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High Temperature Properties and Decomposition of Inorganic Salts

Part 2. Carbonates

U.S. DEPARTMENT OF COMMERCE

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NATIONAL BUREAU OF STANDARDS

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Foreword

The National Standard Reference Data System provides effective access to the quantitative data of physical science, critically evaluated and compiled for convenience, and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, with responsibility to administer it assigned to the National Bureau of Standards.

The System now comprises a complex of data centers and other activities, carried on in academic institutions and other laboratories both in and out of government. 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. In addition, the centers and projects establish criteria for evaluation and compilation of data and make recommendations on needed improvements in experimental techniques. They are normally closely associated with active research in the relevant field.

The technical scope of the NSRDS is indicated by the principal categories of data compilation projects now active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

The NSRDS receives advice and planning assistance from the National Research Council of the National Academy of Sciences-National Academy of Engineering. An overall Review Committee considers the program as a whole and makes recommendations on policy, long-term planning, and international collaboration. Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The NSRDS—NBS series of publications is intended primarily to include evaluated reference data and critical reviews of long-term interest to the scientific and technical community.

Lewis M. Branscomb, *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 alkali and alkaline earth 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, carbonates 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 $S°$ 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.

Since the kinetics of carbonate decomposition have been more extensively studied than those of any other class of inorganic salts, an examination of the relevant literature has revealed many regularities as well as delineated more sharply our areas of ignorance. For example, although it is not yet possible to control all the factors determining rate constants, the conditions for which activation energies are well-defined, reproducible quantities can now be stated rather precisely. Rather than cite the bulk of the extensive literature in this field, much of which is applicable to very special conditions, we have contented ourselves with a brief review of carbonate decomposition kinetics in which the common features rather than the peculiarities of individual compounds are stressed. If such peculiarities are of special interest, they are described in the appropriate section. However, our bibliography is not intended to be exhaustive. In the preparation of this monograph we have consulted many papers not referenced here. Our aim has been to describe for the nonspecialist those features of the decompositions which are generally agreed on, and to illustrate these with representative references of good quality work.

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The literature dealing with the high-temperature behavior of inorganic carbonates 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 and equilibrium constants of reactions were tabulated. Auxiliary data on phase transitions, densities, and kinetics of thermal decomposition have also been included. The literature of the endothermic decomposition kinetics of solids, as it applies to carbonates, has been reviewed.

Key words: Carbonates; thermal decomposition; thermodynamic functions.

The Carbonates

A. Introduction

#### 1. The Structure of the $CO_3^=$ Ion

The carbonate ion is a well-defined entity in which the three oxygens are arranged in the same plane as the carbon atom at a distance of 1.30 ± 0.01 Å and with bond angles of 120°. This value of the C—O distance, calculated by Pauling [103] on the basis of the resonance structures
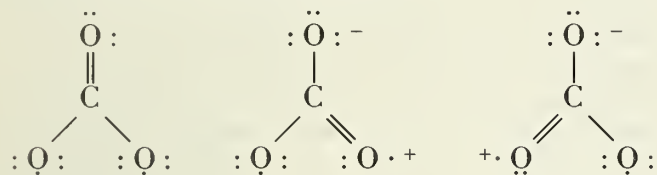
is in good agreement with experimental measurements on calcite [45,117], ranging from 1.29 to 1.31 Å. The resonance energy is 176 kJ (42 kcal) per mole.

2. General Features of Carbonate Decomposition

All carbonates decompose with the evolution of CO_2, the decomposition product being either the corresponding oxide or a basic carbonate, the latter decomposing with further evolution of CO_2 as the temperature is raised. The oxides of some metals are unstable in the same temperature range as the corresponding carbonates so that the decomposition occurs as the simultaneous reactions

$$MCO_3 = MO + CO_2(g)$$

$$MO = M(g) + 1/2\ O_2(g).$$
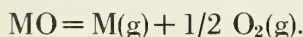
Consequently the vapor phase contains CO_2, M, and O_2. We have not calculated the oxide equilibria but have indicated under the particular element whether it is important, such as for the higher atomic weight alkali metals. Thus the melting points of pure carbonates are generally not measurable directly, though they may be estimated by extrapolation of phase diagrams or by rapid heating, particularly under high CO_2 pressures, which minimizes decomposition. The dissociation, $CO_2 = CO + 1/2\ O_2$, is too slight at temperatures relevant for carbonate decomposition to need taking into account (see below).

As pointed out in out previous paper [121],[3] the thermal stability of a polyatomic anion decreases with increasing polarizing power of the associated cation, since polarization of the anion structure leads to the distortion and consequent weakening of the intra-ionic bonds.

This argument applies to the carbonates. There is, however, some question as to how the polarizing power of the cations is to be measured. For example, Alekseenko [13] noted that the decomposition temperatures ($P_{CO_2} = 1$ atm) of carbonates with 18 electrons in their cation outer shell were lower than those of carbonates with cations of comparable size containing 8 electrons. Ostroff and Sanderson [98] suggested that an anion is most stable when it has the greatest control over its valence electrons and is in a nonpolarizing environment. Since the polarizing power of the cations is inversely proportional to their size and since the electronegativity measures the power of an atom or ion to attract electrons, Ostroff and Sanderson suggested that anion stability should increase as some power of (r/S), where S is the Sanderson stability ratio, a quantity linearly related to other electronegativity

[3] Figures in brackets indicate the literature references at the end of this paper.

scales. As a measure of stability they chose the "lowest temperature at which decomposition could be noted," and found that for several sulfates this temperature varied as $(r/S)^{1/2}$.

In order to define stability in more quantitative terms, it would seem that a thermodynamic measure would be less ambiguous. If one examines the thermodynamic functions for the thermal decomposition of the carbonates, it is evident that the reason for differences in stability are due to $\Delta H°$ since $\Delta S°$ values are nearly the same for all the carbonates and arise primarily from the formation of a gaseous product. Since $\Delta H°$ values at 298 K and those at higher temperatures increase in a parallel manner, the 298 K values are an adequate measure of stability. It has been shown by a semi-empirical method [121a] that $\Delta H°_{298}$ is a linear function of $r^{1/2}/Z^*$, where r is the cation radius and Z^* is the effective nuclear charge, as calculated from Slater's rules
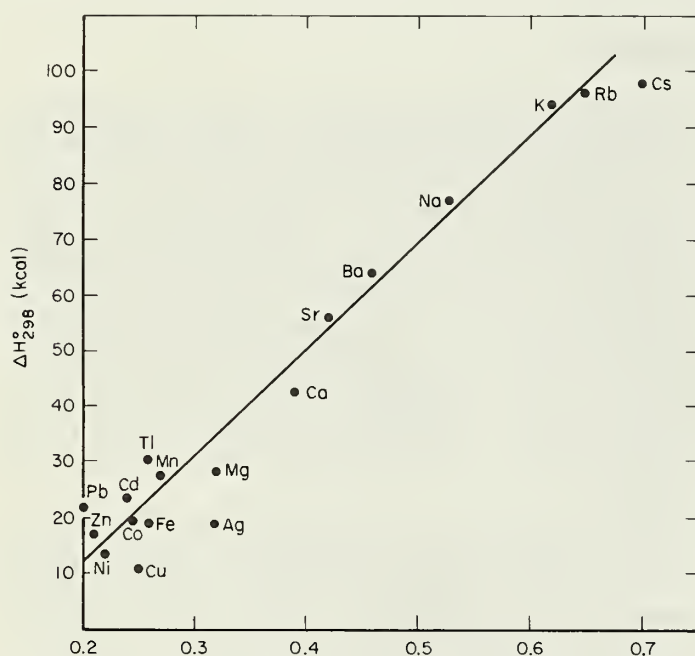

FIGURE 1. *Decomposition enthalpies as a function of cation* $r^{1/2}/Z^*$.

[119a]. The plot is shown in figure 1. Although this correlation is probably not unique, it does illustrate the kind of connections to be expected between atomic and thermodynamic properties.

3. Phase Transitions

a. *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 are so great 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.

b. *Melting Points.* Melting points have been reported for a few of the more stable carbonates. 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. Melting points are usually obtained by rapid heating of the salt to minimize decomposition, but it cannot always be avoided. Another technique is to measure the melting point under a high CO_2 pressure. The listed values should therefore be regarded as lower limits.

c. *Boiling Points.* All carbonates decompose so extensively in the solid or liquid range that boiling points cannot be measured.

4. Density

The total literature of high-temperature density measurements on inorganic carbonates is very small. There exists only one set of reliable values for the liquid salts, those of Janz and Lorenz [75] on the alkali metal carbonates. We have reproduced their original values and also their best fit to a linear equation. On reason for the lack of data is that most carbonates decompose considerably below the melting point so that a measurement of any physical property of the pure liquid is inherently impossible. Except for a few limited studies below 100 °C, there appear to be no studies of the temperature dependence over a wide range of temperature in the solid state.

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 frequently higher than experimental values. Since most crystallographers do not indicate the temperature for which the density is calculated, we have preferentially listed experimental values when these were available. An exception is the careful x-ray work of Swanson and co-workers [123, 124] which has been listed. Units for x-ray densities are g/cm^{-3}. In some cases experimental values seem to depend on the method of preparation, probably because of differences in the defect structure. 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 unity is g/cm^3 of 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. In a few

instances we have listed the thermal expansion coefficients, where these were listed in Vol. III of [9]. The quantities given are:

$$\alpha' = \frac{10^6}{l} \frac{dl}{dt} \text{ at } t°; \text{ or } \alpha = \frac{10^6 \Delta l}{l \Delta t} \text{ over the range } \Delta t°.$$

$$\Delta = 10^9 \frac{d\alpha}{dt} \left(\text{resp. } 10^9 \frac{\Delta \alpha}{\Delta t} \right), \text{ i.e., } 10^9 \times \text{ the rate of}$$

change of α with

t, at $t°$ (resp. over $\Delta t°$).

5. Decomposition Equilibria

As a measure of the stability of each carbonate, we have calculated the equilibrium constants and pressures of CO_2 for each decomposition reaction. Equilibrium pressures may either be obtained from direct measurement in which the carbonate and oxide are allowed to equilibrate with CO_2 at various temperatures or they may be calculated by standard thermodynamic procedures.

Direct measurements are frequently unreliable since in many cases "pseudo-equilibria" appear, i.e., different constant pressures are obtained, depending on whether the equilibrium is approached from above or below [131]. If the same pressure is obtained by both approaches, this possibility is minimized and we have listed a few such values in cases where the necessary thermodynamic values were not available. Whenever possible we have calculated the equilibrium properties by thermodynamic methods.

For these calculations, four items of information are needed:

(1) Knowledge of the course of the decomposition. For the carbonates this is generally quite simple, particularly if the carbonate and oxide coexist as pure solids. In that case the course of the reaction is described by the overall stoichiometry, e.g., $MCO_3 = MO + CO_2$, and the equilibrium pressure of CO_2 is a function of temperature only.

Several carbonates, e.g., lead carbonate, do not decompose directly to the oxide but rather to a basic carbonate such as $PbO \cdot PbCO_3$. These cases are described in the individual sections, but equilibrium pressures can usually not be calculated for the basic carbonates because the necessary thermodynamic data are largely lacking.

(2) High-temperature thermal data such as those tabulated in reference [4] 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 carbonates themselves. Items (3) and (4) are tabulated as "Thermodynamic Data" under each carbonate 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 [6], 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:

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

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 energy change attending the reaction is

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

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

$$\Delta G_T° = - RT \ln K.$$

For the case of simplest stoichiometry:

$$MCO_3 = MO + CO_2 \qquad K = P_{CO_2}.$$

In some cases the decomposing carbonate and the oxide product may form a solid or liquid solution. In that case the equilibrium constant

$$K = \frac{a_{MO}}{a_{MCO_3}} P_{CO_2}$$

where a_{MO} and a_{MCO_3} are the oxide and carbonate activities in the condensed phase and the pressure is now dependent on the solution composition. Such information is not always provided. We would therefore caution against uncritically accepting measured decomposition pressures as meaningful thermodynamic data unless the condensed phases have been examined, for example, by x-ray diffraction of the solids, or direct chemical analysis.

Many of the older decomposition pressure measurements were used by Kelley and Anderson [3] in the calculation of thermodynamic properties of reactions and compounds. When no newer data were available, we incorporated their results into this monograph. The thermodynamic functions in the tables were calculated in 1966 and the literature survey is reasonably complete up to that date. In some cases newer 298 K values have been introduced when these represented major changes from existing values or when this was necessary to be consistent with the ongoing revision of [2]. The values at higher temperatures were then revised accordingly.

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B. Kinetics of Thermal Decomposition

1. General

Although the literature on the thermal decomposition kinetics of carbonates is probably more extensive than that of any other class of compounds, none of the data are of "reference data" quality, as that term is commonly used. One reason for this situation is that it does not yet seem to be possible to prepare duplicate samples of any inorganic solid salt which are identical in all the properties that may determine the rate of decomposition, e.g., the density of dislocations.

Nevertheless, the kinetics of decomposition are of sufficient interest, both for theoretical and for practical reasons, that it seems worthwhile to include the results of at least the more carefully done studies. In this section we summarize those features common to carbonate decompositions and list factors affecting the rate of decomposition. The discussion is essentially limited to solids, since most experimental and theoretical work has been in this area. Kinetics of the individual compounds are treated in their respective sections.

2. Mechanism of Endothermic Solid State Decomposition

Many authors have derived equations for the rate of decomposition, $A(s) \rightarrow B(s) + C(g)$, from theoretical models. The aim of all these studies is to find functional relations between some measurable quantity of the system, such as weight and time, which can be tested against experimental results. Although the usual *caveat* against taking agreement between the predictions of the model and experimental results as evidence for correctness of the mechanism of the model applies, nevertheless such agreement, together with other experimental evidence, e.g., microscopic examination, is frequently very helpful in at least narrowing the possibilities.

In this section some of the models which have been proposed are briefly summarized. Greater detail can be found in books by Garner [54] and Young [129] and in the original references.

Most models try to account for the shape of the experimental $\alpha(=$ fraction decomposed) versus time t curves. These are generally S-shaped with a relatively slow induction period, a steep portion during which the bulk of the material decomposes, and a slow final section. Experimentally determined curves differ primarily in the relative duration of the induction period. This induction period is commonly identified with the formation of nuclei of the new phase B imbedded in A; these nuclei grow, both by spreading over the surface and into the bulk of the decomposing particle. After the surface is covered by B, this phase grows into the bulk of the material. Decomposition thus occurs only at the reactant-product phase boundary, as has been argued by Langmuir from phase rule considerations [87]. It seems to be generally agreed that the evolution of gas C during endothermic solid decomposition is not a rate-limiting step in the process, i.e., the product B is sufficiently porous to permit the gas to escape readily. However, if the gas is generated in the body of the crystal, e.g., as a result of ionizing radiation, and must diffuse out along grain boundaries, the rate of decomposition may depend markedly on the diffusion constant of the gas. This case has been discussed by Gafner [53].

Although the measured decomposition rate of carbonates is not rate-limited by diffusion of the gas out of the crystal, it is clear that in the case of readily reversible decompositions, such as those of the carbonates, the measured rate will depend on the difference between the equilibrium pressure p_e and the actual pressure p at the reaction interface. Thus, although the functional dependence of α on t may be independent of $p_e - p$, the actual rates are not. It is largely for this reason that it is not possible to tabulate "standard reference data" rate constants, since the pressure p is not usually known. Instead one finds decompositions carried out in streams of various inert "sweep gases" which may or may not remove product gas from the reaction interface, or in vacuum. In the latter case, the question as to whether the manometrically measured pressure equals the interface pressure needs to be answered. Small sample size and a porous oxide favor this condition.

(a) Kinetic Equations

The most complete classification of solid decompositions has been worked out by Jacobs and Tompkins [73]. When the decomposition begins at some points on the A lattice where the local energy is most favorable, small fragments of B are imbedded in A. These may at first retain the lattice parameters of A and will therefore possess some strain energy as a result of the deformation. Jacobs and Tompkins show that the Gibbs energy accompanying the formation of a fragment of B containing m molecules is

$$\Delta G = am^{2/3} - bm \qquad (1)$$

where a is proportional to the strain energy and b is the negative of the bulk Gibbs energy per molecule. ΔG passes through a maximum at $m = m^*$ when a fragment has the critical size to be in equilibrium with its surroundings. Smaller fragments are unstable and revert to A; larger ones are stable nuclei and grow. Whether decomposition proceeds from the growth of a few nuclei or whether many small nuclei are formed depends on the relative magnitudes of the activation energies for nucleus formation $(\Delta G_1^{\neq})$ and the growth stage $(\Delta G_2^{\neq})$. If $\Delta G_2^{\neq} < \Delta G_1^{\neq}$, growth of existing nuclei predominates over formation of new ones. If $\Delta G_2^{\neq} \simeq \Delta G_1^{\neq}$, many small nuclei are formed, none of which grow to visible size. In that case the induction period is much reduced. The whole surface then nucleates rapidly and the

kinetics of the remainder of the reaction depends on the rate at which the interface progresses into the crystal.

We next consider various mechanisms for each of the stages in the decomposition.

(1) *Nucleus Formation.* Jacob and Tompkins consider only structure-sensitive nucleation, which occurs at definite sites in the lattice where the activation energy is least, such as lattice defects and dislocations. The rate of nucleus formation thus depends both on the defect density and on the activation energy.

Jacobs and Tompkins distinguish two cases; (1) the decomposition of a single molecule leads to the formation of a nucleus. The probability of this unimolecular decomposition is

$$k_1 = \gamma \exp\left(\Delta G_1^{\neq}/RT\right) \qquad (2)$$

where γ is the frequency of lattice vibrations and $\Delta G_1^{\neq}$ is the activational Gibbs energy for nucleus formation. The rate of nucleus formation at time t then is

$$dN/dt = k_1 N_0 \exp\left(-k_1 t\right) \qquad (3)$$

or

$$N = N_0\left[\left(1 - \exp\left(-k_1 t\right)\right)\right]$$

where N_0 is the total number of potential nucleus forming sites. The possible loss of nucleus-forming sites through their ingestion by growing nuclei is neglected. In the early stages of the reaction and especially for large $\Delta G_1^{\neq}$ and consequently small k_1

$$N \simeq k_1 N_0 t \qquad (4)$$

so that the number of nuclei increases linearly with time.

(2) A power law results from two possible mechanisms: (a) a stable nucleus is formed in a bimolecular combination of two active intermediates, and (b) several decompositions are required to form a stable nucleus. The first of these possibilities may require the surface migration of several B molecules until they coalesce into a stable nucleus. Some aspects of this phenomenon have been discussed by MacDonald [89].

(2) *Growth of Nuclei.* As each nucleus is formed, it grows generally hemispherically, i.e., it spreads across the surface of the crystal and into its interior. Since the laws for the rate of formation of nuclei are different from those for their growth, the overall decomposition rate is likely to be complicated if the two rates are comparable in magnitude. This is particularly true if the complications resulting from overlapping nuclei are taken into account. As nuclei grow, they ingest or overlap sites which would otherwise yield nuclei. Also, as nuclei grow, they impinge on one another and cease to grow along the line of contact. Both of these effects result in rates different from those predicted from models without these refinements.

The simplest decomposition kinetics, commonly observed for carbonates, result from a model in which nucleation and subsequent surface growth are extremely rapid. The rate of decomposition is then determined by the progression of the reaction interface into the crystal. Rate laws have been derived for various geometries, but the one for spherical particles is most useful for carbonate decomposition and has been given in several equivalent forms by various authors. In this derivation it is assumed that the reaction interface proceeds at constant velocity into the crystal, i.e., for a constant interfacial area, the rate of decomposition is a constant. For a spherical particle the reaction proceeds along a constantly diminishing interface. For such particles of initial radius, R_0, the fraction decomposed at time t is

$$\alpha = \frac{4/3\pi R_0^3 - 4/3\pi(R_0 - k_2 t)^3}{4/3\pi R_0^3} \equiv 1 - \left(1 - \frac{k_2 t}{R_0}\right)^3$$

$$= \frac{3k_2 t}{R_0} - \frac{3k_2^2 t^2}{R_0^2} + \frac{k_2^3 t^3}{R_0^3} \qquad (5)$$

and

$$\frac{d\alpha}{dt} = \frac{3k_2}{R_0} - \frac{6k_2^2 t}{R_0^2} + \frac{3k_2 t^2}{R_0^3}. \qquad (6)$$

These equations were first derived by Hume and Colvin [65].

The same, but superficially different, equation was derived by Fischbeck and Schnaidt [50] in a form now frequently used.

$$\frac{d\alpha}{dt} = k_1 A \qquad (7)$$

where A is the total area of the reacting interface. For a spherical particle $A = k_2'(1 - \alpha)^{2/3}$, where k_2' depends on R_0, and hence

$$\frac{d\alpha}{dt} = k_2'(1 - \alpha)^{2/3}. \qquad (8)$$

In this form the equation is frequently referred to as the 2/3 power law. In terms of mass change it can be written (20)

$$-\frac{dm}{dt} = k_2'' m^{2/3} \qquad (9)$$

where k_2'' again depends on R_0. Equation (8) is usually given in integrated form

$$k_2' t = 1 - (1 - \alpha)^{1/3}. \qquad (10)$$

The dependence of rate on particle size can be included by the substitution $k_2 = k_2'/R_0$.

The second limiting case arises when the rate of linear propagation of the reacting interface is so great that each particle decomposes as soon as it has a nucleus. For this case, Hume and Colvin give

$$Rate = k_0 N_t$$

i.e.,

$$dN/dt = k_0 N_t \qquad (11)$$

where N_t is the number of particles at time t. Integration from N_0 to N_t gives

$$\ln(N_t/N_0) = k_0 t \qquad (12)$$

a first-order reaction. This behavior is most likely to be approached by very small particles.

In general the kinetics of decomposition are more complex than in the two limiting cases just outlined. Thus, if nucleation is not extremely rapid, the number of nuclei will increase in time. Each of these nuclei will then begin to grow at a different time. Some of them will spread over sites at which nucleation would have occurred at some future time. These sites are referred to as "phantom nuclei" by Jacobs and Tompkins. The problem has also been studied in great detail by Mampel [92]. Both Jacobs and Tompkins and Mampel assume the rate of nuclei formation to be first order,

$$\frac{dN}{dt} = k_1 N_0 e^{-k_1 t} \qquad (13)$$

where N_0 is the total number of possible sites. For the induction period Mampel finds a t^4 law for α, a relation derived by Jacob and Tompkins for random nucleation and short times, and by Fischbeck and Spingler [51] for the case of no overlap, a constant rate of formation of nuclei, and a large total number of nuclei.

For large radii $(R > k_2 t)$, Mampel finds

$$\frac{k_2 t}{R} \simeq 1 - (1-\alpha)^{1/3}$$

an eq (10) given previously for the contracting sphere case. For small radii the fraction decomposed is

$$X = 1 - ce^{-kt}$$

where c is independent of t, but does depend on R in a rather complicated way. The rates are dependent on particle size and both small and large radii give lower rates than intermediate radii.

A generalized equation has been derived by Erofeyev [47] in terms of probability theory. In his treatment

$$\alpha = 1 - \exp\left(-\int_0^t p\,dt\right) \qquad (14)$$

where p is the probability that a molecule will react in the time interval dt.

The general solution of (14) for thermal decomposition is

$$\alpha = 1 - \exp(-kt^n) \qquad (15)$$

where the constant n depends on the shape of the nucleus and the number of electrons necessary for the formation of a stable nucleus. For example, cylindrical nuclei (the centers of formation are edges or surface cracks) give $n = 3$, flat nuclei give $n = 4$. Thus the evaluation of n, most easily carried out by transforming (15) into

$$\ln[-\ln(1-\alpha)] = \ln k + n \ln t \qquad (16)$$

and plotting the left side of (16) versus $\ln t$, gives some information about the nucleation mechanism.

(b) Surface Area Changes During Decomposition

Since the molar volume of the product oxides is less than that of the corresponding carbonates, decomposition results in a porous structure through which the CO_2 readily escapes. Although not directly related to the decomposition kinetics, the resulting increase in surface area during decomposition is of some interest in the production of "active solids" and has been treated by several authors. Accordingly, we briefly review it here.

The oxide is first formed at sites on the carbonate lattice and is therefore in a strained state. Gregg [61] describes these as small crystallites or micelles. This strained pseudo-lattice will tend to recrystallize into a stable oxide lattice with a resulting decrease in surface area. Three mechanisms for this recrystallization are generally recognized. At temperatures $T/T_m < 0.2$, where T_m is the melting point of the oxide, adhesion predominates. This mechanism results from contact between parts of the micelles which are atomically contiguous. For $0.2 < T/T_m < 0.35$, surface diffusion predominates. Here, mobile atoms or ions in the surface layer leave their position on the lattice to migrate to sites of lower energy, i.e., to stable oxide lattice positions.

In DTA studies of carbonate decomposition [109] small exothermic peaks (200–1000 cal/mol) were observed at temperatures 40 to 80 °C above the main endothermic decomposition peak, consistent with such an oxide lattice rearrangement. The formation of the surface mobile species from the active species on the original lattice is considered by Ilschner [71] to be slower than the prior formation of the active species and the subsequent incorporation of the mobile species into the stable oxide lattice. Above $T/T_m = 0.5$ sintering, i.e., lattice or bulk diffusion, is the most significant process leading to decreased surface area. Thus as decomposition proceeds, there are basically two processes leading to changes in surface area: the formation of the metastable oxide produces an increase in surface, and the formation of stable oxide decreases

the area. Consequently the "surface area" versus "fraction decomposed" plot exhibits a maximum before decomposition is complete. Nicholson [97] has developed a mathematical model for this process which agrees well with experimental observations. If the purpose of the decomposition is the preparation of an "active solid," the reaction should not be carried to completion in order to achieve the desired maximum surface area.

3. The Effect of Pressure on Rate

When the pressure of CO_2 in a carbonate-oxide system is equal to the equilibrium pressure, p_e, no net reaction occurs. When $p < p_e$, the thermodynamic driving force favors oxide formation; conversely, when $p > p_e$, carbonate formation is favored. In actual systems the favored reaction may not occur, however, because kinetic factors prevent it. Particularly when p is not too far from p_e, the reaction may not proceed because some rate-limiting process, such as nucleus formation, is proceeding too slowly. The resulting spurious equilibria [131] give rise to hysteresis effects, i.e., decomposition stops for some $p < p_e$, recombination stops for $p > p_e$. It is for this reason that we have largely relied on thermodynamic methods for the calculation of equilibrium pressures. When the carbonate and oxide are present as pure phases, the value of p_e is completely unambiguous, i.e., at a given temperature $p_e = K_p$, the equilibrium constant for the reaction $MCO_3 = MO + CO_2$. However, when the condensed phase consists of a solid or liquid solution, p_e no longer has a unique value since

$$K = \frac{a_{MO}}{a_{MCO_3}} p_e, \text{ and}$$

p_e now depends on the solution composition. Since the rate of decomposition is generally some function of $p_e - p$, we consider only systems without solution formation. We have also omitted discussion of the effect of "foreign" gases, i.e., gases other than CO_2, on the rate. Such gases, e.g., O_2, H_2O, frequently function as catalysts or inhibitors, but these effects are difficult to relate to well-defined properties of the system [25, 66, 68]. In order to study the dependence of reaction rate on CO_2 pressure, it is necessary that this pressure remains fixed throughout the course of the decomposition while more CO_2 is evolving. Since the significant value of the pressure is that at the reaction interface it is possible that in a closed system where one depends on diffusion to remove the excess CO_2, the pressure at the interface will exceed the nominal value, particularly if the sample size is large and the reaction is rapid. The effect of a pressure gradient on the reaction rate has been investigated [20] by the application of Fick's law. Both for slow and for fast reactions, the rate is proportional to $p_e - p_0$, where p_0 is the pressure at the reaction site but the proportionality constants differ in the two cases. One way to avoid the problem of pressure gradients is to use sweep gases made from a known

mixture of CO_2 and some inert gas. Independence of decomposition rate from flow rate is generally taken as evidence that the reaction is not diffusion-controlled, e.g., [69].

If the surface area is constant, the decomposition rate is proportional to $p_e - p$, i.e.,

$$v = k(p_e - p).$$

Such a relation was also found to hold for both cylindrical pellets of calcite and powdered $CaCO_3$ [72].

Cremer and Nitsch [39], in studying the decomposition of $CaCO_3$, found that for samples which followed a 2/3 rate law the pressure dependence of the rate (in $m^{1/3}t^{-1}$) was given by

$$v = k \left(\frac{1}{p} - \frac{1}{p_0} \right) \tag{17}$$

A similar equation has been derived [69] from a two-step model in which the CaO is assumed to be formed first in some "active" state CaO* which occupies a constant fraction of the surface. The reactions are then

$$CaCO_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CaO* + CO_2$$

$$1-\theta \qquad \theta \qquad P$$

$$CaO* \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CaO$$
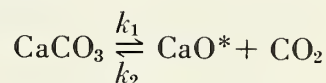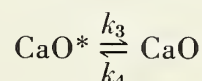
both of which are reversible. The rate

$$R = -dw/dt = \frac{k_0 k_1 k_3 - P k_0 k_2 k_4}{k_1 + k_3 + k_4 + k_2 P} \tag{18}$$

where the constant k_0 is introduced to convert the surface area θ to surface concentration in molecules per square centimeter, to account for the roughness factor, and for the fact that only a portion of the total surface sites may be potentially reactive.

Equation (18) can be written as

$$R = \frac{1 - CP}{VP + D}, \tag{19}$$

When $P = 0$, $R = R_0 = 1/D$.

When $P = P_e$, $R = 0$ and $C = 1/P_e$.

Hence

$$R = \frac{1 - P/P_e}{BP + 1/R_0}. \tag{20}$$

When $1/R_0 \gg BP$

$$R = \frac{1}{BP} - \frac{1}{P_e}, \tag{21}$$

which is essentially the equation given by Cremer and Nitsch [39].

7

4. Activation Energy

The activation energy $E^{\neq}$, as defined by the usual Arrhenius equation

$$k = Ae^{-E^{\neq}/RT}$$

is usually at least as great as the thermodynamic enthalpy for the reaction, ΔH, though it is frequently greater. When $E^{\neq} = \Delta H$, the reaction is often described as occurring "without activation." The question as to whether $E^{\neq} = \Delta H$ for the endothermic carbonate decompositions was first considered by Fischbeck and Schnaidt [50]. In comparing experimental values of $E^{\neq}$ and ΔH, they found approximate agreement, but the scatter of the then available data prevented rigorous comparison.

Shortly thereafter Zawadzki and Bretsznajder [130] showed that for a *reversible reaction*[4] of the type $A_{(s)} = B_{(s)} + C_{(g)}$, the experimental value of $E^{\neq}$ for the forward reaction, as determined from the temperature dependence of k, must necessarily increase with rising pressure and will have its minimum value in the absence of the backward reaction, i.e., in vacuum. This dependence was verified for the decomposition of $CaCO_3$, $CdCO_3$, and Ag_2CO_3. In vacuum the temperature dependence of k was the same as that of the equilibrium pressure p_e, i.e., $E^{\neq} = \Delta H$. The dependence of $E^{\neq}$ on the pressure has recently been reexamined by Pavlyuchenko and Prodan [104], who distinguish two cases: (a) if $E^{\neq}$ is determined from the temperature dependence of the rate, with the pressure p held constant at the various temperatures, then $E^{\neq}$ increases as $p \rightarrow p_e$. (b) If, however, the ratio p/p_e is held constant as the temperature is changed, then $E^{\neq}$ will be independent of the actual numerical value of the ratio and will have the same value as in vacuum. This conclusion was reached by a theoretical argument and verified by data on the decomposition of $CdCO_3$. Since condition (a) is the more usual experimentally, particularly in the older literature, it is not surprising that widely varying values of $E^{\neq}$ for the same reaction have been reported [121] by authors who failed to recognize the dependence of $E^{\neq}$ on pressure.

The atomic mechanism responsible for monomolecular reactions, including thermal decompositions, was first discussed by Polanyi and Wigner [105]. Their model assumes that decomposition occurs when, due to energy fluctuations in the bonds of the molecule, the bond strength is exceeded; or more precisely, that the bond energy "resides in harmonic vibrations and that decomposition occurs when their amplitude is exceeded." The resulting expression for the first-order Polanyi-Wigner rate constant is

$$k = \nu \exp\left(-E/RT\right) \tag{22}$$

where ν is the atomic frequency of vibration and E is the activation energy. Thus a molecule having energy E would leave the surface.

Shannon [118] has analyzed in some detail the theory as it applies to the thermal decomposition of solids. He finds that of the 31 reactions for which he compared experimental rate constants with those calculated from the Polyani-Wigner equation, only a third show order-of-magnitude agreement. In Shannon's view, this lack of agreement stems from neglect of rotational and other vibrational degrees of freedom.

Shannon's is probably the most ambitious attempt to date to calculate a rate constant for the thermal decomposition of a solid from absolute reaction rate theory. The resulting equation is of the same form as eq (22), but ν is replaced by a partition function ratio,

$$k = \frac{kT}{h} \frac{Q^*}{Q} \exp\left(-E/kT\right) \tag{23}$$

where Q^* is the complete partition function for the activated complex excluding that for the reaction coordinate and Q is the complete partition function for the reactant. Detailed calculations of the partition functions were carried out for the decomposition of $CaCO_3$ and $MgCO_3$, using known values of the rotational and vibrational partition functions and several models for the activated complex. The best agreement with experiment was obtained from a model in which the carbonate ion in the lattice is free to rotate and the CO_2 molecule leaves directly from the surface of the solid, rather than from a mobile surface layer.

5. The Effect of Method of Preparation on Rate

Various authors have recognized that the rate of thermal decomposition may depend on the method of preparation and the thermal "history" of the sample, but systematic studies in this area are inherently difficult and few have been carried out. For example, even if the effect of surface structure on the rate of nucleation is recognized, the characterization of the surface in quantitative terms and the reproducible preparation and systematic variation of surface and bulk properties is as yet a largely unsolved problem. Additional problems arise if impurities present in the samples at very low concentrations, such as H_2O, catalyze the decomposition [108]. In that case, the resulting change in mechanism will affect not only the rate but also the activation energy.

If the carbonate is a single crystal, the reaction will propagate from the surface into the interior. In polycrystalline materials the reaction may ad-

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[4] For this type of reaction reversibility implies that the pressure of the gas C is the equilibrium pressure P_e and that infinitesimal changes in this pressure will produce the appropriate shifts in the direction of the reaction, i.e., to the left for $p > P_e$, and to the right for $p < P_e$. Moreover, the solid phases must be the most stable forms, rather than metastable phases.

ditionally propagate along grain boundaries [63].

A systematic study of the effect of sample constitution on decomposition rate was carried out by Cremer and Nitsch [40]. They decomposed four calcite crystal samples at 850 °C and CO_2 pressures ranging from 120 to 220 torr. The CaO product exhibited increasing grain size with increasing pressure. The four CaO samples were then reacted with CO_2 at 850 °C and 420 torr to produce four $CaCO_3$ samples with similarly increasing grain size. When these four samples were then decomposed under identical conditions (850 °C, 200 torr CO_2), the rate of decomposition increased in inverse order of crystallite size. The disappearance of the induction period with decreasing crystal size was particularly noticeable. These results are explained in terms of more rapid nucleus formation at lower pressures, leading to smaller CaO crystals and consequently a larger number of active sites in the $CaCO_3$ subsequently formed.

It is evident from these results that the course of the decomposition is affected by the microstructure of the sample and that the reproducible preparation and characterization of nominally identical materials is an important prerequisite for the understanding and systematization of decomposition kinetics.

6. The Effect of Heat Transfer on Rate

An endothermic solid-state decomposition proceeds as the produce-reactant interface advances into the interior of the sample. The interface can, however, advance only if the necessary heat of reaction is supplied to it. Since the source of heat is outside the sample, the rate of heat transfer to the interface may become rate determining if the inherent rate of reaction is greater than the rate of heat transport. The rate at which heat is transported depends not only on the properties of the product through which heat must be transported, but also on the general experimental arrangement. It is for this reason that one expects and finds the literature to be conflicting.

For example, Narsimhan [96] has derived an equation for the rate of thermal decomposition based on the idea that the entire particle rapidly reaches the decomposition temperature so that there are no internal temperature gradients. All of the heat reaching the reaction interface is used up in the decomposition so that the reaction rate depends on the rate of heat transport. For both spherical and cylindrical particles, good agreement with some literature values is found. Under these conditions the chemical steps are no longer rate-determining.

It can thus be seen that in any solid-state reaction whose enthalphy is appreciable, the establishment, maintenance, and measurement of the temperature at the reaction interface is a complicated problem. Thus, careful studies of the decomposition of $PbCO_3$ [76] and several other inorganic salts [133] have shown that the induction period may disappear if the entire sample is rapidly brought to the reaction temperature. There is therefore now some question whether the commonly reported induction periods in the decomposition of so many substances are artifacts of the experimental arrangement. Considerable care in the experimental design is certainly required to ensure a constant and known temperature at the reaction interface throughout the course of the decomposition.

7. The Influence of Crystal Defect Structure on the Rate of Decomposition

The idea that the defect structure of a solid reactant affects its rate of decomposition seems to be generally accepted; but of all the factors influencing the kinetics, this one is the most difficult to characterize quantitatively. The literature on the subject has been reviewed by Boldyrev [26], who then classified decompositions according to which aspects of the defect structure needed to be considered in particular cases. Because of its general interest, his classification is reproduced here.

Effect of crystal defects on the rate of thermal decomposition of solids (26)

Crystal defects affecting the rate	Decomposition proceeds through		
	Breaking of bonds within cationic and anionic lattice constituents		Electron transfer from anion to cation
	Reversible decomposition	Irreversible decomposition	
Change of habit Growth figures, vicinals, macro-fissures......... Dislocations, and groups of them........	Effect	Effect	Effect
Impurity inclusions in lattice............... Ionic defects Electronic defects	No effect	No effect	

According to this scheme, carbonate decomposition constitutes the simplest type, since it is a reversible reaction in which only intra-ionic bonds are broken. Therefore, only the first two types of defects affect the rate of decomposition.

The main distinction between reversible and irreversible decompositions is the more complex mechanism of the latter, whereas reversible decomposition proceeds through only one step, such as the breaking of a C—O bond in the $CO_3^=$ ion. Since these reactions start on the surface, a change in the crystal habit which affects the surface area ratio of more/less reactive faces will necessarily affect the rate, particularly since such a change of crystal habit also changes the ratio of surface/bulk ions. Growth figures and macrofissures have their greatest effect on the initial rate since nucleation commonly begins at the most reactive surface sites and these are usually defects in the structure.

If Boldyrev's arguments are correct, it would seem that the study of reversible decomposition offers the best chance for a quantitative study of the relation between the various effects discussed above and the rate of decomposition. This is particularly true for the main course of the reactions which is much less affected by the defect structure than is the initial nucleation.

Boldyrev and Medvinskii [27] have attempted a quantum-mechanical interpretation of the above decomposition scheme by considering changes in the electron energy levels which correspond to the various types of decomposition, primarily in the language of band theory. The theory is not yet sufficiently well developed to permit quantitative predictions, although it provides a rational framework for the classification scheme. In terms of this theory, intra-ionic decompositions involve very local changes in the electron levels, i.e., "excitons of small radius." The authors predict that these reactions will in the future be describable by energy level diagrams.

C. Suggestions for Experimental Work

In view of the preceding discussion, it is clear that considerable care in experimental design and execution is required if meaningful thermodynamic and kinetic data on the decomposition of inorganic salts are to be obtained. For the measurement of equilibrium pressures, the requirements are rather simple: (a) the measured temperature must be the temperature of the sample; this requires placing the measuring device close to the sample. (b) The measured pressure must be the equilibrium pressure; precautions against pseudo-equilibria require that the same pressure is obtained when approached from above and below. (c) The condensed phases must be well characterized in order for the measured pressure to be thermodynamically meaningful. In the case of a solid decomposition, both the reactant and product should be examined for evidence of solid solution formation. If a liquid phase forms, pressure measurements are probably of very limited usefulness since not only the composition of this phase, but the component activities must be known in order to calculate the equilibrium constant of the reaction. The characterization of the solid phases is also important for another reason. In cases where the reactant can exist in more than one crystalline modification, it is possible that a form other than the most stable one becomes "frozen" in a metastable state at the temperature of the decomposition. The decomposition pressure and the reaction Gibbs energy calculated from it will be different for the two forms and hence the reaction to which $\Delta G°$ corresponds will not be properly identified. Hence $\Delta G°$ will have its correct equilibrium value only if the solid phases are the most stable ones. (d) Just as the vapor pressure of small drops is greater than that of large ones, so the decomposition pressure of small crystals is larger than that of large ones. Experimental evidence for this phenomenon exists [36A]. For equilibrium measurements, relatively large ($> 10^{-2}$ cm) crystals should probably be used, or the pressure studied for several particle sizes large enough for the pressure to be independent of particle size.

Since the measurement of meaningful decomposition pressures is difficult, work on the determination of high-temperature heat capacities would be appropriate. A perusal of the tables in this monograph shows that only about half of the carbonate decomposition pressures can be calculated from existing thermodynamic data. Most of the remainder (Cu, Fe, Pb, Zn) could be calculated if these C_p values were available. Co and Ni also lack reliable $S°_{298}$ values.

The proper execution of kinetic studies is more difficult since more factors determine the rate of decomposition than determine the equilibrium.

Since these factors have already been discussed in the previous section, we only emphasize here their consequences for the proper experimental approach. We assume that in a chemical study the main interest lies in elucidating the chemical kinetic steps, i.e., the reaction mechanism. Therefore it is desirable to ensure that purely physical steps, such as diffusion of the gas and heat transfer to the reaction site, not be rate-limiting. In planning a kinetic study, the following factors should then be considered:

(a) The significant temperature is that at the reaction site, i.e., at the phase boundary between the reacted and unreacted material. Placement of the temperature-measuring device is thus of critical importance. Particularly in very endothermic or exothermic reactions, temperature gradients within the furnace and even within the sample may be large.

(b) In order to minimize temperature gradients within the sample, to ensure that the rate is not controlled by the diffusion of gaseous products and by the rate of heat transport between sample and surroundings, the sample should be small and consist of a thin layer of finely divided material unless the study is primarily concerned with nucleus formation on the surface, in which case a large sample of known geometry and perhaps surface structure, e.g., a single crystal, may be preferable. If the same rate is attained with samples of different thickness, temperature gradients are probably absent.

(c) Depending on the mechanism of the reaction, the particle size of the sample may or may not affect the rate. Although the theoretical models discussed in section B2 predict such dependence, experimental evidence for both dependence and nondependence exist. It is therefore advisable to use as narrow a size distribution as possible in each experiment and to measure the rate of several such distributions with the total sample size held fixed.

(d) Particularly for readily reversible reactions, the observed decomposition rate depends on the difference between the equilibrium pressure, p_e,

and the actual pressure, p. Therefore, only limiting rates ($p=0$) are meaningful for the forward reaction. Measurement should therefore be carried out at a sufficiently low pressure for the mean free path in the gas to be of the order of the pore size. If an inert sweep gas is used to remove gaseous products, it must be carefully controlled so that the product is really removed from the reaction interface.

(e) Since heat transfer to .the sample is more difficult in a vacuum, special care must be taken to provide good thermal contact between sample and heat source. The sample should be kept from decomposing until the desired temperature is reached by maintaining the pressure above the equilibrium value and then rapidly decreasing it to zero at the beginning of the reaction.

(f) The method of preparation may affect the rate by determining:

(1) The crystal habit. Samples may be crystalline or amorphous. In some cases the crystal structure may depend on the method of preparation, e.g., high-temperature modifications may be frozen on by quenching the molten salt.

(2) Particle size (cf. (c) above).

(3) The nature and concentration of substances adsorbed on the crystal surface. These may function as catalysts or inhibitors for the decomposition.

(4) The defect structure. If decomposition starts at dislocations on the lattice, the rate of decompositions may be anomalously high if the defect density is high.

It is primarily the difficulty of reproducibly preparing well-characterized samples which accounts for the present lack of meaningful rate constants. The measurement of rate constants for solid decompositions which are as significant and reproducible as those for gas reactions will require great care, both in the preparation of materials and in the execution of experiments.

Units, Symbols, and Abbreviations

J = joule

cal   = thermochemical calorie = 4.1840 J

P = pressure; 1 atm = 101325 N m^{-2} = 1013250 dyn cm^{-2}

$T(\text{K})$ = 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

$\Delta Hf°$ = standard enthalpy of formation

$S°$ = standard entropy

$G°$ = standard Gibbs (free) energy

fef   = free energy function = $\dfrac{G_T° - H_{298.15}°}{T}$

TGA = thermogravimetric analysis

DTA = differential thermal analysis.

CO$_2$, CO, and O$_2$

The CO_2 produced by the decomposition of a carbonate dissociates partly to CO and O$_2$. However, at temperatures for which most of the carbonate decomposition equilibrium pressures have been calculated, the decomposition of CO_2 is very slight. We have therefore given the decomposition pressures in terms of CO_2 only. However, for those wishing to refine the calculations still further, we have calculated the free energy functions and equilibrium constant for the reaction $CO_{2(g)} = CO_{(g)} + 1/2\ O_{2(g)}$.

Entropy and enthalpy values at 298.15 K are taken from [2]. Free energy functions above 298.15 K are based on [10] for CO_2 and O$_2$ and on [8] for CO.

Thermodynamic data (298.15 K)

	$S°$		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
CO$_2$	213.64	51.06	2
CO	197.56	47.219	2
O$_2$	205.03	49.003	2

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	References
CO$_2$	393.51	94.051	2
CO	110.52	26.416	2
O$_2$	0	0	2

Dissociation of CO$_2$

$$CO_{2(g)} = CO_{(g)} + 1/2\ O_{2(g)}$$
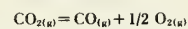
$$\Delta H°_{298.15} = 282.98 \text{ kJ}, 67.635 \text{ kcal}$$

		A. Free Energies			
T	CO$_2$	CO	O$_2$	Reaction	
	fef	fef	fef	Δfef	$\Delta G_T°$
K	J deg^{-1}	J deg^{-1}	J deg^{-1}	J deg^{-1}	kJ
298.15	−213.63	−197.56	−205.04	−86.45	257.21
400	−215.15	−198.71	−206.20	−86.66	248.32
500	−218.15	−200.87	−208.41	−86.95	239.51
600	−221.62	−203.32	−210.93	−87.18	230.60
700	−225.14	−205.80	−213.50	−87.32	221.86
800	−228.81	−208.21	−216.02	−87.40	213.07
900	−232.36	−210.53	−218.44	−87.42	204.31
1000	−235.75	−212.76	−220.77	−87.40	195.59
1100	−239.03	−214.87	−222.99	−87.35	186.90
1200	−242.18	−216.89	−225.10	−87.28	178.24
1300	−245.19	−218.82	−227.12	−87.19	169.64
1400	−248.10	−220.67	−229.05	−87.09	161.06
1500	−250.90	−222.43	−230.89	−86.98	152.52
1600	−253.58	−224.12	−232.66	−86.86	144.00
1700	−256.20	−225.75	−234.36	−86.75	135.52
1800	−258.70	−227.30	−235.98	−86.62	127.07
1900	−261.11	−228.81	−237.55	−86.49	118.65
2000	−263.43	−230.25	−239.06	−86.36	110.26
2100	−265.68	−231.64	−240.51	−86.24	101.89
2200	−267.86	−232.99	−241.91	−86.11	93.55
2300	−269.96	−234.29	−243.22	−85.98	85.23
2400	−272.01	−235.55	−244.58	−85.86	76.93

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T(K)	log K	K
298.15	−45.062	8.67×10^{-46}
400	−32.427	3.74×10^{-33}
500	−25.021	8.53×10^{-26}
600	−20.082	8.28×10^{-21}
700	−16.555	2.79×10^{-17}
800	−13.912	1.22×10^{-14}
900	−11.858	1.39×10^{-12}
1000	−10.216	6.08×10^{-11}
1100	−8.875	1.33×10^{-9}
1200	−7.759	1.74×10^{-8}
1300	−6.816	1.53×10^{-7}
1400	−6.009	9.79×10^{-7}
1500	−5.311	4.89×10^{-6}
1600	−4.701	1.99×10^{-5}
1700	−4.164	6.85×10^{-5}
1800	−3.687	2.06×10^{-4}
1900	−3.262	5.47×10^{-4}
2000	−2.880	1.32×10^{-3}
2100	−2.534	2.92×10^{-3}
2200	−2.221	6.01×10^{-3}
2300	−1.936	1.16×10^{-2}
2400	−1.674	2.12×10^{-2}

The effect of the $BaCO_3$ transitions at 1079 and 1241 K on the calculated equilibrium pressure is virtually nil. Calculations above 1600 K were made by extrapolating the fef values of the individual compounds.

The solid-solid transitions of $BaCO_3$ exhibit pronounced hysteresis, i.e., different temperatures are obtained, depending on whether the transition is approached from above or below [86]. The melting point can only be measured under high CO_2 pressure. ΔH and ΔS for the transitions are taken from (1).

Density of $BaCO_3$

Phase	T(K)	d	References
c	293	4.287	15
c (witherite)	299	4.308 (x-ray)	123a
c (cubic)	1348	3.889 (x-ray)	123c

Transitions of $BaCO_3$

Phase change	T(K)	ΔH	ΔS	References
		kJ mol^{-1}	J mol^{-1} deg^{-1}	
c,orthorhombic $(\gamma) \rightarrow$ c,hexagonal (β)	1076 ⎫			
c,orthorhombic $(\gamma) \leftarrow$ c,hexagonal (β)	1023 ⎭	14.9	13.7	1, 86
c,hexagonal $(\beta) \rightarrow$ c,cubic (α)	1249 ⎫			
c,hexagonal $(\beta) \leftarrow$ c,cubic (α)	1228 ⎭	3.		4, 86
c$(\alpha) \rightarrow$ 1	1653			1

Thermodynamic date (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$BaCO_3$(c, II, witherite)	112.1	26.8	1, 10
BaO	70.3	16.8	1, 5, 6

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	References
$BaCO_3$	−244.7	−297.5	12
BaO	−582.0	−139.1	91

$$BaCO_{3(c)} = BaO_{(c)} + CO_{2(g)}$$
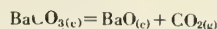
$$\Delta H^\circ_{298.15} = 269.2 \text{ kJ, } 64.35 \text{ kcal}$$

T	BaO	BaCO$_3$	Reaction			
K	fef	fef	Δfef	ΔG°_T	log K	K
	$Jdeg^{-1}$	$Jdeg^{-1}$	$Jdeg^{-1}$	kJ		
298.15	−70.3	−112.1	−171.8	218.0	−38.19$_6$	6.36 × 10^{-39}
400	−72.1	−115.7	−171.5	200.6	−26.20$_0$	6.32 × 10^{-27}
500	−75.8	−122.9	−171.0	183.7	−19.19$_4$	6.39 × 10^{-20}
600	−79.9	−131.1	−170.4	167.0	−14.53$_9$	2.89 × 10^{-15}
700	−84.2	−139.7	−169.7	150.5	−11.22$_9$	5.91 × 10^{-12}
800	−88.4	−148.3	−168.9	134.1	−8.756$_7$	1.75 × 10^{-9}
900	−92.4	−156.7	−168.0	118.0	−6.849$_3$	1.42 × 10^{-7}
1000	−96.2	−164.8	−167.1	102.1	−5.33$_4$	4.63 × 10^{-6}
1079*	−99.1	−171.10(α)	−166.39	89.70	−4.34$_2$	4.55 × 10^{-5}
		−171.08(β)	−166.37	89.72	−4.34$_3$	4.54 × 10^{-5}
1100	−99.9	−173.1	−165.8	86.8$_1$	−4.12$_3$	7.54 × 10^{-5}
1200	−103.4	−182.2$_5$	−163.3	73.2$_8$	−3.19$_0$	6.46 × 10^{-4}
1241*	−104.7	−185.8$_5$(β, γ)	−162.3	67.8$_5$	−2.85$_6$	1.39 × 10^{-3}
1300	−106.7	−191.1	−160.8	60.2$_0$	−2.41$_9$	3.81 × 10^{-3}
1400	−109.9	−199.6	−158.4	47.4$_0$	−1.77$_2$	1.69 × 10^{-2}
1500	−112.9	−207.7	−156.0	35.1$_7$	−1.22$_5$	5.96 × 10^{-2}
1600	−115.8	−215.5	−153.9	23.0$_3$	−0.75$_2$	1.77 × 10^{-1}
(1700)	−118.6	−222.9	−151.8	11.1$_3$	−0.34$_2$	4.55 × 10^{-1}
(1800)	−121.3	−230.0	−150.0	−0.791	+0.23$_0$	1.05
(1900)	−123.9	−236.6	−148.4	−12.6$_6$	+0.348	2.23

Beryllium

Normal anhydrous BeCO$_3$ probably does not exist at ambient temperatures. Dehydration of the hydrate at elevated temperatures probably forms basic carbonates [83]. The value given for ΔHf° of BeCO$_3$ is calculated from a measured value of ΔH for the reaction BeO + CO$_2$ = BeCO$_3$ [83] and the current value of BeO to be published in a continuation of [2].

Thermodynamic data (298.15 K)

	S°		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
BeCO$_3$ BeO	4.15	3.38	2

	ΔHf°		
	kJ mol^{-1}	kcal mol^{-1}	References
BeCO$_3$	−102$_5$	−245	2
BeO		−145.0	2

Cadmium

The rate of decomposition has been measured by Centnerszwer and Bruzs [34] in a CO$_2$ atmosphere and by Prodan and Pavlyuchenko [107] as a function of CO$_2$ pressure. The decomposition yields CdO without the formation of intermediates. In vacuo the activation energy is 36 kcal. The rate of decomposition depends on the method of prepara-

tion. The kinetics follow the contracting sphere model [50, 65]. Experimental dissociation pressure measurements have been reviewed by Kelley and Anderson [3], who selected the measurements of Andrussow [17] for their analysis. For the reaction CdCO$_3$ = CdO + CO$_2$ they obtain

$$\Delta G^\circ(\text{cal}) = 23{,}200 - 10.46 \ T \log T + 8.71$$
$$\times 10^{-3}T^2 - 13.80 \ T.$$

The density must be regarded as very uncertain since there are no 20th-century measurements and DeSchulten reports a value of 4.960 [42].

Density of CdCO$_3$

Phase	T(K)	Density	References
c	293	4.25$_8$ g ml^{-1}	9, Vol. I

Thermodynamic data (298.15 K)

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
CdCO$_3$	92.5	22.1	2
CdO	54.8	13.1	2

	ΔHf°		
	kJ mol^{-1} deg^{-1}	kcal mol^{-1} deg^{-1}	References
CdCO$_3$	−750.6	−179.4	2
CdO	−258.1	−61.7	2

Calcium

More kinetic studies of the thermal decomposition of $CaCO_3$ have been reported than for any other carbonate, and perhaps for any other salt. Many of the general features of carbonate decomposition described in the Introduction have been elucidated from $CaCO_3$ decomposition and will not be repeated here.

The reaction $CaCO_3 = CaO + CO_2$ is reversible. Decomposition occurs without formation of intermediate products. For compacted powders the contracting sphere model applies [72]. A comparison of experiments done with various particle sizes and with single crystals indicates that even the reaction order may vary, depending on which mechanism is rate-determining at each phase of the reaction. For example, in a careful analysis of composition versus distance in a rectangular block of powder, Kappel and Huttig [82] found different rate laws applying at varying distances from the surface. Such apparent changes in mechanism can easily occur if different processes, such as heat transport to the reaction site or escape of CO_2, become rate-determining at various stages of the decomposition. In decomposing a cube of $CaCO_3$ with thermocouples imbedded in it, it was found that the center of the cube was colder by from 15 to 85° than the nominal furnace temperature [18]. The authors suggest from this and other evidence that the decomposition rate is proportional to the heat absorbed. Such a mechanism would most likely not be applicable to thin layers of fine-grained powders.

Many values of the activation energy have been reported, nearly all near 167 kJ (40 kcal)/mol, a value approximately equal to the standard enthalpy of decomposition.

The aragonite $\rightarrow$ calcite transition has been studied as a function of temperature and pressure [37, 90]. At ambient pressure, the transition occurs near 730 K [62, 122]. In addition, a transition from vaterite to calcite occurs in the range 620 to 670 K, with small impurity concentrations producing large changes in the transition temperature [122].

Density of $CaCO_3$

Phase	T(K)	d	References
c, calcite	273	2.771 gml^{-1}	9, Vol. III
c, calcite	298	2.713	15
c, calcite	299	2.711 (x-ray)	123a
c, aragonite	297	2.930	15

Thermal expansion coefficient:

$CaCO_3$: Calcite . .	$\alpha(2°$ to $81°) = 25.1353 + 0.0118t$, $\parallel$ opt. axis; and $-5.5782 + 0.00138t$, $\perp$ opt. axis $\alpha^{40} = 26.21 + 0.0160(t-40)$, $\parallel$ opt. axis; and $= -5.40 \cdot 0.0087(t-40)$, $\perp$ opt. axis 9, Vol. III $a(50°$ to $60°) = 1.447$
$CaCO_3$: Aragonite . .	$20° - 70°$ $\begin{cases} \alpha_1^{40} = 34.60 + 0.0337t \\ \alpha_2^{40} = 17.19 + 0.0368t \\ \alpha_3^{40} = 10.16 + 0.0064t \end{cases}$

Transitions of $CaCO_3$

Phase Change	T(K)	References
c (aragonite) $\rightarrow c$ (calcite)	728	62
c (vaterite) $\rightarrow c$ (calcite)	623–673	122

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$CaCO_3$ (aragonite)	88.7	21.2	1, 5
$CaCO_3$ (calcite)	92.9	22.2	5, 6
CaO	39.7	9.5	5, 6

$\Delta Hf°$

	kJ mol^{-1}	Kcal mol^{-1}	References
$CaCO_3$ (aragonite)	−1207.04	−288.49	1
$CaCO_3$ (calcite)	−1206.87	−288.45	1
CaO	−635.09	−151.7$_9$	6

Decomposition of CaCO$_3$

$$CaCO_{3(c)} = CaO_{(c)} + CO_{2(g)}$$
from calcite $\Delta H^\circ_{298.15} = 178.28$ kJ, 42.61 kcal
from aragonite $\Delta H^\circ_{298.15} = 178.45$ kJ, 42.65 kcal.

A. Calcite

T	CaO	CaCO$_3$	Reaction			
	fef	fef	Δfef	ΔG°_T	log K	K
	J deg^{-1}	J deg^{-1}	J deg^{-1}	kJ		
298.15	-39.7	-92.9	-160.5	130.4	-22.850	1.41×10^{-23}
400	-41.5	-96.4	-160.3	114.2	-14.909	1.23×10^{-15}
500	-44.9	-103.3	-159.7	98.4_3	-10.283	5.21×10^{-11}
600	-48.7	-111.4	-158.9	82.9_2	-7.219	6.04×10^{-8}
700	-52.7	-119.8	-158.1	67.6_1	-5.045	9.01×10^{-6}
800	-56.6	-128.2	-157.2	52.5_4	-3.430	3.71×10^{-4}
900	-60.3	-136.4	-156.3	37.6_3	-2.184	6.55×10^{-3}
1000	-63.8_5	-144.2	-155.4	22.9_0	-1.196	6.36×10^{-2}
1100	-67.2	-151.8	-154.5	8.360	-0.397	4.01×10^{-1}
1200	-70.5	-159.0	-153.6	-6.06_3	$+0.264$	1.84

B. Aragonite

T	CaO	CaCO$_3$	Reaction			
	fef	fef	Δfef	ΔG°_T	log K	K
298.15	-39.7	-88.7	-164.7	129.3	-22.661	2.19×10^{-23}
400	-41.5	-92.0	-164.6	112.6	-14.707	1.97×10^{-15}
500	-44.9	-98.7	-164.3	96.30	-10.060	8.71×10^{-11}
600	-48.7	-106.5	-163.9	80.12	-6.975	1.06×10^{-7}

Cesium

Very little information on Cs$_2$CO$_3$ is available. The decomposition pressure has been measured [88]. Decomposition becomes noticeable near 880 K (2.6×10^{-3} atm at 883 K) and reaches 0.207 atm at 1453 K.

Transitions of Cs$_2$CO$_3$

Phase change	T(K)	References
c → l	1065	111

Thermodynamic data (298.15 K)

	S°		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
Cs$_2$CO$_3$			
Cs$_2$O			

	ΔHf°		
	k Jmol^{-1}	kcal mol^{-1}	References
Cs$_2$CO$_3$	$-1118._8$	-267.4	1, 10
Cs$_2$O	$-318.$	-75.9	10

Cobalt

Information on the thermal decomposition of CoCO$_3$ is scarce. A number of basic oxides have been reported [85], but their existence cannot be regarded as proved. In a more recent study [30], no intermediates were reported, but the decomposition pressure exhibited an unexplained break in the log p versus $1/T$ plot.

In view of several density values in the 4.1–4.2 range, the value of 2.818 for spherocobaltite given in [9, Vol. I] is probably in error.

Density of CoCO$_3$

Phase	d	T(K)	References
c	4.07		116
c	4.24 (x-ray)		48
c (spherocobaltite)	4.214 (x-ray)	299	123

$S°$			
	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$CoCO_3$	88.5	21.2	80
CoO	52.93	12.65	10
Co_3O_4	102.5	24.5	10

$\Delta Hf°$			
	kJ mol⁻¹	kcal mol⁻¹	References
$CoCO_3$	−722.6	−172.7	1, 10
CoO	−238._9	−57.1	10
Co_3O_4	−905.0	−216.3	10

Copper

No high-temperature thermodynamic data are available and decomposition pressures of pure $CuCO_3$ have not been measured. The temperature at which decomposition of the minerals, azurite and malachite, becomes noticeable varies, not surprisingly, with the rate of heating [119].

Thermodynamic data (298.15 K)

$S°$			
	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$CuCO_3$	87.9	21.0	10
CuO	42.63	10.19	5, 6, 10
Cu_2O	92.38 ± 0.42	22.08 ± 0.10	91a

$\Delta Hf°$			
	kJ mol⁻¹	kcal mol⁻¹	References
$CuCO_3$	−595.0	−142.2	10
CuO	−155.77 ± 0.63	−37.23 ± 0.15	91a
Cu_2O	−170.83 ± 1.26	−40.83 ± 0.30	91a

Iron

Anhydrous $FeCO_3$ can be prepared by heating the 1/2 hydrate in CO_2 at high pressure (40 to 50 atm) near 300 °C. The thermal decomposition always leads to a higher-valent oxide, since the CO_2 liberated immediately oxidizes the FeO to Fe_3O_4 [22]. The reaction may also be written as

$$3 FeCO_3 = Fe_3O_4 + 2 CO_2 + CO.$$
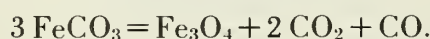
The oxidation occurs so fast that even in vacuum no FeO is formed.

Density of $FeCO_3$

Phase	$T(K)$	d	References
c, siderite	293.9	⸱.851	16

Thermal expansion coefficient:

FeCO₃: Siderite…	$\alpha^{40} = 19.2$ with $\Delta(20°-70°) = 25._5 \|\|$; and $\alpha^{40} = 6.05$ with $\Delta(20°-70°) = 917 \perp$	9, Vol. III

Thermodynamic data (298.15 K)

$S°$			
	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
$FeCO_3$	92.9	22.2	1, 10
FeO ($Fe_{.947}O$)	57.49	13.74	5
Fe_3O_4	146.4	35.0	5
Fe_2O_3	87.4	20.9	5

$\Delta Hf°$			
	kJ mol⁻¹	kcal mol⁻¹	References
$FeCO_3$	−740.6	−177.0	270–3 unpubl.
FeO ($Fe_{0.947}O$)	−266.5	−63.7	1
Fe_3O_4	−1117.	−267.0	1, 10
Fe_2O_3	−822.1_5	−196.5	1, 10

Lead

In a careful study of $PbCO_3$ decomposition, Centnerszwer, Falk, and Awerbuch [36] determined the following successive equilibria at 1 atm CO_2:

$$\overset{274°}{PbCO_3 \longleftrightarrow} 3 PbO \cdot 5 PbCO_3 \overset{286°}{\longleftrightarrow}$$

$$\overset{360°}{PbO \cdot PbCO_3 \longleftrightarrow} 2 PbO \cdot PbCO_3 \overset{412°}{\longleftrightarrow} PbO.$$
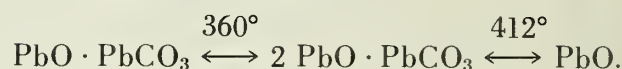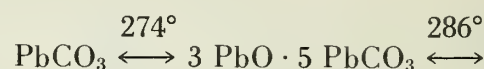
In a kinetic study of $PbCO_3$ decomposition, these authors (31) found an induction period which was accelerated by small amounts of H_2O, and a first-order decomposition for the main course of the reaction independent of moisture content.

Glasner and Hodara [57] have reexamined the basic carbonates and find $2 PbO \cdot 3 PbCO_3$ to be the carbonate of lowest oxide content. They list the following pressures:

	$PbCO_3$		$2 PbO \cdot PbCO_3$			$5 PbO \cdot 6 PbCO_3$	
°C	222	271	240	246	320	290	380
p (mm)	72	690	75	81	690	101	690

	$PbO \cdot PbCO_3$		$3 PbO \cdot 2 PbCO_3$	
°C	350	390	370	430
p (mm)	123	690	150	690

Kelley and Anderson [3] have used the enthalpy data of Marshall and Bruzs [93] to calculate the thermodynamic functions for the reactions

(1) $2 PbCO_3 = PbO \cdot PbCO_3 + CO_2$

$\Delta H(cal) = 20,230 + 4.23 T − 8.21 \times 10^{-3} T^2$

$\Delta G°(cal) = 20,230 − 9.74 \log T + 8.21 \times 10^{-3} T^2 − 13.60 T$
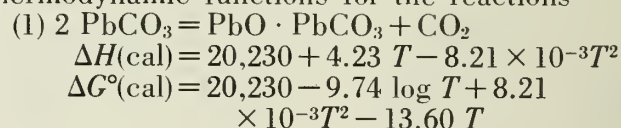
(2) $PbO \cdot PbCO_3 = 2\ PbO + CO_2$

$\Delta H(cal) = 20{,}910 + 4.23\ T - 8.21 \times 10^{-3}T^2$

$\Delta G^\circ(cal) = 20{,}910 - 9.74\ T \log T$
$\qquad + 8.21 \times 10^{-3}T^2 - 12.96T.$

In studying the decomposition of $PbCO_3$ in vacuum as a function of temperature and particle size, Kadlets and Dubinin [81] found that, in contrast to the work of Centnerszwer and Awerbuch, the induction period was absent if the sample was brought to the reaction temperature very rapidly. The rate $(-dm/dt)$ was proportional to the surface area. The expected conformity with eq (10) was observed. Rate constants, expressed in g $s^{-1}cm^{-2}$, were independent of particle size. Hence the decomposition of $PbCO_3$ conforms to the contracting sphere model with rapid surface coverage by nuclei. The kinetic results are summarized by the relation

$k(g\ cm^{-2}s^{-1}) = (0.5 \pm 0.5) \exp(-41{,}500\ kcal/RT)$

in the range 236 to 335 °C.

These results were confirmed by a similar study in nearly the same temperature range [115] for which $E = 40.2$ kcal was found. The reaction rate with freshly prepared and with ground samples differed probably because of changes in the surface structure.

Density of $PbCO_3$

Phase	T(K)	d	References
c	275.3	6.533	16
c	299	6.582 (x-ray)	123a

Thermodynamic data (298.15 K)

S°			
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
PbCO$_3$	131.0	31.3	2
PbO (yellow)	68.70	16.42	2
PbO (red)	66.5	15.9	2
PbO·PbCO$_3$	204.	48.8	2

ΔHf°			
	kJ mol^{-1}	kcal mol^{-1}	References
PbCO$_3$	−699.1	−167.1	2
PbO (yellow)	−217.3	−51.94	2
PbO (red)	−219.0	−52.34	2
PbO·PbCO$_3$	−816.7	−195.2	2

Lithium

The melting point of Li_2CO_3 is still uncertain. Two recent measurements [75, 111] are considerably lower than the value of 1008 K given in (1),

but differ from each other by 6°. In both of these studies, the salt was protected from decomposition by being kept under a pressure of CO_2 high enough to prevent weight changes. ΔH_m values given by [77] and [112] differ by 7 kJ.

Equilibrium pressures of CO_2 above liquid Li_2CO_3 were measured by Janz and Lorenz [75], using a dynamic method in which the temperature was varied until weight changes (losses on heating, gains on cooling) were noted. The resulting pressures are larger by several orders of magnitude than K values determined from thermodynamic data. This apparent discrepancy can be accounted for by considering that $K = (a_{Li_2O}/a_{Li_2CO_3})P_{CO_2}$ and therefore $(a_{Li_2O}/a_{Li_2CO_3}) = K/P_{CO_2}$. For example, at 1000 K we calculate $K = 2 \times 10^{-6}$, whereas $P_{CO_2} \simeq 1.9 \times 10^{-2}$, i.e., $a_{Li_2O}/a_{Li_2CO_3} \simeq 10^{-4}$. This is not unreasonable since Li_2O almost certainly dissolves in molten Li_2CO_3. It is for this reason that we have relied, whenever possible, on thermodynamically calculated equilibrium constants.

Density of Li_2CO_3

Phase	T (K)	d	References
c	290.7	2.111	9, Vol. I
l	1012.2	1.8246	75
	1027.4	1.8189	
	1029.7	1.8190	
	1052.1	1.8119	
	1069.7	1.8036	
	1082.7	1.7987	
	1105.1	1.7910	
	1120.1	1.7843	

The liquid data are fitted by

$$d = 2.2026 - 0.3729 \times 10^{-3}T\ (1010{-}1120\ K).$$

Transitions of Li_2CO_3

Phase change	T (K)	ΔH kJ mol^{-1}	References
c → l	993		111
	999	42.	75
	1008		1

Thermodynamic data (298.15 K)

S°			
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
Li$_2$CO$_3$	90.17	21.55	10b
Li$_2$O	37.89	9.056	10a

ΔHf°			
	kJ mol^{-1}	kcal mol^{-1}	References
Li$_2$CO$_3$	−1216.04	−290.64	10b
Li$_2$O	−598.7	−143.1	10a

$$Li_2CO_{3(c)} = Li_2O_{(c)} + CO_{2(g)}$$
$$\Delta H^\circ_{298.15} = 223.8_0 kJ, 53.49 \text{ kcal}$$
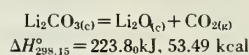
T	Li$_2$O	Li$_2$CO$_3$	Reaction			
	fef	fef	Δfef	ΔG°_T	log K	K
	J deg^{-1}	*J deg^{-1}*	*J deg^{-1}*	*kJ*		
298.15	−37.89	−90.17	−161.35	175.69	−30.780	1.66×10^{-31}
400	−40.15	−94.16	−161.14	159.34	−20.808	1.56×10^{-21}
500	−44.71	−102.1$_9$	−160.65	143.47	−14.988	1.03×10^{-15}
600	−50.08	−111.8$_6$	−159.82	127.90	−11.135	7.33×10^{-12}
700	−55.67	−122.5$_0$	−158.39	112.93	−8.427	3.75×10^{-9}
800	−61.25	−133.5$_7$	−156.50	98.60	−6.438	3.65×10^{-7}
900	−66.71	−144.3$_8$	−154.67	84.60	−4.910	1.23×10^{-5}
1000	−72.00	−192.9$_8$	−114.76	109.04	−5.695	2.02×10^{-6}
1100	−77.12	−203.7$_1$	−112.42	100.13	−4.755	1.76×10^{-5}
1200	−82.06	−214.0$_6$	−110.16	91.60	−3.988	1.03×10^{-4}
1300	−86.82	−224.0$_1$	−108.00	83.40	−3.351	4.46×10^{-4}
1400	−91.41	−233.5$_6$	−105.96	75.46	−2.815	1.53×10^{-3}
1500	−95.85	−242.7$_1$	−104.03	67.75	−2.359	4.37×10^{-3}
1600	−100.13	−251.5$_0$	−102.22	60.25	−1.967	1.08×10^{-2}
1700	−104.3$_6$	−259.9$_4$	−100.50	52.94	−1.627	2.36×10^{-2}
1800	−108.26	−268.0$_4$	−98.90	45.78	−1.329	4.69×10^{-2}
1900	−137.00	−275.8$_3$	−122.25	−8.473	+0.233	1.71
2000	−141.09	−283.3$_4$	−121.16	−18.53	+0.484	3.05

Magnesium

In vacuum, MgCO$_3$ decomposes to MgO at temperatures as low as 320 °C, the solids exhibiting x-ray lines corresponding to MgCO$_3$ and MgO only [60]. In earlier work, Centnerszwer and Bruzs [32, 33] had reported the following series of equilibria at 1 atm CO$_2$ (in °C).

$$MgCO_3 \overset{373°}{\longleftrightarrow} MgO \cdot MgCO_3 \overset{442°}{\longleftrightarrow} 3$$

$$MgO \cdot MgCO_3 \overset{469°}{\longleftrightarrow} 4\ MgO + CO_2$$
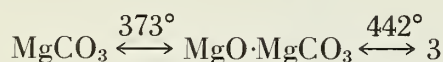
These equilibria are based entirely on pressure measurements and weight loss data. Until structural evidence for the existence of these compounds is produced, their existence must be regarded as doubtful.

The decomposition follows the "rapid nucleation and contracting sphere" kinetics with an activation energy of 150 kJ (36 kcal), somewhat higher than the enthalpy of decomposition [29, 38, 95].

Density of MgCO$_3$

Phase	T(K)	d	References
c	294.6	2.980	15
c	298	3.037	9, Vol. I
c (magnesite)	298	3.009 (x-ray)	123b

Thermal expansion coefficient:

MgCO$_3$:Magnesite	$\alpha^{30} = 21.3$ with $\Delta(20° - 70°)$, $= 33.9\|\|$; and $\alpha^{40} = 5.99$ with $\Delta(20° - 70°) = 24.3 \perp$	9, Vol. III

Thermodynamic data (298.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
MgCO$_3$	65.86	15.74	10b
MgO (periclase)	26.9$_4$	6.44	10b

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	References
MgCO$_3$	−1111.7	−265.7	10b
MgO (periclase)	−601.2	−143.7	10b
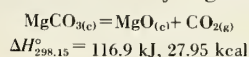
T	MgO	MgCO$_3$	Reaction			
	f~f	fef	Δfef	ΔG°_T	log K	K
	J deg^{-1}	J deg^{-1}	J deg^{-1}	kJ		
298.15	-26.9_4	-65.86	-174.72	64.85	-13.361	4.36×10^{-14}
400	-28.4_8	-69.03	-174.60	47.10	-6.151	7.07×10^{-7}
500	-31.5_3	-75.43	-174.23	29.82	-3.115	7.67×10^{-4}
600	-35.0_9	-83.46	-173.23	13.00	-1.132	7.39×10^{-2}
700	-38.7_5	-91.08	-172.90	-4.088	$+0.305$	2.02
800	-42.3_7	-99.19	-172.00	-20.66	$+1.349$	22.35
900	-45.8_7	-107.19	-171.02	-36.98	$+2.146$	140.
1000	-49.2_4	-115.01	-169.97	-53.03	$+2.770$	539.

Manganese

The thermal decomposition of MnCO$_3$ is complicated by the easy interconvertibility of the various manganese oxides. When MnCO$_3$ is decomposed in O$_2$-containing atmospheres, the oxide formed depends on the temperature. In addition, a number of nonstoichiometric oxides are also formed [24], the particular oxide formed depending primarily on the temperature and partial pressure of oxygen. In the absence of oxygen, the decomposition product is MnO, at least up to 300 or 400 °C [43]. Above this temperature range, MnO may be oxidized by the CO$_2$ formed according to [94]

$$MnO + 1/3 \; CO_2 = 1/3 \; Mn_3O_4 + 1/3 \; CO.$$
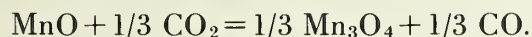
The decomposition can thus also be thought of

$$3 \; MnCO_3 = Mn_3O_4 + 2 \; CO_2 + CO.$$
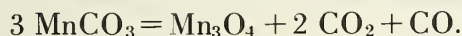
The actual temperature at which such transformations occur therefore depends on the efficiency of CO$_2$ removal and on the partial pressure of O$_2$. The thermodynamics of many reactions involving manganese compounds have been given by Mah [90a]. The predominent mode of decomposition of MnCO$_3$ is MnCO$_3$ = MnO + CO$_2$ and we have therefore given equilibrium constants only for this reaction. Our results agree very closely with Mah's. Thermodynamic functions for other oxides are listed in [11 and 90a]. The kinetics follows the contracting sphere model.

Density of MnCO$_3$

Phase	T(K)	d	References
c	293	3.125 gml^{-1}	9, Vol. I
c, rhodochrosite	294.4	3.633	16

Thermodynamic functions (298.15 K)

	S°		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
MnCO$_3$	85.8	20.5	5, 10
MnO	59.71	14.27	5, 10
Mn$_3$O$_4(\alpha)$	154	36.8	99
Mn$_2$O$_3$	110.$_5$	26.4	5
MnO$_2$	53.05	12.68	5

	ΔHf°		
	KJ mol^{-1}	kcal mol^{-1}	References
MnCO$_3$	-94.96	-213.9	5
MnO	-385.1	-92.05	6, 10
Mn$_3$O$_4(\alpha)$	$-1386._8$	-331.4	6, 10
Mn$_2$O$_3$	-956.9	-228.7	99, 100
MnO$_2$	-520.9	-124.5	1, 10
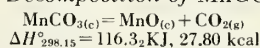
T	MnO	MnCO$_3$	Reaction			
	fef	fef	Δfef	ΔG°_T	log K	K
	J deg^{-1}	J deg^{-1}	J deg^{-1}	kJ		
298.15	-59.71	-85.7_7	-187.5_6	60.39	-10.580	2.63×10^{-14}
400	-61.53	-89.2_0	-187.4_7	41.32	-5.396	4.02×10^{-6}
500	-64.98	-95.9_8	-187.1_3	22.75	-2.377	4.20×10^{-3}
600	-68.95	-103.9_7	-186.6_1	4.34$_3$	-0.378	4.19×10^{-1}
700	-72.97	-112.3_0	-185.9_0	-13.81_5	$+1.031$	10.74

Nickel

There is no evidence for the existence of anhydrous $NiCO_3$, although hydrates are well known. These lose H_2O on heating up to 470 K, but some CO_2 is probably also lost before all the H_2O is removed [41, 52]. In addition, the NiO product seems to lose oxygen rather easily since metallic Ni has been found in NiO formed by the decomposition of $NiCO_3$ below 700 K [114]. $S^o_{298.15}$ of $NiCO_3$ has been calculated from low temperature C_p measurements to be 85.4 J mol^{-1} deg^{-1} [80].

Potassium

The free energy functions of K_2O in [10a] are based on estimated C_p and S^o_{298} values. In the 1966 revision [10b] fef values of K_2CO_3 are listed to 2500 K, but decomposition pressures cannot be calculated above 1100 K because fef data for K_2O are lacking above this temperature. K_2O is sufficiently unstable for its dissociation to $K_{(g)}$ and O_2 to be significant. Equilibrium constants for this reaction are given in [10a] and can be combined with the data in this work to give the partial pressures of all the vapor species.

Density of K_2CO_3

Phase	T (K)	d	
c	293	2.330 gml^{-1}	9, Vol. III
c	288	2.29 gml^{-1}	9, Vol. I
l	1180.8	1.8922 gcm^{-3}	75
	1185.3	1.8904	
	1193.9	1.8864	
	1195.9	1.8848	
	1206.6	1.8824	
	1213.5	1.8778	
	1220.0	1.8749	
	1223.6	1.8735	
	1234.1	1.8684	
	1236.3	1.8670	
	1245.3	1.8640	
	1257.4	1.8584	
	1270.0	1.8527	
	1283.3	1.8467	

The liquid data are fitted by

$$d = 2.4141 - 0.4421 \times 10^{-3}\, T \quad (1180\text{–}1280 \text{ K}).$$

Transitions of K_2CO_3

Phase change	T(K)	ΔH	ΔS	References
		KJ mol^{-1}	J mol^{-1} deg^{-1}	
c, IV → c, III	523			1
c, III → c, II	701			1
c, II → c, I	895			1
c, I → l	1171 ± 2	27		75, 77, 111, 112

Thermodynamic data (298.15 K)

	S^o		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
K_2CO_3	155.5	37.17	10b
K_2O	94.1	22.5	10b

	ΔHf^o		
	KJ mol^{-1}	kcal mol^{-1}	References
K_2CO_3	−1150.2	−274.9	10b
K_2O	−363.2	−86.8	10b

$$K_2CO_{3(c)} = K_2O_{(c)} + CO_{2(g)}$$
$$\Delta H^\circ_{298.15} = 393.5 \text{ KJ}, 94.05 \text{ kcal}$$
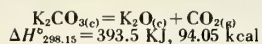
T	K₂O	K₂CO₃	Reaction			
	fef	fef	Δfef	ΔG_T°	log K	K
	$J\,deg^{-1}$	$J\,deg^{-1}$	$J\,deg^{-1}$	kJ		
298.15	−94.1	−155.5	−152.3	348.1	−60.987	1.03×10^{-61}
400	−97.5	−160.2	−152.5	332.5	−43.420	3.80×10^{-44}
500	−104.2	−169.4	−152.9	317.1	−33.123	7.53×10^{-34}
600	−111.8	−180.3	−153.1	301.6	−26.260	5.49×10^{-27}
700	−119.5	−191.6	−153.1	286.3	−21.365	4.31×10^{-22}
800	−127.1	−203.0	−153.0	271.1	−17.703	1.98×10^{-18}
900	−134.5	−214.2	−152.7	256.1	−14.864	1.37×10^{-15}
1000	−141.7	−225.2	−152.2	241.3	−12.603	2.50×10^{-13}
1100	−148.5	−235.9	−151.7	226.7	−10.763	1.73×10^{-11}

Rare Earths

The existence of the anhydrous carbonates at ambient temperatures has not been proved, although hydrates are well known [126]. Such hydrates decompose on heating, losing water at first, and then forming a series of basic carbonates, but it is not certain whether the initial loss of water is also accompanied by some decomposition of the carbonate ion [14]. However, anhydrous carbonates of La, Ce, Pr, Nd, Sa, Eu, and Gd, have been reported by Head and Holley [64], who carefully decomposed the hydrates by TGA and removed the theoretical amount of H_2O.

The formation of carbonates also results from the thermal decomposition of oxalates, but these seem to be formed as basic carbonates or in mixtures with oxides [58, 70, 101]. No thermodynamic data are available.

Similarly, the existence of $Pu(CO_3)_2$ as an intermediate in the decomposition of $Pu(C_2O_4)_2$ has been reported [78].

Rubidium

Very little information is available. The melting point listed is 38° higher than the previously accepted value. However, it has been confirmed by a recently determined value of 1143 K [46].

Transitions of Rb₂CO₃

Phase change	T (K)	Reference
c → l	1146	111

Thermodynamic data (298.15 K)

	S°		
	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
Rb₂CO₃	174.₉	41.8	2 (unpubl.)
Rb₂O	(124.)	(29.7)	1

	ΔHf°		
	kJ mol⁻¹	kcal mol⁻¹	References
Rb₂CO₃	−1128.₀	−269.6	1, 10
Rb₂O	−330.	−78.9	1, 10

Silver

The thermal decomposition of Ag_2CO_3 is complicated by the fact that the decomposition product, Ag_2O, decomposes further ($Ag_2O \rightarrow 2\ Ag + 1/2\ O_2$, for thermodynamic data see [100a]). Therefore weight loss experiments can only be carried out in the relatively narrow temperature region, < 250 °C, where Ag_2CO_3 decomposes but Ag_2O does not. Alternatively, at higher temperatures the reaction can be followed by absorbing CO_2 and O_2 in separate traps and measuring their respective weight changes [81].

The kinetics are most consistent with a model of rapid nucleation followed by contracting sphere kinetics [120]. However, the actual rates are extremely dependent on the method of preparation. Kadlets and Dubinin [81] studied this effect by preparing Ag_2CO_3 by two methods — one by precipitation from concentrated solutions which precipitated rapidly, the other by precipitation from

very dilute solution so that the salt first formed as a supersaturated solution. Although both preparations exhibit the same x-ray diffraction pattern, the second preparation decomposes much more rapidly than the first, an effect which the authors attribute to a higher defect density. Direct evidence is lacking, however.

Free energy functions of Ag_2CO_3 and Ag_2O are calculated from data in [4].

Transitions of Ag_2CO_3

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

Thermodynamic data (298.15 K)

	$S°$		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
Ag_2CO_3	167.$_4$	40.0	2
Ag_2O	121.$_3$	29	5

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	References
Ag_2CO_3	−505.8	−120.9	2
Ag_2O	−31.0$_5$	−7.42	2

Density of Ag_2CO_3

Phase	T (K)	d	References
c	293	6.077 gml^{-1}	9, Vol. I
c	298	6.131 (x-ray)	124

Decomposition of Ag_2CO_3

$$Ag_2CO_{3(c)} = Ag_2O_{(c)} + CO_{2(g)}$$
$$\Delta H°_{298.15} = 81.291 \text{ kJ, } 19.429 \text{ kcal}$$
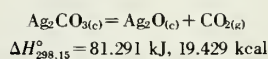
T	Ag_2O	Ag_2CO_3	Reaction			
K	fef	fef	Δfef	$\Delta G°_T$	log K	K
	$J\ deg^{-1}$	$J\ deg^{-1}$	$J\ deg^{-1}$	$\dfrac{kJ}{}$		
298.15	−121.3	−167.4	−167.6	31.32	−5.487	3.26×10^{-6}
350	−122.2	−168.7	−167.5	22.66	−3.381	4.16×10^{-4}
400	−124.0	−171.9	−167.3	14.38	−1.878	1.33×10^{-2}
450	−126.5	−176.0	−167.0	61.4$_3$	−0.713$_0$	1.85×10^{-1}
500	−129.2	−180.7	−166.6	−2.08$_7$	+0.211$_1$	1.63
(550)	−132.0	−185.6	−166.2	−10.09	+0.958$_7$	9.09

Sodium

The literature on the phase transitions is somewhat contradictory. The transitions at 629 and 759 K but not the one at 891° were recently observed by Reisman, as was the melting point. Two other transitions, at 593 and 723 K were observed by Ginzburg [56] and Popov [106], and very similar values also by Jaffrey and Martin [74].

ΔH_m values of [77] and [112] differ by 5 kJ. We have listed the average value. According to Khlapova [84], who studied the polymorphism of Na_2CO_3 by DTA, the actual transition temperature will vary somewhat, depending on sample preparation and treatment, in some cases by 10 to 15°. If this is so, the solid-solid transitions would require careful reinvestigation.

Decomposition pressures were measured by Janz and Lorenz [75], but the same comments apply to them as were made for Li_2CO_3. The difficulties encountered in measuring equilibrium pressures above the liquid salt by the effusion method have been described in great detail by Motzfeld [94a]. He showed that above the melting point CO_2, $Na_{(g)}$, and O_2 vaporize from the melt, but that the activation energy for evaporation of CO_2 is

quite high. Consequently both the observed pressure and the steady-state composition of the melt depend on the size of the effusion orifice.

In this paper we have not calculated the partial pressures of the above three gaseous species, but they can easily be calculated from the equilibrium constants for the dissociation of the oxide given in [10a], and the table in this work.

Density of Na_2CO_3

Phase	T	d	References
c	293	2.533 $g\ ml^{-1}$	9, Vol. I
l	1137.9	1.9685 gcm^{-3}	75
	1146.2	1.9666	
	1165.5	1.9576	
	1178.8	1.9508	
	1184.7	1.9477	
	1223.3	1.9288	
	1233.2	1.9264	
	1244.8	1.9211	
	1260.3	1.9142	
	1277.0	1.9080	

The liquid data are fitted by

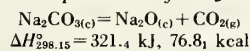$$d = 2.4797 − 0.4487 \times 10^{-3}T \ (1140 − 1280 \text{ K})$$

Transitions of Na_2CO_3

Phase change	T (K)	ΔH	References
		$K\ J\ mol^{-1}$	
c, IV → c, III	629		1
c, III → c, II	759		1
c, II → c, I	891		1
c, I → 1	1129 ± 2	31	75, 77, 112

Thermodynamic data (298.15 K)

	$S°$		
	$J\ mol^{-1}$ deg^{-1}	$cal\ mol^{-1}\ deg^{-1}$	References
Na_2CO_3	138.7	33.17	10b
Na_2O	75.27	17.99	10b

	$\Delta Hf°$		
	$kJ\ mol^{-1}$	$kcal\ mol^{-1}$	References
Na_2CO_3	-1130.7_7	-270.26	10b
Na_2O	$-415._9$	-99.4	10b

Decomposition of Na_2CO_3

$$Na_2CO_{3(c)} = Na_2O_{(c)} + CO_{2(g)}$$
$$\Delta H°_{298.15} = 321._4 \text{ kJ, } 76.8_1 \text{ kcal}$$

T	Na_2O	Na_2CO_3	Reaction			
	fef	fef	Δfef	$\Delta G_T°$	$\log K$	K
	$J\ deg^{-1}$	$J\ deg^{-1}$	$J\ deg^{-1}$	kJ		
298.15	-75.27	-138.7_8	-150.1_1	276.62	-48.462	3.45×10^{-49}
400	-78.19	-143.3_2	-150.0_1	261.36	-34.131	7.40×10^{-35}
500	-83.82	-152.3_3	-149.6_2	246.56	-25.758	1.75×10^{-26}
600	-90.31	-163.1_0	-148.8_1	232.08	-20.205	6.25×10^{-21}
700	-96.98	-174.7_0	-147.5_0	218.12	-16.276	5.29×10^{-17}
800	-103.58	-186.5_8	-145.8_2	204.71	-13.366	4.30×10^{-14}
900	-110.03	-198.0_0	-144.3_7	191.44	-11.111	7.75×10^{-12}
1000	-116.26	-208.9_8	-143.0_3	178.34	-9.316	4.83×10^{-10}
1100	-122.30	-219.5_9	-141.7_2	165.47	-7.858	1.39×10^{-8}
1200	-147.25	-249.0_9	-140.3_2	152.98	-6.659	2.19×10^{-7}
1300	-154.13	-259.4_8	-139.8_5	139.57	-5.608	2.47×10^{-6}
1400	-160.65	-269.4_4	-139.3_2	126.31	-4.713	1.94×10^{-5}
1500	-166.85	-278.9_6	-138.7_8	113.19	-3.942	1.14×10^{-4}
1600	-172.74	-288.0_9	-138.2_9	99.77	-3.271	5.36×10^{-4}
1700	-178.35	-296.8_4	-137.6_9	87.3_0	-2.682	2.08×10^{-3}
1800	-183.70	-305.2_4	-137.1_4	74.51	-2.162	6.88×10^{-3}
1900	-188.82	-313.3_0	-136.6_1	61.81	-1.699	2.00×10^{-2}
2000	-193.73	-321.0_6	-136.0_8	49.21	-1.285	5.19×10^{-2}
2100	-198.44	-328.5_4	-135.5_7	36.68	-0.912	1.22×10^{-1}
2200	-202.97	-335.74	-135.0_6	24.23	-0.575	2.66×10^{-1}
2300	-207.33	-342.6_9	-134.5_8	11.84	-0.269	5.38×10^{-1}
2400	-211.52	-349.4_1	-134.0_9	-0.454	$+0.009_9$	1.02

Strontium

In contrast to the numerous studies of $CaCO_3$ and $MgCO_3$, the decomposition of $SrCO_3$ has received very little attention. Wanmaker and Radielovic [128] studied the decomposition in air thermogravimetrically and report that it commenced at 850 °C and was finished at 1175 °C. The rate for fine and coarse powders was nearly the same. Up to 950 °C the decomposition rate was constant, at higher temperatures a change from zero-order to first-order kinetics occurred as the reaction progressed beyond $\alpha = 0.5$.

Lander [86] observed considerable hysteresis in measuring the orthorhombic-hexagonal transi-

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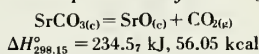tion, but even the higher of his two temperatures is 13° lower than the value given below.

Density of SrCO₃

Phase	T(K)	d	References
c,strontianite	298	3.736	15
c,precipitated salt		3.585	21

Transitions of SrCO₃

Phase change	T(K)	ΔHf	References
		$kJ \cdot mol^{-1}$	
c,orthorhombic → c,hexagonal	1198	17	1, 19, 86
c,hexagonal → c,cubic	1770		19
c → l	1770		1

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
SrCO₃	97.1	23.2	1, 5
SrO	54.4	13.0	10

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	References
SrCO₃	−1220.1	−291.6	12
SrO	−592.0	−141.5	91

Decomposition of SrCO₃

$$SrCO_{3(c)} = SrO_{(c)} + CO_{2(g)}$$
$$\Delta H°_{298.15} = 234.5_7 \text{ kJ, } 56.05 \text{ kcal}$$

T	SrO	SrCO₃	Reaction			
	fef J deg⁻¹	fef J deg⁻¹	Δfef J deg⁻¹	$\Delta G_T°$ kJ	log K	K
298.15	−54.4	−97.1	−171.0	183.7	−32.18	6.5×10^{-33}
400	−56.3	−100.6	−170.8	166.4	−21.72	1.9×10^{-22}
500	−59.8	−107.₆	−170.4	149.5	−15.62	2.4×10^{-16}
600	−63.8	−115.₇	−169.8	132.8	−11.56	2.7×10^{-12}
700	−68.0	−124.₀	−169.2	116.2	−8.67	2.1×10^{-9}
800	−72.0	−132.₂	−168.7	99.7₃	−6.51	3.1×10^{-7}
900	−76.0	−140.₂	−168.1	83.3₇	−4.84	1.4×10^{-5}
1000	−79.7	−147.₉	−167.5	67.1₄	−3.51	3.1×10^{-4}
1100	−83.3	−155.₄	−167.0	51.0₁	−2.42	3.8×10^{-3}
1200	−86.7	−162.₆	−166.2	35.2₀	−1.53	2.9×10^{-2}
1300	−89.9	−170.₈	−164.3	21.1₂	−0.85	1.4×10^{-1}
1400	−93.0	−179.₆	−162.5	7.24	−0.27	5.4×10^{-1}
1500	−95.9	−186.₁	−160.7	6.36	+0.22	1.7

Thallium

There is disagreement about the course of the decomposition. According to TGA studies [44], Tl₂CO₃ is stable well into the liquid range, up to 645 K, and then decomposes to a basic salt. Both Gattow [55] and Rossa [110] find decomposition directly to Tl₂O, without intermediates.

Density of Tl₂CO₃

Phase	T (K)	d	References
c	293	7.11	9, Vol. I
c,γ monoclinic		7.24 (X-ray)	125

Transitions of Tl₂CO₃

Phase Change	T (K)	ΔH	ΔS	References
		$kJ \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot dep^{-1}$	
C, II → c, I	591			127
C, I → I	546	18	36	1
	536			125

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	References
Tl₂CO₃	−155.2	37.1	2
Tl₂O	−126.	30.	2

$\Delta Hf°$

	KJ mol⁻¹	kcal mol⁻¹	References
Tl₂CO₃	−700.0	−167.3	2
Tl₂O	−178.7	−42.7	2

Zinc

The decomposition of ZnCO₃ has been studied by several authors. Huttig, Meller, and Lehman [67] used natural ZnCO₃, smithsonite. Bretsznaider and Cibor [28] used synthetic material. In neither

case was the material pure $ZnCO_3$. There is also some indication that the decomposition is not entirely reversible [113, 132]. It is generally agreed that over most of the concentration range, contracting sphere kinetics are followed, but the details of the induction period are not certain. Various values have been reported for the activation energy and it is not yet certain whether the value at zero pressure is equal to the enthalpy of the reaction.

Density of $ZnCO_3$

Phase	T (K)	d	References
c	293	4.4$_4$	9, Vol. I
c, smithsonite	296	4.348	16
c (smithsonite)	298	4.333 (x-ray)	123c

Transitions of $ZnCO_3$

Phase change	T (K)

Thermodynamic data (298.15 K)

	$S°$		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	References
$ZnCO_3$	82.4	19.7	2
ZnO	43.64	10.43	2

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	References
$ZnCO_3$	-812.78	-194.26	2
ZnO	-348.2_8	-83.24	2

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