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

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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 $(G_T^\circ - H_{298}^\circ)/T$ 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.

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: CO_2 for the carbonates, and the single equilibrium $SO_3 = SO_2 + 1/2\ O_2$ 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 nitrites. 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 O_2, 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 compilations on the one hand, and experimental data on the other. 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 — N_2, 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}
$H°$ = standard enthalpy
$\Delta Hf°$ = standard enthalpy of formation
$S°$ = standard entropy
$G°$ = standard Gibbs energy
fef = free energy function = $\frac{G_T^\circ - H_{298.15}^\circ}{T}$
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: O_2, N_2, NO, NO_2, N_2O_3, N_2O_4, N_2O_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 N_2O_3 and N_2O_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 $\Delta H^\circ_{298.15}$ 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. $\Delta Hf^\circ_{298.15}$ and $S^\circ_{298.15}$ *for some gases in the N-O system*

Gas	$\Delta Hf^\circ_{298.15}$ (kcal mol^{-1})		$S^\circ_{298.15}$ (cal mol^{-1}deg^{-1})	
	270–3	JANAF	270–3	JANAF
N_2	0	0	45.77	45.77 ± 0.01
O_2	0	0	49.003	49.00 ± 0.01
NO	21.57	21.58 ± 0.04	50.347	50.347
NO_2	7.93	7.91 ± 0.2	57.35	57.34 ± 0.03
N_2O_3	20.01	20.01	74.61	73.91 ± 0.5
N_2O_4	2.19	2.19	72.70	72.72
N_2O_5	2.7	2.7 ± 0.3	85.0	82.8 ± 1.0

Gas	$\Delta Hf^\circ_{298.15}$ (kJ mol^{-1}) [2]	$S^\circ_{298.15}$ (J mol^{-1} deg^{-1}) [2]
N_2	0	191.50
O_2	0	205.03
NO	90.29	210.65_2
NO_2	33.10	239.92
N_2O_3	82.84	309.26
N_2O_4	9.08	304.28
N_2O_5	11.3	346.4

TABLE 2. Free energy functions of gases, $-(G_T^\circ-H_{298}^\circ)/T$ (J mol^{-1} deg^{-1})

T(K)	N_2	O_2	NO	NO_2	N_2O_3	N_2O_4	N_2O_5
298.15	191.502	205.033	210.652	239.923	309.260	304.277	346.439
400	192.644	206.196	211.823	241.417	311.930	307.449	350.414
500	194.811	208.413	214.041	244.333	317.189	313.808	358.355
600	197.246	210.932	216.543	247.722	323.314	321.289	367.698
700	199.707	213.501	219.074	251:237	329.670	329.113	377.439
800	202.100	216.061	221.547	254.730	335.984	336.938	387.125
900	204.401	218.442	223.928	258.140	342.142	344.598	396.568
1000	206.598	220.769	226.204	261.437	348.088	352.029	405.672
1100	208.694	222.986	228.375	264.609	353.803	359.188	414.413
1200	210.694	225.103	230.446	267.655	359.288	366.079	422.777

TABLE 3. $N_2+O_2=2NO$

$\Delta H_{298.15}^\circ=180.50$ kJ, 43.16 kcal

T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	−24.769	580.630	−30.329	4.69×10^{-31}
400	−24.806	426.445	−22.275	5.31×10^{-23}
500	−24.858	336.142	−17.588	2.58×10^{-18}
600	−24.908	275.925	−14.412	3.88×10^{-15}
700	−24.940	232.917	−12.166	6.83×10^{-13}
800	−24.933	200.692	−10.483	3.29×10^{-11}
900	−25.013	175.542	−9.169	6.78×10^{-10}
1000	−25.041	155.459	−8.120	7.59×10^{-9}
1100	−25.070	139.021	−7.261	5.48×10^{-8}
1200	−25.095	125.322	−6.545	2.85×10^{-7}

TABLE 4. $2NO_2=2NO+O_2$

$\Delta H_{298.15}^\circ=114.4$ kJ, 27.34 kcal

T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	−146.490	237.210	−12.389	4.08×10^{-13}
400	−148.574	137.426	−7.177	6.65×10^{-8}
500	−147.828	80.972	−4.229	5.90×10^{-5}
600	−148.574	42.092	−2.198	6.34×10^{-3}
700	−149.174	14.254	−0.744	1.80×10^{-1}
800	−149.694	−6.694	0.350	2.24
900	−150.018	−22.906	1.196	15.7
1000	−150.222	−35.822	1.871	74.3
1100	−150.518	−46.518	2.420	269.
1200	−150.685	−55.352	2.891	778.

TABLE 5. $NO+1/2\ O_2=NO_2$

$\Delta H_{298.15}^\circ=-57.20$ kJ, −13.67 kcal

T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	73.245	−118.605	6.194	1.57×10^{6}
400	74.287	−68.713	3.589	3.89×10^{3}
500	73.914	−40.486	2.114	1.30×10^{2}
600	74.287	−21.046	1.099	12.6
700	74.587	−7.127	0.372	2.36
800	74.847	+3.347	−.175	0.669
900	75.009	11.453	−.598	0.253
1000	75.111	17.911	−.935	0.116
1100	75.259	23.260	−1.215	6.10×10^{-2}
1200	75.343	27.675	−1.445	3.59×10^{-2}

TABLE 6. $NO_2=1/2N_2+O_2$

$\Delta H_{298.15}^\circ=-33.09_5$ kJ, −7.91 kcal

T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	−60.861	−171.862	8.976	9.47×10^{8}
400	−61.101	−143.838	7.512	3.25×10^{7}
500	−61.486	−127.676	6.668	4.66×10^{6}
600	−61.833	−116.991	6.110	1.29×10^{6}
700	−62.118	−109.396	5.713	5.17×10^{5}
800	−62.381	−103.749	5.418	2.62×10^{5}
900	−62.503	−99.275	5.185	1.53×10^{5}
1000	−62.631	−95.726	4.999	1.00×10^{5}
1100	−62.724	−92.810	4.848	7.05×10^{5}
1200	−62.795	−90.426	4.723	5.48×10^{4}

On the basis of the data in tables 3 to 10 we draw the following conclusions: (a) N_2O_5 is unstable with respect to dissociation into either N_2O_4 or N_2O_3 from 298 K up. Therefore it need not be considered in the dissociation of the salts. (b) The equilibrium $N_2O_4=2NO_2$ shifts markedly to the right with increasing temperature. Above 400 K the concentration of N_2O_4 is negligible. (c) Although N_2O_3 has been reported as a product of nitrate decomposition it is unstable with respect to dissociation into NO_2 and NO above 400 K. It could therefore exist in equilibrium mixtures only near ambient temperatures. (d) The equilibrium $NO+1/2\ O_2=NO_2$ is very tempera-

TABLE 7. $N_2O_4 = 2NO_2$

$\Delta H^\circ_{298.15} = 13.67$ kcal, 57.19_5 kJ

T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	−175.569	16.263	−0.849	1.42×10^{-1}
400	−175.385	−32.397	+2.256	1.80×10^{2}
500	−174.858	−60.468	3.158	1.44×10^{3}
600	−174.155	−78.830	4.117	1.31×10^{4}
700	−173.261	−91.554	4.782	6.06×10^{4}
800	−172.522	−101.028	5.277	1.89×10^{5}
900	−171.682	−108.132	5.648	4.45×10^{5}
1000	−170.845	−113.650	5.936	8.63×10^{5}
1100	−170.030	−118.035	6.165	1.46×10^{6}
1200	−169.231	−121.569	6.349	2.23×10^{6}

TABLE 8. $NO_2 + NO = N_2O_3$

$\Delta H^\circ_{298.15} = -40.543$ kJ, -9.690 kcal

T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	141.315	5.262	−0.274	5.33×10^{-1}
400	141.310	39.952	−2.086	8.21×10^{-3}
500	141.185	60.100	−3.139	7.27×10^{-4}
600	140.951	73.380	−3.832	1.47×10^{-4}
700	140.641	82.851	−4.327	4.71×10^{-5}
800	140.293	89.613	−4.680	2.09×10^{-5}
900	139.926	94.878	−4.955	1.01×10^{-5}
1000	139.553	99.010	−5.171	6.75×10^{-6}
1100	139.181	102.450	−5.351	4.46×10^{-6}
1200	138.813	105.107	−5.490	3.24×10^{-6}

TABLE 9. $N_2O_5 = N_2O_4 + 1/2\ O_2$

$\Delta H^\circ_{298.15} = -0.53$ kcal, -2.22 kJ

T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	−60.355	−67.801	3.522	3.33×10^{3}
400	−60.133	−65.683	3.430	2.69×10^{3}
500	−59.660	−64.100	3.348	2.23×10^{3}
600	−59.057	−67.757	3.277	1.90×10^{3}
700	−58.425	−61.596	3.217	1.65×10^{3}
800	−57.844	−60.619	3.166	1.47×10^{3}
900	−57.251	−59.718	3.119	1.32×10^{3}
1000	−56.742	−58.962	3.079	1.20×10^{3}
1100	−56.268	−58.286	3.044	1.11×10^{3}
1200	−55.854	−57.704	3.014	1.03×10^{3}

TABLE 10. $N_2O_5 = N_2O_3 + O_2$

$\Delta H^\circ_{298.15} = -37.20$ kJ, -8.89 kcal

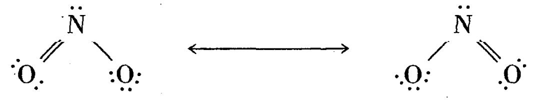
T(K)	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K
298.15	−167.854	−292.693	15.286	1.93×10^{15}
400	−167.712	−260.712	13.615	4.13×10^{13}
500	−167.247	−241.647	12.620	4.17×10^{12}
600	−166.548	−228.548	11.936	8.53×10^{11}
700	−165.732	−218.875	11.431	2.70×10^{11}
800	−164.920	−211.420	11.041	1.10×10^{11}
900	−164.016	−205.349	10.724	5.30×10^{10}
1000	−163.185	−200.385	10.465	2.92×10^{10}
1100	−162.376	−196.194	10.247	1.77×10^{10}
1200	−161.614	−192.614	10.060	1.15×10^{10}

ture dependent. Up to 500 K, NO_2 predominates markedly; above that temperature both species are significant. The equilibrium is quite mobile and must always be considered in the salt decomposition. (e) N_2 and O_2 are very stable with respect to both NO and NO_2. Thus, if N_2 is formed during salt decomposition it will not react further. O_2 may react with NO and with nitrites. (f) If all equilibria were established quickly during decomposition of the salts, N_2 and O_2 would be the only gaseous components. However, the reaction $NO_2 = 1/2\ N_2 + O_2$ is very slow below 1000 K. Thus, if NO_2 is the primary product of the decomposition it will not decompose appreciably by this reaction and only the equilibrium $NO + 1/2\ O_2 = NO_2$ 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 nitrites with the exception of the alkali metal and alkaline earth salts. The nitrite ion is less stable than the nitrate, so that the nitrites 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



or, in MO theory, by assuming that N forms three sp^2 hybrid orbitals, one housing an unshared pair and the other two being used in σ bonding to the oxygens. The p_z orbitals of N and O are used for π bond formation.

The coordination of the nitrite ion to the metal cation appears to differ with the salt. For example, in $AgNO_2$, Ag^+ is closer to N than to O, whereas in $NaNO_2$, Na^+ is closer to O than to N [63]. Since the metal ion-nitrite coordination has not yet been much studied, the periodic table of figure 1 which lists the known nitrites omits bonding information.

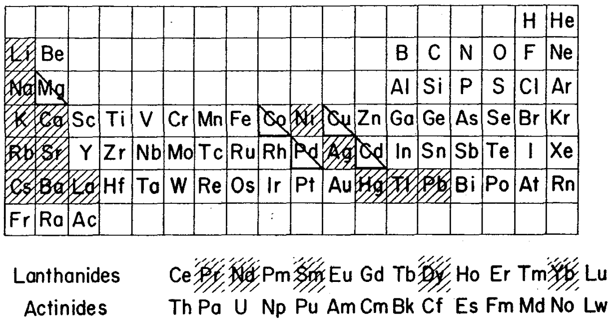


FIGURE 1. The Nitrites: ◺ existence uncertain.

Nitrites decompose at lower temperatures than the corresponding nitrates. The course of the decomposition depends on the nature of the salt and the gas phase composition. Nitrites of the more electropositive metals decompose to form the oxide directly by reactions of the type $2MNO_2 \rightarrow M_2O + NO + NO_2$, but if the gases are not immediately removed the nitrite is easily oxidized to the nitrate by NO_2, if the latter salt is stable at the temperature of the decomposition. In some cases, particularly the rare earth nitrites, the first decomposition product is an oxynitrite. According to Addison and Sutton [20], simple nitrites will be stable only if a higher valence state of the metal is not readily available. Otherwise decomposition to oxynitrites will occur to achieve the more stable valence state of the metal. This view is supported somewhat by the lack of existence of many nitrites of metals in the first two long periods of the periodic table (fig. 1), although the absence of Zn $(NO_2)_2$ is surprising.

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 [48a], 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.

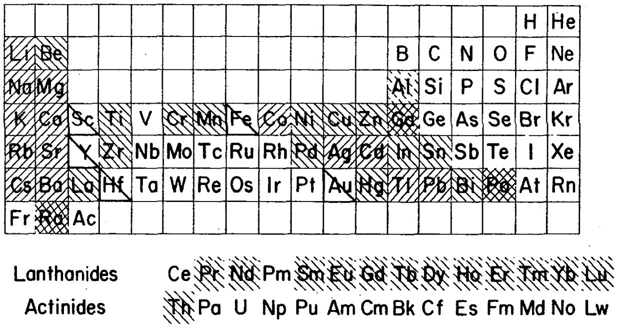


FIGURE 2. The Nitrates: ///// ionic, \\\\\ covalent XXX bonding uncertain, ◺ existence uncertain.

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. $Co(NO_3)_2$ 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_2O_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_2 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-

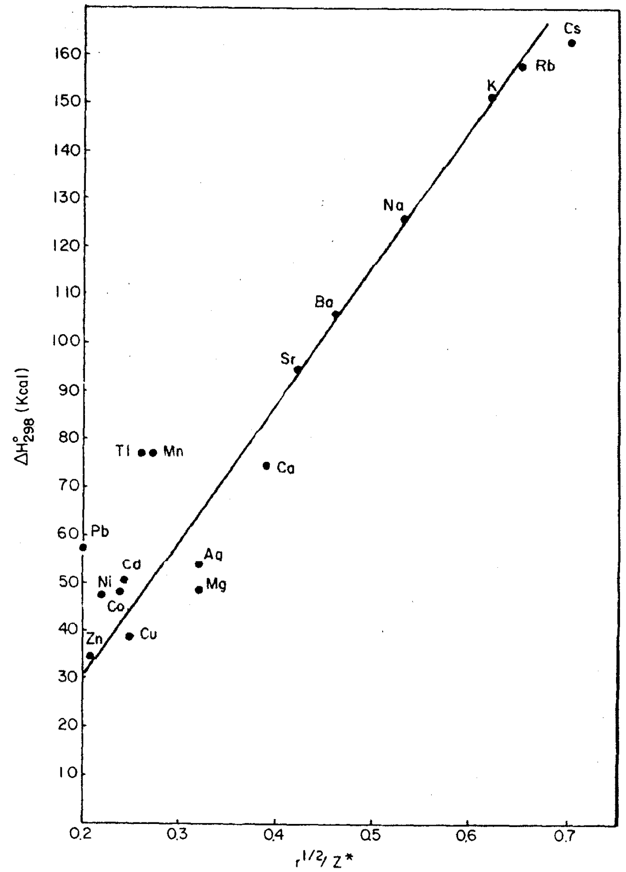


FIGURE 3. Dependence of ΔH°_{298} of the nitrates on the cation $r^{1/2}/Z^*$ For discussion see text and [109].

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,

$$M(NO_3)_2 = MO + 2NO_2 + 1/2\ O_2 \qquad (1)$$

and the gas equilibrium

$$2NO_2 = 2NO + O_2. \qquad (2)$$

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

$$K_1 = \frac{P^2_{NO_2} P^{1/2}_{O_2} a_{MO}}{a_{M(NO_3)_2}}$$

$$K_2 = \frac{P^2_{NO} P_{O_2}}{P^2_{NO_2}}.$$

The partial pressures of the three gases can be calculated if the nitrate and oxide do not form solutions ($a_{MO} = a_{M(NO_3)_2} = 1$) 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

$$P_{O_2} = 1/4(P_{NO_2} + P_{NO}) + 1/2\, P_{NO}$$

or

$$4P_{O_2} = P_{NO_2} + 3P_{NO}.$$

If the condensed phases are pure, a condition which can only hold if both the salt and the oxides are solids, the term $a_{MO}/a_{M(NO_3)_2} = 1$ and appropriate substitutions yield an equation in P_{O_2} alone:

$$\frac{K_1^{1/2}}{P^{1/4}_{O_2}} + \frac{3(K_1K_2)^{1/2}}{P^{3/4}_{O_2}} = 4P_{O_2}\,.$$

Making the substitution $X = P^{1/4}_{O_2}$ this equation can be written in the form

$$X^7 - aX^2 - b = 0$$

where $a = K_1^{1/2}/4$, $b = (3/4)(K_1K_2)^{1/2}$. 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_{O_2} had been obtained P_{NO_2} and P_{NO} were calculated from the equations

$$P_{NO_2} = K_1{}^{1/2}/P^{1/4}_{O_2}$$

$$P_{NO} = (K_1K_2)^{1/2}/P^{3/4}_{O_2}.$$

The pressures thus obtained are those to be expected if the pure nitrate is initially placed into a closed container containing no other reactants, and the system is allowed to reach equilibrium.

Although the pressures in the real systems may differ from those calculated by the above procedure, particularly if nitrites are formed, the values obtained are a useful guide to the stability of the salts.

In several instances the lack of high-temperature thermal data, particularly for the nitrates, prevented the calculation of equilibrium constants at temperatures where it would be useful to have them. In these cases values of log K were obtained by extrapolation of a log K versus $1/T$ plot. The temperatures for these have been put in parentheses. K values calculated in this way are estimated to be uncertain by one order of magnitude. Alternatively, estimation of K by extrapolation of Δfef (uncertainty ± 2 Jdeg^{-1}) would yield approximately the same uncertainty in K.

For those salts for which no high-temperature thermal data are available a very crude estimate of K can be made from $\Delta G^\circ/T = \Delta H^\circ_{298}/T - \Delta S^\circ_{298}$. It should be recognized, however, that the assumption of temperature invariance of ΔS° and ΔH° may result in large errors in K.

All the partial pressures calculated from the equilibrium constants assume a unit activity ratio for the condensed-phase components. This assumption is quite good when these are solid. Above the melting point of the salts, however, continued decomposition of the salt will result in a solution containing dissolved oxide and the partial pressures will depend on the melt composition and will therefore change as the decomposition proceeds. Because of the form of K_1, the partial pressure calculation will be worst for melts containing only small concentrations of oxide ($a_{\mathrm{MO}} \cong 0$), but will be correct when the salt is approximately half decomposed,

$$(a_{\mathrm{MO}}/a_{\mathrm{M(NO_3)_2}}) = 1.$$

An examination of the various tables shows that O_2 and NO are the major products of nitrate decomposition, the concentration of NO_2 being rather minor. This results from the stoichiometry of the equilibrium $2NO_2 = 2NO + O_2$ which lies to the right for low total pressures.

Aluminum

$Al(NO_3)_3$ has been prepared in nearly pure form by vacuum sublimation of its adduct with N_2O_5. It condensed as a white powder at -78 °C. [6]. None of its properties has yet been measured. Its classification as covalent is made on the basis of the spectrum of the N_2O_5 adduct.

Barium

$Ba(NO_2)_2$

The melting point of $Ba(NO_2)_2$ is very much in doubt, Centnerszwer and Piekielny [35] giving 262 °C, Protsenko and Bordyushkova [96] give 284 °C. Neither paper describes any experimental detail. Similarly, solid transitions were reported [97] at 203 and 230 °C, but no details are available.

The decomposition of the salt has been studied by three groups of workers [35, 84, 96] at somewhat different temperatures and under various atmospheres. Although they differ in detail, they are in general agreement as to the main features.

The primary decomposition reaction, which is irreversible, is

$$Ba(NO_2)_2 = BaO + NO_2 + NO. \tag{1}$$

This reaction begins as low as 250 °C. In the temperature range in which $Ba(NO_3)_2$ is stable the NO_2 formed oxidizes $Ba(NO_2)_2$ [118]:

$$Ba(NO_2)_2 + 2NO_2 = Ba(NO_3)_2 + 2NO. \tag{2}$$

Above 400 °C, BaO reacts with NO to form N_2:

$$BaO + 3NO = Ba(NO_2)_2 + 1/2N_2. \tag{3}$$

"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 Bordyushkova [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 O_2 can oxidize 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

$$2Ba(NO_2)_2 = Ba(NO_3)_2 + BaO + NO + 1/2N_2$$

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

$$Ba(NO_3)_2 = BaO + 2NO_2 + 1/2O_2.$$

$Ba(NO_3)_2$

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

$$Ba(NO_3)_2 = Ba(NO_2)_2 + O_2$$

but this salt is very unstable so that the overall decomposition is

$$Ba(NO_2)_3 = BaO + 2NO_2 + 1/2O_2.$$

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.

Density

T(K)	$Ba(NO_2)_2$ ρ(g cm^{-3})	References
298	3.232	31
550	3.254	5
560	3.247	5
570	3.240	5
580	3.233	5
590	3.226	5
600	3.219	5
610	3.212	5
620	3.205	5
	$Ba(NO_3)_2$	
288–298	3.23	57

Transitions

Transition	T(K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} deg^{-1})	References
		$Ba(NO_2)_2$		
c→l	546±11	....	....	35, 96
		$Ba(NO_3)_2$		
c→l	869	[a] 41.6	[b] 47.9	64

[a] at 723 K, from $\Delta H_{sol'n}$.

[b] at the melting point.

Thermodynamic data (298.15 K)

	$S°$ J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Ba(NO_3)_2$	213.8	51.1	1b
$Ba(NO_2)_2$	182.8	43.7	4
BaO	70.42	16.83	1b

	$\Delta Hf°$ kJ mol^{-1}	kcal mol^{-1}	Ref.
$Ba(NO_3)_2$	−992.07	−237.11	1b
$Ba(NO_2)_2$	−768.2	−183.6	1b
BaO	−553.5	−132.3	1b

Decomposition of $Ba(NO_3)_2$

$$Ba(NO_3)_2 = BaO + 2NO_2 + 1/2\ O_2$$

$$\Delta H°_{298.15} = 504.7_2\ \text{kJ},\ 120.6_3\ \text{kcal}$$

T K	$Ba(NO_3)_2$ fef J deg^{-1}	BaO fef J deg^{-1}	Δfef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	log K	K	P_{O_2} atm	P_{NO_2} atm	P_{NO} atm	P_{Tot} atm
298.15	−213.8	−70.3	−438.9	1253.9	−65.499	3.17×10^{-66}	7.03×10^{-23}	6.15×10^{-28}	4.69×10^{-23}	1.17×10^{-22}
400	−220.0	−72.1	−438.0	823.8	−43.031	9.31×10^{-44}	3.83×10^{-15}	1.22×10^{-18}	5.03×10^{-15}	8.94×10^{-15}
500	−232.6	−75.8	−436.1	573.3	−29.948	1.13×10^{-30}	1.46×10^{-10}	3.05×10^{-13}	1.94×10^{-10}	3.40×10^{-10}
600	−247.4	−79.9	−433.4	407.8	−21.301	5.00×10^{-22}	1.64×10^{-7}	1.11×10^{-9}	2.18×10^{-7}	3.84×10^{-7}
700	−263.0	−84.2	−430.4	290.6	−15.181	6.59×10^{-16}	2.40×10^{-5}	3.67×10^{-7}	3.18×10^{-5}	5.61×10^{-5}
800	−278.8	−88.4	−427.1	203.8	−10.645	2.26×10^{-11}	9.75×10^{-4}	2.69×10^{-5}	1.29×10^{-3}	2.29×10^{-3}
(900)	....	....	....	....	−6.8	1.6×10^{-7}	2.2×10^{-2}	1.1×10^{-3}	2.8×10^{-2}	5.1×10^{-2}
(1000)	....	....	....	....	−4.5	3.2×10^{-5}	0.15	9.1×10^{-3}	0.20	0.36
(1100)	....	....	....	....	−3.0	1.0×10^{-3}	0.59	3.6×10^{-2}	0.77	1.40

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 $Be_4O(NO_3)_6$ [21].

Thermodynamic data (298.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Be(NO_3)_2$	184±8	44±2 est.	93
BeO	15	3.7	1a

ΔHf°

	kJ mol^{-1}	k cal mol^{-1}	Ref.
$Be(NO_3)_2$	−602±8	−144±4 est.	93
BeO	−610.9	−146.0	1a

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].

$Cd(NO_3)_2$

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 ΔH_{fus} and ΔS_{fus} are obtained by extrapolation of cryoscopic data in $AgNO_3$ and $TlNO_3$ [65]. The decomposition is reported to be reversible and to yield no intermediates [68].

$$2Cd(NO_3)_2 = 2CdO + 4NO_2 + O_2$$

Transitions

$Cd(NO_3)_2$ transition	T(K)	ΔH(kJ mol^{-1})	ΔS(J mol^{-1} deg^{-1})	Ref.
c → l	633	18.2	28.8	1a, 65

Thermodynamic data (298.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Cd(NO_3)_2$	197.9	47.3	4
$Cd(NO_2)_2$	167 ± 8	40 ± 2 est.	93
CdO	54.8	13.1	1b, 111

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Cd(NO_3)_2$	− 456.31	− 109.06	1b
$Cd(NO_2)_2$	− 331 ± 17	− 79 ± 4 est.	111
CdO	− 258.2	− 61.7	1b, 111

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 ΔH°_{298} for the reaction cited by the authors,

$$Ca(NO_2)_2 = CaO + NO_2 + NO \qquad (1)$$

for which $\Delta H^\circ_{298} = 234.4$kJ. The lack of high-temperature thermodynamic data for $Ca(NO_2)_2$ prevents a comparison of ΔH° at the temperature of the experiment. At somewhat higher temperatures only NO appears as the product, probably because NO_2 oxidizes the $Ca(NO_2)_2$:

$$Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO. \qquad (2)$$

The decomposition was also studied by Protsenko and Bordyushkova [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:

$$4Ca(NO_2)_2 = 2Ca(NO_3)_2 + 2CaO + 2NO + N_2 \qquad (3)$$

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 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 $Ca(NO_3)_2 = CaO + 2NO_2 + 1/2O_2$. 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.

Density

$Ca(NO_2)_2$		
T(K)	$\rho^{\circ}_{\circ}$	Reference
373	2.265	31

Transitions

Transition	T(K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} deg^{-1})	Ref.
$Ca(NO_2)_2$ s → s	539	....	....	97
s → s	633	....	....	97
s → l	665	....	....	96
$Ca(NO_3)_2$ s → l	834	23.4	28.1	1a, 69

Thermodynamic data (298.15 K)

	S°		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Ca(NO_3)_2$	193.3	46.2	1b
$Ca(NO_2)_2$	164.4	39.3	1b
CaO	39.7	9.50	1b

	ΔHf°		
	kJ mol^{-1}	k cal mol^{-1}	Ref.
$Ca(NO_3)_2$	− 938.39	− 224.28	1b
$Ca(NO_2)_2$	− 741.4	− 177.2	1b
CaO	− 635.09	− 151.79	1b

Decomposition of $Ca(NO_3)_2$

$$Ca(NO_3)_2 = CaO + 2NO_2 + 1/2\ O_2$$

$$\Delta H^\circ_{298.15} = 369.4_9\ \text{kJ},\ 88.3_1\ \text{kcal}$$

T K	$Ca(NO_3)_2$ fef J deg^{-1}	CaO fef J deg^{-1}	Δfef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	log K	K	P_{O_2} atm	P_{NO_2} atm	P_{NO} atm	P_{Tot} atm
298.15	−193.3	−39.7	−428.75	810.53	−42.337	4.60×10^{-43}	1.97×10^{-16}	5.72×10^{-18}	2.60×10^{-16}	4.63×10^{-16}
400	−199.6	−41.5	−427.83	495.90	−25.903	1.25×10^{-26}	3.04×10^{-10}	2.68×10^{-11}	3.96×10^{-10}	7.27×10^{-10}
500	−212.0	−44.9	−425.77	313.21	−16.361	4.36×10^{-17}	1.14×10^{-6}	2.02×10^{-7}	1.45×10^{-6}	2.80×10^{-6}
600	−226.8	−48.7	−422.81	193.01	−10.082	8.29×10^{-11}	2.73×10^{-4}	7.08×10^{-5}	3.41×10^{-4}	6.85×10^{-4}
700	−242.3	−52.7	−419.62	108.22	−5.653	2.22×10^{-6}	1.33×10^{-2}	4.40×10^{-3}	1.62×10^{-2}	3.39×10^{-2}
800	−258.0	−56.6	−416.09	45.77	−2.391	4.01×10^{-3}	0.235	9.16×10^{-2}	0.283	0.609

Cesium

$CsNO_2$

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.

$CsNO_3$

This salt exhibits one solid-solid transition. The hysteresis which is frequently exhibited 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°_{298} and C_p values for Cs_2O prevent 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.

Density

$CsNO_2$

T(K)	ρ(gcm^{-3})	References
681	2.844	99
691	2.835	99
701	2.826	99
711	2.815	99
721	2.805	99
732	2.793	99
742	2.783	99
752	2.772	99

$CsNO_3$

T(K)	ρ(gcm^{-3})	References
293	3.643	57
690	2.8160	5
700	2.8044	5
710	2.7927	5
720	2.7810	5
730	2.7694	5
740	2.7577	5
750	2.7461	5
760	2.7344	5

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

Transitions

Salt	Transition	T(K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} deg^{-1})	Ref.
$CsNO_2$	s → l	679	....	....	5
$CsNO_3$	Hexagonal → cubic	425	3.7	8.7	74
	cubic → l	679	14.1	20.8	74

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$CsNO_3$	147.7	35.3	4
Cs_2O	....	....	....

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$CsNO_3$	−509.6	−121.8	1b.
Cs_2O	$-317._6$	−75.9	110

Chromium

$Cr(NO_3)_3$

Anhydrous $Cr(NO_3)_3$ has been prepared. The compound is covalent. When the pale green powder is heated in vacuum or an atmosphere of nitrogen it begins to decompose rapidly at 60°, and the decomposition rate is at a maximum at 100°. Decomposition may proceed through a series of oxide nitrates, but none of these is stable enough to give a plateau on TGA. The first plateau is obtained at 200° and corresponds to Cr_3O_8. [7]

Cobalt

$Co(NO_2)_2$

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

$Co(NO_3)_2$

$Co(NO_3)_2$ decomposes to Co_3O_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)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Co(NO_3)_2$	192.	46.	4
CoO	52.97	12.66	1b
Co_3O_4	102.5	24.5	1b

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Co(NO_3)_2$	−420.5	−100.5	1b
CoO	−237.94	−56.87	1b
Co_3O_4	−891.	−213.	1b

Copper

$Cu(NO_2)_2$

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

$Cu(NO_3)_2$

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 $Cu(NO_3)_2$ 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:

T(K)	430.2	446.0	459.6	462.7	475.2	488.4	495.8
P(torr)	0.32	0.59	0.99	1.15	1.87	2.84	3.59

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

	T(K)	ΔH kJ mol^{-1}	ΔS J mol^{-1} deg^{-1}	Ref.
$Cu(NO_3)_2$ c → l	528	...	...	12
c → g	453–493	65.3	^{a}87.0	12

^{a} At 1 atm.

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Cu(NO_3)_2$	193.3	46.2	4
Cu_2O	93.14	22.26	1b
CuO	42.64	10.19	1b

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Cu(NO_3)_2$	−302.9	−72.4	1b
Cu_2O	−168.6	−40.3	1b
CuO	−157.3	−37.6	1b

Gallium

$Ga(NO_3)_2$ 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 Ga_2O_3 when the temperature reached 200°C.

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Ga(NO_3)_2$	...	...	...
GaO(g)	231.	55.2	1b
Ga_2O_3(c)	84.98	20.31	1b

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Ga(NO_3)_2$	−619 ± 17	−148 ± 4 est.	93
GaO(g)	279.	66.8	1b
Ga_2O_3(c)	−1089.	−260.3	1b

Gold

$Au(NO_3)_3$

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 HNO_3 and N_2O_5. 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 $Hf(NO_3)_4 \cdot N_2O_5$, but this compound sublimed as such, rather than losing N_2O_5.

Indium

The infrared spectrum shows that $In(NO_3)_3$ is covalent and stable to at least 90° C since this was the temperature of its preparation [106].

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$In(NO_3)_3$	...	...	...
In_2O_3	104.	24.9	1b

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$In(NO_3)_3$	−632 ± 17	−151 ± 4 est	93
In_2O_3	−925.79	−221.27	1b

Iron

So far $Fe(NO_3)_3$ has only been prepared as the volatile adduct $Fe(NO_3)_3 \cdot N_2O_4$, although it is possible that $Fe(NO_3)_3$ exists in the vapor state [13].

Lead

$Pb(NO_2)_2$

Very little is yet known about this salt. It has recently been prepared by treatment of the chloride with $AgNO_2$ 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

$$3Pb(NO_2)_2 = Pb(NO_3)_2 + 2PbO + 4NO.$$

The second stage is the decomposition of the nitrate. However, this occurred in the range 320–450° C and seemed to proceed directly to $PbO_{1.7}$, results which are contradictory to other studies of nitrate decomposition (see below).

$Pb(NO_3)_2$

*Although there are as yet no high temperature thermo*dynamic data on $Pb(NO_3)_2$ 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 states, 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 $Pb(NO_3)_2$ 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 (renotated from the original paper) and the temperature ranges over which they were measured are:

	T(K)	
I	539–632	$3Pb(NO_3)_2 = [Pb(NO_3)_2 \cdot 2PbO] + 4NO_2 + O_2$
II	625–719	$2[Pb(NO_3)_2 \cdot 2PbO] = [Pb(NO_3)_2 \cdot 5PbO] + 2NO_2 + 1/2\ O_2$
III	688–809	$[Pb(NO_3)_2 \cdot 5PbO] = 6PbO + 2NO_2 + 1/2\ O_2$.

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.

$$Pb(NO_3)_2 \cdot 2PbO = 3PbO \cdot N_2O_5.$$

Neumann and Sonntag calculated equilibrium constants for the above reactions by calculating the partial pressures of NO_2 and O_2, using the experimental data of Bodenstein [27] for the equilibrium reaction $NO_2 = NO + 1/2\ O_2$. 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. ΔH° values calculated for the various portions are:

Reaction	T(K)	ΔH°(kJ)
I	539–583	694
	583–603	629
	613–632	758
II	625–719	337
III	688–763	390
	763–809	324

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 ΔH° for the reaction

$$6Pb(NO_3)_2 = 6PbO + 12NO_2 + 3\ O_2$$

from the ΔH°'s for reactions I, II, and III. Using for $\Delta H^\circ_{\mathrm{I}}$ 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 $Pb(NO_3)_2$ a direct calculation for this reaction is not possible, but since ΔC_p is generally relatively small, one would not expect ΔH°_{298} and ΔH°_T to differ by more than 5 percent. In fact $\Delta H^\circ_{298} =$ 1794kJ, so that the agreement is reasonable. A choice for $\Delta H^\circ_{\mathrm{II}}$ of 629kJ would have lowered ΔH_T to 1919kJ. If it is assumed that ΔH° for each of three reactions is independent of temperature, ΔHf° values can be estimated for the two oxynitrates. From $\Delta H^\circ_{\mathrm{I}} =$ 629kJ we get ΔHf° of $[Pb(NO_3)_2 \cdot 2PbO]$; $\Delta H^\circ_{\mathrm{III}} = 324$kJ yields ΔHf° of $[Pb(NO_3)_2 \cdot 5PbO]$. The values are

	ΔHf° (kJ)
$Pb(NO_3)_2 \cdot 2PbO$	−867
$Pb(NO_3)_2 \cdot 5PbO$	−1558.

When these values are used to calculate $\Delta H^\circ_{\mathrm{II}}$, 342kJ is obtained, in good agreement with the experimental value of 337kJ.

Recently a TGA study [92] of $Pb(NO_3)_2$ claimed the final product to be $PbO_{1.4}$, but no details were given.

Thermodynamic data (298.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Pb(NO_3)_2$	213.0	50.9	4
PbO (yellow)	68.70	16.42	1b
PbO (red)	66.5	15.9	1b

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Pb(NO_3)_2$	−451.9	−108.0	1b
PbO (yellow)	−217.32	−51.94	1b
PbO (red)	−218.99	−52.34	1b

Lithium

$LiNO_2$

The salt is stable up to 300 °C. It decomposes slowly at 350° and more rapidly with increasing temperature [95]. The product gases, NO and NO_2, may oxidize the salt to $LiNO_3$ if they are not removed.

$LiNO_3$

As is to be expected from the high polarizing power of the cation, $LiNO_3$ is the least stable of the alkali metal nitrates. It decomposes just above its melting point according to $LiNO_3 = LiNO_2 + 1/2\ O_2$. 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 $LiNO_2$ 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 $LiNO_2$ in $LiNO_3$, but in terms of the equilibrium constant $K = (a_{LiNO_2}/a_{LiNO_3})P_{O_2}^{1/2}$, it is clear that the system can be at equilibrium only for some non-zero value of a_{LiNO_2}. Unfortunately there exist no high-temperature thermodynamic data for $LiNO_2$ which would permit an independent evaluation of K. The authors give a value of $\Delta H°$ 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 $LiNO_2$, 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

	$LiNO_2$	
T(K)	ρ(gcm^{-3})	References
493	1.638	98
498	1.636	98
503	1.632	98
512	1.629	98
518	1.626	98
532	1.620	98
543	1.615	98

$LiNO_3$

T(K)	ρ(gcm^{-3})	References
293	2.366	57
550	1.768	5
560	1.762	5
570	1.757	5
580	1.751	5
590	1.746	5
600	1.740	5
610	1.735	5
620	1.729	5
630	1.724	5
640	1.719	5
650	1.713	5
660	1.708	5
670	1.702	5
680	1.697	5
690	1.691	5

$\rho = 2.068 - 0.546 \times 10^{-3}T$

Transitions

	Transition	T(K)	ΔH kJ mol^{-1}	ΔS J mol^{-1} deg^{-1}	Ref.
$LiNO_2$	c→l	493	....	....	5
$LiNO_3$	c→l	526	26.7	50.8	49

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$LiNO_3$	$105._4$	25.2	4
$LiNO_2$	89.1	21.3	4
Li_2O	37.89	9.056	110

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$LiNO_3$	−482.327	−115.279	1a
$LiNO_2$	−401.2	−96.6	1a
Li_2O	−598.7	−143.1	110

Decomposition of $LiNO_3$

$$2LiNO_3 = Li_2O + 2NO_2 + 1/2\ O_2$$

$$\Delta H°_{298.15} = 432.1_2\ \text{kJ},\ 103.2_8\text{kcal}$$

T K	$LiNO_3$ fef J deg^{-1}	Li_2O fef J deg^{-1}	Δfef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	log K	K	P_{O_2} atm	P_{NO_2} atm	P_{NO} atm	P_{Tot} atm
298.15	−105.44	−37.89	−409.38	1039.96	−54.322	4.77×10^{-55}	7.38×10^{-20}	4.19×10^{-23}	9.84×10^{-20}	1.72×10^{-19}
400	−109.08	−40.15	−407.93	672.37	−35.121	7.57×10^{-36}	6.98×10^{-13}	3.01×10^{-15}	9.29×10^{-13}	1.63×10^{-12}
500	−116.19	−44.71	−405.20	459.04	−23.978	1.05×10^{-24}	7.43×10^{-9}	1.11×10^{-10}	9.86×10^{-9}	1.74×10^{-8}
600	−130.57	−50.08	−389.85	330.35	−17.256	5.55×10^{-18}	2.36×10^{-6}	6.01×10^{-8}	3.12×10^{-6}	5.54×10^{-6}

Magnesium

$Mg(NO_3)_2$

Little is known of the high-temperature properties of anhydrous $Mg(NO_3)_2$. 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 $Mg(NO_3)_2 = MgO + 2NO_2 + 1/2O_2$ (see below) which are consistent with complete decomposition at this temperature (fef data for $Mg(NO_3)_2$ 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 $Mg(NO_2)_2$ 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 $Mg(NO_3)_2$ 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)

$S°$			
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Mg(NO_3)_2$	164.0	39.2	1b
MgO	26.94	6.44	1b

$\Delta Hf°$			
	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Mg(NO_3)_2$	−790.65	−188.97	1b
MgO	−601.70	−143.81	1b

Decomposition of $Mg(NO_3)_2$

$$Mg(NO_3)_2 = MgO + 2NO_2(g) + 1/2\,O_2(g)$$

$$\Delta H°_{298.15} = 255.1_4\,\text{kJ},\ 60.9_8\ \text{kcal}$$

T K	$Mg(NO_3)_2$ fef J deg^{-1}	MgO fef J deg^{-1}	Δfef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	log K	K	P_{O_2} atm	P_{NO_2} atm	P_{NO} atm	P_{Tot} atm
298.15	−164.0	−26.95	−445.31	410.43	21.439	3.64×10^{-22}	9.20×10^{-10}	3.46×10^{-9}	7.29×10^{-11}	4.46×10^{-9}
400	−169.9	−28.49	−444.48	193.37	−10.101	7.93×10^{-11}	3.33×10^{-5}	1.17×10^{-4}	5.24×10^{-6}	1.56×10^{-4}
500	−181.9	−31.55	−442.52	67.76	−3.539	2.89×10^{-4}	1.46×10^{-2}	4.89×10^{-2}	3.11×10^{-3}	6.66×10^{-2}
600	−196.0	−35-11	−440.02	−14.79	0.772	5.92	0.811	2.56	0.227	3.60

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:

$$Mn(NO_3)_2 = MnO_2 + 2NO_2.$$

More careful analysis of the remaining solid phase [42] shows that it is $MnO_{1.655}$ and that both NO_2 and O_2 are evolved. Under dry N_2 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 $Co(NO_3)_2$, possesses considerable ionic character.

Thermodynamic data (298.15 K)

$S°$			
	J mol- deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Mn(NO_3)_2$	168.6	40.3	4
MnO	59.71	14.27	1b
MnO_2	53.05	12.68	1b
Mn_2O_3	110.5	26.4	1b
Mn_3O_4	155.6	37.2	1b

$\Delta Hf°$			
	kJ mol^{-1}	k cal mol^{-1}	Ref.
$Mn(NO_3)_2$	−576.26	−137.73	1b
MnO	−385.22	−92.07	1b
MnO_2	−520.03	−124.29	1b
Mn_2O_3	−959.0	−229.2	1b
Mn_3O_4	−1387.8	−331.7	1b

Mercury

$Hg(NO_2)_2$

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 $Hg(NO_3)_2$ appear as products and so the reactions probably are

$$2Hg(NO_2)_2 = 2HgNO_3 + 2NO$$

$$Hg(NO_2)_2 = HgO + N_2O_3.$$

$HgNO_3$

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.

$Hg(NO_3)_2$

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, $HgO \cdot Hg(NO_3)_2$. At 300 °C this compound is unstable and the final product is HgO. In the presence of NO some nitrite and NO_2 are formed [85].

Thermodynamic data (298.15 K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	Ref.
$Hg(NO_3)_2$	230±8	55±2 est	93
HgO (red)	70.29	16.80	1b

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	Ref.
$Hg(NO_3)_2$	−285±17	−68±4 est	93
HgO (red)	−90.83	−21.71	1b

Nickel

$Ni(NO_2)_2$

$Ni(NO_2)_2$ is stable up to 260 °C in an argon atmosphere and decomposes at 220° in vacuum. The compound is slightly volatile [14].

$Ni(NO_3)_2$

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

Thermodynamic data (298.15 K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	Ref.
$Ni(NO_3)_2$	192.0	45.9	4
$Ni(NO_2)_2$	155±8	37±2 est.	93
NiO	37.99	9.08	1b

$\Delta Hf°$

	kJ mol⁻¹	k cal mol⁻¹	Ref.
$Ni(NO_3)_2$	−415.1	−99.2	1b
$Ni(NO_2)_2$	−305±17	−73±4 est.	1b
NiO	−239.7	−57.3	....

Palladium

$Pd(NO_2)_2$

A compound of approximately this composition was reported to result from reaction of $Pd(NO_3)_2$ with NO [45].

$Pd(NO_3)_2$

Anhydrous $Pd(NO_3)_2$ has been prepared [70]. Its infrared spectrum indicates it to be covalent and it is sufficiently stable in the vapor to permit its sublimation in vacuum.

Thermodynamic data (298.15 K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	Ref.
$Pd(NO_3)_2$	....	....	....
PdO	....	....	....

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	Ref.
$Pd(NO_3)_2$	−238±17	−57±4 est.	93
PdO	−85.4	−20.4	1b

Polonium

$Po(NO_3)_4$

The salt was prepared [24] by the reaction of PoO_2 or $PoCl_4$ with N_2O_4. N_2O_4 is lost under vacuum or by standing in dry air. The tetranitrate itself is not very stable as it slowly decomposes in air or under vacuum at ambient temperature to give a basic salt.

Potassium

KNO_2

No solid phase transitions have been reported. The salt begins to decompose noticeably at 410°. The first step in the decomposition sequence is probably 2 $KNO_2 \rightarrow K_2O + NO_2 + NO$. Between 410 and 460° the reaction sequence is [81, 89]:

$$2KNO_2 \rightarrow K_2O + NO_2 + NO. \quad (1)$$

The NO produced in (1) reacts with KNO_2

$$2KNO_2 + 2NO \rightarrow 2KNO_3 + N_2. \quad (2)$$

The NO_2 produced in (1) reacts further

$$K_2O + 2NO_2 \rightarrow KNO_2 + KNO_3 \quad (3)$$

$$KNO_2 + NO_2 \rightarrow KNO_3 + NO. \quad (4)$$

Which reactions are favored will depend largely on the atmospheric composition. For example, in an inert atmosphere which removes the gaseous products reaction (1) will predominate. Otherwise, since KNO_3 is stable in this temperature range and N_2 is unreactive, the net result of reactions (1)–(4) is the production of KNO_3 and N_2. In an oxygen atmosphere, particularly in the temperature range 550–600° the reaction $KNO_2 + 1/2O_2 \rightarrow KNO_3$ goes to completion. In the range 650–750 °C KNO_3 becomes increasingly unstable and this reaction goes to equilibrium (see below) [25, 51, 108]. Above 800 °C the reaction $2KNO_2 \rightarrow K_2O + N_2 + 3/2O_2$ goes to completion [51].

KNO_3

The phase transitions of KNO_3 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.

KNO_3 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° [51], at somewhat lower temperatures at lower oxygen pressures. Between 550° and 750° the quasi-equilibrium $KNO_3 \rightleftarrows KNO_2 + ½O_2$ is set up [25, 51, 108]. The activation energy for the forward reaction is 274kJ (65.6kcal mol^{-1}). If the O_2 is removed, KNO_2 decomposes, various oxides of nitrogen are produced and the reaction is more complicated (see discussion under KNO_2).

$KNO_3(l) = KNO_2(l) + ½O_2(g)$

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 O_2 was established between 650 and 750°. Sirotkin [108] measured melt compositions in equilibrium with air over this temperature range.

The resulting discrepancy in $\Delta H°$ was studied by Bartholemew [25] in the light of his measured values for $H_T - H_{298.15}$ for the salts. He concluded that the gas method, in which the melt composition is calculated from the volume of gas evolved by the decomposing KNO_3, 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. $\Delta H°$ calculated from these thermal data agreed well with those based on the experimentally measured equilibrium constant. The enthalpy increment for KNO_3 at 700 K agreed well with that listed by Kelley [3]. In the range 550–750 °C the equilibrium constant is given by the equation

$$\log K = \frac{-115 \pm 5 \text{ kJ mole}^{-1}}{2.303RT} + \frac{102 \pm 5 \text{ J mole}^{-1} \text{ deg}^{-1}}{2.303R}.$$

The enthalpy increments given by Bartholemew can be used to calculate fef for both KNO_2 and KNO_3. This calculation requires $S°_{298.15}$ and ΔS for the phase changes. For KNO_3 these values are known and fef values at 700 K calculated from Bartholemew's and Kelley's [3] enthalpy increments agree quite well. The former's values have therefore been used to calculate fef for KNO_3 up to 1000 K. However, $S°_{298.15}$ for KNO_2 is somewhat uncertain and no thermodynamic data are available for the phase transition. Therefore, the experimentally determined equilibrium constant for the $KNO_3 - KNO_2$ equilibrium is probably more reliable than a calculated value would be. As usual, the partial pressures given for the reaction

$$2KNO_3 = K_2O + 2NO_2 + 1/2O_2$$

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.

Density

ρ (g cm^{-3})

T	KNO_2	KNO_3	Ref.
293	....	2.109	57
620	....	1.863	5
630	....	1.856	5
640	....	1.848	5
650	....	1.841	5
660	....	1.834	5
670	....	1.827	5
680	....	1.819	5
690	....	1.812	5

Density—Continued

ρ (g cm^{-3})

T	KNO_2	KNO_3	Ref.
700	…	1.805	5
710	1.698	1.797	5
720	1.692	1.790	5
730	1.685	1.783	5
740	1.679	1.776	5
750	1.672	1.768	5
760	…	1.761	5
770	…	1.754	5
780	…	1.746	5
790	…	1.739	5
800	…	1.732	5
810	…	1.725	5
820	…	1.717	5
830	…	1.710	5
840	…	1.703	5
850	…	1.695	5
860	…	1.688	5
870	…	1.681	5

Transitions

	Transition	T(K)	ΔH kJ mol^{-1}	ΔS J mol^{-1}deg^{-1}	Ref.
KNO_2	c → l	713	…	…	1a
KNO_3	III (metastable, rhombohedral) → II (orthorhombic).	386	2.34	6.1	76
	I (rhombohedral) → III.	396	3.01	7.60	76
	II → I	401	5.42	13.5	76
	I → l	607	9.62	15.8	49

Thermodynamic data (298.15 *K*)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
KNO_3	132.93	31.77	1a
KNO_2	116.7	27.9	3 est.
K_2O	94.1	22.5	110

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
KNO_3	−494.633	−118.220	1b
KNO_2	−370.242	−88.490	1b
K_2O	−363.2	−86.8	110

Decomposition of KNO_3

$$2KNO_3 = K_2O + 2NO_2 + 1/2\ O_2$$

$$\Delta H^\circ_{298.15} = 692.2_9 \mathrm{kJ},\ 165.4_6 \mathrm{kcal}$$

T K	KNO_3 fef J deg^{-1}	K_2O fef J deg^{-1}	Δfef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	log K	K	P_{O_2} atm	P_{NO_2} atm	P_{NO} atm	P_{Tot} atm
298.15	−132.93	−94.14	−410.61	1911.34	−99.838	1.45×10^{-100}	1.09×10^{-32}	1.18×10^{-42}	7.24×10^{-33}	1.81×10^{-32}
400	−136.88	−97.55	−409.67	1321.06	−69.005	9.89×10^{-70}	2.16×10^{-22}	8.20×10^{-30}	1.44×10^{-22}	3.60×10^{-22}
500	−147.78	−104.18	−401.51	983.07	−51.350	4.46×10^{-52}	1.12×10^{-16}	2.05×10^{-22}	1.49×10^{-16}	2.61×10^{-16}
600	−159.12	−111.76	−394.48	759.34	−39.664	2.17×10^{-40}	9.30×10^{-13}	1.50×10^{-17}	1.24×10^{-12}	$2.17\times{}^{-12}$
700	−172.51	−119.51	−383.71	605.28	−31.616	2.42×10^{-32}	4.81×10^{-10}	3.32×10^{-14}	6.42×10^{-10}	1.12×10^{-9}
800	−189.03	−127.13	−366.56	498.80	−26.054	8.84×10^{-27}	3.84×10^{-8}	6.72×10^{-12}	5.13×10^{-8}	8.97×10^{-8}
900	−200.33	−134.53	−359.37	409.84	−21.407	3.92×10^{-22}	1.43×10^{-6}	5.73×10^{-10}	1.90×10^{-6}	3.33×10^{-6}
1000	−210.71	−141.66	−353.50	338.79	−17.696	2.01×10^{-18}	2.55×10^{-5}	2.00×10^{-8}	3.40×10^{-5}	5.96×10^{-5}
(1100)	…	…	…	…	−14.7	2.0×10^{-15}	2.7×10^{-4}	3.5×10^{-7}	3.5×10^{-4}	6.2×10^{-4}
(1200)	…	…	…	…	−12.5	3.2×10^{-13}	1.5×10^{-3}	2.9×10^{-6}	2.0×10^{-3}	3.6×10^{-3}

Radium

$Ra(NO_3)_2$

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)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Ra(NO_3)_2$	218	52	1a
RaO	…	…	…

$\Delta Hf°$

	kJ mol^{-1}	k cal mol^{-1}	Ref.
$Ra(NO_3)_2$	−992	−237	1a
RaO	−523	−125	1a

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_6O_{11}, these nitrites 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].

Salt	Initial decomposition temperature (°C)	Minimum oxide formation temperature (°C)
$La(NO_2)_3$	240	580
$Pr(NO_2)_3$	220	450
$Nd(NO_2)_3$	200	510
$Sm(NO_2)_3$	200	500
$Dy(NO_2)_3$	110	500
$Yb(NO_2)_3$	90	350

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 $RONO_3$ 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

$$(R(NO_3)_3 \cdot 6H_2O \rightarrow R(NO_3)_3 \rightarrow RONO_3 \rightarrow R_2O_3)$$

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:

	Stability range of anhydrous nitrate (°C)	Stability range of $RONO_3$ (°C)	Minimum oxide formation temp. (°C)
$La(NO_3)_3$	240–420	515–575	730
$Nd(NO_3)_3$	280–350	460–500	650
$Dy(NO_3)_3$	260–280	420–440	630
$Yb(NO_3)_3$	260–270	340–400	500
$Lu(NO_3)_3$	220–230	370–390	470

$Pr(NO_3)_3$ is exceptional in that the final oxide is Pr_6O_{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 nitrites [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 nitrites, 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: $2RbNO_2 = Rb_2O + NO + NO_2$. 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

	T(K)	ρ(g cm^{-3})	References
$RbNO_2$	696	2.347	99
	706	2.339	99
	715	2.333	99
	726	2.322	99
	734	2.316	99
	745	2.306	99
	755	2.299	99
	759	2.295	99
$RbNO_3$	293	3.112	57
	590	2.476	5
	600	2.466	5
	610	2.456	5
	620	2.446	5
	630	2.437	5
	640	2.427	5
	650	2.417	5
	660	2.407	5
	670	2.398	5
	680	2.388	5

Density—Continued

	$T(K)$	ρ (g cm^{-3})	References
$RbNO_3$	690	2.378	5
	700	2.369	5
	710	2.359	5
	720	2.349	5
	730	2.339	5
	740	2.330	5
	750	2.320	5
	760	2.310	5

$\rho = 3.049 - 0.972 \times 10^{-3}\, T$

Transitions

$RbNO_3$

Transition	T(K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} deg^{-1})	Ref.
rhombic (IV)→cubic (III)	433	3.90	9.00	75
cubic (III)→trigonal (II)	488 ± 3	3.21	6.58	75
II→I	554	0.96	1.74	75
I→l	583	4.64	7.96	75

Rubidium

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$RbNO_3$	140.6	33.6	4
$RbNO_2$			
Rb_2O	(124.)	(29.7)	1a

$\Delta Hf°$

	kJ mol^{-1}	k cal mol^{-1}	Ref.
$RbNO_3$ (C, II)	−489.61	−117.02	1a
$RbNO_2$	−362.8	−86.71	22
Rb_2O	−330	−78.9	1a

Scandium

$Sc(NO_3)_3$

Mellor [72] summarizes earlier work which claims preparation of this salt by heating $Sc(NO_3)_3 \cdot 4H_2O$ in vacuum at 100° C. The melting point is said to lie in the range 125–150°.

Silver

$AgNO_2$

The thermal decomposition of this salt has not yet been studied in detail, but preliminary experiments [92] indicate that it decomposes at 120° to give metallic silver and NO_2 with first-order kinetics and an activation energy of ~25 kJ.

$AgNO_3$

The decomposition equilibria are complicated by the thermal instability of Ag_2O. This means that instead of the usual two simultaneous equilibria the system can be considered in terms of the four reactions only three of which are independent:

$$2\,AgNO_3 = Ag_2O + 2\,NO_2 + \tfrac{1}{2}O_2 \tag{1}$$

$$2\,NO_2 = 2\,NO + O_2 \tag{2}$$

$$2\,AgNO_3 = 2\,Ag + 2\,NO_2 + O_2 \tag{3}$$

$$Ag_2O = 2\,Ag + \tfrac{1}{2}O_2. \tag{4}$$

Equilibrium constants for (1), (3), and (4) have been listed. Ag_2O is quite unstable above 400 K and hence reactions (1) and (4) are not at equilibrium for reasonable pressures of O_2. Below 500 K, P_{O_2} is fixed by reaction (4). P_{NO_2} and P_{NO} can then be calculated from K_1, K_3, and K_4. 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° above the melting point [34].

There has been considerable disagreement about the heat capacity of $AgNO_3$. 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 $Ag_2O = 2\,Ag + \tfrac{1}{2}O_2$ are taken from [111].

Density

$AgNO_3$

T(K)	ρ(g cm^{-3})	References
490	(3.954)	5
500	(3.944)	5
510	(3.934)	5
520	(3.924)	5
530	(3.913)	5
540	(3.903)	5
550	3.893	5
560	3.888	5
570	3.873	5
580	3.862	5
590	3.852	5
600	3.842	5

$\rho = 4.454 - 1.02 \times 10^{-3}\, T$

Transitions

$AgNO_3$

	T(K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1}deg^{-1})	Ref.
C, α(orthorhombic) $\rightarrow$ C, β(rhombohedral)	433	2.4	5.5	104
C, $\beta \rightarrow$ l	483	12.49	25.9	62

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$AgNO_3$	140.92	33.68	1b
$AgNO_2$	128.20	30.64	1b
Ag_2O	121.3	29.0	111
Ag	42.70	10.17	110

$\Delta Hf°$

	kJ mol^{-1}	k cal mol^{-1}	Ref.
$AgNO_3$	−124.39	−29.73	1b
$AgNO_2$	−45.06	−10.77	1b
Ag_2O	−31.05	−7.42	1b

Decomposition of Ag_2O

$$Ag_2O(c) = 2Ag(c) + \tfrac{1}{2}O_2(g)$$

$$\Delta H^{\circ}_{298.15} = +31.0_5 \text{ kJ}, +7.4_2 \text{ kCal}$$

T	Ag fef J deg^{-1}	Ag_2O fef J deg^{-1}	Δfef J deg^{-1}	Reaction $\Delta G°/T$ J deg^{-1}	log K	K
298.15	−42.677	−121.3	−66.55	37.592	−1.963	1.09×10^{-2}
400	−43.694	−124.0	−67.76	9.865	−0.515	0.306
500	−45.564	−129.2	−70.02	−7.920	+0.413	2.59

Decomposition of $AgNO_3$

$$(1)\ 2AgNO_3(c) = Ag_2O(c) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

$$\Delta H^{\circ}_{298.15} = 283.93 \text{ kJ}, 67.86 \text{ kCal}$$

T	$AgNO_3$ fef J deg^{-1}	Δfef J deg^{-1}	Reaction $\Delta G°/T$ J deg^{-1}	log K	K
298.15	−140.92	−421.82	530.49	−27.707	1.97×10^{-28}
400	−144.81	−420.31	289.52	−15.121	7.57×10^{-16}
500	−154.10	−413.87	153.99	−8.042	9.08×10^{-9}
600	−168.07	....	....	....	....
(700)	−186.	....	....	....	....

$$(2)\ 2AgNO_3(c) = 2Ag(c) + 2NO_2(g) + O_2(g)$$

$$\Delta H^{\circ}_{298.15} = 314.97 \text{ kJ}, 75.28 \text{ kCal}$$

298.15		−488.39	568.02	−29.671	2.13×10^{-30}
400		−486.80	300.63	−15.703	1.98×10^{-16}
500		−480.00	149.94	−7.832	1.47×10^{-8}
600		−465.71	59.24	−3.094	8.06×10^{-4}
(700)		−443.80	6.16	−0.322	0.477

Partial pressures (atm) for the decomposition of $AgNO_3$

T(K)	P_{O_2}	P_{NO_2}	P_{NO}	P_{Tot}
298	1.19×10^{-4}	1.35×10^{-13}	8.24×10^{-19}	1.19×10^{-4}
400	9.36×10^{-2}	4.78×10^{-8}	2.22×10^{-15}	9.36×10^{-2}
500	1.89×10^{-3}	2.79×10^{-3}	4.93×10^{-4}	5.17×10^{-3}
600	7.91×10^{-2}	1.01×10^{-1}	2.86×10^{-2}	2.09×10^{-1}
700	7.72×10^{-1}	7.86×10^{-1}	3.79×10^{-1}	1.94

Sodium

$NaNO_2$

$NaNO_2$ is unstable above 330 °C [81]. The first step in the decomposition is probably $2NaNO_2 \rightarrow Na_2O + NO_2 + NO$. ($N_2O_3$ is too unstable at and above this temperature to be significant.) Between 330° and 380° the reaction sequence seems to be as follows:

$$2NaNO_2 = Na_2O + NO + NO_2. \tag{1}$$

The NO produced in (1) reacts with $NaNO_2$

$$2NaNO_2 + 2NO = 2NaNO_3 + N_2. \tag{2}$$

The NO_2 produced in (1) reacts further [118]

$$Na_2O + 2NO_2 = NaNO_2 + NaNO_3 \tag{3}$$

$$NaNO_2 + NO_2 = NaNO_3 + NO. \tag{4}$$

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 $NaNO_3$:

$$NaNO_3 = NaNO_2 + \tfrac{1}{2}O_2. \tag{5}$$

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]

$$2NaNO_2 \rightarrow Na_2O + N_2 + \tfrac{3}{2}O_2. \tag{6}$$

Freeman [50] attributes the evolution of N_2 to the formation of a superoxide which later decomposes to Na_2O 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.

$NaNO_3$

$NaNO_3$ 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 $NaNO_3$ and $NaNO_2$ whose composition is temperature dependent [50, 108]. This equilibrium is discussed above. Enthalpy and entropy increments for $NaNO_3$ have been listed by Kelley [3] up to 700 K, but no such values are available for $NaNO_2$. In the absence of such data no calculation involving $NaNO_2$ 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 $NaNO_3$ in the solid state, we are listing fragmentary calculations which can be made. These include a hypothetical decomposition of $NaNO_3$ and an experimental study [108] of the equilibrium $NaNO_3(l) = NaNO_2(l) + \frac{1}{2}O_2(g)$. Since the liquids are completely miscible and the solution virtually ideal, the equilibrium constant $K = P_{O_2}^{1/2}(X_{NaNO_2}/X_{NaNO_3})$.

Density

ρ (g cm^{-3})

T(K)	$NaNO_2$	$NaNO_3$	References
293	2.266	....	28
570	1.801	1.898	5
580	1.793	1.891	5
590	1.786	1.884	5
600	1.778	1.877	5
610	1.771	1.870	5
620	1.763	1.862	5
630	1.756	(1.855)	5
640	1.749	(1.848)	5
650	1.741	(1.841)	5
660	1.734	(1.834)	5
670	1.726	(1.827)	5
680	1.719	(1.820)	5

Density—Continued

ρ (g cm^{-3})

T(K)	$NaNO_2$	$NaNO_3$	References
690	1.711	....	5
700	1.704	....	5
710	1.696	....	5
720	1.686	....	5

Transitions

Transition	T(K)	ΔH kJ mol^{-1}	ΔS J mol^{-1} deg^{-1}	Ref.
$NaNO_2$				
C→l	554	10.4±.3	18.8±.5	67
$NaNO_3$				
C, II,→C, I	548	3.95	7.21	1a, 73
C, I→l	579	15.5	26.8	49, 69

Thermodynamic data

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$NaNO_3$	116.3	27.8	1a
$NaNO_2$	106.3	25.4	3
Na_2O	75.27	17.99	110

$\Delta Hf°$

	kJ mol^{-1}	k cal mol^{-1}	Ref.
$NaNO_3$	−467.980	−111.850	1b
$NaNO_2$	−358.65	−85.720	1b
Na_2O	−415.9	−99.4	110

Decomposition of $NaNO_3$

(a) $2NaNO_3(c) = Na_2O(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

$\Delta H^\circ_{298.15} = 586.2_6$ kJ, 140.1_2 kcal

T K	$NaNO_3$ fef J deg^{-1}	Na_2O fef J deg^{-1}	Δfef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	log K	K	P_{O_2} atm	P_{NO_2} atm	P_{NO} atm	P_{Tot} atm
298.15	−116.315	−72.80	−422.51	1543.82	−80.641	2.29×10^{-81}	3.32×10^{-27}	1.99×10^{-34}	2.21×10^{-27}	5.53×10^{-27}
400	−120.177	−75.65	−421.26	1044.39	−54.553	2.80×10^{-55}	1.96×10^{-18}	1.41×10^{-23}	2.61×10^{-18}	4.56×10^{-18}
500	−128.281	−81.04	−417.34	755.18	−39.447	3.58×10^{-40}	2.82×10^{-13}	2.60×10^{-17}	3.76×10^{-13}	6.57×10^{-13}
600	−139.034	−87.28	−410.12	566.98	−29.616	2.42×10^{-30}	6.90×10^{-10}	3.04×10^{-13}	9.20×10^{-10}	1.61×10^{-9}
700	−154.816	−93.68	−393.27	444.24	−23.205	6.24×10^{-24}	1.22×10^{-7}	1.34×10^{-10}	1.62×10^{-7}	2.85×10^{-7}
(800)	....	....	....	....	−17.8	1.6×10^{-18}	8.8×10^{-6}	2.3×10^{-8}	1.2×10^{-5}	2.1×10^{-5}
(900)	....	....	....	....	−13.9	1.3×10^{-14}	2.0×10^{-4}	9.6×10^{-7}	2.7×10^{-4}	4.7×10^{-4}
(1000)	....	....	....	....	−11.2	6.3×10^{-12}	1.8×10^{-3}	1.2×10^{-5}	2.4×10^{-3}	4.3×10^{-3}

Decomposition of $NaNO_3$

(b) $NaNO_3(l)=NaNO_2(l)+\frac{1}{2}O_2(g)$

$\Delta H^\circ_{298.15}=$ 109.33 kJ. 26.13 kcal

T(K)	log K	K
800	−1.875	1.34×10^{-2}
850	−1.441	3.62×10^{-2}
900	−1.056	8.80×10^{-2}
950	−0.711	1.95×10^{-1}
1000	−0.400	3.98×10^{-1}

Strontium

$Sr(NO_2)_2$

The melting point of $Sr(NO_2)_2$ 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 $Sr(NO_3)_2$ is stable, the overall reaction is given as [96]

$$4Sr(NO_2)_2=2Sr(NO_3)_2+2SrO+2NO+N_2.$$

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:

$$Sr(NO_2)_2 \rightleftarrows SrO+NO+NO_2. \quad (1)$$

A part of the NO_2 reacts with the remaining nitrite

$$Sr(NO_2)_2+2NO_2 \rightarrow Sr(NO_3)_2+2NO. \quad (2)$$

In a closed system this reaction may be reversible. The rest of the NO_2 reacts with the oxide, if oxygen is present

$$SrO+2NO_2+\tfrac{1}{2}O_2 \rightarrow Sr(NO_3)_2. \quad (3)$$

The oxygen may be produced by the dissociation of NO_2,

$$NO_2 \rightleftarrows NO+\tfrac{1}{2}O_2. \quad (4)$$

Up to 600 °C reaction (3) produces nitrate while above 640° $Sr(NO_3)_2$ decomposes.

N_2 is produced by

$$Sr(NO_2)_2+2NO \rightarrow Sr(NO_3)_2+N_2. \quad (5)$$

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

$Sr(NO_3)_2$

The melting point of $Sr(NO_3)_2$ 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 $Sr(NO_3)_2$ 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 $Ca(NO_3)_2$ and $Ba(NO_3)_2$.

Transitions

Salt	Transition	T(K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} deg^{-1})	Ref.
$Sr(NO_2)_2$	$\gamma\rightarrow\beta$	547	....	....	97
	$\beta\rightarrow\alpha$	558	....	....	97
	$\alpha\rightarrow l$	676 ± 18	....	....	35, 96
$Sr(NO_3)_2$	$c\rightarrow l$	918	44.6	48.6	64

Thermodynamic data

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Sr(NO_3)_2$	198.3	47.4	4
$Sr(NO_2)_2$	176.	42.	4
SrO	54.4	13.0	110

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Sr(NO_3)_2$	−978.22	−233.80	1b
$Sr(NO_2)_2$	−762.3	−182.2	1b
SrO	−592.0	−141.5	110

Thallium

$TlNO_2$

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.

$TlNO_3$

The heat of fusion of $TlNO_3$ 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 H_T-H_{298} values for solid and liquid $TlNO_3$ which differ, particularly at the lower end of the temperature scale, from those given by Kelley [3]. The vaporization of $TlNO_3$ has been studied recently by Cubicciotti [40] in the range 539–613 K. He found that in addition to NO as the decomposition product, $TlNO_3$ also vaporized as the salt. In the range 490–612 K the vapor pressure of $TlNO_3$ is given by $\log_{10} p(\text{atm}) = -7486/T - 10 \log_{10} T + 21.77$, and the enthalpy and entropy of vaporization by ΔH_{vap} (J mol^{-1}) $= 143{,}344 - 41.84T$, ΔS_{vap} (J deg^{-1} mol^{-1}) $= 370.9 - 96 \log T$. He also calculated values of fef for the salt and these have been used in this monograph. The corresponding data for Tl_2O are those of Cubicciotti and Eding [41].

Transitions

Salt	Transition	T(K)	ΔH kJ mol^{-1}	ΔS J mol^{-1} deg^{-1}	Ref.
$TlNO_2$	s → s	442	....	....	97
	s → l	459	....	....	97
$TlNO_3$	Orthorhombic → hexagonal	334.2	1.0	3.0	1a
	hexagonal → cubic	416	3.8	9.1	59, 74
	cubic → liquid	483	8.83	18.3	105

Density

	T(K)	ρ(g cm^{-3})	Ref.
$TlNO_2$	480	4.905	5
	490	4.885	5
	500	4.867	5
	510	4.849	5
	520	4.830	5
	530	4.811	5
	540	4.792	5
	550	4.773	5
	560	4.755	5

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

Thermodynamic Data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$TlNO_3$	160.7	38.4	1b
$TlNO_2$	146 ± 8	35 ± 2 est	93
Tl_2O	126	30	1b

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$TlNO_3$	−243.93	−58.30	1b
$TlNO_2$	−146 ± 63	−35 ± 15	126
Tl_2O	−178.7	−42.7	1b

Decomposition of $TlNO_3$

$$2TlNO_3(c) = Tl_2O(c) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

$$\Delta H^\circ_{298.15} = 375.3_9\,\text{kJ}, 89.7_2\ \text{kcal}$$

T K	$TlNO_3$ fef J deg^{-1}	Tl_2O fef J deg^{-1}	Δfef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	$\log K$	K	P_{O_2}	P_{NO_2}	P_{NO}	P_{Tot}
298.15	−160.7	−125.5	−386.4	872.7	−45.585	2.64×10^{-46}	2.33×10^{-17}	2.34×10^{-19}	3.10×10^{-17}	5.45×10^{-17}
400	−165.3	−128.8	−384.1	554.4	−28.958	1.10×10^{-29}	4.04×10^{-11}	1.32×10^{-12}	5.34×10^{-11}	9.51×10^{-11}
500	−176.9	−134.7	−373.8	377.0	−19.692	2.03×10^{-20}	1.25×10^{-7}	7.57×10^{-9}	1.64×10^{-7}	2.97×10^{-7}
600	−192.3	−141.6	−357.9	267.8	−13.988	1.03×10^{-14}	2.04×10^{-5}	1.51×10^{-6}	2.67×10^{-5}	4.85×10^{-5}
(700)	−206.4	−148.5	−344.9	191.4	−9.997	1.01×10^{-10}	7.33×10^{-4}	6.11×10^{-5}	9.57×10^{-4}	1.75×10^{-3}

Tin

$Sn(NO_3)_4$

$Sn(NO_3)_4$ melts at 364 K and begins to decompose at 371 K. No intermediate oxide-nitrate appears to form, and the final product is SnO_2 [17].

Titanium

$Ti(NO_3)_4$

$Ti(NO_3)_4$ is a covalent salt, stable at least to its melting point at 331 K [48]. It decomposes to TiO_2 with the evolution of O_2 and NO_2 [103].

Zinc

$Zn(NO_3)_2$

$Zn(NO_3)_2$ is stable up to 373 K, and decomposes only slightly even at 513 K. Above this temperature decomposition becomes increasingly rapid, consistent with the equation [15]

$$2Zn(NO_3)_2 = 2ZnO + 4NO_2 + O_2.$$

Thermodynamic data

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Zn(NO_3)_2$.............	193.7	46.3	4
ZnO.....................	43.64	10.43	1b

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Zn(NO_3)_2$	-483.7	-115.6	1b
ZnO	-348.2_8	-83.24	1b

Zirconium

$Zr(NO_3)_4$

Anhydrous $Zr(NO_3)_4$ has been prepared. It can be purified by sublimation. The compound is covalent and very hygroscopic [46].

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General

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[1b] is the ongoing revision of [1a]. Values for $\Delta Hf°$ and $S°$ at 298.15 K for all salts and oxides in the present monograph are taken from [1b], whenever available. In some instances data not yet published by the authors are also included.

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