

MOLTEN SALTS SAFETY AND HAZARDS: AN ANNOTATED BIBLIOGRAPHY

CAROLYN B. ALLEN* and GEORGE J. JANZ**

*Molten Salts Data Center, Department of Chemistry, Rensselaer Polytechnic Institute
Troy, New York 12181 (U.S.A.)*

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Summary

The present information was compiled as a guide to good practice and as an aid in discovering potentially dangerous situations with molten salts in research and technology, and is based on a survey of the primary, secondary, and tertiary scientific literature to December, 1976. The format of an annotated bibliography was selected for this communication; the results are reported with reference to nine categories: hazards; reactive chemical hazards; dangerous mixtures of inorganic compounds; potentially hazardous metal—molten salts mixtures; precautions; applications of molten salts in process design and technology; water in melts; water solubility data; and reviews. A systems index is included. Titles of selected publications are included in the list of references as an additional aid to the user (196 references).

Introduction

Current applications of molten salts in technology include advanced batteries, fuel cells, solar energy storage, coal gasification, environmental pollution, and extractive metallurgy.

The intent of this annotated bibliography is to provide the user with a ready access to important publications and review articles concerning safety and hazards with molten salts in research and technology. The results are based on a survey of the primary, secondary, and tertiary scientific literature to December, 1976, and are organized under nine categories: hazards, reactive chemical hazards, dangerous mixtures of inorganic compounds, potentially hazardous metal—molten salt mixtures, precautions, applications of molten salts in process design and technology, water in melts, water solubility data, and reviews. A tabular format is used in each case to summarize the results and a locator number is included with each entry for use in the systems index. Titles of selected references are included in the bibliography as an additional entry point for the users.

*Postdoctorate research associate; MSDC-RPI (1975–1978). Present address: Department of Chemistry, New York State University at Stonybrook, Long Island, U.S.A.

**To whom correspondence should be directed.

TABLE 1

Hazards

Hazard: Violent chemical reaction.

Comment: If ΔH is greater than ~ 0.7 cal/g, a reaction may take place where the release of energy is too great to be dissipated by the environment.

Nitrates react vigorously and dangerously with carbon and its compounds, and with light metals.

A thermite reaction can occur in an overheated nitrate bath between aluminum and iron oxide sludge. Overheating may also initiate a violent reaction between aluminum and the nitrate bath. This takes place at about 650°C , 1202°F , with the evolution of considerable heat.

References: [2,3,4,9,34,77,79,80]

Locator Number: 1.1.

Hazard: Steam.

Comment: Water introduced into a molten salt bath may turn to steam with explosive effect. Injuries have been fatal.

References: [3,4,14,34,79]

Locator Number: 1.2.

Hazard: Trapped gas or liquid.

Comment: Air, occluded in blow-holes of castings, or trapped in tubes, piping or hollow metal-work, may expand explosively when materials are placed in a molten salt bath without pre-warming.

References: [3,4,34,79]

Locator Number: 1.3.

Hazard: Spattering, fire.

Comment: Although not combustible themselves, molten salts create the hazard of a continuous ignition source for combustibles in their vicinity. Spattering is usually caused by the introduction of foreign material into salt baths. Most of the injuries to personnel working with molten salts have been due to burns.

References: [34,79]

Locator Number: 1.4.

Hazard: Structural failure; overheating.

Comment: Nitrate, nitrite, cyanide, sulfate and carbonate melts decompose to yield noxious gases on overheating. Nitrates begin to decompose at about 400°C (750°F) forming corrosive nitrous fumes, nitrites and hydroxides, but decomposition does not proceed with sufficient rapidity to prevent their use up to about 600°C (1100°F). Above this temperature, decomposition is increasingly rapid until a critical temperature of about 700°C (1300°F) is reached, and violent decomposition is likely to occur.

The introduction of foreign material into salt baths can result in the formation of interior crusts in the tank, leading to serious overheating. Sludge buildup can have the same effect.

Overheating has usually occurred when baths have been left unattended. However, ref. 79 lists "the accidental or uninstructed setting of temperature controls above safe operating limits" as one major cause of fire and explosion in nitrate baths.

References: [1,3,4,5,6,7,34,35,76,79,183,196]

Locator Number: 1.5.

Hazard: Storage, disposal.

Comment: For special hazards associated with molten fluorides, see: Table 2, BeF_2 , 2.43.

The oxides produced in nitrate and carbonate baths by normal deterioration have high exothermic heats of reaction with water and yield strongly caustic solutions.

Fires causing heavy property damage, serious injuries, and loss of life have resulted from the careless handling of sodium nitrate and the waste salts from nitrate baths.

References: [2,3,4,6,7,9,34,79,80]

Locator Number: 1.6.

TABLE 2

Reactive chemical hazards

Hazard	Type	
1	Explosive, or impact-sensitive	
2	Pyrophoric, flammable	
3	Evolves O_2 on heating or on contact with water (creating a hazard in case of fire)	
4	Evolves a noxious gas on heating or on contact with water (creating a hazard in case of fire)	
5	Presents an unusual storage, handling or disposal problem	
6	Preparative hazard	
7	Radioactive	
8	Strong oxidant	
9	Other	

Compound	Hazard	Comments and references
$\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$ 2.1	3,5,8	Sodium perborate. Stable in cool, dry air, but will decompose and give off O_2 when heated or moist [2,9]
$\text{Ba}(\text{BrO}_3)_2$ 2.2	1,3	Thermal decomposition almost explosive at 300°C ($=572^\circ\text{F}$). TOXIC [9]
$\text{Hg}(\text{BrO}_3)_2$ 2.3	2	Deflagrates c. 155°C ($=311^\circ\text{F}$). TOXIC [9]
$\text{Pb}(\text{BrO}_3)_2$ 2.4	1	Two people were killed grinding the material prepared from KBrO_3 and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. It has been established the compound thus formed is diaceto lead (II) bromate. $\text{Pb}(\text{BrO}_3)_2$ is, however, also an explosive salt. It is stable to 180°C ($=356^\circ\text{F}$) when pure. TOXIC [8,9]
NH_4BrO_4 2.5	1	Explosive [9]
$\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ 2.6	1,4	Explodes with liberation of carbon monoxide [9,20]
$\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3$ 2.7	2	Pyrophoric in air [9,20]
$\text{Cu}_2\text{C}_2\text{O}_4$ 2.8	1	Explodes on heating [9]
HgC_2O_4 2.9	1	Explodes 105°C ($=221^\circ\text{F}$), or at room temperature with percussion or grinding. TOXIC [9]

TABLE 2 (cont'd)

Compound	Hazard	Comments and references
CaCO ₃ , Li ₂ CO ₃ , Na ₂ CO ₃ , PbCO ₃ 2.10	2	Ignites and burns on contact with fluorine gas [9]
KCN, NaCN 2.11	1	Oxidizes violently or explosively with hot oxidants. This is one of the most common causes of salt bath explosions. Extremely TOXIC [9,79]
AlCl ₃ , AlBr ₃ 2.12	4,5	Long storage of the anhydrous salts in closed containers has resulted in spontaneous decomposition. Hydrolysis is violent with HCl (HBr) evolved [9]
AuCl ₃ 2.13	1	Gold compounds exhibit a tendency to decompose violently with separation of the metal [9]
TiCl ₂ , TiCl ₃ 2.14	2	Ignites in air. Under inert atmosphere TiCl ₂ disproportionates to TiCl ₄ and pyrophoric titanium [9]
ZrCl ₂ 2.15	2	When warm, ignites in air [9]
Ca(ClO) ₂ 2.16	1,4	There is a long history of explosions involving this compound ("bleaching powder") [9]
AgClO ₂ 2.17	1	Explodes on impact, grinding, friction. Explosive decomposition about 145°C (293°F). TOXIC [9]
Ba(ClO ₂) ₂ 2.18	1	Explodes 190°C (374°F). Explosion is exothermic. TOXIC [36]
Ca(ClO ₂) ₂ 2.19	1	Has been reported to explode due to mechanical shock [8]
Cu(ClO ₂) ₂ 2.20	1	Explodes on impact or being heated. The double salt, Cu(ClO ₂) ₂ · 2KClO ₂ · 2H ₂ O also explodes by percussion. TOXIC [8,9,37]
Hg ₂ (ClO ₂) ₂ 2.21	1	Extremely unstable. Explodes on heating. TOXIC [8,9]
Hg(ClO ₂) ₂ 2.22	1	Unstable at room temperature. TOXIC [8,9]
LiClO ₂ 2.23	1	Disproportionates violently on heating [8]
NaClO ₂ 2.24	1,4	May explode. Forms explosive and poisonous gas on contact with mineral acids [2,8,9]
Ni(ClO ₂) ₂ 2.25	1	Explodes 100°C (212°F). Will explode with percussion even when wet or hydrated [9,38]
Pb(ClO ₂) ₂ 2.26	1	Explodes about 100°C (212°F), or on rubbing with Sb, S or sulfides. TOXIC [8,9,36]
TlClO ₂ 2.27	1	Decomposes above 70°C. Detonates with mechanical shock. TOXIC [8]
Co(NH ₃) ₆ (ClO ₃) ₃ 2.28	1	Hexammine cobalt (III) chlorate. Explosive, as are most other ammine-metal oxosalts [9,17]
KClO ₃ , NaClO ₃ 2.29	1,8	Explodes on contact with H ₂ SO ₄ . Fire hazard. Cellulose impregnated with these salts burns fiercely [2,8]
Pb(ClO ₃) ₂ 2.30	1	Explodes on rapid heating to 240°C (464°F). TOXIC [36]
TlClO ₃ 2.31	4,8	Thermal decomposition yields unstable, explosive gas. Powerful oxidant. TOXIC [9]
Be(ClO ₄) ₂ 2.32	1,8	Powerful oxidant. Insensitive to heat or shock. Used in propellant and igniter systems. TOXIC [9]

Compound	Hazard	Comments and references
Fe(ClO ₄) ₂ , 2.33	6	Prepared by reacting the sulfates with conc. HClO ₄ . Preparation can explode violently [9]
Ga(ClO ₄) ₃ 2.34	6,8	Freshly prepared crystals must not be filtered through filter paper as the mother liquor is concentrated HClO ₄ [9]
Hg ₂ (ClO ₄) ₂ 2.35	4	Melts 210°C (410°F) with evolution of chlorine oxides [7]
KClO ₄ 2.36	1,8	Long history of explosions (in analytical determination of potassium). Mixtures with sulfur used in pyrotechnic devices [2,9]
Mg(ClO ₄) ₂ 2.37	5,8	Skin and eye irritant. High heat of reaction with water (exothermic) may lead to disposal problems. Reported to explode 250°C (482°F) [1,2]
Mn(ClO ₄) ₂ 2.38	1	Explodes 195°C (383°F) [9]
NaClO ₄ 2.39	8	Irritating to skin and eyes [2]
NH ₄ ClO ₄ 2.40	1	Explodes on impact or heating [9,17,20]
PbCrO ₄ 2.41	2	Can be ignited by grinding. Burns fiercely if ignited. TOXIC [9]
AgF 2.42	2	Reaction with titanium metal is highly exothermic. The mixture becomes incandescent at 320°C (608°F). TOXIC [9]
BeF ₂ , all fluorides 2.43	5	It is recommended that fluorides be handled in hoods with adequate ventilation to prevent breathing air containing fluoride dust. This is especially important in the case of BeF ₂ , as beryllium is a highly toxic element itself. Its effect is more damaging when it enters the body via the respiratory tract as dust. Whether beryllium is in its metallic form or in the form of a compound is almost inconsequential to its effect. For some compounds, e.g. BeF ₂ , the damaging effects of HF resulting from hydrolysis is added to that of Be ⁺⁺ . The allowable maximum concentration of beryllium in air is 2μg/m ³ . Hence, the hood exhaust system should be provided with absolute filters. Some people are sensitive to contact with beryllium, manifested by the appearance of dermatitis. For these people, protective clothing, including rubber gloves is essential. However, this practice is recommended for handling fluorides in general. Even when hoods with good ventilation are available, HF-containing exhaust should be sparged through caustic solutions to protect the worker and the hood [13]
NaHSO ₄ 2.44	9	Acid (Lowry-Bronsted). Reaction with oxides and hydroxides is exothermic
NH ₄ IO ₃ 2.45	1	Violent decomposition occurs on touching with a scoop [9]
NH ₄ IO ₄ 2.46	1	Explodes on heating or abrasive impact [9]

TABLE 2 (cont'd)

Compound	Hazard	Comments and references
KMnO ₄ , NaMnO ₄ 2.47	1,5,8	Decomposes on heating; when hot, explodes on contact with organic materials. Fire hazard. Ingestion may be fatal [2]
NH ₄ MnO ₄ 2.48	1	Friction-sensitive. Explodes 60°C (140°F) [9]
AgN ₃ , all azides 2.49	1	Silver azide. All azides are unstable under appropriate conditions. AgN ₃ explodes 340°C (644°F). The presence of impurities lowers the explosion temperature. Impact-sensitive. Explosions are usually violent. TOXIC [9]
Hg(N ₃) ₂ 2.50	1	Friction sensitive, even under water. Explodes spontaneously. TOXIC [9]
Hg ₂ N ₆ 2.51	1	Mercurous azide. Explodes on heating to above 270°C (518°F) in air or 140°C (284°F) in vacuo. TOXIC [9]
LiN ₃ 2.52	1	Insensitve to shock. Decomposes explosively 115–298°C (239–568°F), depending on rate of heating [9]
KN ₃ 2.53	1	Insensitve to shock. On heating it melts, then decomposes evolving N ₂ gas. The residue explodes feebly [9]
NH ₄ N ₃ 2.54	1	Explodes on rapid heating [9]
Hg ₃ N ₂ 2.55	1	Mercuric nitride. Explosive. TOXIC [76]
KNH ₂ , NaNH ₂ 2.56	1,2	Ignites on heating or grinding in air. History of fires or explosions involving these compounds [9]
AgNO ₃ 2.57	1,9	Produces skin burns. Reaction with ammonium compounds can yield silver azide (see above). TOXIC [9]
Ba(NO ₃) ₂ 2.58	2	A mixture of finely-divided Al-Mg alloy with this salt is used as a photoflash composition. Ignites easily. TOXIC. MAY BE LETHAL IF SWALLOWED [2,9]
Ca(NO ₃) ₂ 2.59	5	Evolves considerable heat on solution in water. May pose disposal, storage problems [2]
Cu(NO ₃) ₂ 2.60	9	TOXIC [2]
NH ₄ NO ₃ 2.61	1,2	Fire and explosion hazard. It is difficult, but not impossible to detonate the pure salt. Dangerous mixtures are formed with acetates, (NH ₄) ₂ SO ₄ , KNO ₃ , KMnO ₄ , organics, many metals. Mixtures of NH ₄ NO ₃ and powdered Al are used as an explosive [9,17,18]
NaNO ₃ , NaNO ₂ 2.62	5,8	Fire hazard. Wood impregnated with spilled salt burns fiercely if ignited [2,9,34,79,80]
Pb(NO ₃) ₂ 2.63	9	TOXIC [2]
Th(NO ₃) ₄ 2.64	7	Mildly radioactive [2]
SnO(NO ₃) ₂ 2.65	1,2	Basic tin nitrate. Explodes on shock, friction, or heating above 100°C (212°F). An industrial accident involving this compound and organic dust has been reported [9]
UO ₂ (NO ₃) ₂ 2.66	1,5	Mildly radioactive. Dust can be toxic. Reacts with cellulose to form guncotton [2,9]

Compound	Hazard	Comments and references
Al ₂ O ₃ 2.67	9	Bretherwick [9] cites an accident report saying mixtures of this compound with NaNO ₃ are explosive [9]
Ag ₂ O 2.68	1,2,6	Oxidation of Mg metal with this salt proceeds explosively. Mixtures with Au ₂ S ₃ , Sb ₂ S ₃ , and/or HgS ignite on grinding. TOXIC [9]
Cs ₂ O 2.69	2	Ignites in F ₂ , Cl ₂ [9]
HgO 2.70	8	Under appropriate conditions, HgO can function as a powerful oxidant and/or catalyst. Highly volatile. Thermal decomposition yields free metal. Both salt and metal are toxic [9]
Mn ₂ O ₇ 2.71	1	Explodes 40–70°C (104–158°F) on impact or friction. Sensitivity estimated to be approximately that of mercuric fulminate [9]
BaO ₂ 2.72	3,5,8	Strong oxidant. Avoid breathing dust, contact with skin. Fire hazard. Decomposes slowly in cold water, more rapidly in hot water to yield O ₂ and strongly caustic solution. Thermal decomposition yields O ₂ and BaO. Both BaO and BaO ₂ are toxic [2]
CaO ₂ 2.73	2,3,5,8	As for BaO ₂ , but milder. Grinding with oxidizable materials may cause fire [2]
Li ₂ O ₂ 2.74	2,3,5,8	Decomposes in water yielding O ₂ and heat. Water solution is caustic. Fire hazard [2]
K ₂ O ₂ 2.75	2,3,5,8	As for Li ₂ O ₂ . Does not burn or explode alone, but does when mixed with combustibles. Fire hazard [2]
MgO ₂ 2.76	2,3,5,8	Gradually decomposed by water with release of O ₂ [2]
Na ₂ O ₂ 2.77	2,3,5,8	As for Li ₂ O ₂ . The reaction with water can be explosively rapid. Heat of the reaction is more than enough to ignite nearby combustibles. Mixtures with flammable materials can explode. Sodium peroxide is occasionally shipped in combustible cartons. These must be protected from heat, moisture. In case of fire, large amounts of Na ₂ O ₂ cannot be controlled by water. Salt is caustic. Avoid inhaling dust [2]
SrO ₂ 2.78	2,3,5,8	Decomposes in hot water. Mixtures with combustibles can explode. Strong oxidant [2]
Hg(ONC) ₂ 2.79	1	Mercuric fulminate. Detonates. All fulminates are explosive. Those of Cd, Cu, Ag, and Tl are more powerful and sensitive than Hg(ONC) ₂ [9,18]
BaS, CaS, SrS 2.80	1	Explode weakly on heating with PbO ₂ , KClO ₃ ; strongly with KNO ₃ [9]
Ce ₂ S ₃ 2.81	2	Pyrophoric [9]
CaS ₂ O ₈ 2.82	1,8	Calcium peroxydisulfate. Shock sensitive, explodes violently [9]
K ₂ S ₂ O ₈ 2.83	3,4,8	Potassium peroxydisulfate, also called potassium persulfate. Trade name: Anthion. Strong oxidant. Decomposes to yield O ₂ at 100°C (212°F), when dry. In aqueous solution, yields O ₂ at room temperature. Skin irritant. Thermal decomposition products irritating and toxic [2]

TABLE 2 (cont'd.)

Compound	Hazard	Comments and references
(NH ₄) ₂ S ₂ O ₈ 2.84	3,4,8	Ammonium peroxydisulfate, also called ammonium persulfate. Strong oxidant. Irritating to skin and mucous membranes. Yields SO ₂ , SO ₃ when heated [2]
CdSe 2.85	6	It is prepared directly from the elements. The reaction mixture may explode. TOXIC [9]
Cs ₂ Se 2.86	2	Ignites in air when heated. TOXIC [9]

TABLE 3

Dangerous mixtures of inorganic compounds

Mixture	Comments and references
KBrO ₃ -Pb(C ₂ H ₃ O ₂) ₂ 3.1	Explodes on grinding. See Pb(BrO ₃) ₂ , 2.4 [8,9]
Ca(ClO ₂) ₂ -starch- -NaHSO ₄ -Na ₂ CO ₃ 3.2	Incandescence and explosion on impact [9]
Ca(ClO ₂) ₂ -NH ₄ Cl 3.3	Explosion with formation of NCl ₃ , reported [9]
Cu(ClO ₂) ₂ -KClO ₂ 3.4	Explodes on percussion [37]
NaClO ₂ -H ₂ C ₂ O ₄ 3.5	Explodes on contact with water [9]
All chlorates- -all ammonium salts 3.6	Spontaneously explosive due to formation of NH ₄ ClO ₃ . NH ₄ NO ₃ -NaClO ₃ explodes after 11 h contact at 45°C (113°F), 45 min at 70°C (158°F) [9]
All chlorates- -all cyanides and thiocyanates 3.7	Violent oxidation [9]
KClO ₃ -MnO ₂ -KOH 3.8	Explosive above 80-90°C (176-194°F), and pressures of >19 kbar [9]
KClO ₃ -(NH ₄) ₂ SO ₄ 3.9	Decomposes with incandescence on heating [9]
KClO ₃ -sugar, sulfur, bromides, or phosphorus 3.10	Used in amateur fireworks. Such mixtures are prohibited in Great Britain [9]
Mg(ClO ₃) ₂ -CuS 3.11	Explodes on contact. This is also true of Zn(ClO ₃) ₂ -CuS and Cd(ClO ₃) ₂ -CuS [9]
NaClO ₃ -MS 3.12	MS = metal sulfide. Readily ignitable and potentially explosive [9]
KClO ₄ -CaH ₂ 3.13	Violent explosion [9]
KClO ₄ -CaS 3.14	Explosion [9]
KMnO ₄ -NH ₄ NO ₃ 3.15	Delayed explosion [9]
KNO ₃ -As ₄ S ₄ 3.16	As ₄ S ₄ = realgar. This mixture has been known at least since the Middle Ages as "Greek Fire". Detonates [9,76]

Mixture	Comments and references
KNO_3 -C-S, KNO_3 -nonmetals 3.17	When the carbon is in the form of powdered charcoal, this is gunpowder. KNO_3 forms a dangerously combustible material with carbon alone. The mixture explodes on heating. Mixtures of KNO_3 with nonmetals are generally explosive [9]
KNO_3 -acetates, NaNO_3 -acetates 3.18	May explode. Equal parts of sodium acetate and KNO_3 , or NaNO_3 explode violently on heating [9,21]
KNO_3 -sulfides 3.19	BaS , CsS , GeS , MoS_2 , Sb_2S_3 or TiS_2 mixtures with KNO_3 explode on heating. The CaS mixture explodes violently [9]
NaNO_3 - $\text{Ba}(\text{CNO})_2$ 3.20	Explodes. All cyanates are oxidized violently by fused nitrates [9, 79]
NaNO_3 -C-S 3.21	Black powder. Contact of carbon with molten NaNO_3 causes vigorous reaction, may explode [9,34,79]
NaNO_3 -cyanides 3.22	Common cause of salt bath explosions. The cyanides are introduced into the bath with heat-treated metals [9,34,79]
NaNO_3 - $\text{Na}_2\text{S}_2\text{O}_3$, KNO_3 - $\text{Na}_2\text{S}_2\text{O}_3$ 3.23	Explodes [9]
NH_4NO_3 - KNO_2 3.24	Contact causes incandescence. See also NH_4NO_3 - NaNO_2 [9]
NH_4NO_3 - NaNO_2 3.25	Nitrite salts react with ammonium salts even in the solid state to form NH_4NO_2 , which explodes. Accidental contact of traces of these salts generates enough heat to ignite wood [9,34]
$\text{Pb}(\text{NO}_3)_2$ - $\text{KC}_2\text{H}_3\text{O}_2$ 3.26	Explodes violently on heating [9,21]
$\text{Zn}(\text{NO}_3)_2$ -C 3.27	Explodes on heating [9]
KNO_2 - KNH_2 , NaNO_2 - NaNH_2 3.27,3.28	Vigorous explosion, gas evolution [9]
KNO_2 - $(\text{NH}_4)_2\text{SO}_4$ 3.29	Effervescence and ignition [9]
NaNO_2 -cyanides 3.30	Mixtures of NaNO_2 with various cyanides, including KCN , $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{Hg}(\text{CN})_2$, explode on heating [9]
NaNO_2 - NaCNO 3.31	Explodes on heating [9]
NaNO_2 - NaNO_3 - Na_2S 3.32	Accidental mixing of these three molten salts caused a violent explosion [181]
NaNO_2 - $\text{Na}_2\text{S}_2\text{O}_3$ 3.33	Explodes on heating [7]
Cr_2O_3 - $\text{K}_3\text{Fe}(\text{CN})_6$ 3.34	Inflames above 196°C. Friction may ignite mixture [9]
MnO_2 - KN , 3.35	Violent reaction [9]
PbO_2 -sulfides 3.36	Reaction of PbO_2 with CaS , BaS , SrS is vigorous [9]
Na_2S -C-(O_2) 3.37	Carbon ground with Na_2S reacts exothermically, probably by mutual catalysis of air oxidation [9]
Na_2S_4 - TaC 3.38	Explodes [56]
$\text{K}_2\text{S}_2\text{O}_8$ - KOH 3.39	Two flakes of KOH can render $\text{K}_2\text{S}_2\text{O}_8$ pyrophoric. The vigorous, self-sustaining fire cannot be extinguished with CO_2 , but it can be flooded if cognizance is taken of the fact that the persulfate liberates O_2 when wet [2,9]

TABLE 4

Potentially hazardous metal—salt mixtures; a partial list of reported cases where a metal in contact with a salt led to an explosion or a very vigorous reaction. References: [3,4,9, 34,76,77,79]

Metal	Salt
Aluminum 4.1	CuO; Fe ₂ O ₃ ; NH ₄ NO ₃ , Na ₂ CO ₃ , other nitrates; nitrate—nitrite mixture; KClO ₃
Bismuth 4.2	NH ₄ NO ₃
Calcium 4.3	NH ₄ NO ₃ ; NaNO ₃ ; PbCl ₂
Cadmium 4.4	NH ₄ NO ₃
Chromium 4.5	KClO ₃ ; NH ₄ NO ₃
Cobalt 4.6	NH ₄ NO ₃
Copper; brass 4.7	KClO ₃ ; NH ₄ NO ₃
Iron; stainless steel 4.8	NH ₄ NO ₃ , nitrate—nitrite mixture
Germanium 4.9	KClO ₃
Indium 4.10	HgBr ₂
Potassium 4.11	Bi ₂ O ₃ ; CuBr ₂ ; FeBr ₂ ; FeBr ₃ ; FeI ₃ ; HgO; Hg ₂ O; KO ₂ ; MoO ₃ ; NH ₄ Br; NH ₄ I; NH ₄ NO ₃ ; (NH ₄) ₂ SO ₄ ; PbO ₂ ; PbSO ₄ ; transition metal halides
Magnesium 4.12	BeF ₂ ; metal cyanides; oxides; oxosalts; sulfides; KClO ₃ ; KClO ₄ ; NH ₄ NO ₃ ; NaNO ₃ ; nitrate—nitrite mixture; PbO ₂ ; K ₂ CO ₃ ; SiO ₂
Sodium 4.13	CoBr ₂ ; FeBr ₂ ; FeI ₃ ; NaNO ₃ ; many halides; many oxides; NH ₄ NO ₃
Nickel 4.14	NH ₄ NO ₃ ; nitrate—nitrite mixture
Molybdenum 4.15	PbO ₂
Lead 4.16	NH ₄ NO ₃ ; nitrate—nitrite mixture
Antimony 4.17	NaNO ₃ ; NH ₄ NO ₃
Tin 4.18	NH ₄ NO ₃
Titanium 4.19	KClO ₃
Zinc 4.20	KClO ₃ , MnCl ₂ ; NH ₄ NO ₃ ; nitrate—nitrite mixture
Zirconium 4.21	KClO ₃ ; nitrate—nitrite mixtures

TABLE 5

Precautions

Hazard: Steam explosion.

Comment: The most common cause of a steam explosion in molten salt applications is the accidental introduction of water from the quench tank used in the heat treatment of metals in nitrate baths. Other sources of water include "carry-over" from a previous cleaning step; condensation from overhead service piping; leaky roofs, contact with liquid foods placed on ledges near a salt bath; fresh salt added to replace "drag-out" and the asbestos board used in heat shielding.

Avoidance of water pipes, steam pipes, etc. is an obvious precaution. Buckets of sand should be provided as fire extinguishers for small fires. Precautions and Hazards placards should be used.

References: [3,4,34,79]

Locator Number: 5.1.

Hazard: Trapped gas.

Comment: Where hollow objects are to be introduced into a molten salt bath, care must be taken in the design of the articles and in their method of immersion that trapped air can escape without explosive expansion.

References: [34,79]

Locator Number: 5.2.

Hazard: Addition of carbon containing materials to nitrate melts.

Comment: Oil, grease, cotton-waste, rags, sacking, paper, wood, clothing, food and graphite must be rigorously excluded from nitrate baths. The importance of close supervision and care in this matter cannot be overemphasized, as workmen cannot be expected to recognize carbon-containing compounds. A serious explosion was reported when a workman added case-hardening salt (largely cyanide) to a nitrate bath.

Heating of salt baths with solid-fueled furnaces is rare. It must be emphasized that the reaction between molten nitrates and red hot solid fuel would probably be catastrophic in violence. Even with gas or oil-fired plants, flues may become soot-laden and hazardous.

References: [3,4,9,34,77,79]

Locator Number: 5.3.

Hazard: Reaction between salt-melts and reactive metals.

Comment: A list of potentially hazardous metal-salt combinations is given in Table 4. It is generally accepted that alloys containing more than 3% magnesium should not be treated in nitrate baths at temperatures of 500° C or more. Similarly, aluminum articles must not be treated in nitrate baths over 600° C.

References: [3,4,34,77,79]

Locator Number: 5.4.

Hazard: Spattering, fire.

Comment: Ordinary fire-fighting techniques and protective clothing should suffice for fires associated with carbonate and chloride melts if care is taken to avoid steam explosions. For fluoride melts, see BeF_2 ; 2.43. However, neither water, foam, nor vaporizing liquid should be used to fight fires involving molten nitrates. Dry clean sand appears to be the most suitable fire-fighting material. To reduce the fire risk associated with splashing, fire-proof materials should be used for construction. Wood should not be used as a construction material in the vicinity of a nitrate bath. Fresh salt (and waste

TABLE 5 (cont'd)

salt) should be stored in fire-proof containers.

References: [3,4,34,79]

Locator Number: 5.5.

Hazard: Overheating; structural failure.

Comment: When salt baths can decompose on overheating to yield a toxic gas (e.g., sulfates, nitrates, carbonates, oxyhalogen salts) fume hoods must be used. When a salt can decompose explosively on overheating (e.g., nitrates) adequate protection and training for personnel must be provided. Precautions and Hazards placards should be used.

The use of fully automatic temperature controllers is recommended.

Sludge must not be allowed to accumulate. Nitrate baths used in heat-treating metals must be emptied, cleaned and thoroughly inspected periodically.

If an "idle" salt bath is to be kept molten, reduction of the temperature to a little above the melting point is recommended.

When a solidified bath is remelted, allowance must be made so that thermal expansion of the salt does not place undue stress on the container.

References: [3,4,5,6,34,35,76,79]

Locator Number: 5.6.

Hazard: Storage, disposal, handling.

Comment: Except for those dangers involved in handling hot liquids and reactive chemicals generally, storage, disposal and handling hazards in molten salt applications are primarily those associated with fluorides, NaNO_3 , and waste nitrate salts.

For fluorides, see: BeF_2 , 2.43.

Nitrates should be stored in non-combustible bins and non-combustible materials should be used in the construction of storage buildings. Warning placards (for firemen) are advisable. A program of good housekeeping greatly reduces the hazards of nitrate storage. Waste disposal should be made by properly trained personnel.

Protective clothing: head cover with face visor, asbestos apron, asbestos gloves (high temperature applications); safety glasses (all other).

References: [2,3,4,9,34,79,80,81]

Locator Number: 5.7.

Hazard: Reactive chemical hazard.

Comment: The term "reactive chemical hazard" refers to those compounds and mixtures which may release energy too rapidly to be dissipated by the environment. Careful control of the reaction environment may permit safe handling of such materials. Attention must be paid to the following:

- (i) Proportions of materials used.
- (ii) Purity. Impurities may render reactive materials liable to spontaneous explosion.
- (iii) Rates of addition, heating and cooling.
- (iv) Degree of agitation.
- (v) Reaction pressures, avoidance of friction or shock.
- (vi) Shielding (heat or radiation).

Knowledge of the types of materials and mixtures which may be expected to decompose with explosive violence will help avoid many accidents. In general, if ΔH_f is greater than 0.7 cal/g, the material should be treated as potentially explosive.

Tomlinson and Audreith list precautions to be taken in dealing with reactive chemical hazards. Among these are:

- (1) Avoid the use of open flames.
- (2) Avoid direct applications of electrical energy, electrostatic or that due to live circuits.
- (3) Avoid application of energy deriving from the impact of two hard surfaces,

especially when the contact area is small. The force involved, when considered as localized, may be considerable. Glass-stoppered bottles and fritted glass funnels should not be used.

(4) Protective equipment must be used when applicable. Barricades, goggles, face masks, asbestos gloves, and gas masks should be available.

(5) The dangers of static electricity may be reduced by (a) minimum use of wool clothing; (b) wearing safety shoes; (c) use of conductive flooring; and (d) adequate grounding of containers used to store and transfer ignitable materials.

(6) Adequate fire prevention measures augmented by drills and inspections must be placed in effect.

It is recommended that information on reactive chemical hazards be given to those who receive, store, use, dispose of, dispense or transport such materials, and that all such operations be carried out by trained personnel.

References: [2,3,4,9,16,17,18,19,20,100]

Locator Number: 5.8.

Hazard: Toxic compounds.

Comment: It should be observed that all chemical compounds are toxic in some degree or under some circumstances. Common sense suggests that in working with inorganic salts, the skin and eyes should be protected. The compounds designated as "toxic" in Table 2 are those of barium, beryllium, bismuth, cadmium, lead, mercury, silver, thallium, and vanadium; azides, cyanides, chromates, dichromates and fluorides, and salts containing arsenic, antimony, selenium, and tellurium. Salts known to be poisonous (e.g., $\text{Cu}(\text{NO}_3)_2$) are also listed as toxic. Materials which produce abrasive or caustic dusts are listed as handling hazards. Salts of lithium and cobalt are biologically active, and care must be taken to avoid their ingestion. If a salt listed as toxic in Table 2 is ingested, the exposed person should be taken to a physician.

References: [2,3,10,11,12,15]

Locator Number: 5.9.

TABLE 6

Applications in process design and technology, exclusive of metal extractive electrolyses, metallurgical slags, single crystal growth, and related technologies

Application: Corrosion prevention, alloy coatings.

Comment: Alloy coating, called "metalliding", is carried out in a molten fluoride bath.

Coatings of approximately fifty metals and metalloids can be produced on most metals. In this process the molten salt functions both as a solvent for the alloy metals and the oxide films on the metal surfaces, and as the electrolyte. Specific alloys include: Be-Ti, Cu-Ti, boron alloys with ~ 30 elements; Si, Al, Sc, Zr, Cr, rare earth, Ni, and Ge alloys. The fluoride mixtures used include LiF-NaF-KF , LiF-NaF-CaF_2 , and Na_2BeF_4 .

References: [33,99]

Locator Number: 6.1.

Application: Siliconizing steel.

Comment: The classical gaseous process for siliconizing steel produces an uneven coating, the surface of the steel being corroded by excess chlorine. This problem has been solved through electrolysis of Na_2SiO_3 melts. An even more promising mixture is molten $\text{Na}_2\text{SiO}_3\text{-NaCl}$. The NaCl functions both as an electrolyte and to lower the siliconizing temperature.

References: [39,40,41]

Locator Number: 6.2.

TABLE 6 (cont'd)

Application: Ore enrichment.

Comment: In the reaction of SO_2 and air with ilmenite (FeTiO_3) suspended in molten $\text{NaCl}-\text{FeCl}_3$, the iron constituent of the ore is selectively dissolved. The titanium portion is not attacked and can be recovered in its original particle size.

Reference: [28]

Locator Number: 6.3.

Application: Reactor technology.

Comment: Molten salts are used as fuel solvents for liquid-fueled reactors (molten salt reactors), and also as coolant and flush fluids. Several basic problems, mainly in corrosion and containment, remain to be overcome.

A recent publication describes the use of a molten lithium halide mixture as a solvent extractant to remove tritium from liquid lithium fusion blankets.

High-purity metals, e.g. Th and Cs, used in reactor applications are prepared by the electrolysis of their fused halides. A continuous-feed method whereby uranium oxide is introduced into an electrolytic cell containing a fused mixture of uranium fluoride has been explored. As the uranium metal is formed, it collects in a liquid pool about the cathode at the bottom of the cell.

A method for Li-6 enrichment by countercurrent electromigration in molten

$\text{LiNO}_3-\text{NH}_4\text{NO}_3$ has been described.

References: [31,32,42,43,187-193]

Locator Number: 6.4.

Application: Space technology.

Comment: A system based on the continuous electrolysis of molten Li_2CO_3 has been proposed for closed circuit respiratory systems. The electrolysis produces breathable O_2 while the electrolyte absorbs CO_2 .

Reference: [75]

Locator Number: 6.5.

Application: Thermal energy storage.

Comment: Desired properties for phase change materials in thermal energy storage are (1) high heat of fusion; (2) low melting point; (3) absence of corrosion, toxicity and supercooling problems; and (4) low bulk and cost. It appears that all requirements can be met with molten salt hydrates and/or their eutectic mixtures. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ has already been used for solar energy storage.

References: [44,64,65,66,67,69,70,71,73,84,88,92,101,102,168,194,195]

Locator Number: 6.6.

Application: Waste disposal.

Comment: In the molten salt disposal processes, advantage is taken of the rapid reaction rates in molten salt media (usually carbonates).

References: [24,87]

Locator Number: 6.7.

Application: Atmospheric pollution control (sulfur oxides).

Comment: In the carbonate process, a molten eutectic mixture of Li_2CO_3 , Na_2CO_3 , and K_2CO_3 removes sulfur oxides from power plant stack gases. The resulting solution of sulfates, sulfides and unreacted carbonates is recycled. A similar process has been proposed for reducing atmospheric pollution by fossil-fuel power plants.

References: [72,74,86]

Locator Number: 6.8.

Application: Disposal of high explosives and propellants.

Comment: After a specified storage period, explosives are destroyed since unpredictable characteristics may develop during long storage. Pollutants such as smoke, nitrogen oxides, HCl, etc., are given off in the combustion process. In addition, dust clouds may be formed from detonation.

Molten carbonates (e.g. Na_2CO_3 - K_2CO_3) are used as absorbents for the acidic, gaseous pollutants. In addition, since the molten carbonates have a moderately high thermal conductivity, they act as heat sinks so that detonation does not take place during burning.

Reference: [22]

Locator Number: 6.9.

Application: Scrap tire pyrolysis.

Comment: Pieces of scrap tire immersed in a eutectic mixture of LiCl-KCl yielded oil, residue and gas. The oil consisted of aromatic, olefinic and paraffinic hydrocarbons. The gas was a mixture of C_1 to C_4 paraffins and olefins. The residue resembled carbon black. It is possible to alter the products of this pyrolysis by changing either the physical or the chemical conditions.

Reference: [52]

Locator Number: 6.10.

Application: Wire stripping.

Comment: Organic coatings, used extensively for electrical insulation and wire coating, create a problem when the insulation must be removed without damaging the wire ends. To overcome this, a new stripping process was developed, originally for copper-clad aluminum magnet wire. It consists in immersing the wire to be stripped in a fused salt bath. The insulation reacts chemically and is completely removed.

References: [23,45]

Locator Number: 6.11.

Application: Heat-treating; heat transfer fluids.

Comment: Molten nitrate baths have been used in the heat-treatment of metals for over fifty years. The large-scale use of molten salts as heat transfer fluids began in 1937 with the development of the Houdry units for the catalytic cracking of petroleum. The salt used, called "HTS", is a mixture of 40% NaNO_2 , 7% NaNO_3 and 53% KNO_3 by weight.

Molten nitrates are used in the temperature range 150–550°C (300–1000°F).

Above this range, chlorides may be used.

References: [39,41,45,56,78]

Locator Number: 6.12.

Application: High-output batteries ("super-batteries").

Comment: Ref. [53] is a recent state-of-the-art review of high temperature batteries with emphasis on the Li/S and Na/S cells. Ref. [48] is a bibliography on the sodium-sulfur battery.

An experimental aluminum-sulfur cell using a molten NaCl-KCl-AlCl_3 electrolyte has been described.

It is expected that these high-energy devices will be used mainly as batteries for electric vehicles and load-level storage systems for electric utilities. See especially reference [68].

References: [47–50,53,59,61,62,63,68,82,89,90,91,93,95,96,98,105–123,180,186]

Locator Number: 6.13.

Application: Molten salt fuel cells.

Comment: The process on which molten salt fuel cells are based consists of the thermal

TABLE 6 (cont'd.)

cracking of hydrocarbons in a carbonate melt with the resulting hydrogen functioning as the anode fuel. The oxidant is either air or CO_2 . The molten carbonate also serves as the electrolyte.

References: [47,54,55,184,185]

Locator Number: 6.14.

Application: Thermal batteries.

Comment: Thermal batteries are reserve-type primary batteries activated by heating.

They contain a solid electrolyte which is essentially non-conducting until the temperature is raised sufficiently to melt it. These cells are used where high currents are required for short periods of time, possibly after years of inactive waiting. Although in theory, almost any molten salt electrolyte could be used, in practice most work has been done with the LiCl-KCl eutectic. The cells are mainly used in military and aerospace applications.

References: [47,57,58,94,103,104]

Locator Number: 6.15.

Application: Catalysis, organic synthesis.

Comment: Molten salts as solvent media for organic reactions are highly promising in that the medium can be "tailored" to fit a specific reaction. Thus, Friedel-Craft reactions can be carried out in molten SbCl_3 , in mixtures of alkali chlorides and in NaCl-AlCl_3 melts.

In an industrial process developed during the Second World War, molten salt and gas in direct contact passing countercurrent to each other proved successful in controlling the highly exothermic reactions involved in the condensation of acetylene to aromatic hydrocarbons. The molten salts used were mixtures of NaCl-KCl-CdCl_2 , and NaCl-KCl-ZnCl_2 .

A process has been developed for the chlorination of methane and other light paraffins by means of a continuous multistage process in $\text{KCl-Cu}_2\text{Cl}_2\text{-CuCl}_2$ melts.

Other reactions which have been successfully carried out in salt melts include fluorination (in KF-NaF-LiF , $\text{KF-ZnCl}_2\text{-KCl}$ and $\text{CuF}_2\text{-ZnCl}_2\text{-KCl}$ melts, the choice of melt depending on the desired temperature), the preparation of silanes (in a molten azide eutectic), dehydration of alcohols, hydrochlorination, and exchange reactions. Reference [51] is a review of this field.

References: [27,29,30,51,83,124]

Locator Number: 6.16.

Application: Coal gasification.

Comment: In coal gasification using a molten salt process, the salt can be used as a heat transfer fluid as well as the catalytic material for the endothermic carbon-steam reaction. The product gas, after purification, can be used as a synthesis gas, for hydrogen production, or converted into synthetic natural gas for pipeline use. Reference [85] gives an overview of coal gasification with respect to national energy needs.

References: [25,26,85,97]

Locator Number: 6.17.

Application: Corrosion prevention, electroplating.

Comment: Reference [60] compares the character of coatings deposited electrolytically from molten salts (chlorides and fluorides) with those obtained by electroplating from aqueous solution, and hot plating. The molten salt method gives a better binding between the base and the deposited metal.

Reference: [60]

Locator Number: 6.18.

TABLE 7

Water in melts

System: $\text{LiNO}_3\text{--KNO}_3$ eutectic.

Experimental technique: Polarography.

Comment: System was found to obey Henry's Law 240–330°C. Below 200°C, the saturation of the melt with water vapor proceeded very slowly.

Reference: [125]

Locator Number: 7.1.

System: $\text{LiNO}_3\text{--KNO}_3$, $\text{LiNO}_3\text{--NaNO}_3$.

Experimental technique: Thermogravimetry.

Comment: Temperature range: 230–280°C. Pressure: up to 30 torr. The dissolution is reversible, i.e., no hydrolysis occurs. Henry's Law is obeyed.

Reference: [127]

Locator Number: 7.2.

System: LiCl--KCl .

Experimental technique: Polarography.

Comment: The solubility follows Henry's Law to 18 mm at 480°C, to about 14 mm at 390°C.

Reference: [129]

Locator Number: 7.3.

System: LiClO_3 .

Experimental technique: Gas chromatography.

Comment: The specific conductance, density, viscosity and surface tension of LiClO_3 melts containing up to 0.24 mol fraction water were determined. These properties prove to be strongly dependent on the water concentration, especially the viscosity.

References: [148,149]

Locator Number: 7.4.

Systems: $\text{LiNO}_3\text{--KNO}_3\text{--NaNO}_3$, LiClO_4 , $\text{NaNO}_3\text{--KNO}_3$.

Experimental technique: Equilibrium study.

Comment: The solubility of water in the binary nitrate system is too small to be measured by this technique. The corresponding binary and ternary perchlorate systems decompose. In all cases, at every concentration and in temperature studies, the solubility of water vapor in the melt was found to be a linear function of the pressure (Henry's Law is obeyed).

Reference: [130]

Locator Number: 7.5.

Systems: Chlorides.

Technique: Theoretical (thermodynamics).

Comment: Metal-molten chloride systems were considered with reference to the effect of trace amounts of water on corrosion properties.

For studies of the effect of water in salt melts on corrosion characteristics, see references [153–167].

Reference: [131]

Locator Number: 7.6.

Systems: KNO_3 , LiNO_3 , NaNO_3 .

Experimental technique: Polarography.

TABLE 7 (cont'd.)

Comment: The solubility of water in these salts was observed to follow Henry's Law.

Temperature range: ~ 275 – 340°C .

Reference: [136]

Locator Number: 7.7.

Systems: Fluorides.

Experimental technique: Electroanalytical.

Comment: Anodic overvoltages on nickel electrodes in molten NiF_2 – KF , LiF – NaF – KF , NaF – KF and LiF – KF eutectic mixtures were carried out by means of the galvanostatic, potentiostatic and potential sweep methods at temperatures ranging from 450 to 800°C . Residual water was determined.

Reference: [137]

Locator Number: 7.8.

System: KCl – LiCl .

Experimental Techniques: polarography and chemical techniques.

Comment: The OH^- content of melted, HCl treated, vacuum-dried salt was found to be equivalent to 1.0 ml $N/400$ "acid" per 100 g salt.

Reference: [138]

Locator Number: 7.9.

Systems: Alkali nitrates, nitrites.

Experimental technique: Potentiodynamic.

Comment: The electrochemical oxidation of either NO_3^- or NO_2^- melts in the presence of water yields hydrogen ions.

Reference: [139]

Locator Number: 7.10.

Systems: Nitrates.

Experimental technique: Cryometry.

Comment: The data suggest the solubility of water in nitrate melts occurs interstitially.

Reference: [132]

Locator Number: 7.11.

System: NH_4NO_3 .

Experimental technique: Cryometry.

Comment: Water behaves ideally in this molten salt. The vapor pressure is very low.

Reference: [133]

Locator Number: 7.12.

System: NaCl – KCl .

Experimental technique: Potentiometry.

Comment: Redox potentials in NaCl – KCl melts are not governed by the water activity, but depend on hydrogen and oxide ion concentrations and H_2 and O_2 activities. A rough value for the water activity at 700°C can be calculated from electrochemical data, viz., 10^{-4} , equivalent to a partial pressure of water vapor of approximately 70 microns.

Reference: [134]

Locator Number: 7.13.

System: LiCl – KCl eutectic, LiCl – KCl – NaCl .

Experimental technique: Polarography.

Comments: Drying study. Ordinary dry salt flushed with pure argon contains 3×10^{-4} mol % H_2O at 740°C .

Reference: [135]

Locator Number: 7.14.

Systems: Oxides.

Experimental technique: Viscosity study.

Comment: Dissolved water appreciably lowers viscosity in the molten systems CaO, Al_2O_3 , SiO_2 , Na_2O , B_2O_3 and $\text{PbO}-\text{B}_2\text{O}_3$. The effect decreases with increasing temperature. The dissolved water also lowers the melting points of these melts.

Reference: [140]

Locator Number: 7.15.

System: $\text{VO}_2-\text{V}_2\text{O}_5$.

Experimental technique: Gas transpiration.

Comment: Temperature range: 900–1099°C. The enhancement of melt volatility in the presence of water vapor was measured as a function of water vapor pressure, melt composition and temperature by admixing water vapor at 148, 259 and 456 torr with equilibrating O_2 -Ar mixture.

Reference: [141]

Locator Number: 7.16.

System: $\text{LiNO}_3-\text{KNO}_3$.

Experimental technique: Gas transpiration.

Comment: Temperature range: 383.15–422.66K. System obeys Henry's Law. Results for D_2O also given.

Reference: [142,179]

Locator Number: 7.17.

System: $\text{KNO}_3-\text{NaNO}_3$ eutectic.

Experimental technique: Voltammetry.

Comment: The water solubility in the $\text{NaNO}_3\text{KNO}_3$ eutectic melt was determined by rotating disc electrode voltammetry. The current/concentration calibration curve was found to be slightly non-linear.

Reference: [143]

Locator Number: 7.18.

System: $\text{LiCl}-\text{KCl}-\text{CaCl}_2$.

Experimental technique: Chronopotentiometry.

Comment: The water vapor pressure was varied in the range 0–22.5 torr. Under highly dehydrated conditions, a single wave was found at -1.18 V. However, in a moist melt, two reduction waves were found, at -0.6 V and -1.18 V, resp.

Temperature: $450 \pm 1^\circ\text{C}$.

Reference: [144]

Locator Number: 7.19.

System: $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$.

Experimental technique: Polarography.

Comment: The water dissolved in this melt is in the form of hydrogen ions.

Reference: [145]

Locator Number: 7.20.

System: $\text{Ca}(\text{NO}_3)_2$.

Experimental technique: NMR.

Comment: Diffusion study.

References: [147,182]

TABLE 7 (cont'd.)

 Locator Number: 7.21.

System: LiCl—KCl.

Experimental technique: Tight containment shock tube.

Comment: Study of energy effects when two liquids, one substantially above the boiling point of the other are brought into sudden contact.

Reference: [14]

Locator Number: 7.22.

System: Inorganic salts.

Experimental technique: Drying studies.

Comment: Water can be quantitatively removed from most melts by evacuation at high temperature. Some salts, e.g. LiCl, ZnCl₂, retain water even as high as 1000°C. When salts are heated under vacuum, the rate at which water is lost generally decreases sharply when the salt melts.

Present practice for eliminating water from fused salts is as follows:

(i) The salt is purified, and as much water as possible removed by conventional methods.

(ii) The salt is then dried under a stream of hydrogen halide or other reactive gas while slowly raising the temperature to just above the melting point. The reactive gas functions to restore hydrolysis products.

(iii) The last remaining traces of reactive gas are then removed by bubbling an inert gas through the melt.

References: [103,128,146,150,151,152]

Locator Number: 7.23.

TABLE 8

Water solubility data

The solubility constant, K , is defined as the reciprocal of the Henry's Law Constant, k , and (unless otherwise noted) is expressed in units of:

$$(\text{conc'n})_{\text{H}_2\text{O}}/(\text{pressure})$$

where solubilities are expressed on the Mol Fraction concentration scale and pressures on the mmHg scale. (1 mmHg = 1 torr = $(1.013 \times 10^5/760)$ Pascals).For the Henry's Law concentration range, the mole fraction of dissolved water is (n_2/n_1) where n_2 = moles of (dissolved) water, and n_1 = moles of solvent (molten salt system).

A: Single salts

	LiNO ₃ (8.1)						
$t(^{\circ}\text{C})$	265	268	275	295	310	335	
10^3K	0.232	0.165	0.161	0.11	0.087	0.059	
Ref.	127	127	136	136	136	136	
	NaNO ₃ (8.2)			KNO ₃ (8.3)			
$t(^{\circ}\text{C})$	310	333	342	337			
10^3K	0.022	0.017	0.015	0.02			
Ref.	136	163	136	136			

	LiNO₃ (8.4)	KNO₃ (8.5)	NaNO₃ (8.6)	CsNO₃ (8.7)				
<i>t</i> (°C)	257	335	307	406				
10 ³ <i>n</i> ₂	(1.3)	0.39	1.41	0.92				
Ref.	132	132	132	132				
	LiClO₄ (8.8)							
<i>t</i> (°C)	240	260	290					
10 ³ <i>K</i>	0.055	0.029	0.002					
Ref.	130	130	130					
B: Molten mixtures								
	LiCl—KCl (8.9)							
mol % (LiCl)	50	50	53	60	60	60	68.6	
<i>t</i> (°C)	390	480	480	390	480	480	480	
10 ³ <i>K</i>	0.030	0.014	0.012	0.030	0.011	0.011	0.011	
Ref.	129	129	129	129	129	129	129	
	LiNO₃—NaNO₃ (8.10)							
mol % (LiNO ₃)	75	75	75	50	50	50	25	25
<i>t</i> (°C)	230	265	280	230	265	280	265	280
10 ³ <i>K</i>	0.354	0.165	0.118	0.242	0.110	0.081	0.084	0.064
Ref.	127	127	127	127	127	127	127	127
	LiNO₃—KNO₃ (8.11)							
mol % (LiNO ₃)	75	75	50	50	25	25		
<i>t</i> (°C)	230	265	230	265	230	265		
10 ³ <i>K</i>	0.278	0.137	0.162	0.082	0.099	0.054		
Ref.	127	127	127	127	127	127		
	LiNO₃—KNO₃ eutectic (8.12)							
mol % (KNO ₃)	59	59	59	59	59	59		
<i>t</i> (°C)	147	158	170	170	180	190		
10 ³ <i>n</i> ₂	11.2	13.5	15.0	15.0	15.5	16.1		
Ref.	125	125	125	125	125	125		
	NaNO₃—KNO₃ eutectic (8.13)							
mol % (KNO ₃)	50	50	50	50	50	50	50	50
<i>t</i> (°C)	227	230	241	254	264	274	283	294
10 ³ <i>K</i>	0.089	0.082	0.070	0.057	0.048	0.042	0.037	0.032
Ref.	143	143	143	143	143	134	143	143
	CsNO₃—Ba(NO₃)₂ (8.14)				KNO₃—Ba(NO₃)₂ (8.15)			
mol % (Ba(NO ₃) ₂)	4.33				0.94			
<i>t</i> (°C)	391				332			
10 ³ <i>n</i> ₂	0.63				0.60			
Ref.	132				132			

TABLE 8 (cont'd)

KNO ₃ -K ₂ Cr ₂ O ₇ (8.16)		NaNO ₃ -Ca(NO ₃) ₂ (8.17)	
mol % (KNO ₃)	98.1	mol % (NaNO ₃)	95.98
t(°C)	329		299
10 ³ n ₂	0.60		2.0
Ref.	132		132

LiNO₃(30%)-NaNO₃(23%)-KNO₃(47%) (8.18)

t(°C)	145	170	175	205
10 ³ K	0.024	0.013	0.009	0.003
Ref.	130	130	130	130

LiNO₃-NaNO₃-KNO₃ (8.19)

mol % (LiNO ₃)	mol % (NaNO ₃)	mol % (KNO ₃)	t(°C)	10 ³ K	Ref.
12.5	46.4	41.1	240	0.011	130
24.8	39.9	35.3	240	0.002	130
30.0	37.1	32.9	240	0.002 ₅	130
46.7	28.2	25.1	240	0.010	130
67.0	17.5	15.5	240	0.027	130
86.9	6.9	6.2	240	0.050	130

Molten silicates (8.20)

Silicate	t(°C)	10 ³ K	Ref.
SiO ₂	1000-2000	0.63	169
	1000	0.72	170
	1100-1200	11.4	171
	1400	21.0	126
68-75% SiO ₂ (albite, pegmatite, granite)	900-1200	22.4	172
	900-1000	14.5	173
	660-870	17.6	174
	1200-1300	17.7	173
	1000-1200	13.8	173
50-60% SiO ₂ (andesite, basalt, shale)	900-1000	10.3	173
	1100	15.1	176
	1000-1200	13.1	177
	1400-1600	21.0	126
	1370-1550	10.0	178
40% SiO ₂ (slags)			

Systems index

Ag	Ag 5.9; AgClO ₂ 2.17; AgF 2.42; AgN ₃ 2.49; AgNO ₃ 2.57; Ag ₂ O 2.68; Ag(ONC) ₂ 2.79;
Al	Al 1.1, 2.61, 4.1; AlBr ₃ 2.12; Al[C ₂ H ₃ O ₂] ₃ 2.6; AlCl ₃ 2.12, 6.13, 6.16; Al ₂ O ₃ 2.67, 7.15;
As	As 5.9; As ₂ S ₄ 3.16;
Au	AuCl ₃ 2.13; Au ₂ S ₃ 2.68;

- B** B_2O_3 7.15;
- Ba** Ba 5.9; Ba[BrO₃]₂ 2.2; Ba[ClO₂]₂ 2.18; Ba[CNO]₂ 3.20; Ba[NO₃]₂ 2.58, 8.14, 8.15; BaO 2.72; BaO₂ 2.72; BaS 2.80, 3.19, 3.36;
- Be** Be 2.43, 5.9; Be[ClO₄]₂ 2.32; BeF₂ 2.43, 4.12;
- Bi** Bi 4.2, 5.9; Bi₂O₃ 4.11;
- C** C 3.17, 3.21, 3.27, 3.37;
- Ca** Ca 4.3; CaCl₂ 7.19; Ca[ClO]₂ 2.16, 3.2, 3.3; Ca[ClO₂]₂ 2.19; CaCO₃ 2.10; CaF₂ 6.1; CaH₂ 3.13; Ca[NO₃]₂ 2.59, 7.21, 8.17; CaO 7.15; CaO₂ 2.73; CaS 2.80, 3.14, 3.19, 3.36; CaS₂O₈ 2.82;
- Cd** Cd 4.4, 5.9; CdCl₂ 6.16; Cd[ClO₃]₂ 3.11; Cd[ONC]₂ 2.79; CdSe 2.85;
- Ce** Ce₂S₃ 2.81;
- Co** Co 4.6, 5.9; CoBr₂ 4.13; Co[NH₃]₆ [ClO₃]₃ 2.28;
- Cr** Cr 4.5; Cr[C₂H₃O₂]₃ 2.7; CrO₃ 3.34;
- Cs** CsNO₃ 8.7, 8.14; Cs₂O 2.69; CsS 3.19; Cs₂Se 2.86;
- Cu** Cu 4.7; CuBr₂ 4.11; CuC₂O₄ 2.8; CuCl₂ 6.16; Cu₂Cl₂ 6.16; Cu[ClO₂]₂ 2.20, 3.4; CuF₂ 6.16; Cu[NO₃]₂ 2.60, 5.9; CuO 4.1; Cu[ONC]₂ 2.79; CuS 3.11;
- Fe** Fe 4.8; FeBr₂ 4.11, 4.13; FeBr₃ 4.11; Fe[ClO₄]₂ 2.33; Fe[ClO₄]₃ 2.33; FeI₂ 4.11, 4.13; Fe₂O₃ 1.1; FeTiO₃ 6.3;
- Ga** Ga[ClO₄]₃ 2.34;
- Ge** Ge 4.9; GeS 3.19;
- Hg** Hg 5.9; HgBr₂ 4.10; Hg[BrO₃]₂ 2.3; HgC₂O₄ 2.9; Hg[CN]₂ 3.30; Hg[ClO₂]₂ 2.22; Hg₂[ClO₂]₂ 2.21; Hg₂[ClO₄]₂ 2.35; Hg(N₃)₂ 2.50; Hg₂N₄ 2.51; Hg₃N₂ 2.55; HgO 2.70, 4.11; Hg₂O 4.11; Hg[ONC]₂ 2.79; HgS 2.68;
- In** In 4.10;
- K** K 4.11; KBrO₃ 2.4, 3.1; KC₂H₃O₂ 3.26; KCN 2.11, 3.30; K₂CO₃ 4.12, 6.8, 6.9; KCl 6.10, 6.13, 6.15, 6.16, 7.3, 7.9, 7.13, 7.14, 7.19, 7.22, 8.9; KClO₂ 2.20, 3.4; KClO₃ 2.29, 2.80, 3.8, 3.9, 3.10, 4.1, 4.5, 4.7, 4.9, 4.12, 4.19, 4.20, 4.21; KClO₄ 2.36, 3.13, 3.14, 4.12; K₂Cr₂O₇ 8.16; KF 6.1, 6.16, 7.8; K₃Fe[CN]₆ 3.30, 3.34; KMgCl₂·6H₂O 7.20; KMnO₄ 2.47, 2.61, 3.15; KN₃ 3.35, 2.53; KNH₂ 3.28, 2.56; KNO₂ 2.61, 3.24, 3.28, 3.29; KNO₃ 2.80, 3.16, 3.17, 3.18, 3.19, 3.23, 6.12, 7.1, 7.2, 7.5, 7.7, 7.17, 7.18, 8.3, 8.5, 8.11, 8.12, 8.13, 8.15, 8.16, 8.18, 8.19; KO₂ 4.11; K₂O₂ 2.75; KOH 3.8, 3.39; K₂S₂O₈ 2.83, 3.39;
- Li** Li 5.9, 6.13; Li₂CO₃ 2.10, 6.5, 6.8; LiCl 6.10, 6.15, 7.3, 7.9, 7.14, 7.19, 7.22, 8.9; LiClO₂ 2.23; LiClO₃ 7.4; LiClO₄ 7.5, 8.8; LiF 6.1, 6.16, 7.8; LiN₃ 2.52; LiNO₃ 6.4, 7.1, 7.2, 7.5, 7.7, 7.17, 8.1, 8.4, 8.10, 8.11, 8.12, 8.18, 8.19;
- Mg** Mg 2.68, 4.12; Mg[ClO₃]₂ 3.11; Mg[ClO₄]₂ 2.37; MgO₂ 2.76;

Systems index (cont'd)

- Mn MnCl_2 4.20; $\text{Mn}[\text{ClO}_4]_2$ 2.38; MnO_2 3.8, 3.35; Mn_2O_7 2.71;
- Mo Mo 4.15; MoO_3 4.11; MoS_2 3.19;
- N NH_4Br 4.11; NH_4BrO_4 2.5; NH_4Cl 3.3; NH_4ClO_4 2.40; NH_4I 4.11; NH_4IO_3 2.45; NH_4IO_4 2.46; NH_4MnO_4 2.48; NH_4N_3 2.54; NH_4NO_2 3.25; NH_4NO_3 2.61, 3.6, 3.15, 3.24, 3.25, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.11, 4.12, 4.13, 4.14, 4.16, 4.17, 4.18, 4.20, 6.4, 7.12; $[\text{NH}_4]_2\text{SO}_4$ 2.61, 3.9, 3.29, 4.11; $[\text{NH}_4]_2\text{S}_2\text{O}_8$ 2.84;
- Na Na 4.13, 6.13; $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ 2.1; Na_2BeF_4 6.1; NaCN 2.11; NaCNO 3.31; Na_2CO_3 2.10, 3.2, 4.1, 6.8, 6.9; NaCl 6.13, 6.16, 7.13, 7.14; NaClO_2 2.24, 3.5; NaClO_3 2.29, 3.6, 3.11, 3.12; NaClO_4 2.39; NaF 6.1, 6.16, 7.8; NaHSO_4 2.44; NaMnO_4 2.47; NaNH_2 3.28, 2.56; NaNO_2 2.62, 3.25, 3.28, 3.30, 3.31, 3.32, 3.33, 6.12; NaNO_3 1.6, 2.62, 2.67, 3.18, 3.21, 3.22, 3.20, 3.22, 3.32, 4.1, 4.3, 4.7, 4.12, 4.13, 6.12, 7.2, 7.5, 7.7, 7.18, 8.2, 8.6, 8.10, 8.13, 8.17, 8.18, 8.19; Na_2O 7.15; Na_2O_2 2.77; Na_2S 3.32, 3.37; Na_2S_4 3.38; $\text{Na}_2\text{S}_2\text{O}_3$ 3.23, 3.33; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 6.6; NaSiO_3 6.2;
- Ni Ni 4.14; $\text{Ni}[\text{ClO}_2]_2$ 2.25; NiF_2 7.8;
- Pb Pb 4.16, 5.9; $\text{Pb}(\text{BrO}_3)_2$ 2.4; $\text{Pb}[\text{C}_2\text{H}_3\text{O}_2]_2$ 2.4, 3.1; PbCO_3 2.10; PbCl_2 4.3; $\text{Pb}[\text{ClO}_2]_2$ 2.26; $\text{Pb}[\text{ClO}_3]_2$ 2.30; PbCrO_4 2.41; PbO 7.15; PbO_2 2.80, 3.36, 4.11, 4.12, 4.15; $\text{Pb}[\text{NO}_3]_2$ 2.63, 3.26; PbSO_4 4.11;
- S S 3.17, 3.21, 6.13;
- Sb Sb 4.17, 5.9; SbCl_3 6.16; Sb_2S_3 2.68, 3.19;
- Se Se 5.9;
- Si SiO_2 4.12, 7.15, 8.20;
- Sn Sn 4.18; $\text{SnO}[\text{NO}_3]_2$ 2.65; SnS 3.36;
- Sr SrO_2 2.78; SrS 2.80;
- Ta TaC 3.38;
- Te Te 5.9;
- Th $\text{Th}(\text{NO}_3)_4$ 2.64;
- Ti Ti 2.14, 2.42, 4.19; TiCl_2 2.14; TiCl_3 2.14; TiCl_4 2.14; TiS_2 3.19;
- Tl Tl 5.9; TlClO_2 2.27; TlClO_3 2.31; $\text{Tl}[\text{ONC}]_2$ 2.79;
- U $\text{UO}_2[\text{NO}_3]_2$ 2.66;
- V V 5.9; VO_2 7.16; V_2O_5 7.16;
- Zn Zn 4.20; ZnCl_2 6.16; $\text{Zn}[\text{ClO}_3]_2$ 3.11; $\text{Zn}[\text{NO}_3]_2$ 3.27;
- Zr Zr 4.21; ZrCl_2 2.15.

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