Reactions of Sodium-Potassium Alloys with Inert Gas Impurities − Potential Hazards after Oxidation

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A bibliographical study of the reactions of NaK alloys with their oxides did not explain the related accidents that have occurred in the past, particularly those involving the handling of bubblers installed to remove traces of oxygen and water vapor from blanket gases of LMFR (liquid metal fast reactors). Moreover, it revealed a controversy with respect to the explosive hazard of the NaK alloys + KO_2 reaction. A thermodynamic study of the reaction of a NaK alloy with oxygen as well as experimental work on mixtures containing NaK and different oxides (KO_2, Na_2O, Na_2O_2) led to the conclusion that violent reactions occurring at ambient temperature, were always linked to the presence of hydrated superoxides or hydroxides. On contact with NaK alloys, these hydrated compounds lead to the formation of hydrogen with a release of heat causing the decomposition of potassium superoxide KO_2 and the simultaneous release of oxygen. The oxidation of liquid NaK alloy, by bubbling a mixture of argon and air containing traces of water vapor ($H_2O < 5$ vpm), leads to the formation of mainly KO_2, besides the hydrated compounds $Na_2O_2 \cdot 2H_2O$, $NaOH \cdot H_2O$ and $KOH \cdot H_2O$. The gas follows preferential paths and the product obtained is highly heterogeneous in both composition and hardness (porous parts and dense parts). Hydrated superoxide and hydroxides treated under vacuum result in nearly quantitative dehydration after heating at 100 °C. For storage elements or safety valves, containing NaK that has been submitted to slow surface oxidation and hydration, the oxidized layer contains KO_2, $Na_2O_2 \cdot nH_2O$ and hydrated hydroxides of sodium and potassium. In order to avoid any hazard due to the contact of the oxides with the residual NaK alloy during transport or under impact, it is necessary to freeze the alloy and to reheat it very slowly. Operations such as draining should also be performed slowly, after having calibrated the tanks (temperature and pressure). Therefore the use of NaK liquid alloy to purify gases is questionable; as preferential paths are established, it remains impossible to predict the period of efficiency of a bubbler. Moreover, the NaK alloy does not chemically transform all traces of water vapor; because some remains present in the form of hydrated products, leading to the formation of wastes with a potential hazard during storage or destruction. In our opinion, this method of purification should be abandoned.

Introduction

NaK alloys are liquids at room temperature and this peculiarity explains their common use in the nuclear industry:[1] coolants for fast neutron reactors, fluids in heat transfer systems, gas purifiers, moving barriers of pressure in safety valves, filling liquids of acoustic wave-guides in sonar systems. Nevertheless several accidents due to explosions have been described concerning the use or during storage of NaK alloys or even potassium alone. These accidents have been reviewed,[2] but no clear explanations were given concerning the possible chemical reactions leading to these explosions, although the influence of some of the oxidized products of the alloy seems to be a key factor.

A bibliographical study of the reactions of NaK alloys with their oxides remained scarce and did not allow for the explanation of all related accidents, particularly those linked to the handling of bubblers. Moreover, they revealed a controversy with respect to the NaK + KO_2 reaction, considered explosive by Sloan and Whitby[3] and harmless by Commander.[4] More recent laboratory tests[5,6] did not confirm the explosion hazard linked to the NaK + KO_2 reaction.

In order to have a better understanding of the reaction leading to the potential explosion due to the storage and destruction of NaK wastes, the present study was undertaken with the following objectives:

(i) to review the structural data of the different oxides of sodium and potassium;

(ii) to perform a thermodynamic analysis to obtain further knowledge on the formation of various sodium and potassium oxides and their identification and reactivity;

(iii) to carry out experimental work on different mixtures to confirm literature data concerning the melting and decomposition temperatures of various sodium and potassium oxides and to characterize these products using differential scanning calorimetry, mass spectrometry and X-ray diffraction;

(iv) to study the stability of a mixture of NaK liquid alloy with sodium oxide Na_2O, sodium peroxide Na_2O_2 or potassium superoxide KO_2, using differential calorimetry, mass spectrometry and tests in glove box; and finally

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(v) to define as precisely as possible the conditions for a potential hazard.

The NaK alloy used for the tests was NaK-56 (56 wt-% K) which corresponds to the composition of the NaK alloy used for the cold traps of the Superphenix Reactor.

Finally, NaK oxidation tests have been performed through sweeping or bubbling of argon and dry air containing H_2O or CO_2 as impurities, in order to simulate realistic conditions of oxide formation and to characterize the products thus formed. The results will permit the proposal of new explanations concerning the accidents or incidents linked to the use of bubblers.

Results and Discussion

1. Structural Data

Structural data, density, molar volume and PDF references are gathered in Table 1 for the compounds: Na, K, KNa_2, K_2O, K_2O_2, KO_2, Na_2O, Na_2O_2, NaO_2, $Na_2O_2 \cdot 2H_2O$, $Na_2O_2 \cdot 8H_2O$. From this table the following conclusions can be obtained:
(i) The molar volume of the oxides is smaller than the molar volume of the metals or alloys, therefore the oxides cannot afford a protection against further oxidation.
(ii) Sodium peroxide presents hydrated phases.
(iii) The structure of Na_2O and K_2O are identical.
(iv) The other oxides display different structural data which means that there is no possibility of extended solid solutions.

2. Phase Diagram

The Na-K phase diagram is given in Figure 1.[7] Despite the identical structures of Na and K metals, the solubility in the solid state remains low (< 5% in atoms) which is in agreement with the rather high difference in metallic radii (1.86 Å for Na and 2.30 Å for K); the solubility curves are

represented by dotted lines because the solubility limits are not precisely known. Only one stoichiometric compound Na_2K is present on this diagram, with a non-congruent melting point. Recent theoretical analyses of the liquid curves[8] and of the sodium-potassium eutectic,[9] agree with the experimental diagram. The vertical line corresponding to the NaK-56 alloy cuts the liquid curve and the eutectic segment at 5 and −12.5 °C, respectively. It can be noted that the real alloy composition is not constant and is dependent on the lot and storage conditions. It may vary from 56 to 52 weight% in K, corresponding to 43 to 39 atom%.
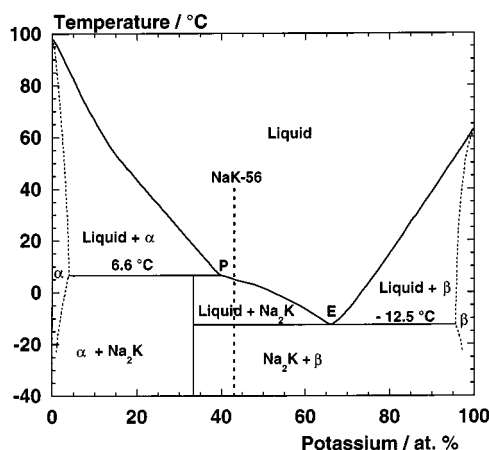

Figure 1. Sodium-potassium liquid solid phase diagram. The diagram was numerized from the figures given in ref.[7]

3. Thermodynamic Analysis

3.1. Formation of Liquid Alloy

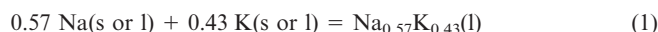The formation of the liquid NaK-56 alloy corresponds to the reaction:

$$0.57 \, \text{Na(s or l)} + 0.43 \, \text{K(s or l)} = \text{Na}_{0.57}\text{K}_{0.43}(l) \qquad (1)$$

Table 1. Crystallographic data and molar volumes

Phase	PDF file number	Molar wt g mol^{-1}	Crystal system and lattice	Formula unit number	Volume Å^3	Density g cm^{-3}	Molar vol. cm^3 mol^{-1}
METALS AND ALLOYS							
K	01−500	39.1	Cubic, I	Z = 2	140.6	0.86	45.5
Na	22−948	23.0	Cubic, I	Z = 2	79.0	0.97	23.7
KNa$_2$	10−244	85.1	Hexagonal, P	Z = 4	594.5	0.95[a]	29.9
POTASSIUM COMPOUNDS							
K$_2$O	23−493	94.2	Cubic, F	Z = 4	268.2	2.33[a]	20.2
K$_2$O$_2$	32−827	110.2	Orthorhombic, C	Z = 4[b]	305.0	2.40[a]	23.0
KO$_2$	43−1020	71.1	Tetragonal, I	Z = 2	109.0	2.16	32.9
KOH	21−645	56.1	Monoclinic, P	Z = 2	87.2	2.14[a]	26.2
KOH·H$_2$O	36−791	74.1	Monoclinic, P	Z = 4	254.9	1.92	38.6
SODIUM COMPOUNDS							
Na$_2$O	23−528	62.0	Cubic, F	Z = 4	171.9	2.27	13.7
Na$_2$O$_2$	09−075	78.0	Hexagonal, P	Z = 3	149.8	2.50	15.6
NaO$_2$	6−500	55.0	Orthorhombic, P	Z = 2	81.2	2.25[a]	24.4
Na$_2$O$_2$·2H$_2$O	15−064	114.0					
Na$_2$O$_2$·8H$_2$O	15−032	222.1	Monoclinic, C	Z = 4[b]	929.1		
NaOH	35−1009	40.0	Orthorhombic, C	Z = 4	131.7	2.02[a]	19.8
NaOH·H$_2$O	30−1194	58.0	Orthorhombic, P	Z = 8	447.9	1.72[a]	33.7

[a] Calculated. − [b] Assumption.

The use of a liquid NaK alloy requires the knowledge of the values of the standard thermodynamic functions H, S and G for this alloy. The enthalpies of mixing versus the composition have been determined at 111 ± 2 °C from liquid sodium and potassium, by Yokokawa and Kleppa.[10] From these data, the authors concluded that the behavior is close to ideality for alloys with a sodium mol fraction x_{Na} higher than 0.5. The work of Cafasso et al.[11] on the determination of the excess Gibbs energies of mixing was performed at the same temperature in order to obtain the activities and activity coefficients of sodium and potassium for such alloys. Their results agree well with the previous conclusion on the range of ideality. From these data and the thermodynamic data of Na and K at 111 °C, it was possible to obtain the thermodynamic values for the formation of $Na_{0.57}K_{0.43}(l)$, as well as the data for the reactants and product at the same temperature (reference temperature 25 °C):

$\Delta_r H° = 0.748$ kJ mol^{-1} $\Delta_r S° = 5.604$ J K^{-1} mol^{-1}
$\Delta_r G° = -1.404$ kJ mol^{-1}
for 0.57 Na(l) + 0.43 K(l):
$H°_{384} = 5.085$ kJ mol^{-1} $S°_{384} = 71.77$ J K^{-1} mol^{-1}
for $Na_{0.57}K_{0.43}(l)$:
$H°_{384} = 5.833$ kJ mol^{-1} $S°_{384} = 77.37$ J K^{-1} mol^{-1}

The standard data at 25 °C were calculated from the melting enthalpies, melting entropies and constant pressure heat capacities for Na and K. The heat capacity of the liquid alloy was estimated from the heat capacities of liquid sodium (31.83 J K^{-1} mol^{-1} at 98 °C) and liquid potassium (32.14 J K^{-1} mol^{-1} at 63 °C) which change very slowly with temperature. The data for the formation of $Na_{0.57}K_{0.43}(l)$ at 25 °C are:

$\Delta_r H° = 3.113$ kJ mol^{-1} $\Delta_r S° = 12.20$ J K^{-1} mol^{-1}
$\Delta_r G° = -0.514$ kJ mol^{-1}
for 0.57 Na(s) + 0.43 K(s):
$H°_{298} = 0$ kJ mol^{-1} $S°_{298} = 57.14$ J K^{-1} mol^{-1}
for $Na_{0.57}K_{0.43}(l)$:
$H°_{298} = 3.113$ kJ mol^{-1} $S°_{298} = 69.34$ J K^{-1} mol^{-1}

The formation of the alloy is endothermic and the driving force is the entropy factor. These values are in agreement with different theoretical calculations using the pseudo-potential model applied to hard sphere mixtures.[12−15]

In comparison with the values calculated for the different oxidation reactions (vide infra), the data given above are lower by two to three orders of magnitude, therefore the corrections needed for the substitution of the pure metals by the liquid alloy can reasonably be neglected.

3.2. Sodium-Oxygen System

Figure 2 represents the Ellingham diagram (Gibbs energy versus temperature) for the formation of the oxygenated compounds of sodium according to the equations:

$$4\ Na(s\ ou\ l) + O_2(g) = 2\ Na_2O(s)\ \Delta_r G°_{298} = -758\ kJ\ mol^{-1} \quad (2)$$

$$2\ Na_2O(s) + O_2(g) = 2\ Na_2O_2(s)\ \ \Delta_r G°_{298} = -141\ kJ\ mol^{-1} \quad (3)$$

$$Na_2O_2(s) + O_2(g) = 2\ NaO_2(s)\ \ \ \ \Delta_r G°_{298} = +12\ kJ\ mol^{-1} \quad (4)$$
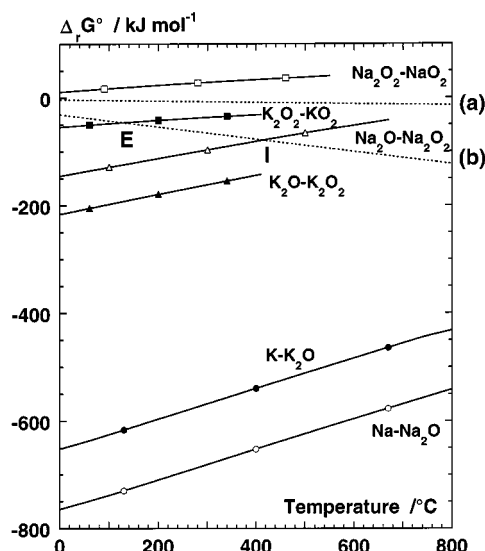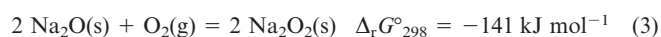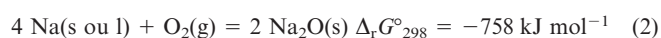

Figure 2. Ellingham diagram for the successive formation of oxygenated compounds of sodium (white points) and potassium (black points). The dotted lines represent the free enthalpy of dioxygen for a partial pressure of (a) 0.2 bar and (b) 10^{-6} bar. E and I are the crossing points between line (b) and the formation curves of KO_2 and Na_2O_2

This diagram shows that in the presence of excess sodium, the stable product is Na_2O, therefore, metallic sodium will reduce the higher oxides. The presence of an excess of oxygen leads to the formation of a stable peroxide, Na_2O_2, at atmospheric pressure. For the sodium superoxide NaO_2, the corresponding values are positive, implying that this compound is only stable under high oxygen pressure.

Figure 2 also represents the variations of the Gibbs energy of gaseous oxygen for the partial pressure of O_2 in air (0.2 bar, dotted line a), and also for a partial pressure of 10^{-6} bar (dotted line b) which corresponds to a dioxygen concentration of only 1 ppmv (part per million in volume). The latter is in line with the magnitude of the impurity level in the gases. The stability of the peroxide Na_2O_2, with regard to the decomposition at atmospheric pressure, can be deduced from the respective positions of the corresponding curve and line b; this peroxide is stable up to a temperature of about 420 °C which corresponds to the crossing point I. Sodium superoxide is not stable in the considered temperature range and decomposes according to the reverse of Equation (4). Therefore, in the presence of an excess of oxygen , there is a predominant formation of sodium peroxide Na_2O_2 on the oxide crust, while Na_2O is stable only in direct contact with sodium. From a kinetic point of view, Na_2O_2 represents the primary product of the reaction which maintains the O−O bond, while the formation of Na_2O requires the full breaking of this bond.

3.3. Reactions with Water Vapor

In the presence of water vapor, the oxide Na_2O can transform into sodium hydroxide NaOH and can then form the successive hydrates NaOH·nH_2O (n = 1, 2, ...). Sodium peroxide can also form hydrates Na_2O_2·nH_2O (n = 1, 2, 8) which should remain stable provided they are not in direct

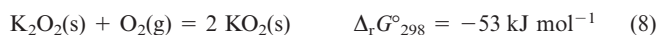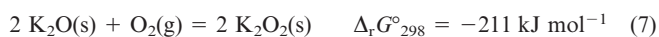contact with metallic sodium. Data are available for the octa-hydrate $Na_2O_2 \cdot 8H_2O(s)$ that allows for the checking of its stability according to the equation:

$$Na_2O_2(s) + 8\ H_2O(g) = Na_2O_2 \cdot 8H_2O(s)$$
$$\Delta_r G°_{298} = -193\ kJ\ mol^{-1}\quad (5)$$
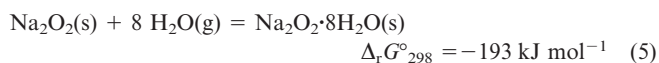
The equilibrium at room temperature corresponds to a partial pressure $p(H_2O)$ of about 6×10^{-5} bar.[16] These data show that the hydrates can be formed in the presence of traces of water, in agreement with the highly hygroscopic nature of sodium peroxide.

3.4. Potassium-Oxygen System

The successive formation of oxygenated compounds of potassium are also displayed in Figure 2, according to the balanced equations:
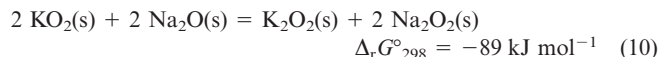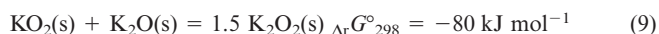
$$4\ K(s\ or\ l) + O_2(g) = 2\ K_2O(s)\quad \Delta_r G°_{298} = -646\ kJ\ mol^{-1}\quad (6)$$

$$2\ K_2O(s) + O_2(g) = 2\ K_2O_2(s)\quad \Delta_r G°_{298} = -211\ kJ\ mol^{-1}\quad (7)$$

$$K_2O_2(s) + O_2(g) = 2\ KO_2(s)\quad \Delta_r G°_{298} = -53\ kJ\ mol^{-1}\quad (8)$$

All the species are stable at 20 °C with regard to decomposition. K_2O_2 is also stable with regard to disproportionation into KO_2 and K_2O. At ambient temperature, the superoxide KO_2 is in equilibrium with a very low partial pressure of oxygen $p(O_2)$ of about 10^{-9} bar at 20 °C. According to the diagram, KO_2 begins to decompose at 130 °C at a pressure of 10^{-6} bar (crossing point E on Figure 2). It will thus form and remain stable at ambient temperature, even if gaseous oxygen is present in trace amounts only.

As the superoxide is the first product to be formed (kinetic product), the stable product on the outer layer of the oxide crust will be $KO_2(s)$, which should constitute the predominant species in accordance with the results of Gardener.[6] Therefore, the conditions favorable to the formation of the superoxide are those in which oxygen is in the presence of a small proportion of metal, mainly on the walls and on the outer surface of the crusts that form above the NaK alloy. According to Gardener,[6] KO_2 begins to decompose at around 130 °C under 8×10^{-6} bar, a value of the same order of magnitude that can be deduced from the thermodynamic data (10^{-6} bar).
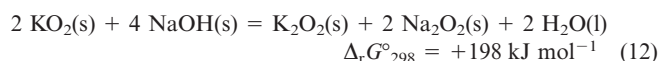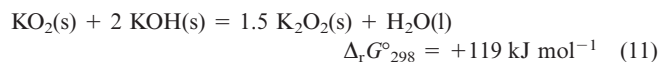
3.5. Sodium-Potassium Comparison: The Case of NaK Alloys

Figure 2 clearly shows differences in stability with respect to the decomposition of higher oxides into lower oxides: Na_2O is more stable than K_2O, whereas K_2O_2 and KO_2 are more stable than Na_2O_2 and NaO_2, respectively. At 25 °C and above 10^{-6} bar (dotted line b), KO_2 is stable and will be formed, whereas even with an oxygen pressure of 1 bar, NaO_2 cannot be formed from Na_2O_2 ($\Delta_r G > 0$).

The oxides Na_2O or K_2O can react with KO_2 according to the equations:

$$KO_2(s) + K_2O(s) = 1.5\ K_2O_2(s)\ \Delta_r G°_{298} = -80\ kJ\ mol^{-1}\quad (9)$$

$$2\ KO_2(s) + 2\ Na_2O(s) = K_2O_2(s) + 2\ Na_2O_2(s)$$
$$\Delta_r G°_{298} = -89\ kJ\ mol^{-1}\quad (10)$$

For both reactions, $\Delta_r G°$ is negative in the temperature range 0−100 °C. On the other hand, KOH, NaOH and $NaOH \cdot H_2O$ cannot react with KO_2:

$$KO_2(s) + 2\ KOH(s) = 1.5\ K_2O_2(s) + H_2O(l)$$
$$\Delta_r G°_{298} = +119\ kJ\ mol^{-1}\quad (11)$$
$$2\ KO_2(s) + 4\ NaOH(s) = K_2O_2(s) + 2\ Na_2O_2(s) + 2\ H_2O(l)$$
$$\Delta_r G°_{298} = +198\ kJ\ mol^{-1}\quad (12)$$

For all these reactions, $\Delta_r G°$ is positive in the same temperature range.

4. Model for Oxidation of Na-K Alloys

According to the above results, the most likely predominant phases in the presence of oxygen are: sodium peroxide Na_2O_2 and potassium superoxide KO_2. On direct contact with the alloy, a $Na_2O + K_2O$ mixture may occur since Na_2O and K_2O are the only thermodynamically stable oxides in the presence of an excess of NaK alloy.

All the oxygenated compounds display a higher density than the NaK alloy, and should therefore fall to the bottom of the containers, thus being protected against any further reactions. This behavior is not observed as the oxide layers remain on the surface of the alloy. This experimental result could be explained by the formation of a porous oxide layer that cannot be wetted by the metallic alloy. As the liquid alloy cannot penetrate this layer, the apparent density of the oxide layer (i.e. including the pore volume) has to be taken into account. This apparent density is therefore less than the bulk density of the alloy and leads to an apparent molar volume greater than that of the alloy.

Moreover, some oxygenated compounds are very hygroscopic and in the presence of traces of water vapor, the formation of hydrates such as $Na_2O_2 \cdot 8H_2O$, $Na_2O_2 \cdot 2H_2O$, $NaOH \cdot H_2O$ or $KOH \cdot H_2O$ is likely to occur.

Under these conditions, the layer of oxides can come off from the surface of the alloy, making any subsequent reduction of sodium peroxide or potassium superoxide by the alloy impossible. The layer or crust of oxides can be schematized as presented in Figure 3. In the areas that are in contact with the alloy, a thin layer of a $K_2O + Na_2O$ mixture can play the role of buffer between the alloy and the external part of the crust.
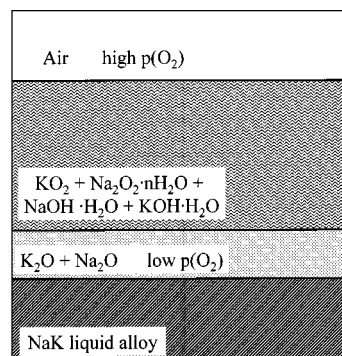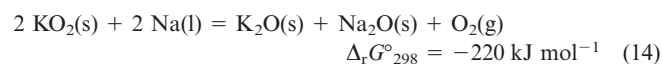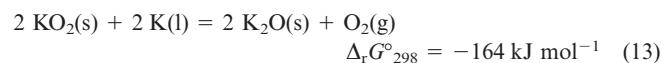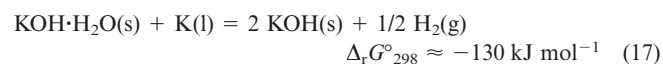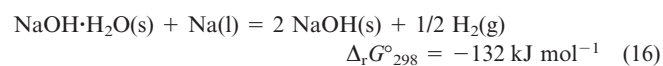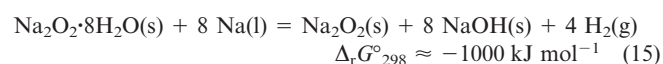

Figure 3. Model for the oxide layers on the surface of Na-K alloys

The accidents and explosions that occurred during handling or upon impact may be explained by the contact of the external part of the oxide crust with the liquid alloy. This contact is likely to cause an exothermic reduction of the potassium superoxide KO_2 by the NaK alloy if, the kinetics is not too slow. The heat released could then favor the decomposition or further reaction of KO_2 according to the strongly exothermic equations:

$$2\ KO_2(s) + 2\ K(l) = 2\ K_2O(s) + O_2(g)$$
$$\Delta_r G°_{298} = -164\ kJ\ mol^{-1} \quad (13)$$

$$2\ KO_2(s) + 2\ Na(l) = K_2O(s) + Na_2O(s) + O_2(g)$$
$$\Delta_r G°_{298} = -220\ kJ\ mol^{-1} \quad (14)$$

In the case of hydrated oxides, other possible reactions can lead to the release of hydrogen:

$$Na_2O_2·8H_2O(s) + 8\ Na(l) = Na_2O_2(s) + 8\ NaOH(s) + 4\ H_2(g)$$
$$\Delta_r G°_{298} \approx -1000\ kJ\ mol^{-1} \quad (15)$$

$$NaOH·H_2O(s) + Na(l) = 2\ NaOH(s) + 1/2\ H_2(g)$$
$$\Delta_r G°_{298} = -132\ kJ\ mol^{-1} \quad (16)$$

$$KOH·H_2O(s) + K(l) = 2\ KOH(s) + 1/2\ H_2(g)$$
$$\Delta_r G°_{298} \approx -130\ kJ\ mol^{-1} \quad (17)$$

The heat released by these reaction is likely to cause the endothermic decomposition of KO_2 and the simultaneous release of oxygen, which could lead to an explosion of the $H_2(g) + O_2(g)$ mixture.

On the basis of these assumptions, an experimental program was initiated, including the following tests:

(i) Reactions of pure KO_2, Na_2O_2 and Na_2O with the alloy NaK-56;

(ii) Reaction of hydrated peroxide or hydroxide with the alloy;

(iii) Reaction of a $Na_2O_2·nH_2O + KO_2$ mixture placed in contact with the alloy;

(iv) Oxidation tests on NaK-56 and characterization of the products obtained.

5. Reactions of NaK-52 Alloy with Oxides, Peroxides, and Superoxides

5.1. Thermal Stability of Pure Compounds

The differential scanning calorimetry (DSC) measurements performed on pure NaK alloy show the eutectic point at -12.7 °C and that the liquid form exists at 8.3 °C in accordance with the phase diagram (Figure 1). The melting enthalpy of the alloy is 2.17 kJ mol^{-1} a value in good agreement with the calculated data for Na (2.21 kJ mol^{-1}) and K (2.11 kJ mol^{-1}).[22]

The stability of pure and hydrated oxides was studied using DSC and mass spectrometry. The reactants have been characterized by X-ray diffraction. The results are gathered in Table 2 and they give rise to the following observations: Na_2O is stable up to 1000 °C (not given in Table 2); For Na_2O_2, the endothermic phenomenon at 490 °C seems to be the melting of the peroxide. This value is slightly higher than that given in the literature i.e. 460 °C;[17]

KO_2 decomposes slowly under our operating conditions above 130 °C. From the literature, the melting point lies between 380 and 500 °C.

Hydrated Na_2O_2 releases water and oxygen above 50 °C with a maximum at 100 °C for H_2O and at 200 °C for oxygen.

The diffractograms show that pure sodium and potassium oxides are hygroscopic, as the hydrated compounds $NaOH·H_2O$, $KOH·H_2O$ and $Na_2O_2·nH_2O$ were also observed. The hydration of Na_2O_2, performed in an exsiccator with water vapor under a water-pump vacuum, results in the formation of $Na_2O_2·2H_2O$; when the hydration reaction is performed in air, there is the predominant formation of Na_2CO_3, $Na_2O_2·2H_2O$ and $Na_2O_2·8H_2O$.

For the superoxide KO_2, the mass spectrometry analysis revealed a release of oxygen at the beginning of heating (estimated between 50 and 100 °C), whereas the thermodynamic calculation predicted decomposition from 130 °C for an oxygen pressure of 10^{-6} bar. These values are not in

Table 2. Stability and characterization of pure and hydrated oxides.

Compounds	Na_2O_2	KO_2	Hydrated Na_2O_2
Supplier (purity)	Osi (95%)	Merck (96.5%)	Prepared
Phase identification	Na_2O_2 major	KO_2 major	$Na_2O_2·2H_2O$
by X-ray diffraction	$Na_2O_2·2H_2O$	$KOH·H_2O$	Na_2O_2 and $NaOH·H_2O$
Calorimetry:			
Reactant mass	0.538 g	0.520 g	
Temperature range	20−600 °C	20−600 °C	
Main thermal events	Slight exotherm, 444 °C (-2.4 J g^{-1})	Endotherm, 130 °C (50.3 J g^{-1})	
under heating	Endotherm, 490 °C (53 J g^{-1})	Slight exotherm, 153 °C (-14 J g^{-1})	
	(melting)	From 430 °C, reaction leading to loss of tightness at 500 °C	
Conclusion	Melting at 480−490 °C	Decomposition above 130 °C	
Mass spectrometry	1.49 g	0.996 g	3.72 g
Temperature range	20−500 °C	20−500 °C	20−300 °C
Gas release	Main but slight release of H_2O above 100 °C. Slight release of O_2; max. at 200 °C	Release of oxygen from 50−100 °C. Max. at 200 °C.	Release of water (predominant) and oxygen above 50 °C O_2 max. at 200 °C

disagreement as the vacuum needed for the MS measurements is much lower than this value. The maximum for oxygen release is situated at 200 °C and corresponds to a partial pressure of 10^{-6} bar (Figure 4).
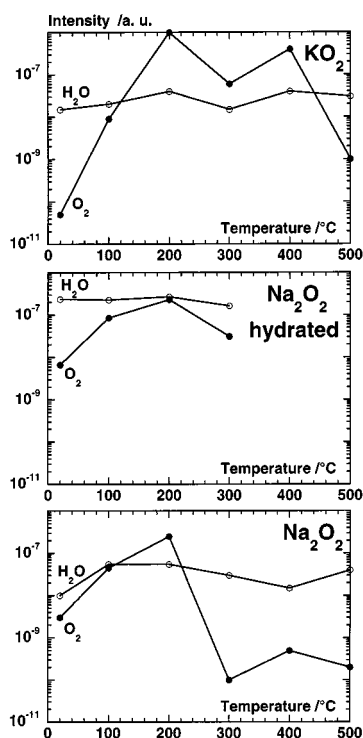

Figure 4. Mass spectra results for the release of water vapor and oxygen, versus temperature for the compounds KO_2, Na_2O_2 and hydrated Na_2O_2

Sodium peroxide displays a mass loss of 8.7 wt-% at the end of the test. This loss indicates the likely and partial formation of Na_2O, the whole decomposition corresponding to a loss of mass of 20.5%. In addition, Na_2O_2 contains impurities (H_2O, CO_2, etc.) evidenced by mass spectrometry in agreement with the very hygroscopic and basic character of Na_2O_2 (higher than that of KO_2). Its decomposition rate is lower than that of KO_2 by more than one order of magnitude.

The decomposition of hydrated sodium peroxide $Na_2O_2 \cdot nH_2O$ shows a constant predominant loss of H_2O

from the very beginning of heating (Figure 4), and a minor loss of oxygen with a maximum at 200 °C.

5.2. Reactions of NaK Alloy with Na_2O_2

Using the DSC 111 calorimeter, two tests were performed, with the aim to vary the temperature around 0 °C (cycles between − 20 and + 20 °C) in order to simulate natural thermal cycling, then followed by high temperature cycles. The results are given in Table 3.

1st test: 18 cycles −20 to 20 °C; 4 cycles 20 to 390 °C; 4 cycles −20 to 20 °C.

2nd test: 10 cycles −20 to 20 °C; 2 cycles 20 to 420 °C; 4 cycles −20 to 20 °C.

A significant part of the results of the second test are presented in Figure 5. Before the temperature rise, the thermograms of the thermal cycling around ambient temperature show the characteristic NaK melting and solidification peaks corresponding to the liquid and eutectic lines and we can see only minor changes between the first cycle and the tenth cycle. The heating leads to slightly endothermic reactions between 33 and 53 °C, followed by an exothermic reaction above 170 °C; after the first temperature rise, we observe the formation of metallic potassium which is revealed by the appearance of a peak at about 60 °C (Figure 5). For test 2 the weight of potassium is estimated to be about 10 mg.

From the thermodynamic data, an exothermic reaction is expected between the alloy and Na_2O_2 which would lead to the formation of the more stable oxide Na_2O:

$$2\ NaK(l) + Na_2O_2(s) \rightarrow 2\ Na_2O(s) + 2\ K(l)$$
$$\Delta rH°_{298} = -327\ kJ\ mol^{-1} \quad (18)$$
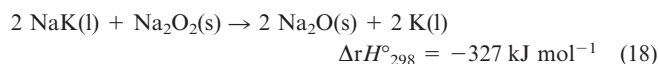
This reaction consumes sodium and therefore leads to a change in the composition of the alloy, up to the formation of metallic potassium. The weight balance is given in Table 4 and takes into account the excess peroxide Na_2O_2 which can react with potassium in a second step giving, as final products, a mixture of Na_2O, K_2O and K. The calculated weight of remaining potassium (7.8 mg) is in agreement with the value deduced from DSC measurements (10 mg).

Table 3. Reaction of NaK-56 alloy with Na and K oxides. Results of differential scanning calorimetry

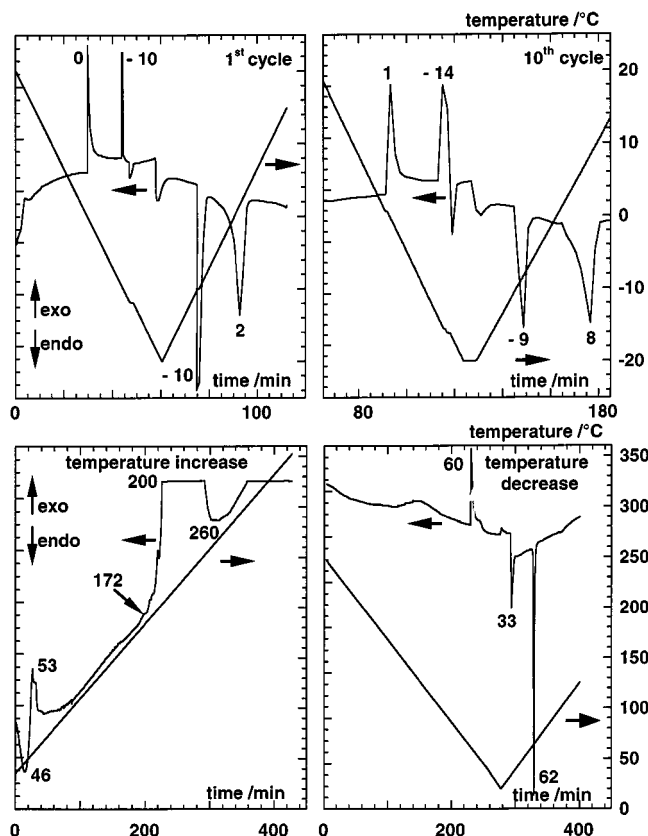| | NaK + Na_2O_2 | | NaK + KO_2 | | |
	Test 1	Test 2	Test 1	Test 2	Test 3
Mass of NaK-56	0.037 g	0.024 g	0.024 g	0.0082 g	0.049 g
Mass of Na_2O_2 or KO_2	0.041 g	0.024 g	0.027 g	0.0057 g	0.050 g
Main thermal phenomena under heating	Endotherm at 45 °C Endotherm at 60 °C (melting of K) Exotherm at 166 °C Large exotherm at 240 °C	Endotherm 33 to 53 °C Large exotherm above 172 °C	Exotherm > 167 °C Large exotherm above 195 °C	Exotherm > 167 °C	Exotherm > 167 °C Large exotherm at 190 °C
NaK consumed	Yes	Yes	Yes, partially	Yes	
Potassium formation	Yes	Yes (0.010 g)	No	Yes (≈ 0.001 g)	Yes
Apparatus	DSC 111	DSC 111	DSC 111	DSC 111	HTC

Figure 5. DSC curves for the reaction between NaK alloy and Na$_2$O$_2$:1st cycle between 20 and −20 °C; 10th cycle between 20 and −20 °C; increase from 20 to 420 °C and cooling from 420 to 20 °C. See test 2 in Table 3

Table 4. Example of mass and mol balance for the reaction NaK + Na$_2$O$_2$ (Test 2)

| | NaK (24.3 mg) | | Na$_2$O$_2$ (24.4 mg) | | | |
	Na	K	Na	O	Na$_2$O	K$_2$O
Initial mass/48.7 mg	10.7	13.6	14.4	10.0	0	0
Initial amount/mmol	0.47	0.35	0.62	0.62	0	0
Intermediate amount/mmol	0	0.35	0.15	0.15	0.47	0
Final amount /mmol	0	0.2	0	0	0.545	0.075
Final mass/48.7 mg	0	7.8	0	0	33.8	7.1

Intermediate reaction: Na$_2$O$_2$(s) (excess) + 2 Na(l) → 2 Na$_2$O(s);
Final reaction: Na$_2$O$_2$(s) + 2 K(l) (excess) → Na$_2$O(s) + K$_2$O(s).

After the temperature rise, the low temperature cycles (−20 to +20 °C) do not show the previous NaK peaks, which is in agreement with the proposed reactions. Therefore, these results are consistent with the thermodynamic calculations which suggested the enrichment of the alloy in potassium due to the formation of the more stable Na$_2$O.

Another mixture of the NaK alloy (0.41 g) and Na$_2$O$_2$ (1.00 g) was analyzed by mass spectrometry, but no significant gas release was observed, in agreement with the explanations given in Table 4.

5.3. Reactions of the NaK Alloy with KO$_2$

Two tests were performed using the DSC 111 calorimeter and one test using the HTC calorimeter. The test conditions

and results are gathered in Table 3. For test 1 and test 2 the same cycling as with Na$_2$O$_2$, i.e. between 20 and −20 °C, displays the characteristic peaks of the NaK alloy, even after heating at 150 °C. During heating (up to 300 °C), exothermic peaks appear above 167 °C (Figure 6 for test 3). For test 1, the expected reaction would lead, after completion, to the disappearance of the alloy and to the formation of a mixture of Na$_2$O, K$_2$O and K$_2$O$_2$; experimentally, the alloy is only partially consumed and no potassium can be evidenced, showing an incomplete reaction. Test 2, performed with more NaK alloy, displays the same exothermic peaks above 167 °C, but leads to a complete disappearance of the alloy and to the formation of potassium (about 1.0 mg). This is in agreement with a complete reaction leading to the formation of Na$_2$O, K$_2$O and K (calculated weight 1.1 mg).
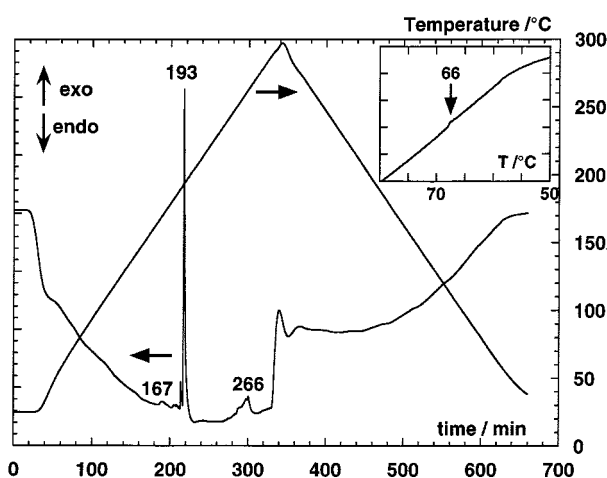

Figure 6. HTC curves for the reaction between NaK alloy and KO$_2$ (Table 3, test 3). The window represents an enlargement of the last part of the curve versus temperature

The exothermic reactions that appear at 167 °C (Figure 6) are reproducible since this temperature is strictly identical on both instruments, with different reactant masses and different proportions. Below this temperature, there is no violent reaction, even after an induction period. This is in agreement with Sloan.[1] Moreover, the low temperature thermal cycling has little effect on the reaction between the NaK alloy and KO$_2$ superoxide. For test 3, the reaction is incomplete and leads to a heterogeneous mixture of the products; the formation of potassium is seen by a very tiny exothermic peak at 66 °C (see window in Figure 6).

The influence of these exothermic events on the endothermic decomposition of potassium superoxide was examined by means of mass spectrometry. A mixture of NaK alloy (0.46 g) and KO$_2$ (0.49 g) was placed under inert atmosphere (glove box) into the sample container equipped with a tight connection. The temperature was increased in steps from ambient temperature up to 300 °C. The measurements performed in the 150−160 °C range showed a considerable increase in oxygen corresponding to the decomposition of KO$_2$. The same reaction performed in the presence of Na$_2$O from 20 to 200 °C displayed similar results,

showing that sodium oxide is very stable and plays no role in the reaction between the NaK alloy and KO_2.

5.4. Reaction of NaK + KO_2 + Na_2O_2

One test was performed using the DSC 111 calorimeter and one using the HTC calorimeter. The results are given in Table 5. Figure 7, obtained with the HTC apparatus (test 2), shows a rapid and significant exothermic reaction from 170 °C, greater than that observed during the NaK + KO_2 reaction. The formation of potassium is evidenced during the cooling (see window in Figure 7).
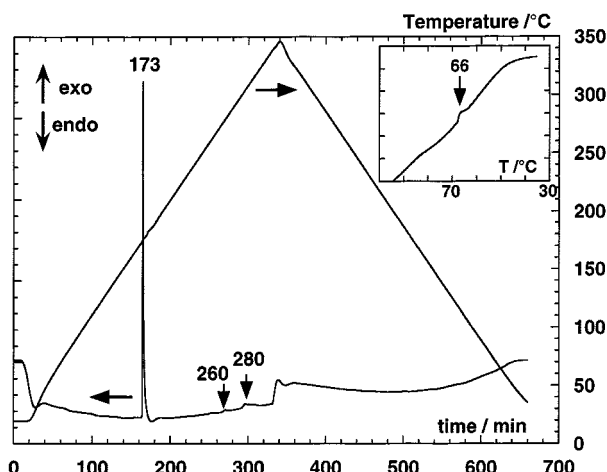

Figure 7. HTC curves for the reaction between NaK alloy and KO_2 + Na_2O_2 (Table 4, test 2). The window represents an enlargement of the last part of the curve versus temperature

5.5 Discussion About the Role of Potassium Superoxide

The tests carried out between the NaK alloy and sodium peroxide and/or potassium superoxide, revealed significant exothermic reactions above 170−180 °C. Therefore, KO_2 is effectively responsible for a significant heat release, but only above a temperature of about 170 °C, with subsequent consumption of the sodium of the NaK alloy. Na_2O_2 is also responsible for significant exothermic reactions above 200 °C, but only slight reactions with the alloy occur as soon as ambient temperature is reached. Therefore, the explosive behavior of such mixtures at ambient temperature imply another kind of reactions; KO_2 alone cannot be responsible for the triggering of this phenomenon.

The formation of metallic potassium during several tests was confirmed, displaying the selective consumption of the sodium of the NaK alloy, in accordance with the formation of the more stable Na_2O oxide. The completed reactions deduced from the thermodynamic data can be experimentally evidenced, but some tests leads to incomplete reactions and the products are more relevant to the kinetics of the processes (heterogeneous mixtures) than to the reaction thermodynamics.

6. Reactions of NaK-52 Alloy with Hydrated Oxides and Peroxides

These tests were performed in a glove box under argon in a 20 mL glass flask equipped with a thermocouple. The oxides were added separately or simultaneously to about two grams of NaK alloy. The mixture was then manually agitated so as to ensure good contact between the alloy and the oxides. The operating conditions and the results of all the tests are given in Table 6. Preliminary tests were carried out with KO_2 and non hydrated Na_2O_2 for comparison purposes. The reaction was slightly exothermic, but neither the addition of Na_2O_2, nor that of KO_2 caused a violent reaction, in agreement with the results of Gardener.[6] These results confirm, on larger scale (than that used in the calorimetric experiments), that there is no significant reaction at ambient temperature between NaK alloy and sodium peroxide or potassium superoxide, whether they are added successively or simultaneously (Table 6, tests 1 and 2). The results described by Commander,[4] i.e. ignition after an induction period of 18 minutes under inert gas, were therefore not confirmed.

6.1. Reaction of NaK with $Na_2O_2 \cdot nH_2O$
Test on NaK + Na_2O_2 Hydrated in Air

The sodium peroxide was hydrated in ambient air before the test and corresponds to a mixture of dihydrate $Na_2O_2 \cdot 2H_2O$ (minor) and octahydrate $Na_2O_2 \cdot 8H_2O$ (major), aside from sodium carbonate Na_2CO_3. Three tests were performed and the operating conditions and results are given in Table 6. The NaK + hydrated peroxide reaction, performed in a glove box, is violent (Photo 1) and occurs at ambient temperature when the two reagents come into contact (Tests 3a and 3b, Table 6). These tests are the
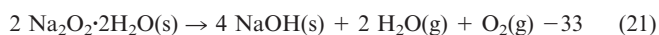
Table 5. Differential calorimetric analysis of the reactions of NaK-56 alloy with sodium peroxide and potassium superoxide

	NaK + KO_2 + Na_2O_2 Test 1	Test 2
Temperature range	+20 to −20 to +20 °C 20 to 250 to 44 °C 44 to 250 to 20 °C	20 to 350 °C to 20 °C 5 cycles
Mass of NaK	0.0411 g	0.0752 g
Mass of Na_2O_2	0.0206 g	0.0366 g
Mass of KO_2	0.008 g	0.0376 g
Main thermal events during heating	Large exothermic reaction above 180 °C	Large exothermic reaction at 170 °C
NaK consumed	About 1/3 of the initial alloy	Not measured
Formation of potassium	Yes	Yes
Apparatus	DSC	HTC

Table 6. Evolution of the reaction temperature of NaK-56 alloy in the presence of pure or hydrated oxides and hydroxides

Test N°	Initial conditions					Temperature evolution
1	NaK 2.035 g	+	Na_2O_2 0.604 g	+	KO_2 0.320 g	Slightly exothermic reaction 22 to 28 °C in 4 min
	Reactants added successively					
2	NaK 2.030 g	+	Na_2O_2 0.250 g	+	KO_2 0.321 g	Slight exothermic reaction 24 to 27 °C NaK brilliant under the film
	Reactants added simultaneously					
3a	NaK 2.04 g	+	Na_2O_2 hydrated in air 0.577 g			Violent reaction: 21 to 146 °C in 3 min, explosion, grey smoke. Glass flask broken
3b	NaK 2.05 g	+	Na_2O_2 hydrated in air 0.212 g			Violent reaction: smoke, sparks 23 to 78 °C in 3 min.
4	NaK 2.2 g	+	Na_2O_2 hydrated in air 0.632 g			Slightly exothermic reaction: 21 to 27 °C. Brilliant NaK alloy mixed with parts of oxide
	Na_2O_2 stored in glove box for one week					
5	NaK 2.74 g	+	hydrated Na_2O_2 0.326 g			Violent reaction: 25 to 306 °C in 2 min; flames, smoke
	Hydration in water vapor under vacuum					
6	NaK 2.45 g	+	KO_2 0.250 g	+	hydrated Na_2O_2 0.578 g	Violent reaction: 23 to 380 °C in 30 s; flames, smoke
	Hydration in water vapor under vacuum; oxides added simultaneously					
7	NaK 2.14 g	+	NaOH slightly hydrated 1.01 g + 0.519 + 0.52 g + 0.69 g			NaOH as received; slight reaction: 22 to 34 °C in 5 min 34 to 38 °C in 3 min 38 to 51 °C in 3 min
8	NaK 2.14 g	+	KOH slightly hydrated 0.63 g + 1.19 g			KOH as received Slight reaction: 25 to 31 °C in 1 min 31 to 33 °C in 3 min; dull grey mixture

first ones showing that the occurrence of an explosion is linked to the presence of water in the hydrated peroxide; moreover, the final temperature depends on the amount of hydrated peroxide (compare 3a and 3b). A possible explanation of these results is as follow: in a first step, a surface reaction between the water molecules and the liquid alloy alters the wetting ability of the oxide crust by the alloy; then the alloy penetrates rapidly into the porosity of the peroxide and the reaction becomes violent, resulting in the exothermic formation of hydrogen which first reacts with the peroxide, then with the oxygen released by the temperature increase. The explosion is therefore due to the simultaneous formation of hydrogen and oxygen from the following strongly exothermic reactions ($\Delta rH°$ in kJ mol^{-1}):

$$NaK(l) + Na_2O_2 \cdot 2H_2O(s) \rightarrow NaOH(s) + KOH(s) + Na_2O_2(s) + H_2(g) \quad -242 \quad (19)$$

$$Na_2O_2(s) + H_2(g) \rightarrow 2\,NaOH(s) \quad -339 \quad (20)$$

$$2\,Na_2O_2 \cdot 2H_2O(s) \rightarrow 4\,NaOH(s) + 2\,H_2O(g) + O_2(g) \quad -33 \quad (21)$$

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \quad -483 \quad (22)$$
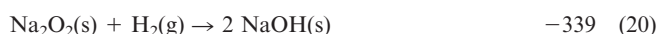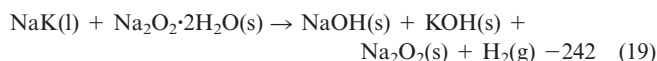
The values for equations (19) and (21) are based on a value of about -1121 kJ mol^{-1} for the formation enthalpy of $Na_2O_2 \cdot 2H_2O$; this value was estimated from the corresponding value given for $Na_2O_2 \cdot 8H_2O$ (-2943 kJ mol^{-1}).[18]

Photo 1. Results of the reaction between NaK alloy and sodium peroxide hydrated in air (Table 6, test 3b)

The storage of hydrated Na_2O_2 for one week in glove box, apparently dried the compound with a loss of its reactivity (Test 4, Table 6). This test confirms that the water molecules of the hydrate are responsible for the highly exothermic reaction or explosion.

Test on NaK + Na₂O₂ Hydrated Under Water Pump Vacuum

The diffractogram (Figure 8) of the hydrated product protected by a layer of polyethylene film, displays the presence of the phases Na_2O_2, $Na_2O_2 \cdot 2H_2O$ and the hydrated hydroxide $NaOH \cdot H_2O$, showing that the peroxide was only partially hydrated. Although the hydrates formed are not the same as those observed in the previous tests ($Na_2O_2 \cdot 8H_2O$ in one case and $Na_2O_2 \cdot 2H_2O$ plus $NaOH \cdot H_2O$ in another case), the reaction is violent in both cases (Table 6, Test 5). These very violent exothermic reactions are due to the presence of hydration water in the solid mixtures. The release of hydrogen exhibits a limited risk as these operations were performed in a glove box, but in air, actual explosions could occur.

Test on NaK + KO₂ + Hydrated Na₂O₂

The previous hydrated peroxide was mixed with KO_2 inside the glove box and then inserted together into the NaK alloy (Table 6, Test 6). In comparison with Test 1, the very violent resulting reaction is clearly due to the hydrated peroxide.

Test on NaK + NaOH

Slightly hydrated sodium hydroxide pellets (97%) were ground in air, and analyzed using X-ray diffraction: NaOH is found to be the predominant species besides the hydrates $NaOH \cdot H_2O$ and $Na_2CO_3 \cdot 7H_2O$ (Table 6, Test 7). The alloy reacts only slightly in the presence of sodium hydroxide, with a release of hydrogen. Repeated additions of hydroxide does not produce significant reactions.

Test on NaK + KOH

Potassium hydroxide pellets (87%) were ground and analyzed. KOH is the predominant phase besides $KOH \cdot H_2O$ and K_2CO_3 (Table 6, Test 8). The reaction is less exothermic than that with the sodium hydroxide due to the the lower hygroscopic behavior of KOH.

In conclusion, the violence of the reaction between NaK alloys and hydrated sodium peroxide, sodium hydroxide or potassium hydroxide, depends on the degree of hydration of the reagents and therefore on their history. The reaction remains difficult to predict and therefore portrays a random character. The simultaneous presence of hydrated sodium peroxide and potassium superoxide leads to a faster and more exothermic reaction.

7. Oxidation of NaK Alloy by Oxygen in Presence of H₂O Impurities

7.1. Preparation of Oxidized NaK Alloy by Sweeping Argon and Air

Two tests were performed in glass crucibles and the operating conditions and results are given in Table 7. The first test was carried out in one day and shows that sweeping with argon and air containing H_2O impurities (<5 vpm) results in the formation of a yellow mixture containing hydrated peroxide and hydroxides, in addition to the predominant species KO_2 (Photo 2). The phases observed are in agreement with the thermodynamic data: the oxides Na_2O and K_2O can react with KO_2 and are therefore absent, whereas the hydrates $KOH \cdot H_2O$ and $NaOH \cdot H_2O$ do not react with KO_2 and can coexist.

The second test was performed over one week and the behavior of the NaK alloy differs from the one observed in the previous test. A few hours after the beginning of the oxidation, the ball of NaK shows numerous excrescences; after a few days, the swellings took on a cauliflower-like appearance (Photo 3) with two predominant phases: KO_2 and $Na_2O_2 \cdot 2H_2O$ (Table 7, test 2). In this case, the water impurities in the argon during the first step seem to play an important role.

In conclusion, sweeping with a gas containing water impurities leads to a concentration of the water molecules through the formation of hydrated hydroxides and peroxides and not to the reduction of water into hydrogen. The traces of water vapor are only partially eliminated and therefore the role assigned to the NaK alloy is not fulfilled
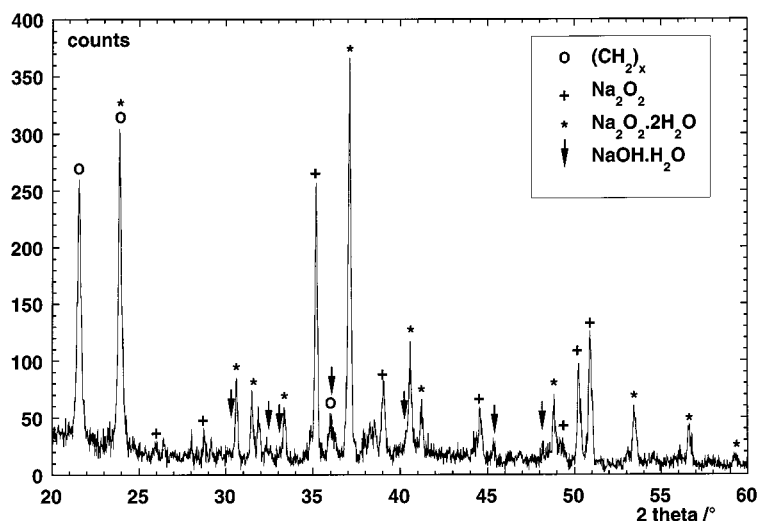

Figure 8. Raw diffractogram of sodium peroxide after hydration under water pump vacuum. The polyethylene peaks are due to the protecting layer. Dwell time 1 s; step 0.02 °

Table 7. Oxidation of the NaK alloy by argon and air sweeping

	Conditions	Aspect	Composition
Test 1 1.03 g	Sweeping 23 h with argon (3 L min^{-1}) and air (3 to 5 L min^{-1}), then storage in a closed flask	Intense yellow product	KO_2 predominant + $Na_2O_2 \cdot 2H_2O$ + $NaOH \cdot H_2O$ + $KOH \cdot H_2O$
Test 2 2.28 g	Sweeping 13 h with argon (6 L min^{-1}) then 8 h with argon and air (5 L min^{-1}) followed by 150 h with air (3 L min^{-1})	Cauliflower-like aspect, yellow at end of test	KO_2, major + $Na_2O_2 \cdot 2H_2O$, major + $NaOH \cdot H_2O$

Photo 2. Yellow product obtained during the oxidation of NaK alloy by argon and air sweeping (Table 7, test 1)
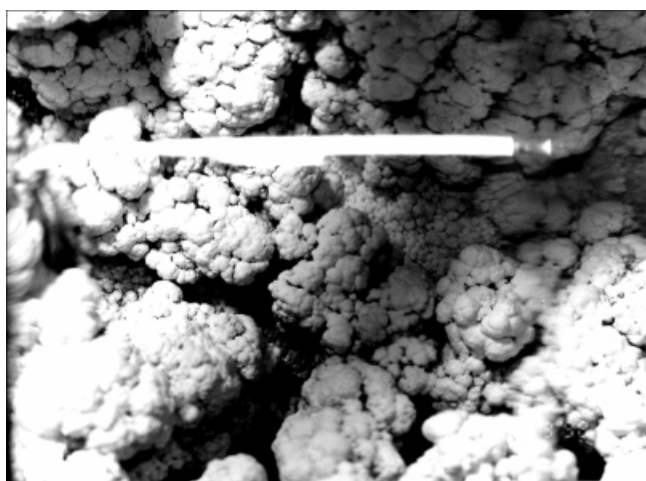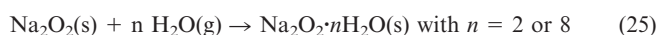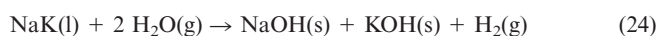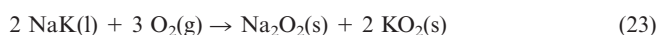

Photo 3. Product obtained during the oxidation of NaK alloy by argon and air sweeping (Table 7, test 2)

because it leads predominantly to an accumulation of the H_2O impurities. The products thus obtained confirm the reactions expected from a thermodynamic basis (NaK-56 is represented by the approximate formula NaK):

$$2\ NaK(l) + 3\ O_2(g) \rightarrow Na_2O_2(s) + 2\ KO_2(s) \qquad (23)$$

$$NaK(l) + 2\ H_2O(g) \rightarrow NaOH(s) + KOH(s) + H_2(g) \qquad (24)$$

$$Na_2O_2(s) + n\ H_2O(g) \rightarrow Na_2O_2 \cdot nH_2O(s)\ \text{with } n = 2 \text{ or } 8 \qquad (25)$$

$$NaOH(s) + H_2O(g) \rightarrow NaOH \cdot H_2O(s) \qquad (26)$$

$$KOH(s) + H_2O(g) \rightarrow KOH \cdot H_2O(s) \qquad (27)$$

7.2. Preparation of Oxidized NaK Using Argon and Air Bubbling

The purpose of this test was to represent a real bubble chamber at a laboratory scale, with a continuous circulation of gas containing water impurities (≤ 5 vpm) in the NaK liquid alloy. Air was added to the argon flow in order to accelerate the oxidation of the NaK alloy. The oxidation was performed in a glove box.

The test lasted three months (including 500 h of bubbling) during which a total of 30 m^3 of argon and 60 m^3 of azoxy (reconstituted dry air) were alternatively or simultaneously bubbled into the liquid alloy (9.95 g). The mass of water impurities passing through the alloy totals 0.36 g and it serves either to hydrolyze the NaK alloy into NaOH and KOH, or to hydrate Na_2O_2, NaOH and KOH.

During the argon bubbling, the previously very brilliant NaK alloy first becomes dull gray, then starts to whiten in selected areas due to the water and oxygen impurities. The bottom of the reactor is coated with very fine gray beads that are ejected. Bubbling with air results in the formation of yellowish areas, which then become clear yellow. This always occurs along the preferential paths. The start of the azoxy gas flow sometimes causes orange flames and grayish smoke which are then extinguished by argon sweeping. Throughout the test, the ejection of small gray beads is observed. At the end of the test, the mixture is very heterogeneous: orange crusts adhering closely to the walls, grayish parts and metallic NaK. After the test, four samples were taken from these various parts and the results of the X ray diffraction analyses are given in Table 8. Figure 9 represents the diffractogram of the sample BAG 2 and five species could be identified. After 30 min in air, we observe a swelling of the sample and the disappearance of the peaks corresponding to sodium hydroxide due the very hygroscopic behavior of these compounds.

These series of tests show that when the NaK alloy is exposed to the sweeping or bubbling of argon and dry air containing water impurities, the products KO_2, $KOH \cdot H_2O$, $NaOH \cdot H_2O$ and $Na_2O_2 \cdot 2H_2O$ are always formed The mixture is heterogeneous, certain areas are very hard, whereas others are flaky. Differences in color can be observed. It is also observed that the gas follows preferential paths due to the heterogeneous nature of the crust. Therefore certain areas are oxidized and hydrated whereas other parts of the alloy remain in the metallic state. The argon is likely to circulate without being really purified.

Table 8. Products obtained after oxidation of the NaK alloy by argon and air bubbling for three months

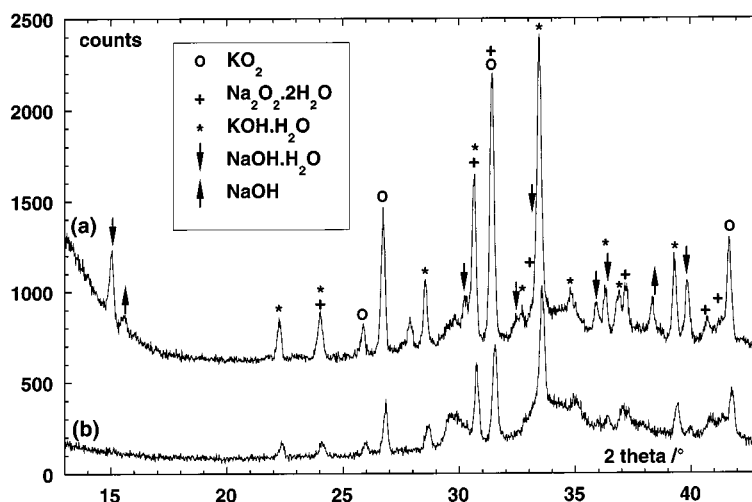|	Aspect	Identified products (XRD)
BAG 1	Yellow crust taken from the surface of the NaK during the test	KO_2 predominant + $KOH \cdot H_2O$ + $Na_2O_2 \cdot 2H_2O$
BAG 2	Grey ashes and yellow crusts taken during the test	KO_2 + $KOH \cdot H_2O$ + $Na_2O_2 \cdot 2H_2O$ + $NaOH \cdot H_2O$+ $NaOH$ + amorphous phase
BAG 3	Grey area (end of test)	KO_2 + $Na_2O_2 \cdot H_2O$ + $KOH \cdot H_2O$ + $NaOH \cdot H_2O$+ $NaOH$
BAG 4	Yellow area (end of the test)	KO_2 + $KOH \cdot H_2O$ + $Na_2O_2 \cdot 2H_2O$ + $NaOH \cdot H_2O$

Figure 9. Raw diffractogram of NaK alloy after oxidation by argon and air bubbling during 3 months (Table 8, sample BAG 2).(a) Initial; (b) after 30 min in air. Dwell time 0.5 s; step 0.02 °

Photo 4. Product obtained during the oxidation of NaK alloy by argon and air bubbling for three months (Table 8)

These observations are very important as they explain the hazards of oxidized NaK alloy. Porous crusts containing superoxides, hydrated peroxides and hydroxides, can form on the surface or along the walls and can violently come into contact with the remaining alloy following impact. A slow surface reaction then occurs that can result in the modification of the wetting ability of the oxide crust. The NaK penetrates the pores, which then leads to a violent reaction.

8. Hydration and Dehydration of Sodium and Potassium Oxides and Hydroxides

The aim of these experiments was to examine the possibility to reduce or eliminate the hydration water of the oxidation crust through treatment in vacuum. Hydration was performed using water vapor under water pump vacuum for 12 h. The product was then placed under vacuum (10^{-2} to 10^{-3} bar) for 24 to 60 h at ambient temperature. Dehydration was completed by heating for 24 to 48 h at 110 °C under primary vacuum, followed by cooling. All the results are given in Table 9.

During the dehydration treatment, hydrated peroxide $Na_2O_2 \cdot 2H_2O$ disappears and is partially transformed into NaOH. The hydrated products $NaOH \cdot H_2O$ and $Na_2CO_3 \cdot 10H_2O$ are present only in minute amounts, and therefore less likely to react further. After being placed under vacuum, the sample of sodium peroxide becomes harder, but its apparent volume does not change. After

Table 9. Oxide and hydroxide hydration and dehydration tests. (tr = traces)

	Na_2O_2	KO_2	NaOH	KOH
Hydration				
Mass	8.274 g	1.301 g	23.076 g	6.091 g
Increase in mass	1.235 g	Change into liquid KOH	2.963 g	1.308 g
Hydrate obtained	$Na_2O_2 \cdot 2H_2O$ + Na_2O_2	No hydrate formation	$NaOH \cdot H_2O$ + NaOH	$KOH \cdot H_2O$ + KOH
Dehydration				
Mass	4.086 g		6.406 g	2.673 g
Weight loss after vacuum and heating	0.442 g		0.616 g	0.414 g
% initial water eliminated	83%		85%	86%
Products after dehydration	Na_2O_2 + NaOH + $NaOH \cdot H_2O$ (tr) + $Na_2CO_3 \cdot 10H_2O$		NaOH + $NaOH \cdot H_2O$ (tr)	KOH + $KOH \cdot H_2O$ (tr)

heating under vacuum, the sample expands considerably and migrats up to the upper level of the recipient.

Potassium superoxide KO_2 does not form hydrated products but is decomposed, giving KOH. For NaOH, the hydration leads to the formation of $NaOH \cdot H_2O$ and the vacuum treatment eliminates at least 85% of the water previously fixed. The product is practically dry. The same results are obtained for potassium hydroxide (Table 9).

The products rehydrate very rapidly, as soon as they are no longer under vacuum. Dehydration had to be completed by heating at 100 to 110 °C in order to reach irreversible dehydration levels of about 85%. It is observed during the tests that the hydrated products become partially dehydrated in the glove box (water content < 1 vpm). Therefore, it may be possible to dehydrate a product by circulating hot argon, provided the latter is completely dried. Before performing this type of dehydration on a larger scale in a bubbler containing liquid NaK, laboratory tests are essential to check whether the crust layers that detach and expand, could fall into the liquid NaK and cause exothermic reactions. Laboratory tests have to be developed in order to study the complex geometry, similar to that in real bubblers.

General Conclusion

To the best of our knowledge this is the first laboratory demonstration of an explosion due to gas contaminants (oxygen and water vapor). The previous results were obtained by addition of water or hydrocarbon to the alloy.[4]

The main results of the structural and thermodynamic analysis are as follows:
(i) All the oxygenated compounds of sodium and potassium are denser than the NaK alloy and should therefore fall to the bottom of recipients, which is not observed. The molar volumes of the different oxides are lower than the molar volumes of the metals or alloys.
(ii) The oxide layer that is formed must contain predominantly Na_2O_2 and KO_2. This crust is porous and cannot be wetted by the alloy.
(iii) There is a possible formation of hydrated compounds such as $Na_2O_2 \cdot 8H_2O$; $Na_2O_2 \cdot 2H_2O$; $NaOH \cdot H_2O$ and $KOH \cdot H_2O$.

(iv) If the oxide crust comes in contact with the NaK alloy, the hydration water can react, leading to a release of hydrogen. As the thermal decomposition of KO_2 results in a release of oxygen, a violent reaction could occur, resulting in an explosion.

The experimental study leads to the following conclusions:
(i) Sodium peroxide Na_2O_2 is stable up to 490 °C and potassium superoxide KO_2 decomposes above 130 °C, resulting in oxygen release.
(ii) The NaK + Na_2O_2 reaction shows great instability which results in the formation of several non-identified compounds. The exothermic reactions begin above 166 °C and increases considerably at 204 °C, but does not release any significant amount of gas.
(iii) The NaK + KO_2 reaction starts at 167 °C and is easily reproducible, with the formation of potassium metal and the release of oxygen due to the thermal decomposition of KO_2. Thermal cycling between −20 and +20 °C has little effect.
(iv) The NaK + KO_2 + Na_2O_2 reaction is highly exothermic above 170 °C; the presence of Na_2O_2 contributes significantly to an increase in released heat.

Tests performed in a glove box on greater quantities display the same results, in disagreement with the high exothermicity mentioned by several authors. On the other hand, the use of hydrated sodium peroxide leads to violent or even explosive reactions. The hydration of Na_2O_2 results in the formation of $Na_2O_2 \cdot 2H_2O$ and/or $Na_2O_2 \cdot 8H_2O$ and $NaOH \cdot H_2O$ and the quantity of water absorbed and the degree of hydration determine the random explosive character of the reaction.

The laboratory preparation of oxidized NaK alloy by the sweeping or bubbling of argon and air mixture, containing less than 5 vpm of H_2O, leads to the formation of potassium superoxide KO_2 and hydrated peroxide and oxides: $Na_2O_2 \cdot 2H_2O$, $KOH \cdot H_2O$ and $NaOH \cdot H_2O$. The water impurities are therefore not eliminated, but they are concentrated into the oxide product crust. In the presence of initial alloy, these products can produce exothermic or explosive reactions, depending on the degree of hydration of the peroxide and hydroxides.

The product mixture is very heterogeneous containing gray parts, orange crusts adhering closely to the walls together with metallic NaK alloy. The gas flow follows preferential paths, certain parts of the alloy are oxidized and hydrated, while other parts remain in the metallic state. These important observations explain the danger of oxidized NaK crusts formed at the surface or along the walls of the bubblers containing hydrated oxides; if they can rapidly come in contact with the remaining metallic alloy following impact, explosions can occur.

The bubblers in service on fast reactors are generally largely oversized. When argon follows preferential paths through the crust forming hydrates, and when saturation is reached, the argon is likely to circulate without being purified. It is therefore impossible to assess the duration of the efficiency of these bubblers. Therefore, in our opinion, this method of purification should be abandoned.

The dehydration tests performed on hydrated peroxide and hydroxide show that the products can be dried under primary vacuum at 100 °C. Drying of the products placed in glove boxes under purified argon ($\leq$ 1 vpm H_2O) is also observed. However, as these hydrated products expand when heated, the crusts could detach and come into contact with the remaining alloy. Therefore, to achieve dehydration on complex geometry, such as those of real bubblers, it is indispensable to perform laboratory tests in order to check whether exothermic reactions can occur, resulting in the accidental contact of these reagents.

Experimental Section

Structural Data: The structural data needed for this work (space group, cell parameters, density) were extracted from Powder Diffraction Files (PDF).[19] They are related to the sodium-potassium alloy phases and the different oxides of sodium and potassium. The main data are given in Table 1.

Thermodynamic Data: The purpose of this analysis was to establish the thermodynamic values concerning the various possible reactions: reaction enthalpy $\Delta_r H°$, entropy $\Delta_r S°$ and Gibbs energy $\Delta_r G°$. These values were calculated and tabulated according to the temperature in the 25−500 °C range and involve all the possible Na-K-O combinations available in the literature. The primary thermodynamic data concern the values tabulated for the following species:

K(s and l), KO_2(s), K_2O(s), K_2O_2(s); Na(s and l), NaO_2(s), Na_2O(s), Na_2O_2(s); O_2(g), H_2O(g), CO_2(g)

They were extracted from two recent data bases[20,21] or from the NIST files.[18] The HSC program was used for part of the calculations.[22] The effect of water vapor and carbon dioxide was taken into account. As standard thermodynamic data concerning NaK alloys were not found, all the diagrams, therefore, refer to sodium and potassium.

Chemicals: The commercially available potassium and sodium oxides are: sodium oxide Na_2O (Osi, France, 98%), sodium peroxide Na_2O_2 (Osi, France, 95%, aggregate size $\approx$ 1.5 mm) and potassium superoxide KO_2 (Merck, Germany, 96.5%, aggregate size $\approx$ 0.2 mm). They were ground before use. The NaK-56 liquid alloy was purchased from Callery Company, PA, USA. It corresponds to 56 wt-% K or 43 at-% K and will be denoted $Na_{0.57}K_{0.43}$. Data for $Na_{0.57}K_{0.43}$ alloy are: molar mass 29.8 g mol^{-1}; molar volume 33.5 cm^3 mol^{-1}; density 0.89 g cm^{-3}. The purity of the gases are: argon quality U, O_2 < 5 vpm, H_2O < 5 vpm; Azoxy N_2/O_2: 80%/ 20%, H_2O < 5 vpm. They were used without any further purification.

Apparatus and Measurements

Differential Scanning Calorimetry: The tests involving pure oxides were performed between ambient temperature and 1300 °C by means of a Multi HTC SETARAM calorimeter with alumina as a reference. Inconel crucible (Ni-Cr-Fe alloy), volume 6.5 cm^3. The samples were studied under argon. Most of the calorimetric tests were performed using a DSC 111 SETARAM type calorimeter (temperature range −120 °C to 800 °C) in order to observe the melting point of NaK, (solid at −12.6 °C) and to calculate the amount of remaining NaK alloy. Volume of the stainless steel crucible: 0.170 cm^3. The samples were placed under argon. The results from the DSC 111 apparatus were numerized afterwards. For both apparatus, the calibration in temperature and enthalpy was performed with pure metals and the Joule effect. The heating rate was 1 K min^{-1}. The reported temperatures corresponded to the onset of the peaks.

Mass Spectrometer: The laboratory mass spectrometer used was a quadripole-type residual gas analyzer, model Anagaz 200, marketed by the Quad/Service company. The samples were placed in a container equipped with a tight stainless steel connection, or in a crucible inserted into the container. They were first placed under primary vacuum, then swept with argon (N55 quality, H_2O < 2 vpm; N_2 < 0.5 vpm; O_2 < 0.5 vpm). The temperature of the sample was raised from ambient temperature up to 500 °C in a 100 °C step at a heating rate of 5 K min^{-1} between each 1 h plateau. The calibration was performed with the pure corresponding gases (H_2O, O_2).

X-ray Diffraction: The diffractograms were obtained at room temperature with a Siemens D500 (Poitiers) or D5000 diffractometer (Cadarache) equipped with a copper anode [$\lambda(K_a)$ = 1.54188 Å] and a back graphite monochromator, under the following conditions: dwell time 1 or 0.5 s; step 0.02 °; 2 theta range 5 to 80 °; divergence slit 1°. As most of the samples are air and particularly moisture sensitive, the samples were placed on the sample holder under argon and protected with polymer film for the D5000 diffractometer (Parafilm M, American National Can; XRD profile corresponding to polyethylene) or measured twice under air without protection for the D500 apparatus. The identified phases were the same but no quantitative analysis could be undertaken. The identification of the peaks was obtained by comparison with the PDF file (program Search of the Diffract-AT package, Socabim, France). Examples of raw diffractograms are given in Figure 8 and 9.

Reactivity Apparatus

Measurement of the Reaction Temperature: In a glove-box filled with argon, about 2 g of liquid NaK alloy were introduced into a 20 mL glass flask equipped with a thermocouple. The oxide(s) were added separately or simultaneously and the mixture was manually stirred in order to ensure good contact between the alloy and the oxides.

FULL PAPER

***Preparation of Oxidized NaK by Sweeping*:** The apparatus (Figure 10) was made of a glass tube containing the boat (1 to 2 g of NaK alloy) and supplied by two inlets equipped with a flowmeter, one for argon and the other for the Azoxy mixture. The two gases were introduced independently or together. A coil was used to homogenize the mixture of argon and azoxy gases.
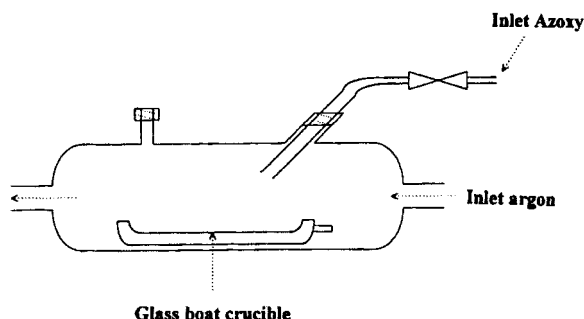

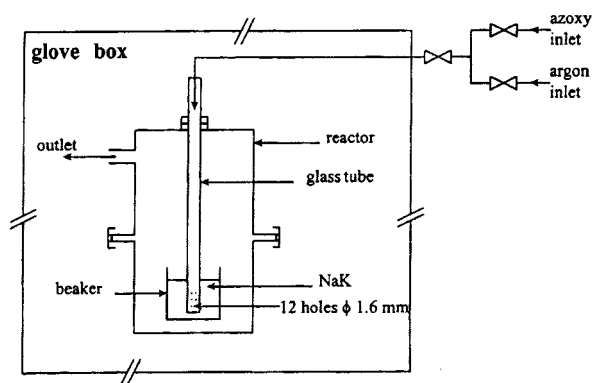Figure 10. Device used for the preparation of oxidized NaK by sweeping

Figure 11. Device used for the preparation of oxidized NaK by bubbling

***Preparation of Oxidized NaK by Bubbling*:** Figure 11 shows the apparatus placed in a glove box. The NaK alloy (9.95 g) was placed in a beaker, which was itself enclosed in a reactor, with two gas inlet tubes (argon and Azoxy), permitting to bubble directly in the liquid alloy.

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