are thought to be too high because of attack on the boat. Knopf and Staude [64] made measurements (1144–1313 °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 $MgSO_4$, 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 $MgSO_4$ has been studied in a flow system in the range 1223 to 1323 °K [98]. When N_2 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 $SO_3 = SO_2 + 1/2\ O_2$ is not established.

If these gases flow over the salt at 3 l/hr the reaction rate is nearly independent of oxygen content, but the proportion of SO_3 relative to SO_2 decreases with decreasing O_2 content. The activation energy in the range 1293 to 1333 °K is 661 kJ (158.0 kcal) [103].

Density of $MgSO_4$

Phase	T	d	References
	°K		
c, II	288	2.71	130
c, II	298	2.66	7

Transitions of Mg $MgSO_4$

Phase change	T	ΔH		ΔS	References
	°K	*kJ mol⁻¹*		*J mol⁻¹ deg⁻¹*	
c, II → c, I	1283		No data		5
c, I → l.	1400	$14._6$		$10._4$	5, cf. 114

Thermodynamic data (298.15 °K)

$S°$

	J mol⁻¹ deg⁻¹	*cal mol⁻¹deg⁻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

$\Delta Hf°$

	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 $MnSO_4$, 700 °C, quoted in handbooks, is erroneous. Decomposition begins before melting. The product usually observed on pyrolysis in air is Mn_3O_4, as in TGA [28, 90], though Mn_2O_3 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 °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 $MnSO_4$ to 1200 °K. We also calculated the pressures for decomposition to Mn_2O_3. A comparison of these two sets of pressures with the calculated oxygen pressures for pairs of the four oxides of manganese show that Mn_3O_4 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 $P_{SO_2}=3P_{O_2}$, obtaining pressures slightly lower than those tabulated here.

Mn (III). $Mn_2(SO_4)_3$ is said to be stable at 473 °K, decomposition beginning about 100° higher, to $MnSO_4$, O_2, and SO_3.

Mn (IV). $Mn(SO_4)_2$ is somewhat unstable at room temperature.

Calculation of Partial Pressures

There are four equilibrium equations and corresponding equilibrium constants:

(a) $SO_3 \rightleftarrows SO_2 + 1/2\ O_2$

$$K_1=\frac{(P_{SO_2})(P_{O_2})^{1/2}}{(P_{SO_3})}$$

(b) $3\ MnSO_4 \rightleftarrows Mn_3O_4 + 3\ SO_2 + O_2$

$$K_2=(P_{SO_2})^3(P_{O_2})$$

(c) $3\ MnSO_4 \rightleftarrows Mn_3O_4 + 2\ SO_3 + SO_2$

$$K_3=(P_{SO_3})^2(P_{SO_2})$$

(d) $6\ MnSO_4 + O_2 \rightleftarrows 2\ Mn_3O_4 + 6\ SO_3$

$$K_4=\frac{(P_{SO_3})^6}{(P_{O_2})}.$$

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: $K_2=K_1^2K_3$. The required third relation is obtained from:

SO_2	O_2	SO_3	
x	$\frac{x}{3}$	0	moles formed in reaction *b*
$-n$	$\frac{-n}{2}$	$+n$	moles formed in reaction *a*
$(x-n)$	$\left(\frac{x}{3}-\frac{n}{2}\right)$	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:

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

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

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

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

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:

$$P_{SO_3}=n$$

$$P_{SO_2}=\frac{K_3}{(P_{SO_3})^2}$$

$$P_{O_2}=\frac{P_{SO_2}}{3}-\frac{P_{SO_3}}{6}.$$

Densities

Phase	T	d	References
	°K		
$MnSO_4$(c)	298	3.181 (25/4)	81
$Mn_2(SO_4)_3$(c)	288	3.24 (g/cm³)	16

Thermodynamic data (298.15 °K)

$S°$

	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
$Mn_3O_4(\alpha)$	154.	36.8	91
Mn_2O_3	$110._5$	26.4	3, 8
MnO_2(I)	53.05	12.68	1, 3, 8

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	References
$MnSO_4$	-1063.7_4	−254.24	1, 4, 8
MnO	−385.1	−92.05	1, 4, 8
$Mn_3O_4(\alpha)$	$-1386._6$	−331.4	4, 8
Mn_2O_3	−956.9	−228.7	91
MnO_2(I)	−520.9	−124.5	1, 8

Decomposition of $MnSO_4$

$$3\ MnSO_4(c) \rightleftarrows Mn_3O_4(\alpha) + 3\ SO_2(g) + O_2(g)$$
$$\Delta H^\circ_{298} = 914.1\ kJ,\ 218.4_7\ kcal.$$

A. Free energies

T	Mn_3O_4	$MnSO_4$	Δfef	ΔG°_T
	fef	fef		
°*K*	*J*	*J*	*J*	*kJ*
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

T	log K	K
°*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)

T	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 Hg_2SO_4 as unstable to light, disproportionating to Hg° and $HgSO_4$, and melting with decomposition to Hg°, O_2, and SO_2.

Hg (II). According to a recent study by Hoschek [57], $HgSO_4$ is unchanged after 2 hr at 673 °K, but by 773 °K decomposition occurs to $HgO \cdot HgSO_4$ and then $2HgO \cdot HgSO_4$, 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 $HgSO_4$ is heated rapidly to 973 °K, some Hg_2SO_4 appears along with the oxysulfates before volatilization is complete. No thermal data above 298 °K exist for any of these compounds.

Densities

Phase	T	d	References
	°*K*		
$HgSO_4(c)$	298	6.49 (pycnometric)	13
	298	6.50 (crystallographic)	13

Thermodynamic data (298.15 °K)

S°

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$HgSO_4$			
Hg_2SO_4	201.	48.0	1, 3, 9, 8
Hg_2O			
HgO (red)	70.3	16.8	3, 8, 10
HgO (yellow)	72.4	17.3	3

ΔHf°

	kJ mol⁻¹	kcal mol⁻¹	References
$HgSO_4$	−704.2	−168.3	1, 8
Hg_2SO_4	-743.1_2	−177.61	9
Hg_2O	−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 $Nd_2(SO_4)_3$

Phase	T	d	References
c	°K 294	3.961	17

Thermodynamic data (298.15 °K)

	$S°$		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Nd_2(SO_4)_3$			
Nd_2O_3			

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	References
$Nd_2(SO_4)_3$			
Nd_2O_3	−1782.4	−426.0	8

Nickel

$NiSO_4$ 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 $CoSO_4$ and agree that $NiSO_4$ 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 $NiSO_4$. Such data are available for NiO [2]. The necessary thermodynamic constants at 298 °K are known, as tabulated below, except the entropy of $NiSO_4$. [1] gives a value for it that seems much too low; [3] does not list one.

Density of $NiSO_4$

Phase	T	d	References
c	°K 288	3.543(25/4)	81

Transitions of $NiSO_4$

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

Thermodynamic data (298.15 °K)

	$S°$		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$NiSO_4$			
NiO	38.0	9.08	3, 8

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	References
$NiSO_4$	$-870._7$	-208.1 ± 0.2	11
NiO	$-239._7$	-57.3 ± 0.1	19

Palladium

Anhydrous $PdSO_4$ has not been prepared free of H_2O or H_2SO_4. The hydrate $PdSO_4 \cdot 2H_2O$ on heating loses H_2O, then SO_2, yielding ultimately the metal.

Density of $PdSO_4$

Phase	T	d	References
c	°K 287	4.012	17

Plutonium

For the oxidation states Pu (III) and Pu (VI) (PuO_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 $Pu(SO_4)_2$ by heating materials initially containing H_2O and H_2SO_4 let to a product of composition varying with conditions. TGA showed a $Pu(SO_4)_2$ plateau that was not quite level, followed by a drop to the $PuO_{2.09}$ level.

Polonium

Like tellurium, Po forms a basic sulfate, $2PoO_2 \cdot SO_3$, but in contrast to Te it also forms a normal sulfate $Po(SO_4)_2$ 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	*T*	*d*	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	*T*	Δ*H*	Δ*S*	References
	°K	*kJ mol*$^{-1}$	*J mol*$^{-1}$ *deg*$^{-1}$	
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)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
K_2SO_4(II)	$175._7$	42.0	1, 3, 8
K_2O			
KO_2	$116._7$	27.9	3, 8

Δ*Hf*°

	kJ mol^{-1}	kcal mol^{-1}	References
K_2SO_4(II)	−1436.9	−342.66	1, 8
K_2O	$-361._5$	−86.4	1, 8
KO_2	$-28_0.$	−67.	1
	−283.	−67.7	8

Praseodymium

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

Density of $Pr_2(SO_4)_3$

Phase	T	d	References
	°K		
c	297	3.797	17

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Pr_2(SO_4)_3$			
Pr_2O_3			
$PrO_{1.72}$			
$PrO_{1.833}$			
PrO_2			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Pr_2(SO_4)_3$			
Pr_2O_3	−1827.6	−436.8	8
$PrO_{1.72}$	−937.2	−224.0	8
$PrO_{1.833}$	−952.3	−227.6	8
PrO_2	−1004.2	−240.0	8

Radium

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$RaSO_4$	$14_2.$	34	1
RaO			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$RaSO_4$	$-147_3.$	−352	1
RaO	−523.	−125	1

Rare Earths

On heating, all of the anhydrous sulfates of the trivalent rare-earth elements and yttrium, type formula $R_2(SO_4)_3$, decompose, without first melting, to basic salts (oxysulfates) of the type $R_2O_3 \cdot SO_3$, 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.

$$R_2(SO_4)_3 \rightarrow R_2O_3 \cdot SO_3 + 2SO_3 \qquad (a)$$

$$R_2O_3 \cdot SO_3 \rightarrow R_2O_3 + SO_3. \qquad (b)$$

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 °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 °K and of reaction (b) at 1573 °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, $Sc_2(SO_4)_3$ 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).

$Ce_2(SO_4)_3$ is much less stable than the sulfates of the other rare earths [83, 142, 143], and less stable than $Sc_2(SO_4)_3$ [143]. The product is CeO_2 rather than Ce_2O_3, but the mechanism is unknown. Least stable by far is $Ce(SO_4)_2$ 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 $2Ce(SO_4)_2 \rightleftarrows Ce_2(SO_4)_3 + SO_3 + 1/2\ O_2$. Duval [34] by TGA found an intermediate $3CeO_2 \cdot 4SO_3$.

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 $R_2(SO_4)_3$ and $R_2O_3 \cdot SO_3$, 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:

La-Y-Lu— —Gd-Sc-Ce(III)-Ce(IV).

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 $Rh_2(SO_4)_3$ is difficult to prepare in pure form. The reported density needs confirmation.

Density of $Rh_2(SO_4)_3$

Phase	T	d	Reference
	°K		
c	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	T	d	References
	°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	T	References
	°K	
c, II → c, I	923	1
c, I → l.	1347	1

Thermodynamic data (298.15 °K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
Rb_2SO_4			
Rb_2O			

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	References
Rb_2SO_4	−1424.7	−340.5	1, 8
Rb_2O	−330.	−78.9	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
	°K		
$SmSO_4(c)$			
$Sm_2(SO_4)_3(c)$	297	4.059	17

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$SmSO_4$			
$Sm_2(SO_4)_3$			
Sm_2O_3			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$SmSO_4$			
$Sm_2(SO_4)_3$	−3884.8	−928.5	82
Sm_2O_3	−1815.4	−433.9	8, 82

Scandium

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

Density of $Sc_2(SO_4)_3$

Phase	*T*	*d*	References
	°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 °K, but not beyond. Marchal [76] measured decomposition pressures by the static method in the range 1090 to 1493 °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 °K was obtained by [52].

Density of Ag_2SO_4

Phase	*T*	*d*	Reference
	°K		
c, II	298	5.363	145

Transitions of Ag_2SO_4

Phase change	*T*	ΔH	ΔS	References
	°K	*kJ* mol^{-1}	*J* mol^{-1} deg^{-1}	
c, II → c, I	685	8.0	$11._7$	1, 5; see text
c, I → l.	933	$1_7.$	$1_7.$	1, 5

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Ag_2SO_4(II)$	$200._4$	47.9	3, 8
Ag_2O	$121._3$	29.0	3, 9, 8
Ag	42.70	10.20	3, 9, 8

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Ag_2SO_4(II)$	−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 °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 °K, 0.04 percent at 1273 °K and 1.05 percent at 1473 °K. The composition of the residue showed that both decomposition and volatilization had occurred. Kröger and Stratmann [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. $Na_2SO_4(V)$ 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 kcal mol^{-1}, in [1] was calculated there from data of Pitzer and Coulter [113] who used $Na_2SO_4(V)$. According to Coughlin [26] there is a constant $\Delta H = 0.74$ kcal mol^{-1} between types V and III from 298 to 450 °K, whence the heat of formation of $Na_2SO_4(III)$ at 298.15 °K is taken to be

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

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

18.2 ± 1.0 cal mol^{-1} deg^{-1} (= 72.8 J mol^{-1} deg^{-1}).

Density of Na_2SO_4

Phase	T	d	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	T	ΔH	ΔS	References
	°K	*kJ mol^{-1}*	*J mol^{-1} deg^{-1}*	
c, V → c, III	450	3.1_0	6.9	5
c, III → c, I	515	7.49	14.5_6	5
c, I → l.	1157	23.8_5	20.6_3	5

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Na_2SO_4(V)$	149.5	35.73	1, 3, 8
$Na_2SO_4(III)$	$156._5$	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

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Na_2SO_4(V)$	−1384.5	−330.90	1
$Na_2SO_4(III)$	−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) $Na_2SO_4(c) \rightleftarrows Na_2O(c) + SO_3(g)$
from Na_2SO_4 (III): $\Delta H^\circ_{298.15} = 570.3_2$ kJ, 136.3_1 kcal
from Na_2SO_4(V): $\Delta H^\circ_{298.15} = 573.4_2$ kJ, 137.0_5 kcal
(2) $Na_2SO_4(c) \rightleftarrows Na_2O(c) + SO_2(g) + 1/2\ O_2(g)$
from Na_2SO_4 (III): $\Delta H^\circ_{298.15} = 668.7_3$ kJ, 159.8_3 kcal
from Na_2SO_4 (V): $\Delta H^\circ_{298.15} = 671.8_2$ kJ, 160.5_7 kcal.

A. Free energies

T	Na_2O	Na_2SO_4	Reaction (1)	
	fef	fef	Δfef	ΔG°_T
°K	*J*	*J*	*J*	*kJ*
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 → 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

T	log K_1	K_1	log K_2	K_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)

T	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

$SrSO_4$(II) is the mineral celestite (celestine). There has been some disagreement on the thermal stability of $SrSO_4$. 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 $SrSO_4$, though available for the SrO product [2]. The other necessary data are listed below. The entropy of $SrSO_4$ is uncertain. [3] does not accept the value listed by [1], but has an estimated 28.2 ± 1.0 cal mol^{-1} deg^{-1} (118.0 ± 4 J mol^{-1} deg^{-1}) taken from the earlier [60]. We would estimate 28.7 cal mol^{-1} deg^{-1} (120.1 J mol^{-1} deg^{-1}).

Density of $SrSO_4$

Phase	T	d	Reference
	°K		
c, II	ambient	3.91	129

Transitions of $SrSO_4$

Phase changes	T	References
	°K	
c, II → c, I	1425	1, 5
c, I → l.	1878	1, 5

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$SrSO_4$	121.8	29.1	1
	118.0	28.1±1.0(2.0)	3, 8
SrO	54.4	13.0	1, 3, 8

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$SrSO_4$	−1445.	−345.3	1, 8
SrO	−590.4	−141.1	1, 8

Terbium

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

Density of $Tb_2(SO_4)_3$

Phase	T(°K)	d	References

Thermodynamic data (298 °K)

$S°$

	J mol^{-1} deg	cal mol^{-1} deg	References
$Tb_2(SO_4)_3$			
Tb_2O_3			
$TbO_{1.71}$			
$TbO_{1.8}$			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Tb_2(SO_4)_3$			
Tb_2O_3	−1827.6	−436.8	8
$TbO_{1.71}$	−934.3	−223.3	8
$TbO_{1.8}$	−947.3	−226.4	8

Thallium

Tl(I). According to most of the older literature, as collected in the handbooks of Gmelin, etc., Tl_2SO_4 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 Tl_2O_3. 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 Tl_2O_3, 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 Tl_2SO_4 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 Tl_2O listed by [1] is ignored by [3].

Tl(III). Little is known about $Tl_2(SO_4)_3$. It has been reported (see Gmelin, etc.) to decompose readily to Tl_2SO_4.

Densities

Phase	T	d	References
	°K		
Tl_2SO_4(c)	298	6.77 ± 0.02	46
Tl_2SO_4(c)	303	6.768 ± 0.003	24
$Tl_2(SO_4)_3$(c)	288	5.22	16

Transitions

Phase change	T	ΔH	ΔS	References
	°K	kJ mol^{-1}	J mol^{-1} deg^{-1}	
Tl_2SO_4, II → I	765			46
Tl_2SO_4, c → l.	905	23	25.$_5$	1

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
Tl_2SO_4			
$Tl_2(SO_4)_3$			
Tl_2O	99.0	23.8	1
Tl_2O_3			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
Tl_2SO_4	−927.6	−221.7	1
$Tl_2(SO_4)_3$			
Tl_2O	−175.$_3$	−41.9	1
Tl_2O_3			

Thorium

$Th(SO_4)_2$ 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 ThO_2 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 $\Delta G°$, $\Delta S°$, $\Delta H°$, 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 ThO_2 but not for $Th(SO_4)_2$.

Density of $Th(SO_4)_2$

Phase	T	d	References
	°K		
c	291	4.37	16

Transitions of $Th(SO_4)_2$

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

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$Th(SO_4)_2$	148.	35.4	78
ThO_2	65.3	15.6	3, 8

$\Delta Hf°$

	kJ mol^{-1} deg^{-1}	kcal mol^{-1} deg^{-1}	References
$Th(SO_4)_2$	−2541.4	−607.4	78
ThO_2	−1226.7	−293.2	8

Decomposition of $Th(SO_4)_2$

(1) $Th(SO_4)_2(c) \rightleftarrows ThO_2(c) + 2SO_3(g)$
$\Delta H^\circ_{298.15} = 524.2$ kJ, 125.3 kcal
(2) $Th(SO_4)_2(c) \rightleftarrows ThO_2(c) + 2SO_2(g) + O_2(g)$
$\Delta H^\circ_{298.15} = 720.9$ kJ, 172.3 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 $Tm_2(SO_4)_3$

Phase	T	d	References
	°*K*		
c	297	3.906	17

Tin

Sn (II). At room temperature $SnSO_4$ is stable for several months in air and much longer in the dark in vacuo, but on heating it undergoes self-oxidation to $SnO_2 + SO_2$. Thus above 633 °K in O_2-free N_2 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, $SnSO_4 + SnO_2$ (but no oxysulfate) at 623 °K, and only SnO_2 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 SnO_2 by about 870 °K [28].

Sn (IV). Anhydrous $Sn(SO_4)_2$, 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 SnO_2 by about 860 °K [28].

No calculation of decomposition pressures is possible. High-temperature thermal data exist only for SnO_2 [2], and the 298.15 °K data are incomplete as shown below.

Densities

Phase	T	d	References
	°K		
$SnSO_4$(c)	ambient	4.185 g/cm³ (crystallographic)	118
$Sn(SO_4)_2$(c)	291	3.45	16

Thermodynamic data (298.15 °K)

$S°$

	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

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	References
$SnSO_4$			
$Sn(SO_4)_2$	−1646.	−393.4	1, 8
SnO	$-286._2$	−68.4	1, 8
SnO_2	−580.7	−138.8	1, 8

Titanium

Ti (II). $TiSO_4$, uncertain existence.

Ti (III). $Ti_2(SO_4)_3$ Thermal properties unknown except that it yields TiO_2 on ignition.

Ti (IV). Anhydrous $Ti(SO_4)_2$ has only recently been prepared [51, 23]. Hayek and Engelbrecht [51] found that it decomposed in 2 steps, beginning at 423 °K, ultimately yielding TiO_2. Chuklantsev [23], by a procedure resembling TGA, heating at 1.7°/min in dry argon, found decomposition beginning at 423 °K to produce $TiOSO_4$; then near 703 °K this began decomposing to TiO_2, complete by about 873 °K. The decomposition pressures reported by [144] for $TiOSO_4$ (741–853 °K) are not to be trusted. No pressures can be calculated thermodynamically because high-temperature thermal data are available only for TiO_2 [2].

Densities

Phase	T	d	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)

$S°$

	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

$\Delta Hf°$

	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 H_2O.

U (IV). It is not certain that a pure anhydrous $U(SO_4)_2$ has been obtained, although hydrates are well known. The latter, on heating, are said to yield first the anhydrous salt (near 570 °K), then UO_2SO_4 even in the absence of air.

U (VI). Anhydrous UO_2SO_4 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 UO_3 and UO_2. Formulas such as U_3O_8 and U_4O_9 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 UO_2SO_4 in the range 373 to 820 °K. These high-temperature thermal data could be used along with those in [2] for UO_2 and UO_3 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 UO_2SO_4 entropy at 298.15 °K upon which such calculations would strongly depend.

Densities

Phase	T	d	References
	°K		
$U(SO_4)_2(c)$	291	4.60	16
$UO_2SO_4(c)$			

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$U(SO_4)_2$			
UO_2SO_4	155±25	37±6	92
U_3O_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_4O_9	336	80.3	3, 116a, 8

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$U(SO_4)_2$	−2259	−540	116a
UO_2SO_4	−1888±6	−451.2±1.5	92
U_3O_8	−3574	−854.1	116a
UO_2	−1084	−259.2	4, 116a, 8
UO_3	−1226	−293	116a
U_4O_9	−4510	−1078	116a

Vanadium

V (II). Only the hydrate $VSO_4 \cdot 7H_2O$ is known.

V (III). Rivenq [119] described the preparation and pyrolysis of anhydrous $V_2(SO_4)_3$. 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 V_2O_5, while above 681 °K a mixture of V_2O_4 and V_2O_5 was formed. The results need confirmation by other methods.

V (IV). Anhydrous $VOSO_4$ decomposes, without melting, above about 673 °K, with oxidation to V_2O_5, SO_3, and SO_2. 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 V_2O_5 [2], and the entropy of $VOSO_4$ is unknown.

V (V). Anhydrous $V_2O_5 \cdot 2SO_3$, $V_2O_5 \cdot 3SO_3$, and $V_2O_5 \cdot 4SO_3$ 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)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$VOSO_4$			
V_2O_5	131	31.3	1, 3, 4, 8

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$VOSO_4$	−1307.$_5$	−312.5	1
V_2O_5	−1561	−373	1, 4

Ytterbium

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

Density

Phase	T	d	References
	°K		
$YbSO_4(c)$			
$Yb_2(SO_4)_3(c)$	297	3.964	17

Yttrium

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

Density of $Y_2(SO_4)_3$

Phase	T	d	References
	°K		
c	297	2.949	17

Thermodynamic data (298.15 °K)

$S°$

	J mol^{-1} deg	cal mol^{-1} deg	References
$Y_2(SO_4)_3$			
Y_2O_3			

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Y_2(SO_4)_3$			
Y_2O_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 $2ZnO \cdot 3ZnSO_4$. 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

$$5ZnSO_4 = 3ZnSO_4 \cdot 2ZnO + 2SO_3$$

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

$$3ZnSO_4 \cdot 2ZnO = 5ZnO + 3SO_3$$

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 $ZnSO_4 \rightarrow ZnO$, they are intermediate between the somewhat higher pressures expected for $ZnSO_4 \rightarrow$ oxysulfate and the lower pressures for Oxysulfate → 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	T	d	References
c	288	3.74_4	7
c	298	3.546	81

Transitions of $ZnSO_4$

Phase change	T	References
	°K	
$\alpha \rightarrow \beta$	1013	see text

Thermodynamic data (298.15 °K)

$S°$

	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

$\Delta Hf°$

	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) $ZnSO_4(c) \rightleftarrows ZnO(c) + SO_3(g)$
$\Delta H^\circ_{298.15} = 235.4$ kJ, 56.26 kcal
(2) $ZnSO_4(c) \rightleftarrows ZnO(c) + SO_2(g) + 1/2\ O_2(g)$
$\Delta H^\circ_{298.15} = 333.8_0$ kJ, 79.78 kcal.

A. Free energies

T	ZnO	$ZnSO_4$	Reaction (1)	
	fef	fef	Δfef	ΔG°_T
°K	J	J	J	kJ
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

T	log K_1	K_1	log K_2	K_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)

T	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

Zirconium

Von Hevesy and Cremer [135] attempted to measure equilibrium decomposition pressures of $Zr(SO_4)_2$ in the range 849 to 905 °K, but were not sure of obtaining true equilibrium. Decomposition was direct to ZrO_2, not through an intermediate oxysulfate, and the sulfate appeared to be less stable than $Hf(SO_4)_2$. A TGA curve [68] also shows no sign of an oxysulfate.

We calculated decomposition pressures using high-temperature thermal data for $Zr(SO_4)_2$ from [124] and for ZrO_2 from [2], estimating the entropy of $Zr(SO_4)_2$; 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 $Zr(SO_4)_2$.

Density of $Zr(SO_4)_2$

Phase	T	d	Reference
	°K		
c	289	3.22	16

Transitions of $Zr(SO_4)_2$

Phase change		References
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}	References
$Zr(SO_4)_2$	133.1	31.8	estimated
$ZrO_2(\alpha)$	50.71	12.12	3, 4, 8

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$Zr(SO_4)_2$	−2500.	−597.4	1 (see text)
$ZrO_2(\alpha)$	$-1080._3$	−258.2	1
	$-1085._7$	−259.5	8
	−1094.1	−261.5	4, 10

Relative Thermal Stability of Some Sulfates

In order of increasing stability; criterion: equilibrium partial pressure of SO_3 at 1000 °K. Note that the products are not always the first actually formed.

Sulfate	Product	P_{SO_3}
		atm
$Al_2(SO_4)_3$	Al_2O_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_3O_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_2SO_4	Na_2O	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}
	atm
$Sn(SO_4)_2$	2×10^{-13}
$Al_2(SO_4)_3$	2×10^{-24}
$NiSO_4$	6×10^{-32}
$CoSO_4$	1×10^{-34}
$Th(SO_4)_2$	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
		kJ
$Fe_2(SO_4)_3$	Fe_2O_3	83.3, 154.
$FeSO_4$	Fe_2O_3	253.
$Al_2(SO_4)_3$	Al_2O_3	268.
$CoSO_4$	CoO	319.
$PbSO_4$	PbO	385.
$ZnSO_4$	$2ZnO.3ZnSO_4$	212, 271.
$CuSO_4$	$CuO.CuSO_4$	212, 238.
$2ZnO.3ZnSO_4$	ZnO	77, 385.
$CuO.CuSO_4$	CuO	346, 269.

Melting Points in Increasing Order

Compound	MP	MP
	°K	*°C*
Tl_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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