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High Temperature Properties and Decomposition of Inorganic Salts
Part 3. Nitrates and Nitrites

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The literature dealing with the high-temperature behavior of inorganic nitrates and nitrites has been critically reviewed. Values of \((G - H_{298})/T\) of the reactants and products of the decomposition reactions were calculated and have been tabulated from 298 K up to as high a temperature as possible. Equilibrium constants and partial pressures were tabulated. Auxiliary data on phase transitions and densities have also been included. Qualitative information about the thermal decomposition of the salts is reviewed.

Key words: Nitrates; nitrites; thermal decomposition; thermodynamic functions.

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1. Introduction

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 most important 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 many of these salts might have useful properties, 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.

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In the preceding two volumes dealing with carbonates and sulfates, respectively, it was possible to calculate thermodynamic functions for the decomposition reactions of many salts because (1) the reactions were well known, and (2) heat capacities for the salts and the decomposition products were known. Moreover the composition of the gas phase is simple in both cases: \( \text{CO}_2 \) for the carbonates, and the single equilibrium \( \text{SO}_2 = \text{SO}_2 + 1/2 \text{O}_2 \) for the sulfates.

The situation with respect to nitrate decomposition is different: (1) Many nitrates, particularly those of the transition metals, have only recently been prepared in the anhydrous state and very little is known of their thermal behavior, (2) The decomposition of the alkali and alkaline earth nitrates first proceeds to the corresponding nitrates. Over certain temperature ranges nitrates and nitrites may be in equilibrium. Therefore these two groups of salts are treated in a single volume. (3) The course of most of the decompositions is not well understood. The gas phase composition is complex and may contain \( \text{O}_2 \), \( \text{N}_2 \), and several oxides of nitrogen. All of these gases may react with the salts and each other, reversibly or irreversibly. The course of the decomposition thus depends on experimental conditions. (4) For very few nitrates are there any thermodynamic data above 298 K; for nitrites there are virtually none.

The procedure that has been followed represents a compromise between total reliance on thermodynamic data above 298 K; for nitrites there are virtually none. When experimental studies exist, these are discussed and, when possible, used in the calculations. When no experimental data about the decompositions exist, the thermodynamic data are used to calculate equilibrium constants and partial pressures for the reactions that probably occur. Since knowledge of the gas phase properties — \( \text{N}_2 \), \( \text{O}_2 \), and the nitrogen oxides — is important for these calculations, these are discussed in a separate section. Following the procedure established in the preceding monographs of this series subsidiary data on phase transitions and densities have also been listed.

### 2. Units, Symbols, and Abbreviations

- **J** = joule
- **cal** = thermochemical calorie = 4.1840 J
- **P** = pressure; 1 atm = 101325 N m\(^{-2}\) = 1013250 dyn cm\(^{-2}\)
- **T(K)** = temperature in degrees Kelvin, defined on 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\(^{o}\)** = standard enthalpy
- **\( \Delta H^o \)** = standard enthalpy of formation
- **S\(^{o}\)** = standard entropy
- **G\(^{o}\)** = standard Gibbs energy
- **fef** = free energy function = \( \frac{G^o - H^o}{T} \)
- **TGA** = thermogravimetric analysis
- **DTA** = differential thermal analysis

### 3. Gaseous Equilibria in the N-O System

When nitrates and nitrites are thermally decomposed, nitrogen, oxygen, and their compounds are produced. A survey of the literature produces the following list of substances which appear in one or another decomposition: \( \text{O}_2 \), \( \text{N}_2 \), \( \text{NO} \), \( \text{NO}_2 \), \( \text{N}_2\text{O}_3 \), \( \text{N}_2\text{O}_4 \), \( \text{N}_2\text{O}_5 \). Which of these substances are produced in any specific case depends on the salt, the temperature, and the experimental conditions. Since reactions between these substances occur quite readily, thermodynamic functions for these substances and reactions between them have been listed up to 1200 K. (Nitrates and nitrites decompose well below this temperature.)

There are two major sources for enthalpies and entropies: (1) the ongoing revision of NBS Circular 500, Wagman et al. [1b] lists values at 298.15 K; (2) the JANAF tables [2] list these as well as free energy functions up to 6000 K. The two compilations agree quite closely (cf. table 1) except for the entropies of \( \text{N}_2\text{O}_3 \) and \( \text{N}_2\text{O}_5 \), although even these probably agree within experimental error. They represent different evaluations of the same data [1b]. For internal consistency we have selected the JANAF values. Free energy functions used in the calculations are listed in table 2. Tables 3 to 10 list thermodynamic functions for chemical gas phase reactions which may occur during the decomposition of nitrates and nitrites. To preserve differences, fef values in these tables are given to more significant figures than the values at 298.15 K listed in table 1. This policy is the same as used by [2]. For similar reasons \( \Delta H^{298.15} \) values are frequently listed to more significant figures than warranted by the data. In these cases the uncertain digits have been subscripted. In listing thermodynamic values in joules enough significant figures have been retained to permit recovery of the original calories.

#### Table 1. \( \Delta H_{298.15}^{o} \) and \( S_{298.15}^{o} \) for some gases in the N-O system

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \Delta H_{298.15}^{o} ) (kJ mol(^{-1})) [2]</th>
<th>( S_{298.15}^{o} ) (J mol(^{-1})deg(^{-1})) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>270–3</td>
<td>JANAF</td>
<td>JANAF</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>0</td>
<td>45.77</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>0</td>
<td>49.00</td>
</tr>
<tr>
<td>NO</td>
<td>21.57</td>
<td>50.347</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
<td>7.93</td>
<td>57.357</td>
</tr>
<tr>
<td>( \text{N}_2\text{O}_3 )</td>
<td>20.01</td>
<td>74.61</td>
</tr>
<tr>
<td>( \text{N}_2\text{O}_4 )</td>
<td>2.19</td>
<td>72.70</td>
</tr>
<tr>
<td>( \text{N}_2\text{O}_5 )</td>
<td>2.7</td>
<td>82.8 ± 1.0</td>
</tr>
</tbody>
</table>

On the basis of the data in tables 3 to 10 we draw the following conclusions: (a) \( \text{N}_2 \text{O}_3 \) is unstable with respect to dissociation into either \( \text{N}_2 \text{O}_4 \) or \( \text{N}_2 \text{O}_5 \) from 298 K up. Therefore it need not be considered in the dissociation of the salts. (b) The equilibrium \( \text{N}_2 \text{O}_3 = 2 \text{NO} \) shifts markedly to the right with increasing temperature. Above 400 K the concentration of \( \text{N}_2 \text{O}_3 \) is negligible. (c) Although \( \text{N}_2 \text{O}_3 \) has been reported as a product of nitrate decomposition it is unstable with respect to dissociation into \( \text{NO}_2 \) and \( \text{NO} \) above 400 K. It could therefore exist in equilibrium mixtures only near ambient temperatures. (d) The equilibrium \( \text{NO} + 1/2 \text{O}_2 = \text{NO}_2 \) is very tempera-
ture dependent. Up to 500 K, NO₂ predominates markedly; above that temperature both species are significant. The equilibrium is quite mobile and must always be considered in the salt decomposition. (e) N₂ and O₂ are very stable with respect to both NO and NO₂. Thus, if N₂ is formed during salt decomposition it will not react further. O₂ may react with NO and with nitrates. (f) If all equilibria were established quickly during decomposition of the salts, N₂ and O₂ would be the only gaseous components. However, the reaction NO₂ = 1/2 N₂ + O₂ is very slow below 1000 K. Thus, if NO₂ is the primary product of the decomposition it will not decompose appreciably by this reaction and only the equilibrium NO + 1/2 O₂ = NO₂ need be considered. For similar reasons the decomposition of NO to the elements can be neglected. The same conclusion was reached by Kelley [62a] in examining the decomposition of a few nitrates.

4. The Nitrites

Relatively little is known about the anhydrous nitrates with the exception of the alkali metal and alkaline earth salts. The nitrite ion is less stable than the nitrate, so that the nitrates of magnesium and beryllium, small and highly charged cations, are quite unstable.

The nitrite ion is bent, but there is still some disagreement about the bond angle (116° or 132°) and, the N-O distance (1.13 or 1.23 Å) [63, 128]. Cotton and Wilkinson [39] describe the bent structure in terms of the resonance

\[ \text{NO}_2^- \]
This view is factor: infrared spectra. Chasan and Norwitz [36] have prepared long time, the anhydrous nitrates of many other metals the metal. The distinction between ionic and covalent here. have also recently written extensive reviews of nitrate examination of the literature, and covalent nitrate nitrates can most easily be made on the basis of their existence of some earth metals have been known and widely used for a a listing of ionic and covalent solid salts based on an complexes have been reviewed by Addison and Sutton [20]. Otherwise the rare earth nitrites, the first decomposi­

5. The Nitrates

Although anhydrous nitrates of the alkali and alkaline earth metals have been known and widely used for a long time, the anhydrous nitrates of many other metals have been prepared only recently. The existence of some is still in doubt. Methods for preparing these nitrates have been described by Addison and Logan [16]. These authors [16a], as well as Field and Hardy [43a], have also recently written extensive reviews of nitrate chemistry. In view of these, only a brief summary of factors relevant to thermal decomposition is provided here.

In the hydrated salts and in aqueous solution the nitrate ion is a distinct entity. This is also true for the anhydrous nitrates of the electropositive metals, but in many other salts the nitrate ion is covalently bonded to the metal. The distinction between ionic and covalent nitrates can most easily be made on the basis of their infrared spectra. Chasan and Norwitz [36] have prepared a listing of ionic and covalent solid salts based on an examination of the literature, and covalent nitrate complexes have been reviewed by Addison and Sutton [20]. Spectra of liquid nitrates have been discussed by Wait and Janz [122]. Figure 2 represents the author’s evaluation of the literature with respect to the existence and bonding of anhydrous nitrates, but no attempt was made to classify the covalent nitrates with respect to the number of oxygens bonded to the metal atom. This topic, which is of great structural interest, is discussed in the review by Addison and Logan [16a]. In some instances the type of bonding has not clearly been established. In others, which are discussed in this monograph, evidence for the existence of the compound is shaky.

The alkali metal nitrates and the alkaline earth salts, except Be(NO$_3$)$_2$, are ionic, but otherwise there are no obvious criteria. For example AgNO$_3$ and Cd(NO$_3$)$_2$ are ionic, but Cu(NO$_3$)$_2$ and Zn(NO$_3$)$_2$ are covalent. Co(NO$_3$)$_3$ exhibits characteristics of both ionic and covalent bonding.

The ionic nitrates generally melt to liquids which are stable to various degrees above their melting points. These liquids can be distilled under reduced pressure [58]. The covalent nitrates are generally not stable as liquids. When heated, they first sublime, frequently giving stable molecular vapors, and then decompose. The cation influences the decomposition through its ability to distort the nitrate ion. The decomposition enthalpies of the nitrates to N$_2$O$_5$ and the metal oxide are linear functions of the cation property $r^{1/2}/Z^*$, where $r$ is the cationic radius and $Z^*$ the effective nuclear charge [109]. A plot is shown in figure 3.

Since the nitrite of a given metal is generally much less stable than the nitrate, the former can only appear as an unstable intermediate in the decomposition of the nitrate. This is particularly true for the covalent nitrates. In the case of the ionic nitrates, however, both salts may be more or less equally unstable over some temperature range so that the decomposition reactions can become quite complex. This is particularly so since the salts may be oxidized or reduced by the gaseous decomposition products. For example, NO$_3$ produced by the decomposition of the nitrate may oxidize the nitrite also formed back to the nitrate. Since the experimental arrangement usually determines the gas phase composition, reports by different authors frequently conflict. In such cases the common features have been empha-
sized in this monograph. A consequence of the complexity of most nitrate decompositions is that the kinetic studies have usually been restricted to identifying the reactions. Even when rate constants and activation energies are reported it is frequently not clear with which particular reaction they are to be identified.

6. Decomposition Equilibria

In view of the complexities of nitrate decomposition the tabulation of system composition requires some compromises. For example, although it is known that over some temperature ranges alkali metal and alkaline earth nitrates decompose to nitrites as a first step, no high-temperature thermodynamic data for the latter salts are available. Therefore the following procedure has been adopted: when good quality experimental decomposition studies are available these are discussed. The decomposition of the above-mentioned nitrates and a few others is treated in terms of decomposition to the oxide, e.g. for a divalent salt,

\[
M(\text{NO}_3)_2 = \text{MO} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2 \quad (1)
\]

and the gas equilibrium

\[
2\text{NO}_2 = 2\text{NO} + \text{O}_2. \quad (2)
\]

The reasons for neglecting other gaseous species have been discussed in the previous section. The approach is that used previously by Kelley [62a] and in all cases where nitrates are not stable represents the best approximation to the physical situation. The equilibrium constants for reactions (1) and (2) are

\[
K_1 = \frac{P_{\text{NO}} P_{\text{O}_2}^{1/2} a_{\text{MO}}}{a_{\text{M(\text{NO}_3)_2}}}
\]

\[
K_2 = \frac{P_{\text{NO}} P_{\text{O}_2}}{P_{\text{N}_2}^{1/2}}
\]

The partial pressures of the three gases can be calculated if the nitrate and oxide do not form solutions \((a_{\text{MO}} = a_{\text{M(\text{NO}_3)_2}} = 1)\) and if the only source of the gases is the salt. In addition to the equations for \(K_1\) and \(K_2\) a third relation is derived from the fact that \(N\) and \(O\) must be liberated in a fixed atomic ratio. Thus

\[
P_{\text{O}_2} = \frac{1}{4}(P_{\text{NO}} + P_{\text{NO}}) + \frac{1}{2} P_{\text{NO}}
\]

or

\[4P_{\text{O}_2} = P_{\text{NO}} + 3P_{\text{NO}}\]

If the condensed phases are pure, a condition which can only hold if both the salt and the oxides are solids, the term \(a_{\text{MO}} a_{\text{M(\text{NO}_3)_2}} = 1\) and appropriate substitutions yield an equation in \(P_{\text{O}_2}\) alone:

\[
\frac{K_1^{1/2}}{P_{\text{O}_2}^{1/4}} + \frac{3(K_1 K_2)^{1/2}}{P_{\text{O}_2}^{3/4}} = 4P_{\text{O}_2}.
\]

Making the substitution \(X = P_{\text{O}_2}^{1/4}\) this equation can be written in the form

\[X^2 - aX^2 - b = 0\]

where \(a = K_1^{1/2}/4, b = (3/4) (K_1 K_2)^{1/2}\). This equation has only one real positive root for positive values of \(a\) and \(b\) but cannot be solved in closed form. Newton's method was used to solve it by iteration. After the solution for \(P_{\text{O}_2}\) had been obtained \(P_{\text{NO}}\) and \(P_{\text{NO}}\) were calculated from the equations

\[
P_{\text{NO}} = K_1^{1/2} P_{\text{O}_2}^{1/4}
\]

\[P_{\text{NO}} = (K_1 K_2)^{1/2} P_{\text{O}_2}^{3/4}\]

The pressures thus obtained are those to be expected if the pure nitrate is initially placed into a closed con-
DECOMPOSITION OF NITRATES AND NITRITES

The primary decomposition reaction, which is irreversible, is

\[
\text{Ba(NO}_2\text{)}_2 = \text{BaO} + \text{NO}_2 + \text{NO}.
\]

(1)

This reaction begins as low as 250 °C. In the temperature range in which \(\text{Ba(NO}_2\text{)}_2\) is stable the \(\text{NO}_2\) formed oxidizes \(\text{Ba(NO}_2\text{)}_2\) [118]:

\[
\text{Ba(NO}_2\text{)}_2 + 2\text{NO}_2 = \text{Ba(NO}_2\text{)}_2 + 2\text{NO}.
\]

(2)

Above 400 °C, \(\text{BaO}\) reacts with \(\text{NO}\) to form \(\text{N}_2\):

\[
\text{BaO} + 3\text{NO} = \text{Ba(NO}_3\text{)}_2 + 1/2\text{N}_2.
\]

(3)

"Overall" reactions given by the various authors are obtained from various combinations of reactions (1)–(3). The speed of the overall reaction and the distribution of products is evidently affected by the composition of the gas phase and the manner of its removal. For example, Protsentko and Bondyushkova [96] observed that in the range 410–440 °C the rate varied in the order air > vacuum > argon. The rate in air may be greatest since \(\text{O}_2\) can oxidize \(\text{NO}\) which may increase the rate of (2). In argon the Arrhenius activation energy for a first order reaction is 65.3 kJ.

The effect of gas composition and pressure on the temperature range over which the decomposition reactions occur can be seen by comparing the above results with a TGA study under vacuum [92]. The first stage of the decomposition, corresponding to

\[
2\text{Ba(NO}_2\text{)}_2 = \text{Ba(NO}_3\text{)}_2 + \text{BaO} + \text{NO} + 1/2\text{N}_2
\]

occurs between 90 and 150 °C. The second stage beginning at 450° and complete at 600°, is the decomposition of the nitrate

\[
\text{Ba(NO}_3\text{)}_2 = \text{BaO} + 2\text{NO}_2 + 1/2\text{O}_2.
\]

\[
\text{Ba(NO}_2\text{)}_2
\]

Decomposition has been observed as low as 525 °C, but is still slow at 550° [85]. In fact, even the liquid salt decomposes only slowly just above its melting point [9, 55]. The first stage of the reaction is formation of the nitrite

\[
\text{Ba(NO}_2\text{)}_2 = \text{Ba(NO}_3\text{)}_2 + \text{O}_2.
\]
but this salt is very unstable so that the overall decomposition is

\[
\text{Ba(NO}_2\text{)}_2 = \text{BaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2.
\]

As can be seen from the calculated dissociation pressures in the table below, the dissociation might be expected to be inhibited in air. This may account for the stability observed by Addison and Coldrey [9].

The salt appears to have no solid-state transitions.

<table>
<thead>
<tr>
<th>Density</th>
<th>(\text{Ba(NO}_2\text{)}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T(K))</td>
<td>(\rho(g, cm^3))</td>
</tr>
<tr>
<td>298</td>
<td>3.232</td>
</tr>
<tr>
<td>550</td>
<td>3.254</td>
</tr>
<tr>
<td>560</td>
<td>3.247</td>
</tr>
<tr>
<td>570</td>
<td>3.240</td>
</tr>
<tr>
<td>580</td>
<td>3.233</td>
</tr>
<tr>
<td>590</td>
<td>3.226</td>
</tr>
<tr>
<td>600</td>
<td>3.219</td>
</tr>
<tr>
<td>610</td>
<td>3.212</td>
</tr>
<tr>
<td>620</td>
<td>3.205</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\text{Ba(NO}_3\text{)}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(288-298)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Decomposition of (\text{Ba(NO}_2\text{)}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba(NO}_2\text{)}_2 = \text{BaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2)</td>
</tr>
</tbody>
</table>

\[\Delta H_{298.15} = 504.7 \text{ kJ}, 120.6 \text{ kcal}\]

<table>
<thead>
<tr>
<th>(T)</th>
<th>(\text{Ba(NO}_2\text{)}_2)</th>
<th>(\text{BaO})</th>
<th>(\Delta f_{\text{ef}})</th>
<th>(\delta_{\text{eff}})</th>
<th>(\log K)</th>
<th>(K)</th>
<th>(P_{01})</th>
<th>(P_{02})</th>
<th>(P_{03})</th>
<th>(P_{p01})</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>-218.8</td>
<td>-70.3</td>
<td>-438.9</td>
<td>1253.9</td>
<td>-65.499</td>
<td>3.17 \times 10^{46}</td>
<td>7.03 \times 10^{-28}</td>
<td>6.15 \times 10^{-29}</td>
<td>4.69 \times 10^{-28}</td>
<td>1.17 \times 10^{-25}</td>
</tr>
<tr>
<td>400</td>
<td>-220.0</td>
<td>-72.1</td>
<td>-438.0</td>
<td>823.8</td>
<td>-43.031</td>
<td>9.31 \times 10^{-44}</td>
<td>3.83 \times 10^{-16}</td>
<td>1.22 \times 10^{-16}</td>
<td>5.93 \times 10^{-16}</td>
<td>8.94 \times 10^{-16}</td>
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<tr>
<td>500</td>
<td>-232.6</td>
<td>-75.8</td>
<td>-436.1</td>
<td>573.3</td>
<td>-29.948</td>
<td>1.13 \times 10^{-20}</td>
<td>1.46 \times 10^{-28}</td>
<td>3.06 \times 10^{-28}</td>
<td>1.94 \times 10^{-28}</td>
<td>3.49 \times 10^{-28}</td>
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<td>600</td>
<td>-247.4</td>
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<td>407.8</td>
<td>-21.301</td>
<td>5.00 \times 10^{-22}</td>
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<td>1.11 \times 10^{-17}</td>
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<td>203.8</td>
<td>-10.645</td>
<td>2.26 \times 10^{-11}</td>
<td>9.75 \times 10^{-4}</td>
<td>2.69 \times 10^{-4}</td>
<td>1.29 \times 10^{-4}</td>
<td>2.29 \times 10^{-4}</td>
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<td>(900)</td>
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<td>-6.8</td>
<td>1.6 \times 10^{-7}</td>
<td>2.2 \times 10^{-2}</td>
<td>2.8 \times 10^{-2}</td>
<td>5.1 \times 10^{-2}</td>
<td></td>
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<td>(1000)</td>
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<td></td>
<td></td>
<td>-4.5</td>
<td>3.2 \times 10^{-5}</td>
<td>0.15</td>
<td>9.1 \times 10^{-3}</td>
<td>0.20</td>
<td>0.36</td>
</tr>
<tr>
<td>(1100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-3.0</td>
<td>1.0 \times 10^{-3}</td>
<td>0.59</td>
<td>3.6 \times 10^{-2}</td>
<td>0.77</td>
<td>1.40</td>
</tr>
</tbody>
</table>

\(a\) at 723 K, from \(\Delta H_{723}\).

\(b\) at the melting point.

**References**

DECOMPOSITION OF NITRATES AND NITRITES

Beryllium
Be(NO$_3$)$_2$

Be(NO$_3$)$_2$ is a white, hygroscopic solid. The bonding between the metal and the nitrate group is covalent. On being heated above 125 °C it rapidly loses NO$_2$, with the formation of the oxide nitrate Be$_2$O(NO$_3$)$_2$ [21].

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th></th>
<th>$S^e$</th>
<th>$J$ mol$^{-1}$ deg$^{-1}$</th>
<th>cal mol$^{-1}$ deg$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be(NO$_3$)$_2$</td>
<td>184±8</td>
<td>44±2 est.</td>
<td>3.7</td>
<td>93</td>
</tr>
<tr>
<td>BeO</td>
<td>15</td>
<td></td>
<td></td>
<td>1a</td>
</tr>
</tbody>
</table>

$\Delta H^o$

<table>
<thead>
<tr>
<th></th>
<th>$kJ$ mol$^{-1}$</th>
<th>$k$ cal mol$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be(NO$_3$)$_2$</td>
<td>−602±8</td>
<td>−144±4 est.</td>
<td>93</td>
</tr>
<tr>
<td>BeO</td>
<td>−610.9</td>
<td>−146.0</td>
<td>1a</td>
</tr>
</tbody>
</table>

Bismuth

The preparation of Bi(NO$_3$)$_3$ has been reported. Bonding appears to be covalent [112].

Cadmium
Cd(NO$_2$)$_2$

The pure anhydrous salt has apparently never been prepared, although it has been reported in reaction mixtures [53a].

Cd(NO$_2$)$_2$

The infrared spectrum [11] indicates the salt to be a typically ionic solid. Since it decomposes rapidly above 573 K [65] the reported melting point is uncertain. The values of $\Delta H_{fus}$ and $\Delta S_{fus}$ are obtained by extrapolation of cryoscopic data in AgNO$_3$ and TiNO$_3$ [65]. The decomposition is reported to be reversible and to yield no intermediates [68].

2Cd(NO$_2$)$_2$ = 2CdO + 4NO$_2$ + O$_2$

Transitions

<table>
<thead>
<tr>
<th>Cd(NO$_2$)$_2$ transition</th>
<th>$T$(K)</th>
<th>$\Delta H$(kJ mol$^{-1}$)</th>
<th>$\Delta S$(J mol$^{-1}$ deg$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c \rightarrow l$</td>
<td>633</td>
<td>18.2</td>
<td>28.8</td>
<td>1a, 65</td>
</tr>
</tbody>
</table>

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th></th>
<th>$S^e$</th>
<th>$J$ mol$^{-1}$ deg$^{-1}$</th>
<th>cal mol$^{-1}$ deg$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(NO$_2$)$_2$</td>
<td>197.9</td>
<td>47.3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Cd(NO$_2$)$_2$</td>
<td>167±8</td>
<td>40±2 est.</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>CdO</td>
<td>54.8</td>
<td>13.1</td>
<td>1b, 111</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta H^o$

<table>
<thead>
<tr>
<th></th>
<th>$kJ$ mol$^{-1}$</th>
<th>kcal mol$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(NO$_2$)$_2$</td>
<td>−456.31</td>
<td>−109.06</td>
<td>1b</td>
</tr>
<tr>
<td>Cd(NO$_2$)$_2$</td>
<td>−331±17</td>
<td>−79±4 est.</td>
<td>111</td>
</tr>
<tr>
<td>CdO</td>
<td>−958.2</td>
<td>−61.7</td>
<td>1b, 111</td>
</tr>
</tbody>
</table>

Calcium
Ca(NO$_2$)$_2$

The solid-state transitions were obtained from heating curves. The nature of the phases was not characterized [97].

The decomposition reactions of Ca(NO$_2$)$_2$ are similar to those for the Ba and Sr salts. Centnerszwer and Pickielny [35] measured the decomposition pressure over the temperature range 540–588 K. In an inert atmosphere log $p$ is linear in 1/T. $p$ varied from 0 at 540 K to 693 torr at 588 K. This suggests that a single reaction is responsible for the measured pressure, but it is not at all clear what this reaction is since the enthalpy change calculated by the authors from the pressure data (147.7kJ, 35.3kcal) differs considerably from $\Delta H_{298}$ for the reaction cited by the authors,

\[
\text{Ca(NO}_2\text{)}_2 = \text{CaO} + \text{NO}_2 + \text{NO}
\]

for which $\Delta H_{298} = 234.4kJ$. The lack of high-temperature thermodynamic data for Ca(NO$_2$)$_2$ prevents a comparison of $\Delta H^o$ at the temperature of the experiment. At somewhat higher temperatures only NO appears as the product, probably because NO$_2$ oxidizes the Ca(NO$_2$)$_2$:

\[
\text{Ca(NO}_2\text{)}_2 + 2\text{NO}_2 = \text{Ca(NO}_3\text{)}_2 + 2\text{NO}.
\]

The decomposition was also studied by Protsenko and Bondyushkova [96] at somewhat higher temperatures, 693 and 723 K, which is still sufficiently low for the Ca(NO$_3$)$_2$ to be stable, or at least for its decomposition to be negligible compared to that of the nitrite. They noted that the rate of decomposition varied with the gas phase in the order argon < air < vacuum. From an analysis of the gas phase and the weight loss of the sample they conclude that in argon the main reaction is the formation of the nitrate with partial reduction of the NO to N$_2$:

\[
4\text{Ca(NO}_2\text{)}_2 = 2\text{Ca(NO}_3\text{)}_2 + 2\text{CaO} + 2\text{NO} + \text{N}_2
\]

which is fairly consistent with reactions (1) and (2) above. From the first-order rate constants they calculate an Arrhenius activation energy of 33.2kJ(7.94 kcal).

Reactions (1) and (2) have also been found by Oza and Oza [87] who find that these reactions are reversible. Thus, since the nitrate is unstable in the presence of NO, the production of N$_2$ is inhibited and reaction (3) will be minor unless the product gases are continually removed from the system.

The interpretation of the pressure measurements of Centnerszwer and Pickielny would therefore need to take not only reaction (1), but also (2) and (3) into account. In reaction schemes as complicated as the

KURT H. STERN

present one, equilibrium pressure measurements alone are likely to be of limited utility, particularly since the partial pressures of the component gases depend not only on the equilibrium constants of the reactions, but also on the composition of the condensed phase(s).

**Ca(NO$_3$)$_2$**

The salt exhibits no crystalline transitions [55]. Its decomposition has apparently not yet been studied in detail. Some indication of its stability may be gained from the thermodynamic data calculated for the reaction $\text{Ca(NO}_3\text{)}_2 = \text{CaO} + 2\text{NO}_2 + 1/2\text{O}_2$. Enthalpy and entropy increments listed by Kelley [3] were used in the calculation. Although the calculated dissociation pressures are substantial above 700 K, it must be noted that Addison and Coldrey [9] found the liquid to be clear at 828 K and small bubbles to form at 833 K, but both of these temperatures lie below the generally accepted melting point of 834 K. The behavior of this salt near the melting point evidently needs more careful study.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$T$ (K)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ deg$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca(NO}_3\text{)}_2 \rightarrow \text{CaO} + 2\text{NO}_2 + 1/2\text{O}_2$</td>
<td>834</td>
<td>23.4</td>
<td>28.1</td>
<td>1a, 69</td>
</tr>
</tbody>
</table>

**Thermodynamic data (298.15 K)**

<table>
<thead>
<tr>
<th>$S^0$</th>
<th>J mol$^{-1}$ deg$^{-1}$</th>
<th>cal mol$^{-1}$ deg$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca(NO}_3\text{)}_2$</td>
<td>193.3</td>
<td>46.2</td>
<td>1b</td>
</tr>
<tr>
<td>$\text{Ca(NO}_3\text{)}_2$</td>
<td>164.4</td>
<td>39.3</td>
<td>1b</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>39.7</td>
<td>9.50</td>
<td>1b</td>
</tr>
</tbody>
</table>

Decomposition of $\text{Ca(NO}_3\text{)}_2$

$\text{Ca(NO}_3\text{)}_2 = \text{CaO} + 2\text{NO}_2 + 1/2\text{O}_2$

$\Delta H_{\text{f}298.15} = 369.4$, kJ, 88.3, kcal

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\text{Ca(NO}_3\text{)}_2$</th>
<th>$\text{CaO}$</th>
<th>$\Delta G^\circ/T$</th>
<th>$\log K$</th>
<th>$P_{\text{O}_2}$ atm</th>
<th>$P_{\text{NO}_2}$ atm</th>
<th>$P_{\text{NO}}$ atm</th>
<th>$P_{\text{Tot}}$ atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>-193.3</td>
<td>-39.7</td>
<td>-428.75</td>
<td>810.53</td>
<td>-42.337</td>
<td>4.60 x 10$^{-43}$</td>
<td>1.97 x 10$^{-16}$</td>
<td>5.72 x 10$^{-18}$</td>
</tr>
<tr>
<td>400</td>
<td>-199.6</td>
<td>-41.5</td>
<td>-427.83</td>
<td>495.90</td>
<td>-25.903</td>
<td>1.25 x 10$^{-16}$</td>
<td>3.04 x 10$^{-10}$</td>
<td>2.68 x 10$^{-11}$</td>
</tr>
<tr>
<td>500</td>
<td>-212.0</td>
<td>-44.9</td>
<td>-425.77</td>
<td>313.21</td>
<td>-16.361</td>
<td>4.36 x 10$^{-17}$</td>
<td>1.14 x 10$^{-6}$</td>
<td>2.02 x 10$^{-7}$</td>
</tr>
<tr>
<td>600</td>
<td>-226.8</td>
<td>-48.7</td>
<td>-422.81</td>
<td>193.04</td>
<td>-10.682</td>
<td>8.29 x 10$^{-15}$</td>
<td>2.73 x 10$^{-4}$</td>
<td>7.08 x 10$^{-5}$</td>
</tr>
<tr>
<td>700</td>
<td>-242.3</td>
<td>-52.7</td>
<td>-419.62</td>
<td>108.22</td>
<td>-5.653</td>
<td>2.22 x 10$^{-6}$</td>
<td>1.33 x 10$^{-8}$</td>
<td>4.40 x 10$^{-9}$</td>
</tr>
<tr>
<td>800</td>
<td>-258.0</td>
<td>-56.6</td>
<td>-416.09</td>
<td>45.77</td>
<td>-2.391</td>
<td>4.01 x 10$^{-3}$</td>
<td>0.235</td>
<td>9.16 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

**Cesium**

CsNO$_3$

The salt is stable to 450 °C and decomposes to the oxide above that temperature if the product gases, NO and NO$_2$, are removed [95]. In their presence the nitrite is partially oxidized to the nitrate.

CsNO$_2$

This salt exhibits one solid-solid transition. The hysteresis which is frequently noted by this transformation leads to some uncertainty in the enthalpy change. This problem is discussed in detail by Rao and Rao [100]. The new heat capacity measurements by Mustajoki [74] permit calculation of the free-energy function of this salt up to 723 K, but the lack of $S_2^{\text{gas}}$ and $C_p$ values for Cs$_2$O prevents carrying out thermodynamic calculations for the decomposition reactions.

A semi-quantitative study [29] indicates that the salt decomposes only slowly up to 828 K, 0.05 percent nitrite appearing in the melt after heating for ten minutes.
DECOMPOSITION OF NITRATES AND NITRITES

Density

<table>
<thead>
<tr>
<th>$T(K)$</th>
<th>$\rho(\text{g cm}^{-3})$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>681</td>
<td>2.844</td>
<td>99</td>
</tr>
<tr>
<td>691</td>
<td>2.835</td>
<td>99</td>
</tr>
<tr>
<td>701</td>
<td>2.826</td>
<td>99</td>
</tr>
<tr>
<td>711</td>
<td>2.816</td>
<td>99</td>
</tr>
<tr>
<td>721</td>
<td>2.806</td>
<td>99</td>
</tr>
<tr>
<td>732</td>
<td>2.793</td>
<td>99</td>
</tr>
<tr>
<td>742</td>
<td>2.783</td>
<td>99</td>
</tr>
<tr>
<td>752</td>
<td>2.772</td>
<td>99</td>
</tr>
</tbody>
</table>

$\rho(690-760\text{K}) = 3.6206 - 1.6605 \times 10^{-3}T$.

Transitions

<table>
<thead>
<tr>
<th>Salt</th>
<th>Transition</th>
<th>$T(K)$</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ deg$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsNO$_3$</td>
<td>s → l</td>
<td>679</td>
<td>3.7</td>
<td>8.7</td>
<td>74</td>
</tr>
<tr>
<td>CsNO$_3$</td>
<td>Hexagonal → cubic → l</td>
<td>679</td>
<td>14.1</td>
<td>20.8</td>
<td>74</td>
</tr>
</tbody>
</table>

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th>Salt</th>
<th>$S^\circ$</th>
<th>J mol$^{-1}$ deg$^{-1}$</th>
<th>cal mol$^{-1}$ deg$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsNO$_3$</td>
<td>147.7</td>
<td>35.3</td>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>

$\Delta H^\circ$

<table>
<thead>
<tr>
<th>Salt</th>
<th>kJ mol$^{-1}$</th>
<th>kcal mol$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsNO$_3$</td>
<td>-509.6</td>
<td>-121.8</td>
<td>lb.</td>
</tr>
<tr>
<td>Cs$_2$O</td>
<td>-317.4</td>
<td>-75.9</td>
<td>110</td>
</tr>
</tbody>
</table>

Cobalt

$\text{Co(NO}_3\text{)}_2$

The existence of the salt has been reported [38] but it must still be regarded as doubtful. It supposedly begins to evolve NO at $\sim 100^\circ$C.

$\text{Co(NO}_3\text{)}_2$

$\text{Co(NO}_3\text{)}_2$ decomposes to $\text{Co}_2\text{O}_4$ in a single step without formation of an intermediate [19]. The decomposition begins at 100–105 °C [19, 56], but there is some question as to the temperature at which the decomposition rate is a maximum. Both [19] and [16] state that the rate is a maximum at 270 °C, but the experimental curve published by [19] shows this maximum approximately 100° lower.

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th>$S^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co(NO}_3\text{)}_2$</td>
<td>-420.6</td>
<td>-100.5</td>
<td>1b</td>
</tr>
<tr>
<td>$\text{Co}_2\text{O}_4$</td>
<td>-237.94</td>
<td>-56.87</td>
<td>1b</td>
</tr>
<tr>
<td>$\text{CoO}_2$</td>
<td>-891.2</td>
<td>-213.1</td>
<td>1b</td>
</tr>
</tbody>
</table>

Copper

$\text{Cu(NO}_3\text{)}_2$

Reports about the existence of this salt are conflicting [53a]. Its preparation is doubtful.

$\text{Cu(NO}_3\text{)}_2$

Below 500 K heating of the solid salt results primarily in the vaporization of the covalent molecule as a monomer. In this temperature range the only thermal decomposition, into NO$_2$ + O$_2$, is exhibited by the solid. The vapor is more stable. The vapor pressure of $\text{Cu(NO}_3\text{)}_2$ was determined by Addison and Hathaway [12] by extrapolating pressure-time curves to zero time in order to subtract the pressures of NO$_2$ and O$_2$. Their results are:

<table>
<thead>
<tr>
<th>$T(K)$</th>
<th>430.2</th>
<th>446.0</th>
<th>459.6</th>
<th>462.7</th>
<th>475.2</th>
<th>488.4</th>
<th>495.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(\text{torr})$</td>
<td>0.32</td>
<td>0.59</td>
<td>0.99</td>
<td>1.15</td>
<td>1.87</td>
<td>2.84</td>
<td>3.59</td>
</tr>
</tbody>
</table>

A plot of log $P$ versus 1/$T$ is linear and yields a sublimation enthalpy of 67.0 kJ. Above 500 K both the solid and vapor phase salt decompose to NO$_2$ + O$_2$.

Transitions

<table>
<thead>
<tr>
<th></th>
<th>T(K)</th>
<th>ΔH</th>
<th>ΔS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO₃)₂</td>
<td>528</td>
<td>453-493</td>
<td>65.3</td>
</tr>
<tr>
<td>α → β</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

*At 1 atm.*

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th></th>
<th>J mol⁻¹ deg⁻¹</th>
<th>cal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO₃)₂</td>
<td>193.3</td>
<td>46.2</td>
<td>4</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>93.14</td>
<td>22.26</td>
<td>1b</td>
</tr>
<tr>
<td>CuO</td>
<td>42.64</td>
<td>10.19</td>
<td>1b</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>kJ mol⁻¹</th>
<th>kcal mol⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NO₃)₂</td>
<td>-302.9</td>
<td>-72.4</td>
<td>1b</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>-168.6</td>
<td>-40.3</td>
<td>1b</td>
</tr>
<tr>
<td>CuO</td>
<td>-157.3</td>
<td>-37.6</td>
<td>1b</td>
</tr>
</tbody>
</table>

**Gallium**

Ga(NO₃)₂ was probably prepared in the anhydrous state by Dupré [43], using vacuum dehydration of the hydrate at 40°C. A large fraction of the salt had decomposed to Ga₂O₃ when the temperature reached 200°C.

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th></th>
<th>J mol⁻¹ deg⁻¹</th>
<th>cal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(NO₃)₂</td>
<td>231</td>
<td>55.2</td>
<td>1b</td>
</tr>
<tr>
<td>Ga₂O₃(c)</td>
<td>84.98</td>
<td>20.31</td>
<td>1b</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>kJ mol⁻¹</th>
<th>kcal mol⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(NO₃)₂</td>
<td>-619 ± 17</td>
<td>-148 ± 4 est.</td>
<td>93</td>
</tr>
<tr>
<td>Ga(O)</td>
<td>279</td>
<td>66.8</td>
<td>1b</td>
</tr>
<tr>
<td>Ga₂O₃(c)</td>
<td>-1089</td>
<td>-260.3</td>
<td>1b</td>
</tr>
</tbody>
</table>

**Gold**

Au(NO₃)₃

Evidence for the existence of this compound seems to be based solely on a report by Field and Hardy [45] who treated hydrated gold nitrate successively with HNO₃ and N₂O₅. Although the gold content corresponded to the trinitrate, no quantitative nitrate analysis was performed. Further information is lacking.

**Hafnium**

Although Addison and Logan [16] indicated the existence of an anhydrous nitrate in their periodic table (fig. 2) there is some question whether such a compound actually has been prepared. Field and Hardy [45] succeeded in preparing the addition compound Hf(NO₃)₂ · N₂O₅, but this compound sublimes as such, rather than losing N₂O₅.

**Indium**

The infrared spectrum shows that In(NO₃)₃ is covalent and stable to at least 90°C since this was the temperature of its preparation [106].

**Iron**

So far Fe(NO₃)₃ has only been prepared as the volatile adduct Fe(NO₃)₃ · N₂O₅, although it is possible that Fe(NO₃)₃ exists in the vapor state [13].

**Lead**

Pb(NO₃)₂

Very little is yet known about this salt. It has recently been prepared by treatment of the chloride with AgNO₃ and its decomposition measured by TGA [92]. The decomposition occurs in two stages, the first stage beginning at ~110°C being consistent with the stoichiometry

3Pb(NO₃)₂ = Pb(NO₃)₃ + 2PbO + 4NO.

The second stage is the decomposition of the nitrate. However, this occurred in the range 320-450°C and seemed to proceed directly to PbO₂, results which are contradictory to other studies of nitrate decomposition (see below).

**Pb(NO₃)₂**

Although there are as yet no high temperature thermodynamic data on Pb(NO₃)₂ available, the thermal decomposition of the salt has been studied by a number of workers [23, 78, 120]. There is general agreement that decomposition occurs without oxidation of the Pb (II) ion to higher valence state, but it is not yet
clear whether a nitrite may be an intermediate in the decomposition.

Bakeland [23] was the first to report a reversible decomposition of Pb(NO₃)₂ involving a basic nitrate intermediate, but the most careful study seems to have been carried out by Neumann and Sonntag [78] who measured the total pressure involved in three reversible equilibria and analyzed the solid phases. The equilibria (rearranged from the original paper) and the temperature ranges over which they were measured are:

\[
\begin{align*}
I & : T(K) = 539-632 \quad 3\text{Pb(NO}_3\text{)}_2 = [\text{Pb(NO}_3\text{)}_2 \cdot 2\text{PbO}] + 4\text{NO}_2 + \text{O}_2 \\
II & : T(K) = 625-719 \quad 2[\text{Pb(NO}_3\text{)}_2 \cdot 2\text{PbO}] = [\text{Pb(NO}_3\text{)}_2 \cdot 5\text{PbO}] + 2\text{NO}_2 + 1/2 \text{O}_2 \\
III & : T(K) = 688-809 \quad [\text{Pb(NO}_3\text{)}_2 \cdot 5\text{PbO}] = 6\text{PbO} + 2\text{NO}_2 + 1/2 \text{O}_2.
\end{align*}
\]

The overlapping of the temperature ranges is accounted for by the fact that the continued removal of product gas will result in the disappearance of a lower oxide and the formation of a higher one, with the resulting establishment of a new equilibrium.

Nothing seems to be known as yet of the structure of the oxinitrates so that the writing of the formula is somewhat arbitrary, e.g.

\[
\text{Pb(NO}_3\text{)}_2 \cdot 2\text{PbO} = 3\text{PbO} \cdot \text{N}_2\text{O}_5.
\]

Neumann and Sonntag calculated equilibrium constants for the above reactions by calculating the partial pressures of NO₂ and O₂, using the experimental data of Bodenstein [27] for the equilibrium reaction NO₂+NO+1/2 O₂. Since these differ but little from those given in this monograph they were used to reanalyze the above three reactions. It was noted that a plot of ln K of reaction I versus 1/T could only very approximately be described as linear, but rather consisted of three linear portions. A plot of ln K versus 1/T for reaction III could also more accurately be described as consisting of two linear portions. For reaction II the plot was linear over the entire temperature range. \( \Delta H^o \) values calculated for the various portions are:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( T(K) )</th>
<th>( \Delta H^o (kJ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>539-583</td>
<td>694</td>
</tr>
<tr>
<td></td>
<td>583-603</td>
<td>629</td>
</tr>
<tr>
<td></td>
<td>613-632</td>
<td>758</td>
</tr>
<tr>
<td>II</td>
<td>625-719</td>
<td>337</td>
</tr>
<tr>
<td>III</td>
<td>688-763</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>763-809</td>
<td>324</td>
</tr>
</tbody>
</table>

There seems to be no simple way to choose among the enthalpies for the various slopes, although the high-temperature plot of I does not join smoothly to the lower two and may represent experimental error. The low-temperature plot of I shows more scatter than the plot at the higher temperature.

Using Hess' law it is possible to calculate \( \Delta H^o \) for the reaction

\[
6\text{Pb(NO}_3\text{)}_2 = 6\text{PbO} + 12\text{NO}_2 + 3 \text{O}_2
\]

from the \( \Delta H^o \)'s for reactions I, II, and III. Using for \( \Delta H^o \) the average of the lower two temperature ranges and the high-temperature range of III gives 1983kJ for this reaction. In the absence of high-temperature thermodynamic data for Pb(NO₃)₂ a direct calculation for this reaction is not possible, but since \( \Delta C_p \) is generally relatively small, one would not expect \( \Delta H^0_{298} \) and \( \Delta H^o \) to differ by more than 5 percent. In fact \( \Delta H^0_{298} = 1794kJ \), so that the agreement is reasonable. A choice for \( \Delta H^0_{298} \) of 629kJ would have lowered \( \Delta H^o \) to 1919kJ. If it is assumed that \( \Delta H^o \) for each of three reactions is independent of temperature, \( \Delta H^o \) values can be estimated for the two oxynitrates. From \( \Delta H^0_{298} = 629kJ \) we get \( \Delta H^o \) of \([\text{Pb(NO}_3\text{)}_2 \cdot 2\text{PbO}] \), \( \Delta H^0_{298} = -324kJ \) yields \( \Delta H^o \) of \([\text{Pb(NO}_3\text{)}_2 \cdot 5\text{PbO}] \). The values are

<table>
<thead>
<tr>
<th>( \Delta H^o ) (kJ)</th>
<th>Pb(NO₃)₂ ( \cdot 2)PbO</th>
<th>-867</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb(NO₃)₂ ( \cdot 5)PbO</td>
<td>-1558.</td>
</tr>
</tbody>
</table>

When these values are used to calculate \( \Delta H^0_{298} \), 342kJ is obtained, in good agreement with the experimental value of 337kJ.

Recently a TGA study [92] of Pb(NO₃)₂ claimed the final product to be PbO₁.₄, but no details were given.

<table>
<thead>
<tr>
<th>Thermodynamic data (298.15 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S^o )</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
</tr>
<tr>
<td>PbO (yellow)</td>
</tr>
<tr>
<td>PbO (red)</td>
</tr>
</tbody>
</table>

\( \Delta H^o \)

<table>
<thead>
<tr>
<th>kJ mol⁻¹</th>
<th>kcal mol⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(NO₃)₂</td>
<td>-451.9</td>
<td>-108.0</td>
</tr>
<tr>
<td>PbO (yellow)</td>
<td>-217.32</td>
<td>-51.94</td>
</tr>
<tr>
<td>PbO (red)</td>
<td>-218.99</td>
<td>-52.34</td>
</tr>
</tbody>
</table>

**Lithium**

\( \text{LiNO}_2 \)

The salt is stable up to 300°C. It decomposes slowly at 350°C and more rapidly with increasing temperature [95]. The product gases, NO and NO₂, may oxidize the salt to LiNO₃ if they are not removed.
As is to be expected from the high polarizing power of the cation, LiNO₃ is the least stable of the alkali metal nitrates. It decomposes just above its melting point according to LiNO₃ = LiN0₂ + 1/2 O₂. If the container material is inert (glass is not) oxides of nitrogen are absent. “Equilibrium pressures” were measured by Centnerszwer and Blumenthal [33] but since the LiN0₂ dissolves in the melt the measured pressures depend on the melt composition. These authors therefore refer to the measured pressures as applying to “infinitely dilute” solutions of LiN0₂ in LiNO₃, but in terms of the equilibrium constant \( K = \frac{a_{\text{LiN0}_2}}{a_{\text{LiN0}_3}} P_{\text{O}_2} \), it is clear that the system can be at equilibrium only for some non-zero value of \( a_{\text{LiN0}_2} \). Unfortunately there exist no high-temperature thermodynamic data for LiN0₂ which would permit an independent evaluation of \( K \). The authors give a value of \( \Delta H^\circ \) of -52.5kJ for the dissociation reaction for the temperature range (656-693 K) over which their measurements extended, but this value differs too sharply from the calculated \( \Delta H^{+298.15} \) of 81.1kJ to represent a thermodynamic value.

The qualitative features observed by Centnerszwer and Blumenthal have been confirmed [29], i.e. decomposition of the nitrate above the melting point results in the formation of LiN0₂, very slight decomposition being noted only 40° above the melting point. Only above 720 K does the decomposition become appreciable, however.

As can be seen from the table below, decomposition to the oxide is negligible up to 600 K.

### Density

<table>
<thead>
<tr>
<th>T(K)</th>
<th>LiNO₃</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>493</td>
<td>1.638</td>
<td>98</td>
</tr>
<tr>
<td>498</td>
<td>1.636</td>
<td>98</td>
</tr>
<tr>
<td>503</td>
<td>1.632</td>
<td>98</td>
</tr>
<tr>
<td>512</td>
<td>1.629</td>
<td>98</td>
</tr>
<tr>
<td>518</td>
<td>1.626</td>
<td>98</td>
</tr>
<tr>
<td>532</td>
<td>1.620</td>
<td>98</td>
</tr>
<tr>
<td>543</td>
<td>1.615</td>
<td>98</td>
</tr>
</tbody>
</table>

\[
\rho = 2.068 - 0.546 \times 10^{-5} T
\]

<table>
<thead>
<tr>
<th>Transition</th>
<th>T(K)</th>
<th>( \Delta H ) J mol⁻¹</th>
<th>( \Delta S ) J mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃ c→l</td>
<td>493</td>
<td>26.7</td>
<td>50.8</td>
<td>49</td>
</tr>
<tr>
<td>LiNO₃ c→l</td>
<td>526</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Thermodynamic data (298.15 K)**

\[
S^\circ = \begin{vmatrix} J \text{ mol}^{-1} \text{ deg}^{-1} \end{vmatrix} = \begin{vmatrix} \text{cal} \text{ mol}^{-1} \text{ deg}^{-1} \end{vmatrix}
\]

| LiNO₃     | 105.4 | 25.2           | 4     |
| LiNO₂     | 89.1  | 21.3           | 4     |
| Li₄O      | 37.89 | 9.056          | 110   |

\[\Delta H^\circ\] J mol⁻¹ kcal mol⁻¹ Ref.

| LiNO₃     | -487.377 | -115.279 | 1  |
| LiNO₂     | -401.2   | -96.6    | 1  |
| Li₄O      | -598.7   | -143.1   | 110|

**Decomposition of LiNO₃**

\[2\text{LiNO₃} = \text{Li}_4\text{O} + 2\text{NO}_2 + 1/2 \text{O}_2\]

\[\Delta H^\circ_{298.15} = 432.1 \text{kJ}, 103.2 \text{kcal}\]

<table>
<thead>
<tr>
<th>T K</th>
<th>LiNO₃ fef</th>
<th>Li₄O fef</th>
<th>( \Delta fef ) J deg⁻¹</th>
<th>( \Delta G/\Delta T ) J deg⁻¹</th>
<th>( \log K )</th>
<th>K</th>
<th>( P_{\text{O}_2} ) atm</th>
<th>( P_{\text{NO}_2} ) atm</th>
<th>( P_{\text{NO}} ) atm</th>
<th>( P_{\text{tot}} ) atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>-105.4</td>
<td>-37.99</td>
<td>-409.38</td>
<td>1039.96</td>
<td>-54.322</td>
<td>4.77 × 10⁻¹⁵</td>
<td>7.38 × 10⁻⁹³</td>
<td>4.19 × 10⁻¹³</td>
<td>8.84 × 10⁻¹³</td>
<td>1.72 × 10⁻¹⁵</td>
</tr>
<tr>
<td>400</td>
<td>-110.08</td>
<td>-40.15</td>
<td>-407.93</td>
<td>672.37</td>
<td>-35.121</td>
<td>7.57 × 10⁻¹⁶</td>
<td>6.98 × 10⁻⁹³</td>
<td>3.01 × 10⁻¹³</td>
<td>9.29 × 10⁻¹³</td>
<td>1.63 × 10⁻¹³</td>
</tr>
<tr>
<td>500</td>
<td>-116.19</td>
<td>-44.71</td>
<td>-405.20</td>
<td>459.04</td>
<td>-23.978</td>
<td>1.05 × 10⁻¹⁴</td>
<td>7.43 × 10⁻⁹⁵</td>
<td>1.11 × 10⁻¹⁰</td>
<td>9.86 × 10⁻⁵</td>
<td>1.74 × 10⁻⁶</td>
</tr>
<tr>
<td>600</td>
<td>-130.57</td>
<td>-50.08</td>
<td>-389.85</td>
<td>330.35</td>
<td>-17.256</td>
<td>5.55 × 10⁻¹⁸</td>
<td>2.36 × 10⁻⁸</td>
<td>6.01 × 10⁻⁸</td>
<td>3.12 × 10⁻⁸</td>
<td>5.54 × 10⁻⁸</td>
</tr>
</tbody>
</table>

DECOMPOSITION OF NITRATES AND NITRITES 761

Magnesium

Mg(NO₃)₂

Little is known of the high-temperature properties of anhydrous Mg(NO₃)₂. The salt is ionic and stable in the solid state up to approximately 600 K [21, 90]. This observation contrasts with the equilibrium pressures calculated for the reaction Mg(NO₃)₂ = MgO + 2NO₂ + 1/2O₂ (see below) which are consistent with complete decomposition at this temperature (ref data for Mg(NO₃)₂ were calculated from [3] and for MgO from [90]). Some of the difference may arise from the dependence of the stability on the nature of the gas phase. For example, in an atmosphere of NO, decomposition has been observed as low as 400 K [86]. At this temperature some Mn(NO₃)₂ was observed as product. This latter salt decomposes at 380 K and can therefore appear only as an unstable intermediate in the decomposition of the nitrate. The latter is unstable in the liquid state [21]. The thermal decomposition of Mg(NO₃)₂ was also studied in some detail by Oza and Dipali [82] but although their results are consistent with those of other nitrates, their use of the dihydrate salt casts some doubts on their findings since the effect of water on the course and temperature of the decomposition reactions is not known.

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th>Species</th>
<th>S° J mol⁻¹ deg⁻¹</th>
<th>S° kcal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(NO₃)₂</td>
<td>164.0</td>
<td>39.2</td>
<td>lb</td>
</tr>
<tr>
<td>MgO</td>
<td>26.94</td>
<td>6.44</td>
<td>lb</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔH° Reaction (kJ mol⁻¹)</th>
<th>ΔH° Reaction (kcal mol⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(NO₃)₂</td>
<td>-790.6</td>
<td>-188.9</td>
<td>lb</td>
</tr>
<tr>
<td>MgO</td>
<td>-601.7</td>
<td>-143.8</td>
<td>lb</td>
</tr>
</tbody>
</table>

Decomposition of Mg(NO₃)₂

Mg(NO₃)₂ = MgO + 2NO₂(g) + 1/2O₂(g)

ΔH° Reaction = 255,1 kJ, 60.9 kcal

Manganese

Reports as to the course of the decomposition differ somewhat. According to the older work of Guntz and Martin [56] decomposition begins near 160° and produces the dioxide:

Mn(NO₃)₂ = MnO₂ + 2NO₂.

More careful analysis of the remaining solid phase [42] shows that it is MnO₁.₆₅₅ and that both NO₂ and O₂ are evolved. Under dry N₂, the decomposition rate reaches a maximum near 230 °C [16].

The salt is characterized as covalent by Addison and Gatehouse [11], but Dehnicke and Strahle [42] find that it, like Co(NO₃)₂, possesses considerable ionic character.

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th>Species</th>
<th>S° J mol⁻¹ deg⁻¹</th>
<th>S° kcal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(NO₃)₂</td>
<td>168.6</td>
<td>40.3</td>
<td>4</td>
</tr>
<tr>
<td>MnO</td>
<td>59.71</td>
<td>14.27</td>
<td>lb</td>
</tr>
<tr>
<td>MnO₂</td>
<td>53.05</td>
<td>12.68</td>
<td>lb</td>
</tr>
<tr>
<td>MnO₃</td>
<td>110.5</td>
<td>26.4</td>
<td>lb</td>
</tr>
<tr>
<td>MnO₄</td>
<td>155.6</td>
<td>37.2</td>
<td>lb</td>
</tr>
</tbody>
</table>

ΔH° Reaction

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔH° Reaction (kJ mol⁻¹)</th>
<th>ΔH° Reaction (kcal mol⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(NO₃)₂</td>
<td>-576.26</td>
<td>-137.73</td>
<td>lb</td>
</tr>
<tr>
<td>MnO</td>
<td>-385.22</td>
<td>-92.07</td>
<td>lb</td>
</tr>
<tr>
<td>MnO₂</td>
<td>-520.03</td>
<td>-124.29</td>
<td>lb</td>
</tr>
<tr>
<td>MnO₃</td>
<td>-959.0</td>
<td>-229.2</td>
<td>lb</td>
</tr>
<tr>
<td>MnO₄</td>
<td>-1387.8</td>
<td>-331.7</td>
<td>lb</td>
</tr>
</tbody>
</table>

**Mercury**

**Hg(NO₃)₂**

This salt appears to have been prepared for the first time by Ray [102] and in the pure state by Oza and Ezekiel [85]. It is a yellow powder which begins to decompose at 50 °C and readily decomposes at 90°. HgO and Hg(NO₃)₂ appear as products and so the reactions probably are:

\[2\text{Hg(NO}_3\text{)}_2 = 2\text{HgNO}_3 + 2\text{NO}\]

\[\text{Hg(NO}_3\text{)}_2 = \text{HgO} + \text{N}_2\text{O}_5\]

**Hg(NO₃)₂**

The salt has only recently been prepared [94] in the anhydrous state. It decomposes to a yellow solid with the evolution of brown fumes when heated above 100 °C. It appears to be covalent.

**Hg(NO₃)₂**

The anhydrous salt has been prepared [11], but aside from infrared studies which indicate that the compound is covalent [11, 45] little has been done to determine its properties.

The decomposition of the salt is appreciable at 160 °C and appears to lead to a basic nitrate, HgO · Hg(NO₃)₂. At 300 °C this compound is unstable and the final product is HgO. In the presence of NO some nitrite and NO₂ are formed [85].

### Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th></th>
<th>(S^\circ)</th>
<th>J mol⁻¹ deg⁻¹</th>
<th>cal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(NO₃)₂</td>
<td>230 ± 8</td>
<td>55 ± 2 est.</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>HgO (red)</td>
<td>70.29</td>
<td>16.80</td>
<td>1b</td>
<td></td>
</tr>
</tbody>
</table>

### \(\Delta H^\circ\)

<table>
<thead>
<tr>
<th></th>
<th>kJ mol⁻¹</th>
<th>kcal mol⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(NO₃)₂</td>
<td>-285 ± 17</td>
<td>-68 ± 4 est.</td>
<td>93</td>
</tr>
<tr>
<td>HgO (red)</td>
<td>-90.83</td>
<td>-21.71</td>
<td>1b</td>
</tr>
</tbody>
</table>

**Nickel**

**Ni(NO₂)₂**

Ni(NO₂)₂ is stable up to 260 °C in an argon atmosphere and decomposes at 220° in vacuum. The compound is slightly volatile [14].

**Ni(NO₃)₂**

The salt decomposes on heating, the initial decomposition, near 260 °C, resulting in formation of the nitrite [16].

**Palladium**

**Pd(NO₃)₂**

A compound of approximately this composition was reported to result from reaction of Pd(NO₃)₂ with NO [45].

### Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th></th>
<th>(S^\circ)</th>
<th>J mol⁻¹ deg⁻¹</th>
<th>cal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(NO₃)₂</td>
<td>-305 ± 17</td>
<td>-73 ± 4 est.</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>PdO</td>
<td>-239.7</td>
<td>-57.3</td>
<td>1b</td>
<td></td>
</tr>
</tbody>
</table>

## Polonium

**Po(NO₃)₄**

The salt was prepared [24] by the reaction of PoO₂ or PoCl₄ with N₂O₄. N₂O₄ is lost under vacuum or by standing in dry air. The tetrinitrate itself is not very stable as it slowly decomposes in air or under vacuum at ambient temperature to give a basic salt.

**Potassium**

**KNO₂**

No solid phase transitions have been reported. The salt begins to decompose noticeably at 410°. The first
DECOMPOSITION OF NITRATES AND NITRITES

step in the decomposition sequence is probably 2 KNO₃ → K₂O + NO₂ + NO. Between 410 and 460°C the reaction sequence is [81, 89]:

\[ 2 \text{KNO}_3 \rightarrow \text{K}_2\text{O} + \text{NO}_2 + \text{NO}. \]  

(1)

The NO produced in (1) reacts with KNO₂

\[ 2 \text{KNO}_3 + 2 \text{NO} \rightarrow 2 \text{KNO}_2 + \text{N}_2. \]  

(2)

The NO₂ produced in (1) reacts further

\[ \text{K}_2\text{O} + 2 \text{NO}_2 \rightarrow \text{KNO}_2 + \text{KNO}_3. \]  

(3)

\[ \text{KNO}_2 + \text{NO}_2 \rightarrow \text{KNO}_3 + \text{NO}. \]  

(4)

Which reactions are favored will depend largely on the atmospheric composition. For example, in an inert atmosphere which removes the gaseous reaction products (1) will predominate. Otherwise, since KNO₂ is stable in this temperature range and N₂ is unreactive, the net result of reactions (1)-(4) is the production of KNO₂ and N₂. In an oxygen atmosphere, particularly in the temperature range 550–600°C the reaction KNO₂ + 1/2O₂ → KNO₂ goes to completion. In the range 650–750°C KNO₂ becomes increasingly unstable and this reaction goes to equilibrium (see below) [25, 51, 108]. Above 800°C the reaction 2KNO₂ → K₂O + N₂ + 3/2O₂ goes to completion [51].

KNO₂

The phase transitions of KNO₂ are fairly complicated and have been discussed by several authors [76, 80, 113]. In addition to the stable low-temperature orthorhombic form II which transforms at 401 K to the rhombohedral I, there exists a metastable form III which can be obtained by cooling I to 396 K. III then transforms to II on further cooling at 386 K.

KNO₂ melts without decomposition to a liquid which is stable in air at least to 530°C [29]. When heated in air it begins to decompose near 650°C [51], at somewhat lower temperatures at lower oxygen pressures. Between 550° and 750°C the quasi-equilibrium KNO₂ ⇌ KNO₂ + 1/2O₂ is set up [25, 51, 108]. The activation energy for the forward reaction is 274kJ (65.6kcal mol⁻¹). If the O₂ is removed, KNO₂ decomposes, various oxides of nitrogen are produced and the reaction is more complicated (see discussion under KNO₃).

\[ \text{KNO}_2(l) = \text{KNO}_2(l) + 1/2\text{O}_2(g). \]  

As pointed out above, the two salts tend to interconvert over a limited temperature range. Above the melting points this leads to solutions containing both salts. For some specified oxygen partial pressure, e.g. air, the solution composition is then a unique function of temperature if equilibrium is established. In the range 550–750°C the equilibrium has been studied by several authors [25, 51, 108].

Freeman [51] studied forward and reverse reactions between 550° and 800°C by a gas evolution method and found that equilibrium in one atmosphere O₂ was established between 650 and 750°C. Sirotkin [108] measured melt compositions in equilibrium with air over this temperature range.

The resulting discrepancy in ΔΗ° was studied by Bartholemew [25] in the light of his measured values for HT-H₂S. For the melts. He concluded that the gas method, in which the melt composition is calculated from the volume of gas evolved by the decomposing KNO₂, is more nearly in agreement with the thermodynamic calculation. In this calculation it was assumed that the enthalpy increments for the salts could be extrapolated from the region in which they were measured to the decomposition region. ΔΗ° calculated from these thermal data agreed well with those based on the experimentally measured equilibrium constant. The enthalpy increment for KNO₂ at 700°C agreed well with that listed by Kelley [3]. In the range 550–750°C the equilibrium constant is given by the equation

\[
\log K = \frac{-115 \pm 5 \text{ kJ mol}^{-1} + 102 \pm 5 \text{ J mol}^{-1} \text{ deg}^{-1}}{2.303 RT}.\]

The enthalpy increments given by Bartholemew can be used to calculate K for both KNO₂ and KNO₃. This calculation requires S°₂₉₈. and ΔS for the phase changes. For KNO₂ these values are known and for values at 700°C calculated from Bartholemew’s and Kelley’s [3] enthalpy increments agree quite well. The former’s values have therefore been used to calculate K for KNO₂ up to 1000°C. However, S°₂₉₈. for KNO₂ is somewhat uncertain and no thermodynamic data are available for the phase transition. Therefore, the experimentally determined equilibrium constant for the KNO₂–KNO₂ equilibrium is probably more reliable than a calculated value would be. As usual, the partial pressures given for the reaction

\[ 2 \text{KNO}_3 = \text{K}_2\text{O} + 2 \text{NO}_2 + 1/2\text{O}_2 \]

assume unit activity for the condensed phases and the absence of other reactions. They can only provide a rough approximation to the actual behavior of a complicated system.

<table>
<thead>
<tr>
<th>Density (ρ g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>293</td>
</tr>
<tr>
<td>620</td>
</tr>
<tr>
<td>630</td>
</tr>
<tr>
<td>640</td>
</tr>
<tr>
<td>650</td>
</tr>
<tr>
<td>660</td>
</tr>
<tr>
<td>670</td>
</tr>
<tr>
<td>680</td>
</tr>
<tr>
<td>690</td>
</tr>
</tbody>
</table>

Density—Continued

\[ \rho \text{ (g cm}^{-3}\text{)} \]

<table>
<thead>
<tr>
<th>( T )</th>
<th>( \text{KNO}_2 )</th>
<th>( \text{KNO}_3 )</th>
<th>( \text{Ref.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1.805</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>710</td>
<td>1.698</td>
<td>1.797</td>
<td>5</td>
</tr>
<tr>
<td>720</td>
<td>1.692</td>
<td>1.790</td>
<td>5</td>
</tr>
<tr>
<td>730</td>
<td>1.685</td>
<td>1.783</td>
<td>5</td>
</tr>
<tr>
<td>740</td>
<td>1.679</td>
<td>1.776</td>
<td>5</td>
</tr>
<tr>
<td>750</td>
<td>1.672</td>
<td>1.768</td>
<td>5</td>
</tr>
<tr>
<td>760</td>
<td>1.671</td>
<td></td>
<td></td>
</tr>
<tr>
<td>770</td>
<td>1.674</td>
<td></td>
<td></td>
</tr>
<tr>
<td>780</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>790</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1.732</td>
<td></td>
<td></td>
</tr>
<tr>
<td>810</td>
<td>1.725</td>
<td></td>
<td></td>
</tr>
<tr>
<td>820</td>
<td>1.717</td>
<td></td>
<td></td>
</tr>
<tr>
<td>830</td>
<td>1.710</td>
<td></td>
<td></td>
</tr>
<tr>
<td>840</td>
<td>1.703</td>
<td></td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>1.695</td>
<td></td>
<td></td>
</tr>
<tr>
<td>860</td>
<td>1.688</td>
<td></td>
<td></td>
</tr>
<tr>
<td>870</td>
<td>1.681</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Transitions

<table>
<thead>
<tr>
<th>Transition</th>
<th>( T(K) )</th>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>( \text{Ref.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{KNO}_2 \rightarrow \text{I} )</td>
<td>713</td>
<td>2.34</td>
<td>6.1</td>
<td>76</td>
</tr>
<tr>
<td>( \text{KNO}_3 \rightarrow \text{II} )</td>
<td>386</td>
<td>3.01</td>
<td>7.60</td>
<td>76</td>
</tr>
<tr>
<td>( \text{KNO}_3 \rightarrow \text{III} )</td>
<td>401</td>
<td>5.42</td>
<td>13.5</td>
<td>76</td>
</tr>
<tr>
<td>( \text{KNO}_3 \rightarrow \text{IV} )</td>
<td>607</td>
<td>9.62</td>
<td>15.8</td>
<td>49</td>
</tr>
</tbody>
</table>

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th>( S^o )</th>
<th>( J \text{ mol}^{-1} \text{ deg}^{-1} )</th>
<th>( \text{Ref.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{KNO}_2 )</td>
<td>132.93</td>
<td>31.77</td>
</tr>
<tr>
<td>( \text{KNO}_3 )</td>
<td>116.7</td>
<td>27.9</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
<td>94.1</td>
<td>22.5</td>
</tr>
</tbody>
</table>

\[ \Delta H_f^o \]

<table>
<thead>
<tr>
<th>( \text{kJ mol}^{-1} )</th>
<th>( \text{Ref.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{KNO}_2 )</td>
<td>-494.633</td>
</tr>
<tr>
<td>( \text{KNO}_3 )</td>
<td>-370.242</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
<td>-363.2</td>
</tr>
</tbody>
</table>

Decomposition of \( \text{KNO}_3 \)

\[ 2\text{KNO}_3 = \text{K}_2\text{O} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2 \]

\[ \Delta H_{\text{f,15}} = 692.2 \text{kJ} , 165.4 \text{kcal} \]

Radium

\( \text{Ra(NO}_3\text{)}_2 \)

According to Mellor [72a] the salt was first prepared by M. S. Curie, but its properties seem not to have been studied since.

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th>( \text{Ra(NO}_3\text{)}_2 )</th>
<th>( J \text{ mol}^{-1} \text{ deg}^{-1} )</th>
<th>( \text{Ref.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ra(NO}_3\text{)}_2 )</td>
<td>218</td>
<td>52</td>
</tr>
</tbody>
</table>

Rare Earths

Nitrites

Several anhydrous nitrites have recently been prepared and their decomposition studied by TGA [92]. They all decompose at lower temperatures than the...
corresponding nitrates. With the exception of praseodymium nitrite whose decomposition product is Pr$_6$O$_{11}$, these nitrates decompose according to

$$4R(NO_2)_3 = 2R_2O_3 + 12NO + 3O_2.$$  

Below are listed the initial decomposition and minimum oxide formation temperatures as given by [92].

<table>
<thead>
<tr>
<th>Salt</th>
<th>Initial decomposition temperature (°C)</th>
<th>Minimum oxide formation temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(NO$_2$)$_3$</td>
<td>240</td>
<td>580</td>
</tr>
<tr>
<td>Pr(NO$_2$)$_3$</td>
<td>220</td>
<td>450</td>
</tr>
<tr>
<td>Nd(NO$_2$)$_3$</td>
<td>200</td>
<td>510</td>
</tr>
<tr>
<td>Sm(NO$_2$)$_3$</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Dy(NO$_2$)$_3$</td>
<td>110</td>
<td>500</td>
</tr>
<tr>
<td>Yb(NO$_2$)$_3$</td>
<td>90</td>
<td>350</td>
</tr>
</tbody>
</table>

These authors also measured the decomposition kinetics of Nd, Dy, and Tb nitrite. The reactions were first-order with very low (4–15 kJ) activation energies which they attributed to metal-oxygen interaction.

**Nitrates**

There has recently been considerable discussion as to (a) whether the anhydrous nitrates are stable intermediates in the thermal decomposition of the corresponding hydrates and (b) whether some of the anhydrous nitrates are ionic or covalent.

A study of the infrared spectra by Walker and Ferraro [123] seems to have established rather firmly that the anhydrous nitrates are covalent. Unfortunately, there appear to have been no TGA or other thermal decomposition studies of rare earth nitrates originally prepared in the anhydrous state. Both Wentland [124, 125] and Patil, Gosavi, and Rao [92] studied the thermal decomposition of the hydrated salts. They agree that oxynitrates of composition RONO$_2$ are formed as intermediates in nearly all cases, but differ as to whether the anhydrous nitrates are also intermediates. Wentland [125] found that the lighter rare earths—La, Pr, Nd—gave the anhydrous salt as stable intermediate

$$(R(NO_2)_3 \cdot 6H_2O \rightarrow R(NO_3)_3 \rightarrow RONO_2 \rightarrow R_2O_3)$$

whereas the heavier rare earths decomposed directly to the oxynitrate. However, Patil et al. [92] claimed that most rare earths on careful decomposition do give the anhydrous nitrate as intermediate. However, they list definite thermal stability ranges only for those listed below:

<table>
<thead>
<tr>
<th>Salt</th>
<th>Stability range of anhydrous nitrate (°C)</th>
<th>Stability range of RONO$_2$ (°C)</th>
<th>Minimum oxide formation temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(NO$_2$)$_3$</td>
<td>240–420</td>
<td>515–575</td>
<td>730</td>
</tr>
<tr>
<td>Nd(NO$_2$)$_3$</td>
<td>230–350</td>
<td>460–500</td>
<td>650</td>
</tr>
<tr>
<td>Dy(NO$_2$)$_3$</td>
<td>260–280</td>
<td>420–440</td>
<td>630</td>
</tr>
<tr>
<td>Yb(NO$_2$)$_3$</td>
<td>260–270</td>
<td>340–400</td>
<td>500</td>
</tr>
<tr>
<td>Lu(NO$_2$)$_3$</td>
<td>220–230</td>
<td>370–390</td>
<td>470</td>
</tr>
</tbody>
</table>

Pr(NO$_3$)$_3$ is exceptional in that the final oxide is Pr$_6$O$_{11}$. The hydrated cerium salt shows no stable intermediates, but goes to CeO$_2$.

The above uncertainties could probably be cleared up by TGA studies of anhydrous nitrates. The above data indicate that these should be stable to ~300 °C. The kinetics of the nitrate decompositions of Nd, Dy, and Yb were found to be first order with activation energies ranging from 23 to 46 kJ higher than corresponding nitrates [92].

**Rubidium**

**RbNO$_2$**

The salt appears to be quite stable up to 450 °C and decomposes increasingly rapidly above that temperature [95]. The decomposition reactions appear to be similar to those of the other alkali metal nitrates, i.e., the course of the decomposition depends on the gas phase. If the gas is continually removed the reaction proceeds directly to the oxide: 2RbNO$_2$ = Rb$_2$O + NO + NO$_2$. In the presence of the nitrogen oxides the salt may be oxidized to the nitrate, particularly in the temperature range where the nitrate is stable.

**RbNO$_3$**

The salt is stable up to 600 °C and begins to lose weight above that temperature [44]. The phase transitions and high-temperature heat capacity have been studied by Mustajoki [75], but the lack of a reliable entropy value for the salt and high-temperature data for the oxide prevent the calculation of decomposition equilibria. Although no experimental studies of the decomposition seem to have been reported, it is expected to resemble that of the other alkali metal nitrates. Like the other alkali metal nitrates, the salt can be vacuum-distilled above 350 °C [58].

**Density**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>ρ (g cm$^{-3}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbNO$_2$</td>
<td>696</td>
<td>2.347</td>
</tr>
<tr>
<td>706</td>
<td>2.339</td>
<td>99</td>
</tr>
<tr>
<td>715</td>
<td>2.333</td>
<td>99</td>
</tr>
<tr>
<td>726</td>
<td>2.322</td>
<td>99</td>
</tr>
<tr>
<td>734</td>
<td>2.316</td>
<td>99</td>
</tr>
<tr>
<td>745</td>
<td>2.306</td>
<td>99</td>
</tr>
<tr>
<td>755</td>
<td>2.299</td>
<td>99</td>
</tr>
<tr>
<td>759</td>
<td>2.295</td>
<td>99</td>
</tr>
<tr>
<td>RbNO$_3$</td>
<td>293</td>
<td>3.112</td>
</tr>
<tr>
<td>590</td>
<td>2.476</td>
<td>5</td>
</tr>
<tr>
<td>600</td>
<td>2.466</td>
<td>5</td>
</tr>
<tr>
<td>610</td>
<td>2.456</td>
<td>5</td>
</tr>
<tr>
<td>620</td>
<td>2.446</td>
<td>5</td>
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<tr>
<td>630</td>
<td>2.437</td>
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<tr>
<td>640</td>
<td>2.427</td>
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<tr>
<td>650</td>
<td>2.417</td>
<td>5</td>
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<tr>
<td>660</td>
<td>2.407</td>
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<tr>
<td>670</td>
<td>2.398</td>
<td>5</td>
</tr>
<tr>
<td>680</td>
<td>2.388</td>
<td>5</td>
</tr>
</tbody>
</table>

KURT H. STERN

Density—Continued

<table>
<thead>
<tr>
<th>T(K)</th>
<th>ρ (g cm⁻³)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbNO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>690</td>
<td>2.378</td>
<td>5</td>
</tr>
<tr>
<td>700</td>
<td>2.369</td>
<td>5</td>
</tr>
<tr>
<td>710</td>
<td>2.359</td>
<td>5</td>
</tr>
<tr>
<td>720</td>
<td>2.349</td>
<td>5</td>
</tr>
<tr>
<td>730</td>
<td>2.339</td>
<td>5</td>
</tr>
<tr>
<td>740</td>
<td>2.330</td>
<td>5</td>
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<tr>
<td>750</td>
<td>2.320</td>
<td>5</td>
</tr>
<tr>
<td>760</td>
<td>2.310</td>
<td>5</td>
</tr>
</tbody>
</table>

ρ = 3.049 − 0.972 × 10⁻³ T

Transitions

RbNO₃

<table>
<thead>
<tr>
<th>Transition</th>
<th>T(K)</th>
<th>ΔH (kJ mol⁻¹)</th>
<th>ΔS (J mol⁻¹ deg⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>rhombic(IV) → cubic(III)</td>
<td>433</td>
<td>3.90</td>
<td>0.90</td>
<td>75</td>
</tr>
<tr>
<td>cubic(III) → trigonal(II)</td>
<td>448±3</td>
<td>3.21</td>
<td>6.58</td>
<td>75</td>
</tr>
<tr>
<td>II → I</td>
<td>554</td>
<td>0.96</td>
<td>1.74</td>
<td>75</td>
</tr>
<tr>
<td>I → I</td>
<td>583</td>
<td>4.64</td>
<td>7.96</td>
<td>75</td>
</tr>
</tbody>
</table>

Rubidium

Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th></th>
<th>J mol⁻¹ deg⁻¹</th>
<th>cal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbNO₃</td>
<td>140.6</td>
<td>33.6</td>
<td>4</td>
</tr>
<tr>
<td>RbNO₂</td>
<td>(124.)</td>
<td>(29.7)</td>
<td>1a</td>
</tr>
</tbody>
</table>

ΔH°

<table>
<thead>
<tr>
<th></th>
<th>kJ mol⁻¹</th>
<th>k cal mol⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbNO₃(C, II)</td>
<td>−489.61</td>
<td>−117.02</td>
<td>1a</td>
</tr>
<tr>
<td>RbNO₂</td>
<td>−362.8</td>
<td>−86.71</td>
<td>22</td>
</tr>
<tr>
<td>RbO</td>
<td>−330</td>
<td>−78.9</td>
<td>1a</td>
</tr>
</tbody>
</table>

Scandium

Sc(NO₃)₃

Mellor [72] summarizes earlier work which claims preparation of this salt by heating Sc(NO₃)₃·4H₂O in vacuum at 100°C. The melting point is said to lie in the range 125−150°C.

Silver

AgNO₃

The thermal decomposition of this salt has not yet been studied in detail, but preliminary experiments [92] indicate that it decomposes at 120°C to give metallic silver and NO₂ with first-order kinetics and an activation energy of ~25 kJ.

Equilibrium constants for (1), (3), and (4) have been listed. Ag₃O is quite unstable above 400 K and hence reactions (1) and (4) are not at equilibrium for reasonable pressures of O₂. Below 500 K, P₀₂ is fixed by reaction (4). P NO₂ and P NO can then be calculated from K₁, K₃, and K₄. Above 400 K the partial pressures were calculated by a procedure analogous to that used for the other nitrates by assuming that only reactions (2) and (3) come to equilibrium. The partial pressures of the three gases calculated in this way are listed in a separate table. Qualitatively, decomposition is negligible in the solid state, but becomes appreciable 30−40°C above the melting point [34].

There has been considerable disagreement about the heat capacity of AgNO₃. It was measured twice by Janz and coworkers [61, 62] who used drop calorimetry to obtain data that differed considerably from those listed by Kelley [3]. Their work was criticized by Reinsborough and Wetmore [104] who pointed out that the sluggish transformation at 433 K may cause hysteresis. They therefore employed adiabatic colorimetry and obtained agreement with Kelley’s [3] compilation. The latter data were therefore used in this work. Data for the reaction Ag₃O = 2 Ag + ½O₂ are taken from [111].

### Decomposition of Nitrites and Nitrites

#### Thermodynamic data (298.15 K)

<table>
<thead>
<tr>
<th>Transitions</th>
<th>$T$ (K)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, ortorhombic$^c$</td>
<td>433</td>
<td>2.4</td>
<td>5.5</td>
<td>104</td>
</tr>
<tr>
<td>$\rightarrow$ C, $\beta$ (rhombohedral)</td>
<td>483</td>
<td>12.49</td>
<td>25.9</td>
<td>62</td>
</tr>
</tbody>
</table>

**Partial pressures (atm) for the decomposition of AgNO$_3$**

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P_{\text{NO}_2}$</th>
<th>$P_{\text{NO}_3}$</th>
<th>$P_{\text{N}_2}$</th>
<th>$P_{\text{O}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$1.19 \times 10^{-4}$</td>
<td>$1.35 \times 10^{-10}$</td>
<td>$8.24 \times 10^{-10}$</td>
<td>$1.19 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>$9.36 \times 10^{-2}$</td>
<td>$4.78 \times 10^{-6}$</td>
<td>$2.22 \times 10^{-10}$</td>
<td>$9.36 \times 10^{-2}$</td>
</tr>
<tr>
<td>500</td>
<td>$1.89 \times 10^{-3}$</td>
<td>$2.79 \times 10^{-6}$</td>
<td>$4.93 \times 10^{-4}$</td>
<td>$5.17 \times 10^{-3}$</td>
</tr>
<tr>
<td>600</td>
<td>$7.91 \times 10^{-4}$</td>
<td>$1.01 \times 10^{-4}$</td>
<td>$2.86 \times 10^{-4}$</td>
<td>$2.09 \times 10^{-1}$</td>
</tr>
<tr>
<td>700</td>
<td>$7.72 \times 10^{-1}$</td>
<td>$7.86 \times 10^{-4}$</td>
<td>$3.79 \times 10^{-4}$</td>
<td>$1.94$</td>
</tr>
</tbody>
</table>

**Sodium**

NaNO$_2$ is unstable above 330 °C [81]. The first step in the decomposition is probably 2NaNO$_2$ → Na$_2$O + NO$_2$ + NO. (N$_2$O$_3$ is too unstable at and above this temperature to be significant.) Between 330° and 380° the reaction sequence seems to be as follows:

1. $2\text{NaNO}_2 \rightarrow \text{Na}_2\text{O} + \text{NO} + \text{NO}_2$. (1)

The NO produced in (1) reacts with NaNO$_2$:

2. $2\text{NaNO}_2 + 2\text{NO} = 2\text{NaNO}_3 + \text{N}_2$. (2)

The NO$_2$ produced in (1) reacts further [118]

3. $\text{Na}_2\text{O} + 2\text{NO}_2 = \text{NaNO}_2 + \text{NaNO}_3$. (3)

4. $\text{NaNO}_2 + \text{NO}_2 = \text{NaNO}_3 + \text{NO}$. (4)

Of these, at least reaction (4) is reversible [116]. Since NaNO$_3$ is stable in this temperature range and N$_2$ is unreactive the net result of reactions (1)–(4) is the production of NaNO$_3$ and N$_2$. If the gas phase is continuously removed only (1) will occur.

At higher temperatures, 600–750 °C, NaNO$_2$ reacts with O$_2$ to establish the equilibrium with NaNO$_3$:

5. $\text{NaNO}_3 = \text{NaNO}_2 + \frac{3}{2}\text{O}_2$. (5)

If the decomposition is carried out in an inert atmosphere the first decomposition product is N$_2$, accompanied by increasing concentrations of O$_2$ in the later stages of the reaction [50]. The stoichiometry of this reaction can be written as [28]

6. $2\text{NaNO}_2 \rightarrow \text{Na}_2\text{O} + \text{N}_2 + \frac{3}{2}\text{O}_2$. (6)

Freeman [50] attributes the evolution of N$_2$ to the formation of a superoxide which later decomposes to Na$_2$O and O$_2$. This view is also supported by Bond and Jacobs [28] who report that this reaction also proceeds in air. For reaction (5) the Arrhenius activation energy is given by [50] as 187 kJ (44.7 kcal) and by [28] as 169 kJ (40.3 kcal). For reaction (6) $E_a = 179$ kJ (42.8 kcal) [28]. Both reactions are fitted by the equation

$$[-\ln (1 - \alpha)]^{1/3} = kt$$
(α = fraction decomposed), an equation which was originally derived for solid state decompositions. Equations of this type generally describe sigmoid α versus t curves.

**NaNO₃**

NaNO₃ melts without decomposition to a liquid which is stable in air at least to 500 °C [29] and begins to decompose slowly at 600° [50]. Between 600 and 750° a pseudoequilibrium is established between air and a liquid containing NaNO₃ and NaNO₂ whose composition is temperature dependent [50, 108]. This equilibrium is discussed above. Enthalpy and entropy increments for NaNO₃ have been listed by Kelley [3] up to 700 K, but no such values are available for NaNO₂. In the absence of such data no calculation involving NaNO₂ can be carried out. In view of the complexity of the decomposition reactions there is some question about the usefulness of such calculations.

As an example of the stability of NaNO₃ in the solid state, we are listing fragmentary calculations which can be made. These include a hypothetical decomposition of NaNO₃ and an experimental study [108] of the equilibrium NaNO₃(1) = NaNO₂(1) + O₂(g). Since the liquids are completely miscible and the solution virtually ideal, the equilibrium constant

\[ K = P_{O_2}^{1/2} (X_{NaNO_3}/X_{NaNO_2}). \]

### Density

\[ \rho (g \text{ cm}^{-3}) \]

<table>
<thead>
<tr>
<th>T(K)</th>
<th>NaNO₂</th>
<th>NaNO₃</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.266</td>
<td>1.898</td>
<td>28</td>
</tr>
<tr>
<td>570</td>
<td>1.801</td>
<td>1.898</td>
<td>5</td>
</tr>
<tr>
<td>580</td>
<td>1.793</td>
<td>1.891</td>
<td>5</td>
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<td>590</td>
<td>1.786</td>
<td>1.884</td>
<td>5</td>
</tr>
<tr>
<td>600</td>
<td>1.778</td>
<td>1.877</td>
<td>5</td>
</tr>
<tr>
<td>610</td>
<td>1.771</td>
<td>1.870</td>
<td>5</td>
</tr>
<tr>
<td>620</td>
<td>1.763</td>
<td>1.862</td>
<td>5</td>
</tr>
<tr>
<td>630</td>
<td>1.756</td>
<td>1.855</td>
<td>5</td>
</tr>
<tr>
<td>640</td>
<td>1.749</td>
<td>1.849</td>
<td>5</td>
</tr>
<tr>
<td>650</td>
<td>1.741</td>
<td>1.841</td>
<td>5</td>
</tr>
<tr>
<td>660</td>
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<td>5</td>
</tr>
<tr>
<td>680</td>
<td>1.719</td>
<td>1.820</td>
<td>5</td>
</tr>
</tbody>
</table>

### Energy changes (kJ mol⁻¹)

\[ \Delta H_{298.15} = 586.2 \text{kJ}, 140.1 \text{kcal} \]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>NaNO₃</th>
<th>NaNO₂</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td>298.15</td>
<td>-116.35</td>
<td>72.89</td>
<td>242.51</td>
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<tr>
<td>400</td>
<td>-120.177</td>
<td>75.65</td>
<td>421.26</td>
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<tr>
<td>500</td>
<td>-128.281</td>
<td>81.04</td>
<td>417.34</td>
</tr>
<tr>
<td>600</td>
<td>-139.034</td>
<td>87.28</td>
<td>410.12</td>
</tr>
<tr>
<td>700</td>
<td>-154.816</td>
<td>93.68</td>
<td>393.27</td>
</tr>
<tr>
<td>800</td>
<td>-166.315</td>
<td>100.04</td>
<td>378.34</td>
</tr>
<tr>
<td>900</td>
<td>-178.625</td>
<td>106.45</td>
<td>365.12</td>
</tr>
<tr>
<td>1000</td>
<td>-190.935</td>
<td>112.86</td>
<td>352.94</td>
</tr>
</tbody>
</table>

DECOMPOSITION OF NITRATES AND NITRITES

Decomposition of NaNO₃

(b) NaNO₃(ℓ) → NaNO₂(ℓ) + 1/2O₂(ℓ)

ΔH°₂₉₈,₁₅ = 109.33 kJ, 26.13 kcal

<table>
<thead>
<tr>
<th>T(K)</th>
<th>log K</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>-1.875</td>
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<td>850</td>
<td>-1.441</td>
<td>3.62 × 10⁻²</td>
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<tr>
<td>900</td>
<td>-1.056</td>
<td>8.80 × 10⁻²</td>
</tr>
<tr>
<td>950</td>
<td>-0.711</td>
<td>1.95 × 10⁻¹</td>
</tr>
<tr>
<td>1000</td>
<td>-0.400</td>
<td>3.98 × 10⁻¹</td>
</tr>
</tbody>
</table>

Strontium

Sr(NO₃)₂

The melting point of Sr(NO₃)₂ is in doubt since the determinations of it [35, 96] vary by 37°. The solid phases have not been characterized.

The thermal decomposition has been studied by several authors [35, 88, 96]. It is similar to those of the barium and calcium salts. A measurable decomposition pressure has been reported at 264 °C, but most studies have been carried out at higher temperatures. At 400–500°, where Sr(NO₃)₂ is stable, the overall reaction is given as [96]

4Sr(NO₃)₂ → 2Sr(NO₃)₃ + 2SrO + 2NO + N₂.

From a careful analysis of all the condensed and vapor phase components in the range 540–700 °C, Oza and Patel [88] deduce the following reaction sequence:

Sr(NO₃)₂ → SrO + NO + NO₂.

(1)

A part of the NO₂ reacts with the remaining nitrite

Sr(NO₃)₂ + 2NO₂ → Sr(NO₃)₃ + 2NO.

(2)

In a closed system this reaction may be reversible. The rest of the NO₂ reacts with the oxide, if oxygen is present

SrO + 2NO₂ + 1/2O₂ → Sr(NO₃)₂.

(3)

The oxygen may be produced by the dissociation of NO₂,

NO₂ ⇌ NO + 1/2O₂.

(4)

Up to 600 °C reaction (3) produces nitrate while above 640° Sr(NO₃)₂ decomposes.

N₂ is produced by

Sr(NO₃)₂ + 2NO → Sr(NO₃)₃ + N₂.

(5)

Reaction (5) probably occurs only at the higher temperatures since it was not reported by [35] below 369 °C.

Sr(NO₃)₂

The melting point of Sr(NO₃)₂ is uncertain. The value listed is that selected by Lumsden [69], but Campbell and Gordon [55] report 891 K and Addison and Coldrey [9] give 878 K. Similarly, reports on the stability of the salt above its melting point vary from slight bubbling starting at 888 [9] to 945 [55]. Crystalline transitions appear to be absent [55]. The thermal decomposition of Sr(NO₃)₂ has not yet been studied in any detail and the absence of high-temperature data prevent carrying out thermodynamic calculations. Its stability would be expected to lie between that of Ca(NO₃)₂ and Ba(NO₃)₂.

Strontium

Sr(NO₃)₂

<table>
<thead>
<tr>
<th>Salt</th>
<th>Transition</th>
<th>T(K)</th>
<th>ΔH (kJ mol⁻¹)</th>
<th>ΔS (J mol⁻¹ deg⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr(NO₃)₂</td>
<td>γ → β</td>
<td>547</td>
<td></td>
<td></td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>β → α</td>
<td>558</td>
<td></td>
<td></td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>α → l</td>
<td>676 ± 18</td>
<td></td>
<td></td>
<td>35, 96</td>
</tr>
<tr>
<td>Sr(NO₃)₂</td>
<td>c → l</td>
<td>918</td>
<td>44.6</td>
<td>48.6</td>
<td>64</td>
</tr>
</tbody>
</table>

Thermodynamic data

<table>
<thead>
<tr>
<th>Salt</th>
<th>S°</th>
<th>J mol⁻¹ deg⁻¹</th>
<th>cal mol⁻¹ deg⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr(NO₃)₂</td>
<td>198.3</td>
<td>47.4</td>
<td>44.6</td>
<td>4</td>
</tr>
<tr>
<td>Sr(NO₃)₂</td>
<td>176.</td>
<td>42.</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>SrO</td>
<td>54.4</td>
<td>13.0</td>
<td></td>
<td>110</td>
</tr>
</tbody>
</table>

Thallium

TINO₂

Very little is known about this salt. Phase transitions have been reported but no details are given by the authors [97]. The thermodynamic data are estimates.

TINO₂

The heat of fusion of TINO₂ has been determined also by Kleppa and McCarthy [66] who obtained 9.47 kJ, but their melting point was 5° lower than the commonly accepted one.

Rolla, Francosini and Riccardi [105] determined H₁ − H₂₉₈ values for solid and liquid TINO₂ which differ, particularly at the lower end of the temperature scale, from those given by Kelley [3]. The vaporization of TINO₂ has been studied recently by Cubicciotti [40]

in the range 539–613 K. He found that in addition to NO as the decomposition product, TINO₃ also vaporized as the salt. In the range 490–612 K the vapor pressure of TINO₃ is given by

$$\log_{10} p(\text{atm}) = -7486/T - 10$$

and the enthalpy and entropy of vaporization by

$$\Delta H_{\text{vap}} (\text{J mol}^{-1}) = 143344 - 41.84T$$

and

$$\Delta S_{\text{vap}} (\text{J deg}^{-1} \text{mol}^{-1}) = 370.9 - 96 \log T.$$ 

He also calculated values of $\Delta G$ for the salt and these have been used in this monograph. The corresponding data for TbO are those of Cubicciotti and Eding [41].

<table>
<thead>
<tr>
<th>Salt</th>
<th>Transition</th>
<th>$T$ (K)</th>
<th>$\Delta H$ J mol$^{-1}$</th>
<th>$\Delta S$ J mol$^{-1}$ deg$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TINO₂</td>
<td>$s \rightarrow s$</td>
<td>442</td>
<td></td>
<td>97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$s \rightarrow 1$</td>
<td>459</td>
<td></td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>TINO₃</td>
<td>Orthorhombic $\rightarrow$ hexagonal</td>
<td>334.2</td>
<td>1.0</td>
<td>3.0, 1a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hexagonal $\rightarrow$ cubic</td>
<td>416</td>
<td>3.8</td>
<td>9.1, 59.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cubic $\rightarrow$ liquid</td>
<td>483</td>
<td>8.83</td>
<td>18.3, 105</td>
<td></td>
</tr>
</tbody>
</table>

$\rho = 5.8041 - 1.8737 \times 10^{-3} T$

### Decomposition of TINO₃

$$2\text{TINO}_3(c) = \text{Tl}_2\text{O}(c) + 2\text{NO}_2(g) + \text{O}_2(g)$$

$$\Delta H_{298.15} = 375.3 \text{kJ}, 89.7 \text{kcal}$$

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>TINO₃ fef</th>
<th>Tl₂O fef</th>
<th>$\Delta S$ J deg$^{-1}$</th>
<th>$\Delta C_p/T$ J deg$^{-1}$</th>
<th>log $K$</th>
<th>$K$</th>
<th>$P_{\text{O}_2}$</th>
<th>$P_{\text{NO}_2}$</th>
<th>$P_{\text{O}_2}$</th>
<th>$P_{\text{NO}_2}$</th>
<th>$P_{\text{O}_2}$</th>
</tr>
</thead>
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<tr>
<td>298.15</td>
<td>-160.7</td>
<td>-125.5</td>
<td>-386.4</td>
<td>872.7</td>
<td>-45.585</td>
<td>2.64 $\times 10^{-4}$</td>
<td>2.33 $\times 10^{-17}$</td>
<td>3.10 $\times 10^{-17}$</td>
<td>5.45 $\times 10^{-17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>-165.3</td>
<td>-128.8</td>
<td>-391.1</td>
<td>872.7</td>
<td>-28.958</td>
<td>1.10 $\times 10^{-10}$</td>
<td>4.04 $\times 10^{-11}$</td>
<td>5.34 $\times 10^{-11}$</td>
<td>9.51 $\times 10^{-11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>-176.9</td>
<td>-134.7</td>
<td>-373.8</td>
<td>377.0</td>
<td>0.000</td>
<td>2.03 $\times 10^{-9}$</td>
<td>1.25 $\times 10^{-9}$</td>
<td>1.64 $\times 10^{-9}$</td>
<td>2.97 $\times 10^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>-192.3</td>
<td>-141.6</td>
<td>-357.9</td>
<td>267.8</td>
<td>-13.908</td>
<td>1.03 $\times 10^{-8}$</td>
<td>2.04 $\times 10^{-8}$</td>
<td>2.67 $\times 10^{-8}$</td>
<td>4.85 $\times 10^{-8}$</td>
<td></td>
<td></td>
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<tr>
<td>700</td>
<td>-206.4</td>
<td>-148.5</td>
<td>-344.9</td>
<td>191.4</td>
<td>-9.997</td>
<td>1.01 $\times 10^{-7}$</td>
<td>7.33 $\times 10^{-8}$</td>
<td>6.11 $\times 10^{-8}$</td>
<td>9.57 $\times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Tin

Sn(NO₃)₄

Sn(NO₃)₄ melts at 364 K and begins to decompose at 371 K. No intermediate oxide-nitrate appears to form, and the final product is SnO₂ [17].

### Titanium

Ti(NO₃)₄

Ti(NO₃)₄ is a covalent salt, stable at least to its melting point at 331 K [48]. It decomposes to TiO₂ with the evolution of O₂ and NO₂ [103].

---

Zirconium

Zr(NO₃)₄

Anhydrous Zr(NO₃)₄ has been prepared. It can be purified by sublimation. The compound is covalent and very hygroscopic [46].

Acknowledgements

I am greatly indebted to Miss Brenda Gibson of the International Telecomputer Network and Mr. Curtis T. Ewing of the Naval Research Laboratory for working out appropriate computer programs for the solution of the equations in section 6.

References

General

The following references in this bibliography have proved to be generally useful in the preparation of this paper and were used so frequently that no specific page numbers are given:


This compilation was used for all the thermodynamic properties of nitrogen, oxygen, and their compounds.


All density values of molten nitrates and nitrites which were listed in this monograph have been transcribed into the present work.

Specific References


