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Survey & Selection Of Inorganic Salts For Application To Thermal Energy Storage

Report To
U.S. Energy Research & Development
Administration

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SURVEY AND SELECTION OF INORGANIC SALTS FOR APPLICATION TO THERMAL ENERGY STORAGE

REPORT

to

U.S. ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION

by

Alina Borucka

June, 1975

CONTENTS

1. SUMMARY AND RECOMMENDATIONS

This report was prepared with the object of selecting the best inorganic salts for application to the storage of thermal energy at temperatures from about 200 to 1000^{o}C, taking advantage of the fact that the latent heat involved in the process of fusion is recoverable reversibly.

The report contains a section dealing with the theoretical aspects and the present status of knowledge concerning the structure of fused salts and the predictability of their properties on the basis of different theoretical models and proposed methods.

Relative to the selection criteria adopted (Sec. 1), 36 single salts and their relevant properties, 32 binary salts and 12 ternary salts are listed and discussed in Sec. 3, together with a general discussion and conclusions concerning their applicability to thermal energy storage.

Corrosion aspects of these salts are discussed briefly and only generally because the subject is extensive and will be covered separately by a BRC report especially devoted to this topic. Supplementing the data of Sec. 3, a large number of additional property tables and all relevant phase diagrams are given in the Appendix.

Section 4 of the report is devoted to a critical summary of the experimental methods used for the evaluation of the physical and thermal properties of fused salts, including many detailed diagrams showing the necessary apparatus.

Conclusions and recommendations deriving from this report are as follows:

- From the standpoint of practical application to thermal energy storage, the most suitable salts are those with good thermal storage properties coupled with existing and reliable knowledge (scientific or engineering) concerning their properties and corrosiveness. This indicates alkali chlorides, fluorides and a number of related binary and ternary salts discussed in Sec. 3 of the report.

- With a few exceptions, inorganic salts in general show a very large increase in volume upon melting (up to 40%) which must be tolerated by proper hardware design if molten salts are to be successfully used in the storage of thermal energy at high temperatures.

- Available experimental data on properties of many salts (and especially on the binary and ternary systems) is deficient and not fully reliable in many cases. The same applies to their corrosion properties.

- Further accurate property and corrosion studies are mandatory for the particular salts selected.

II. REPORT

1. Object of Survey and Selection Criteria

This survey was prepared with the object of selecting suitable molten salt systems for application to the storage of thermal energy as economically and efficiently as possible. Considering this task, the following selection criteria were identified and adopted:

Primary Criteria

1. Melting point temperature between 200 and 1000°C.
2. High value of the latent heat of fusion per unit weight and per unit volume.
3. Low change in volume upon fusion.
4. Low corrosiveness.
5. Good chemical and physical stability with time; low vapor pressure.
6. Low cost.

Secondary Criteria

1. High thermal conductivity.
2. High specific heat.
3. Low coefficient of expansion.
4. Low viscosity.

Discussion of these criteria is presented in Sec. 3 of this report.

2. Theoretical Background

2.1 Summary of the Current Concepts and Knowledge Concerning the Structure of Molten Salts

The early belief that liquids are in all respects (except their density) more similar to gaseous than solid bodies, and the misconception that the molecular forces in liquids are long range ones, instead of very short (as we know them to be now), gave rise to treatment of liquids by van der Waal's theory of condensed gases.

In more recent years, a number of new facts have been discovered which suggest that liquids, especially in the vicinity of the melting point, are much nearer in character to solids than gases, not only with respect to density, but also their thermal motion and structure.

The early distinction between a crystalline solid and a liquid, based on the regularity of structure of the former and irregularity of the latter, is now known to be quantitative and not qualitative in nature. The same is the concept of "rigidity" of solids and "fluidity" of liquids.

It was found that the irregularity in the structure of liquids has its analogue in the solid state. It has been proved that crystals exhibit appreciable irregularity in the form of vacancies in their normal lattice structure or atoms situated in the interstices of the ionic lattice.[1-6] This phenomenon was especially noted in the neighbourhood of the melting point, while a certain amount of regularity (decreasing with increase of temperature) was still observed in the liquid state. In the case of the ionic crystals this irregularity is manifested by the phenomena of diffusion and ionic conductance.

The following facts indicate the quasi-crystalline structure of liquids rather than "gaslike".

(a) The approximate equality of specific heats in the solid and liquid states indicates that the heat motion in liquids is similar to that in solids and consists largely of oscillations about an equilibrium position. Both the translational and rotational motion of molecules in liquids are confined to the vicinity of the equilibrium position. There is no translational contribution to the specific heat as in the case of gases.[4,7]

(b) The increase in molecular volume on fusion (from below 0 to 30%) is often not negligible, yet still relatively small, suggesting that the atomic distances in the liquid phase are comparable with those in the solid.

(c) The heat of fusion is much smaller than that of vaporization; typically, for inorganic salts, the latent heat of vaporization exceeds that of fusion by a factor of 5 to 15. This indicates that the cohesive forces between the molecules decrease only very slightly on fusion, in agreement with the fact that their distance apart is increased by approximately 3 - 4%.

(d) X-ray diffraction studies[2,8,9] indicate a quasi-crystalline structure existing above the melting point. The quasi-crystalline arrangement appears to be interrupted occasionally by small proportions of random molecules.

From the above facts Frenkel[2] drew the conclusion that there is no fundamental discontinuity between solid, liquid and gaseous states and that a liquid is a true transition phase between the two others. At temperatures near the melting point, liquid structure resembles that of the solid, while at temperatures approaching the boiling point the character of the liquid becomes more and more "gas-like". This is well illustrated by the X-ray results of Wood and Ritter,[10] shown in Table 2.1.

TABLE 2.1 Comparison of X-ray Results for Solid Liquid and Gas

Phase	Cd-I	I-I	I-Cd-I
Solid	2.99 Å	4.23 Å	90°
Liquid	2.90 Å	4.75 Å	110°
Gas	3.58 Å	5.16 Å	180°

The six modern theories of the structure of liquids are briefly summarized below:

i. Quasi-Lattice or Vacancy Model

This simple theory was originally proposed by Frenkel in 1935[7] and independently conceived and extended by Bresler in 1939.[11] It suggests that the increase of volume on melting and the thermal expansion of the crystal and of the liquid are due to the increase in the number of holes, while the lattice constant remains unaltered. According to Frenkel, the thermal expansion is fundamentally due to an increase in the interatomic distances. A treatment of the equilibrium was presented by Müller and Stupegia in 1957.[12]

ii. The Hole Model

This model was originated in 1937 by Altar[13] and extended by Früth in 1941.[14] The hole model differs from the quasi-lattice model in that holes are not Schottky defects in cell-like positions but are randomly distributed and arise by means of density fluctuations. According to this theory, the free volume of a liquid body is not distributed uniformly as in the case of a crystal lattice, but is concentrated in form of separate micro-cavities or holes. These holes can be regarded as a particular case of heterophase fluctuations. The theory also suggests that the distance between neighbouring atoms of the liquid outside the regions of holes remains the same as in a solid body. This, however, is only a simplification of the problem since in reality the free volume of a liquid body must be distributed partly in a discontinuous way in the form of separate holes, and partly as a general increase of the average distances between the particles in those regions which preserve their homogeneity. In the case of crystals the concept of a "hole" refers to a vacant lattice site and does not include the interstitial areas, while in the case of a liquid such a distinction is no longer possible, owing to the lack of the long-range order. In liquids the gaps between molecules have neither a definite size nor shape. As in the case of the crystal vacancies, these holes can migrate and give rise to such processes as self-diffusion and, in the case of ionic liquids, to electrical conduction.

iii. The Crystallite Model

This model derives from the concept of microdefects in solids. According to Rothstein,[15] near the melting point the Schottky-type defects diffuse to the dislocation lines in the crystal. As they approach each other, the energy required to form an additional defect is reduced and at the melting point "sheets" of vacancies are thus formed. The melting process consists, therefore, of the crystal breakdown along these "sheets" to form crystallites with fluctuating boundaries.[16]

iv. The Polyhedral-hole Model

Mendenhall and Ingersoll observed in 1908[17] that not only liquids containing complex molecules but also those composed of small and simple ones can be supercooled. This implies that in the liquid state the individual component entities do not pack well on cooling. Frank, in 1952,[18] considered that individual particles of substances with coordination number 12, arranged in contact with others are at the center of the face of a dodecahedron which results in:

a) the short-range cohesive energy being larger than that of other arrangements

and b) the arrangement being non-space filling, i.e., having holes which do not permit close-packed geometry and thus cause difficulty in crystallization.

This model is attractive in that it includes the concepts of holes, dislocations and crystallites and some ideas whereby a liquid is essentially different from a solid. As suggested by Bernal in 1960,[19] this model indicates that solids are regular and coherent, liquids are irregular and coherent, while gases are irregular and incoherent.

v. The Liquid Free-volume Model

This model originates in the early work of Zernicke and Prins[20] and the concept that liquids can be treated as compressed gases. The "cell" in which a molecule spends most of its time has a certain cell free volume[21] which is the difference between the total volume available for the movement of the particle and that of the particle itself. Different models based on this initial concept have been subjected to a more thorough mathematical analysis than those above.[22-26] It was shown that the (cell) free-volume model suffers not only from a difficulty in interpretation of the entropy of fusion but is also qualitatively inconsistent with the volume expansion on fusion while the internuclear distance remains constant or decreases. By introducing a modified concept of the (liquid)-free volume in which free space per cell is randomly distributed, the above difficulties are eliminated but with the random amount of extra free space per cell which is also assumed to be variable, this modified model resembles the hole theory and the quasi-lattice model.

vi. The Significant-structure Model

This model was proposed by Eyring, et.al., in 1958[27] and combines concepts from the vacancy model, the crystallite model and the compressed-gas model. It interprets the process of fusion as the creation of two types of defects: holes and dislocations. The holes are of the Schottky and Frenkel type. The two "significant structures" are particles which are essentially those of an Einstein solid but which have their properties modified by the presence of "strain centers": areas near defects and the holes which exist (gas-like) in the passageways associated with the dislocations. This model lends itself well to the mathematical development[27,28] and is consistent with experiment with respect to reduction of coordination number and constancy of internuclear distance upon fusion. Applied to ionic liquids quantitatively, it accounts very well for the change of volume and entropy on fusion. Nevertheless, as other models, it suffers from a number of unrealistic assumptions such as the "gas-like" rather than a "liquid-like" behavior of the dislocation area.[29]

2.2 Prediction of Data from Theoretical Models

A theoretical model is useful only if it leads to correct calculation of physical, thermal and other properties. In the case of the ionic liquids, properties which are useful for the comparison of the experimental and predicted values are: entropy of fusion, volume change on fusion, compressibility and self-diffusion coefficient. Values of these and other experimentally determined properties for the ionic salts have been tabulated by Bloom and Bockris[30] and, more recently and extensively, by Janz.[9]

Bloom and Bockris[31] reported a series of quantitative comparisons of the data predicted by the different theoretical models with those observed experimentally. These are shown in Tables 2.2 to 2.9 below and their qualitative summary in Table 2.10.[31]

It should be noted that even when the agreements between the calculated and observed values are described as being "good" in Table 2.10, this refers to discrepancies both positive and negative and in some cases as large as 40%.

This shows that while the prediction of some properties from some of the models proposed can be conducted on basis of the work reported in references 1 through 31, no high accuracy predictions of data should be expected at this stage of the development of the quantitative aspects of these theories. For binary and ternary salt mixtures the situation is, of course, correspondingly worse.

PREDICTION OF VOLUME CHANGE ON FUSION

TABLE 2.2

Hole Model

Liquid	$\frac{\Delta V_f}{V_s}$ at m.pt.	
	Calc.%	Obs.%
NaCl	21	25
NaI	16	19
KBr	17	17
KI	22	16

TABLE 2.3

Liquid Free-volume Model

Liquid	$\frac{\Delta V_f}{V_s}$ at m.pt.	
	Obs.%	Calc.%
NaCl	25	20
RbCl	14	18
CsCl	11	18
NaI	19	15

TABLE 2.4

Significant-structures Model

Liquid	Calculated, cc mole^{-1}	Observed, cc mole^{-1}
KCl	8.5	7.2
NaCl	7.9	7.5

TABLE 2.5 Prediction of Entropy of Fusion by Cavity Models

Liquid	Single holes	Coalesced holes	Single vacs.	Single vacs.+ paired vacs.	Single vacs.+ paired vacs.+ rotation	Obs. e.u.
NaCl	1.5	5.5	2.6	2.6	7.2	6.7
KCl	1.4	5.4	2.2	2.1	5.8	6.2
RbCl	1.3	5.3	1.7	1.7	4.4	4.4
CsCl	1.2	5.2	1.4	1.3	3.4	3.9
NaI	1.6	5.4	2.0	2.0	5.5	5.6

TABLE 2.6 Prediction of Compressibilities and Expansivities: Hole Model

Liquid	Isothermal compressibility X 10^{12} (exptl.,cm^2 dyne^{-1})	Hole Model	Expansivity X 10^4 {exptl.,(°C)$^{-1}$}	Hole Model
NaCl	28.7 (800°C)	27.8	3.3	3.6
CsBr	76.0 (800°C)	67.1	4.0	4.4
CsCl	72.5 (1000°C)	76.3	4.4	4.5
NaI	43.7 (1000°C)	47.3	3.9	4.2
$CaBr_2$	18 (800°C)	12	1.6	1.4
$SrBr_2$	16 (800°C)	14	2.1	2.1
$BaCl_2$	15 (1000°C)	13	2.2	1.8
CdI_2	60 (600°C)	71	2.7	4.4
$ZnCl_2$	49 (600°C)	55	2.1	3.0

TABLE 2.7 Prediction of Free Volume: Cell Model

Liquid	Free volume from sound velocity, cc mole^{-1}	Compressed-gas model, cc mole^{-1}
NaCl	0.42	ca. 10^{-10}
CsBr	0.88	
CsCl	1.85	
NaI	2.31	

TABLE 2.8 Prediction of Energy of Activation for Self-diffusion: Hole Model

Liquid	Experimental values, kcal $mole^{-1}$		Furth Hole Model
	$E_{cat.}$	$E_{an.}$	
NaCl	5.2	5.3	7.5
NaI	4.9	5.8	6.5
RbCl	7.0	6.2	6.4
CsCl	7.0	7.5	6.8

TABLE 2.9 Prediction of Parameters of Self-diffusion: Liquid Free-volume Model

Salt	A, LFV model $(T = T_m)$	Mean E_{exptl}, kcal $mole^{-1}$	E, LFV model $(T_o=1/3T_b, V^*=V_m)$	Mean A (exptl)
NaCl	5×10^{-4}	5.3	16.7	3×10^{-3}
NaI	2×10^{-4}	5.4	16.6	0.5×10^{-3}
CsCl	2×10^{-4}	7.3	14.6	2.2×10^{-3}
RbCl	3×10^{-4}	6.6	14.1	2.2×10^{-3}

TABLE 2.10 Summary of Ability of Various Models of Ionic Liquids to Predict Data

Quantity Concerned	Hole	Quasi-Lattice	Crystallite	Polyhedral Hole	Liquid free volume	Significant structure
ΔV_f	Good	Not yet calculated	Indicates particles ion-sized	....	Good	Very good
ΔS_f	Fair	Very good if rotation of vacancy pairs	Indicates particles ion-sized	....	Theory not yet formulated	Very good
α,β*	Very good	....	....	Model is qualitative	(Cell free volume of compressed gas model grossly discrepant with experiment)	Theory not yet formulated
$D=Ae^{-E/RT}$	A good, E excellent	A good, E qualitative	Indicates particles ion-sized	....	Satisfactory if cavity assumed about 0.4 V_{ion} but predicts curvature of $\ln D_1/(1/T)$	Not yet calculated

* α = expansivity, β= compressibility

2.3 Practical Consequences

The above summary of the various structural models proposed for molten salts shows that in spite of the existing diversity of views and theories, these liquids, especially near the melting point, have structurally very little in common with other liquids and even less in common with gases. Near the melting point, they undoubtedly resemble their solid crystalline structure even if considerably expanded by the process of melting.

While some of their physical properties are similar in order of magnitude to those of other liquids, their thermal properties (with the exception of the specific heat) differ very substantially as shown on Table 2.11 below.

TABLE 2.11 Properties of Molten Salts vs Other Liquids

PROPERTY		Sodium Chloride	Potassium Chloride	Water	Benzene
PHYSICAL	Temperature, °C	850	800	25	25
	Surface Tension, dynes cm^{-1}	118.8	96.8	72	28.2
	Viscosity, millipoise	12.5	11.0	8.9	6.2
	Density, gm cm^{-3}	1.55	1.51	1.0	0.88
	Refractive Index	1.41	1.39	1.33	1.50
THERMAL	Melting point, °C	801	776	0.0	5.53
	Boiling point, °C	1,413	1,500	100.0	80.1
	Heat of fusion, cal/mole	6,730	6,410	1,436	2,351
	Heat of vaporization, cal/mole	40,810	38,840	9,729	7,353
	Specific Heat (liquid, near m.pt.), cal $^{o}K^{-1}$ $mole^{-1}$	16.0	16.0	18.0	32.7
	Thermal Conductivity (near m.pt.), 10^{3} cal cm sec^{-1} $^{o}C^{-1}$ cm^{-2}	3.8 (s)	3.6(s)	1.43(1)	0.38(1)

Additionally, most common inorganic salts are fully ionized and thus have much higher value transport properties such as the ionic mobilities, ionic conductivities and the ionic self-diffusion coefficients. For example, the specific ionic conductivity of molten NaCl at 850°C is 3.74 $\text{ohm}^{-1}\ \text{cm}^{-1}$ compared with $6.2 \times 10^{-8}\ \text{ohm}^{-1}\ \text{cm}^{-1}$ for H_2O at 25°C; molten KCl at 800°C has a specific ionic conductivity about 22 times greater than that of its 1 molar solution in water at 20°C.

Resulting from their fully or highly ionized structure and the high temperatures at which they operate, molten salts are generally corrosive to many metals and non-metals. Practically, this characteristic is very important yet any thermodynamic predictions of their interactions with other materials by the classical methods are again far from fully reliable.

As with the physical and thermal properties of these salts and their mixtures, their corrosion properties should best be determined experimentally.

As will be seen from the following sections of this report, the necessary physical, thermal, and corrosion data even for the single salts are only partially available while for the binary and ternary salt mixtures of interest to this project, there are even fewer.

3. SELECTED SALTS AND THEIR PROPERTIES

3.1 Introduction

The selection criteria listed in Sec. 1 of this report represent a large number of often conflicting property requirements and dictate the need for an "optimized" compromise. An additional difficulty in proper selection of the salts for the thermal energy storage application arises from the lack of complete data especially for the binary and ternary salt mixtures.

Because of the practical importance of the requirement for low corrosiveness, salts such as: sulfates, sulfides, chlorates, phosphates, etc., were rejected. Additionally, salts of metals such as: Ag, Cd, Hg, etc., were rejected either on the grounds of high cost or toxicity or both. Lithium salts are quoted in Table 3.1, but mainly for comparison purposes, as the Li^+ ion is particularly corrosive and lithium salts are very expensive. Resulting from this type of selection process, only the least "offensive" and best studied salts such as: nitrates, chlorides, bromides, a few hydroxides, fluorides and carbonates were considered.

The selected salts and their properties are listed and discussed in the next sections of this report.

3.2 Selected Single Salts

The list of 36 single salts selected as being of interest to the thermal energy storage application, either directly or as components of suitable binary or ternary mixtures, is given in Table 3.1 together with their physical and thermal properties found in literature.[9,32-60]

While very extensive literature was surveyed for purposes of this report (see REFERENCE section), no claim can be made at this stage

TABLE 3.1 SUMMARY OF DATA FOR SELECTED SINGLE SALTS

Reference	32	32	32, 47	CALC.	32 - 35	34 - 41	CALC.	9	9, 42, 43			44 - 48, 53			49 - 53			40, 47, 54, 55 - 59				34, 36, 40, 56 - 58		60	
SALT	MOL. WT.	m.pt.	b.pt.	Δt_L	DENSITY gm/cc		VOL. CHANGE ON FUSION %		VAPOR PRESSURE mm Hg			LATENT HEAT OF FUSION			SPECIFIC HEAT cal/°K mole			THERMAL CONDUCTIVITY 10^3 x cal/sec °C cm^2				VISCOSITY (centipoise)		RELATIVE COST (\$/1lb, cert. salts Fisher Cat. 1974)	
					SOLID	LIQUID									SOLID		LIQUID	SOLID		LIQUID					
		°C	°C	°C.	25°C	m.pt.	25°C to m.pt.	at m.pt.	(T = °K) Log P =	at m.pt.	at m.pt. +100°C	cal/mol	cal/gm	cal/cc	(T = °K) Cp =	Cp m.pt.	Cp m.pt.	TEMP °C	k	TEMP °C	k	TEMP °C	η	\$/ 1 lb	cal/\$
$SnCl_2$	189.60	246	652	406	3.95	3.36	1.76					3,000	15.8	53.1	$16.2 + 9.26 \times 10^{-3}T$	21.01								8.73	821
$LiNO_3$	68.95	264	d600	336	2.38	1.77	34.4	21.4				6,100	88.5	156.7	$9.17 + 36.0 \times 10^{-3}T$	28.50	26.6					277	5.85	15.10	2,659
$NaNO_2$	69.00	271	d320	49	2.17	1.80	20.6													314	1.70	297	3.04	4.00	
$ZnCl_2$	136.28	283	732	449	2.91	2.52	15.5	11.6	$10.1233 - 7,030.6/T$	.0003	.254	2,450	18.0	45.4	$15.9 + 8.00 \times 10^{-3}T$	20.35	24.1			283	0.75	327	2.9×10^3	6.19	1,319
$NaNO_3$	84.99	307	d380	73	2.26	1.90	18.9	10.7				3,696	43.5	82.7	$4.56 + 58.0 \times 10^{-3}T$	38.20	37.0	307	1.35	314	1.45	317	2.86	6.75	8,180
$NaOH$	40.00	318	1390	1072	2.13	1.78	19.7		$7.030 - 6,984.4/T$	.00002	.001	1,520	38.0	67.6	19.2	19.20	20.4			319	2.20	357	3.79	2.56	6,733
KNO_3	101.11	334	d400	66	2.11	1.87	12.8	3.32				2,413	23.9	44.7	$\alpha = 6.42 + 53.0 \times 10^{-3}T \quad \beta = 28.8$	28.80	29.5	334	1.03	393	1.30	357	2.63	5.30	2,045
KOH	56.11	360	1320	960	2.04	1.73	17.9		$7.472 - 7,103.3/T$	.00013	.006	1,800	32.1	55.5			19.9					407	2.21	2.99	4,870
$LiOH$	23.45	450	d924	474	1.46							5,010	209.2		$3.96 + 13.60 \times 10^{-3}T$	13.79	22.1							17.20	5,517
$LiBr$	86.86	547	1265	718	3.46	2.53	37.0	24.3	$8.068 - 7,975.5/T$	.0220	.250	4,220	48.6	122.8	22.6	22.60						597	1.52	11.75	1,917
$Ca(NO_3)_2$	164.09	561	d		2.56			10.0				5,120	31.2		$29.37 + 36.8 \times 10^{-3}T - 4.13 \times 10^5T^{-2}$	59.47								4.91	2,882
$CdCl_2$	183.32	569	677	108	4.05	3.39	19.5		$-9,183/T - 5,04 \text{ Log } T + 25,907$			6,780	29.7	100.6	$14.64 + 9.60 \times 10^{-3}T$	22.72	24.0					597	2.31	21.36	631
$Sr(NO_3)_2$	211.63	570	d		2.99							12,700	60.0			38.3								7.83	3,476
$Ba(NO_3)_2$	261.35	592	d		3.24	3.22	0.6					5,900	22.6	72.7	$30.05 + 35.70 \times 10^{-3}T - 4.07 \times 10^5T^{-2}$	60.39								8.26	1,241
$LiCl$	42.30	614	1325	711	2.07	1.50	37.6	26.2	$7.939 - 8,142.7/T$	.0574	.4887	4,740	112.1	168.6	$11.0 + 3.39 \times 10^{-3}T$	14.01	15.0					637	1.59	11.00	4,621
$MnCl_2$	125.84	650	1190	540	2.98	2.35	26.8					8,970	71.3	167.6	$16.2 + 5.20 \times 10^{-3}T$	21.00	22.6							5.83	5,547
$MgBr_2$	184.13	700	d		3.72	2.62	42.2					8,300	45.1	118.0			24.0							13.36	9,348
$MgCl_2$	95.23	708	1412	704	2.32	1.68	38.1	30.5	$-11735/T - 4.0765 \log T + 23.15$	.0982	.8451	10,300	108.2	181.8	$17.3 + 3.77 \times 10^{-3}T$	21.00	22.0							5.25	9,348
Li_2CO_3	73.89	723	d1310	587	2.11	1.83	15.3					10,700	144.8	265.0	$3.82 + 42.74 \times 10^{-3}T$	39.38	40.6					777	4.64	16.60	3,957
$CaBr_2$	199.91	730	806	76	3.35	3.11	7.7	4.0				6,900	34.5	107.3			27.0								
KBr	119.01	730	1345	615	2.75	2.12	29.5	16.6	$8.2475 - 8,779.9/T$	.3118	1.9274	6,100	51.3	109.0	$11.49 + 3.60 \times 10^{-3}T$	15.10	16.0	100	11.3			747	1.18	5.40	4,309
$NaBr$	102.91	755	1390	635	3.20	2.34	36.8	22.4	$8.9567 - 9,686.7/T$	.3419	2.3400	6,250	60.7	142.0	$11.74 + 2.33 \times 10^{-3}T$	14.14	15.0					787	1.28	3.93	7,006
$CaCl_2$	110.99	772	1600	828	2.15	2.07	4.1	0.09	$9.220 - 1,356.8/T$	.00017	.0023	6,780	61.1	126.2	$16.90 + 3.86 \times 10^{-3}T$	20.93	23.6					787	3.34	5.44	5,095
KCl	74.60	776	1500	724	2.07	1.50	37.6	26.2	$-11023/T - 3.526 \log T + 20.798$	.4352	2.5927	6,410	75.3	113.7	$10.93 + 3.76 \times 10^{-3}T$	14.87	16.0	776	3.6			787	1.14	2.95	11,578
$NaCl$	58.44	801	1413	612	2.17	1.56	39.5	25.0	$-11495/T - 3.526 \log T + 20.929$	.3457	2.0608	6,730	115.2	178.9	$10.79 + 4.20 \times 10 \quad T$	15.30	16.0	801	3.8			817	1.38	2.25	23,224
LiF	25.94	842	1676	834	2.64	1.83	44.0	29.4	$8.797 - 11,409 \times T^{-1}$	.037	.255	6,474	249.6	465.7	$10.41 + 3.90 \times 10^{-3}T - 1.38 \times 10^5T$	14.7	15.5	499	13.8					13.30	15,880
KF	58.10	846	1505	659	2.48	1.92	29.3	17.2				6,750	116.2	223.1	$11.88 + 2.22 \times 10^{-3}T - 0.72 \times 10^5T^{-2}$	14.3	16.0							9.80	10,324
Na_2CO_3	105.99	851	d		2.53	1.97	28.6					7,000	66.0	129.9	28.9	28.90	43.1					887	3.40	3.66	8,180
$SrCl_2$	158.53	873	1250	377	3.05	2.73	11.7					4,100	25.9	70.6	$18.2 + 2.45 \times 10^{-3}T$	20.95	27.0					887	3.43	6.09	1,929
K_2CO_3	138.21	891	d		2.43	1.90	28.2					7,800	56.4	106.9	29.9	29.90	49.3					917	3.03	3.81	6,719
$BaCl_2$	208.25	963	1560	597	3.84	3.17	21.1					3,900	18.7	59.3	$17.0 + 3.30 \times 10^{-3}T$	21.08	26.3					997	4.60	3.50	2,424
$NiCl_2$	129.62	973s	subl		3.55							18,470	142.5		$13.10 + 13.00 \times 10^{-3}T$	29.66	24.0							10.14	6,375
NaF	41.99	988	1695	707	2.56	1.95	31.3	27.4	$9.4188 - 12,428 \times T^{-1}$	.366	1.938	7,920	188.6	367.8	$10.40 + 3.88 \times 10^{-3}T - 0.33 \times 10^5T^{-2}$	15.29	16.4							7.75	21,523
MgF_2	62.31	1270	2239	969	3.00	2.43	23.5					13,900	223.1	542.1	$16.93 + 2.52 \times 10^{-3}T - 2.20 \times 10^5T^{-2}$	19.87	22.6							9.46est.	25,983
CaF_2	78.08	1360	2500	1140	3.18	2.54	25.2		$8.8930 - 21,826 \times T^{-1}$	.00003	.0002	7,100	90.9	231.0	$25.81 + 2.50 \times 10^{-3}T \quad (\beta)$	30.04	23.9							9.80	10,690
$CaCO_3$	100.09	1339	d		2.93							12,700	126.9		$19.68 + 11.89 \times 10^{-3}T - 3.076 \times 10^5T^{-2}$	38.85		60	1.30					7.05	8,164

that the search is fully complete because the existing literature is extremely large and because much of the original material on molten salt studies is published in old Russian and German journals which are difficult to obtain.

An additional important fact which must be pointed out concerning the data presented in Table 3.1 is that their accuracy is, in many cases, questionable mainly because many molten salt property measurements conducted by different workers show considerable differences. (In some cases disagreements on the values for thermal properties are as large as 40%, e.g. ΔH_f.[9,45])

To resolve this problem, the values quoted in Table 3.1 are those reported most recently, or by well known and reliable researchers. Nevertheless, it would be safer to assume that most of the available thermal data, such as the latent heat of fusion, volume change on fusion, and thermal conductivity are, at best only ±10% accurate.

Specific comments on particular properties listed in Table 3.1 are as follows:

a. The molecular weights and the melting points of the single salts[32] are accurate but the boiling points[32,47] are no longer so. In many cases, when the salt decomposes below the boiling point, the decomposition temperatures are apt to be not fully accurate, and many are not reported at all. The temperature difference, Δt_L, is shown as a rough guide to the thermal stability of the melt and as a measure of the operating temperature range.

(In most cases it is, of course, much higher than that for water.).

b. The room temperature density for the solid salts[32-35] is likely to be fully accurate but the melt density[34-41]had to be extrapolated back to the melting temperature from density equations such as those shown in the Appendix (Sec.A-1 of this report, Table A-1). For this reason, only two decimal places are quoted in the density values in Table 3.1. The %volume change on fusion was calculated from the density data quoted or, in some cases,as reported in literature.[9] (See also Fig. A-1 in the Appendix). Molar and free volumes are not quoted in Table 3.1 but some data found in literature are given in the Appendix in Tables A-2, A-3, and Fig. A-2.

c. Vapor pressure equations and data[9,42,43] were found for only 15 out of 36 salts listed in Table 3.1. It is possible that some more may exist in literature but so far these have not been discovered.

d. Latent heat of fusion data[44-48,53]are especially important to the purpose of this report and were therefore presented in three different ways, on molar, weight and volume basis. Some data on the entropy of fusion are given in the Appendix, in Table A-4 and Fig. A-3.

e. Apart from the specific heat data[49-53] given in Table 3.1, Tables A-5, A-6, and Fig. A-4 in the Appendix compare the Cp and C_v values for various salts.

f. Thermal conductivity data[40,47,55-59] are the least complete and, very probably, the least accurate.

g. Viscosity data[34,36,40,56,58] of Table 3.1 are supplemented with viscosity equations listed in the Appendix in Tables A-7 and A-8.

h. The cost figures presented in Table 3.1 are only intended for purposes of approximate comparison. They are based on the 1974 Fisher catalog[60] cost for 1 lb. quantities of the certified quality chemicals and, as such, they may have little to do with large - quantity commercial prices. (For the more common salts, such as NaCl for instance, the bulk commercial price is likely to be very much lower than that for the less common salts).

3.2 Selected Binary Salts

The thirty-two binary salt mixtures listed in Table 3.2 were selected so as to represent the best combination of salts from Table 3.1 for which, so far as was found, both the phase diagrams and the composition data are available.

The salts selected for Table 3.2 are mainly binary chlorides with a few cases of fluorides, nitrates and the better known carbonates. These salts offer a choice of melting points from 220 to 1000°C at small intervals and are therefore likely to prove useful in considering candidate salts for relatively narrow ranges of temperatures at which thermal energy may have to be stored.

They fall into five different groups as regards the features of their phase diagrams as marked in Table 3.2:

A. Simple eutectic without intermediate compounds or solid solutions.

B. Eutectic with compounds and congruent melting points.

C. Eutectic with peritectic features.

D. Non-eutectic systems with a single solid solution with a minimum melting point.

E. Systems with conjugate solid solutions.

Most of these binaries are obviously not "ideal" mixtures and, therefore, their properties are not additive relative to the properties of the component salts, and, without the relevant activity data, cannot be subjected to calculations for reasonably accurate prediction of their properties.[59,67-69]

Unfortunately, the experimentally measured properties for the binary salts are extremely scarce (see Table 3.2), often incomplete (such as those given by Holm for fluoride mixtures[70]), and often not fully reliable. Therefore, to achieve some measure of expedient comparison at this stage, however inaccurate in detail, Table 3.2 shows averaged densities, heats of fusion and relative costs (using data for pure components as listed in Table 3.1 and allowing for the composition of the particular mixture as given in Table 3.2).

(It should be noted that in some specific cases these calculated values may be grossly inaccurate.)

3.4 Selected Ternary Salts

Again, as above, the selection of the ternary salts shown in Table 3.3 covers mainly the most promising chlorides, fluorides and the well studied alkali carbonate eutectics.[71-74] As in the case of the binaries, the measured properties for the ternaries are very scarce. Therefore, Table 3.3 shows only the simple averaged calculations which serve as a broad comparison basis for the mixtures selected.

TABLE 3-2 SELECTED BINARY SALT MIXTURES

Reference		9,62	CALC.	62		9,62				CALC.		CALC.			9	60
BINARY SALT		m.pt. °C	AVERAGE MOL. WT.	PHASE DIAG.†		COMPOSITION				AVG. DENSITY*		AVERAGED HEAT* OF FUSION			OTHER MEASURED PROPERTIES AVAILABLE	RELATIVE COST cal/$
						MOL%		WT.%		SOL. 25°C	LIQ. m.pt.	cal/mol	cal/gm	cal/cc		
A	B			NO.	TYPE	A	B	A	B							
$NaNO_3$	KNO_3	220	93.06	A-8	D	50	50	45.7	54.3	2.18	1.88	3055	32.8	61.7	ρ, ΔHmix, η, k	4849
KCl	$ZnCl_2$	228	107.91	A-9	B	46	54	31.8	68.2	2.61	2.20	4272	39.6	87.1		4581
KCl	$ZnCl_2$	262	118.39	A-9	B	29	71	18.3	81.7	2.74	2.34	3598	30.4	71.1		3196
NaCl	$ZnCl_2$	262	104.76	A-10	C	40.5	59.5	22.6	77.4	2.74	2.30	4183	39.9	91.8		6270
KNO_3	$Ba(NO_3)_2$	287	120.98	A-11	B	87.6	12.4	73.2	26.8	2.41		3348	27.7			1830
KBr	$MgBr_2$	334	141.80	A-12	C	65	35	54.6	45.4	3.19	2.35	6870	48.4	113.9		6597
NaBr	$MgBr_2$	431	136.21	A-13	A	59	41	44.6	55.4	3.49	2.50	7091	52.1	130.1		15537
KCl	$ZnCl_2$	432	94.03	A-9	B	68.5	31.5	54.3	45.7	2.41	1.97	5163	54.9	108.2		6890
KCl	$MgCl_2$	435	81.41	A-14	B	67	33	61.4	38.6	2.11	1.58	7694	94.5	149.3	η	9250
NaCl	$MgCl_2$	450	76.10	A-15	C	52	48	60.1	39.9	2.23	1.61	8444	111.0	178.6	ρ, η, ΔHmix	16171
KCl	$MgCl_2$	470	86.56	A-14	B	42	58	36.2	63.8	2.20	1.62	8666	100.1	162.2	ρ, ΔHmix	7730
LiF	KF	492	41.38	A-16	A	52	48	32.6	67.4	2.53	1.89	6606	159.7	301.7	η, ΔHmix	12135
NaCl	$CaCl_2$	500	85.76	A-16	E	48	52	32.7	67.3	2.16	1.89	6756	78.8	148.9	ρ, η	11023
$MgCl_2$	$SrCl_2$	535	126.88	A-17	A	50	50	37.5	62.5	2.78	2.34	7200	56.7	132.8		4470
$BaCl_2$	$MgCl_2$	560	134.79	A-18	A	35	65	54.1	45.9	3.14	2.49	8060	59.8	148.9	ρ	5602
NaCl	$SrCl_2$	564	108.48	A-19	A	50	50	26.9	73.1	2.81	2.42	5415	49.9	120.8		7212
NaCl	$NiCl_2$	574	82.43	A-20	A	35	65	47.0	53.0	2.90		10686	129.69			14294
KCl	Na_2CO_3	587	87.78	A-21	A	58	42	49.3	50.7	2.46	1.74	6658	75.8	132.0		9855
KCl	$CaCl_2$	600	83.70	A-22	B	66	34	66.8	33.2	2.10	1.69	6503	77.7	131.3		9008
$CaCl_2$		614	103.11	A-23	E	50	50	53.8	46.2	2.25	1.89	8540	82.8	156.5	ρ, η	7060
KCl	$CaCl_2$	640	97.17	A-22	A	38	62	29.2	70.8	2.13	1.90	6639	68.3	129.8	ρ	6988
LiF	NaF	652	32.20	A-25	A	61	39	49.1	50.9	2.60	1.89	7038	218.6	413.1		18752
KCl	NaCl	658	66.52	A-24	D	50	50	56.1	43.9	2.06	1.53	6570	98.8	151.1	ρ, η, ΔHmix	16691
Na_2CO_3	K_2CO_3	710	120.60	A-25	D	56	44	49.2	50.8	2.48	1.94	7352	61.0	118.3	ρ, ΔH_f, C_{pl}	7438
KF	NaF	710	51.59	A-28	A	59.5	40.5	67.1	32.9	2.51	1.93	7223	140.0	270.2		14008
LiF	MgF_2	741	38.21	A-29	E	66	34	44.9	55.1	2.84	2.16	8991	235.3	508.3		21450
LiF	CaF_2	765	37.00	A-30	A	79	21	55.3	44.7	2.88	2.15	6607	178.6	383.9		13560
KF	MgF_2	778	58.74	A-31	C	85.5	14.5	84.5	15.5	2.56	2.00	7794	132.7	265.4		12752
NaF	CaF_2	810	54.02	A-32	A	66.7	33.3	51.8	48.2	2.86	2.23	7647	141.6	315.7		16301
NaF	MgF_2	830	46.58	A-33	B	77.4	22.6	69.8	30.2	2.69	2.09	9271	199.0	416.0		20896
CaF_2	MgF_2	944	69.48	A-34	A	45.7	54.3	51.3	48.7	3.09	2.49	10792	155.3	386.8		18140
NaF	MgF_2	1000	54.18	A-35	B	40.0	60.0	31.0	69.0	2.86	2.24	11508	212.4	475.8		24604

† See Appendix, Sec. A-3.

* Not accurate. Calculation based on assumed ideality, not true in most cases.

ρ = density; η = viscosity; $C_{p(\ell)}$ = sp. heat of liquid; k = thermal conductivity;
ΔHmix = heat of mixing; ΔH_f = heat of fusion.

TABLE 3-3 Selected Ternary Salt Mixtures

Reference			62	CALC	62	9 and CALCULATED FROM 62						CALCULATED		CALCULATED			9	60
TERNARY SALT			m. pt.	AVG. MOL. WT.	PH. DIAG.† NO.	COMPOSITION*						AVG. DENSITY*		AVERAGED HEAT OF FUSION*			OTHER PROPERTIES AVAILABLE	RELATIVE COST cal/$
						MOL %			WEIGHT %			SOL	LIQ					
A	B	C	°C			A	B	C	A	B	C	25°C	m. pt.	cal/mol	cal/gm	cal/cc		
KCl	NaCl	$CdCl_2$	375	113.01	A-35	47.9	14.6	37.5	31.6	7.6	60.8	3.28	2.65	6595	58.4	154.7		5807
KCl	NaCl	$MgCl_2$	385	84.03	A-36	12.9	15.5	71.6	14.5	22.3	63.2	2.25	1.63	9245	110.0	179.3		12766
K_2CO_3	Li_2CO_3	Na_2CO_3	397	100.08	A-37	25.0	43.5	31.5	34.5	32.1	33.4	2.36	1.90	8810	88.0	167.2	ρ, η, $C_{p(\ell)}$, ΔH_f, d.d.	6320
NaCl	$BaCl_2$	$MgCl_2$	418	94.74	A-38	46.0	14.5	39.5	28.4	31.8	39.8	2.76	2.12	7730	81.6	173.0		4430
NaF	KF	LiF	454	41.29	A-39	11.5	42.0	46.5	11.7	59.1	29.2	2.53	1.90	6756	163.6	310.9	η, K_{500}	13257
KCl	$CaCl_2$	$MgCl_2$	487	92.35	A-40	30.9	22.2	46.9	25.0	26.7	48.3	2.53	1.74	8317	90.1	156.7		8770
KCl	NaCl	$CaCl_2$	504	86.55	A-41	5.8	42.5	51.7	5.0	28.7	66.3	2.15	1.90	6737	77.8	147.9		10622
KCl	NaCl	$SrCl_2$	504	107.51	A-42	19.2	34.9	45.9	13.3	19.0	67.7	2.75	2.34	5461	50.8	118.9		6838
KCl	NaCl	$BaCl_2$	542	105.29	A-43	39.7	33.3	27.0	28.1	18.5	53.4	3.03	2.40	5841	55.5	133.1		8844
KCl	$BaCl_2$	$CaCl_2$	551	123.91	A-44	39.6	28.1	32.3	23.9	47.2	28.9	2.93	2.45	5824	47.0	115.2		5384
K_2CO_3	Na_2CO_3	$CaCO_3$	700	118.05	A-45	40.8	33.3	25.9	48.1	29.9	22.0	2.57		8805	74.6			7474
KF	LiF	MgF_2	713	38.65	A-46	5.6	64.4	30.0	8.4	43.2	48.4	2.80	2.13	8717	225.5	480.4		20274

† See Appendix, Sec. A-4.

* Not accurate when calculated with assumption of ideality (for comparison only).

ρ = density; η = viscosity; $C_{p(\ell)}$ = sp. heat of liquid; k = thermal conductivity; ΔH_{mix} = heat of mixing; ΔH_f = heat of fusion; d.d.- dissociation data.

3.5 Corrosion and Handling Aspects

3.51 General

As with other properties of molten salts, their corrosiveness has not been studied fully or accurately in most cases, and not discussed directly in any of the most prominent modern books on fused salts.[9,40,59,66-68,75] Such data and theoretical understanding as exist are mostly in scattered literature (mostly electrochemical) pertaining to specific single or mixed salts. Additionally, corrosion data quoted are often unreliable because in most cases they were obtained without proper control of the ambient atmosphere, elimination of melt impurities, of residual water content of the melt, etc. Similarly, the literature data do not correspond to the specific realistic conditions prevailing in particular industrial applications of modern salts, such as metal electrowinning or electrolysis[76]; they are, therefore, not too useful and difficult (if not impossible) to interpret theoretically.

The thermodynamic calculations and predictions based on Pourbaix method[77-79] are helpful, but cannot truly replace the necessary reliable kinetic data in this field.

A full discussion of the theory and the analysis of data available on the corrosion characterisitcs of molten salts is outside the scope of the present report. It will be available shortly in a separate BRC report on this topic. Here we include only a brief outline and comments on this subject to the extent necessary for the preliminary selection of the best salts for the thermal energy storage application.

3.52 Summary of Basic Considerations

As with any type of corrosion, the basic driving force for the reaction of a metal or a non-metal with a molten salt depends on the free energy change, ΔG, for the reaction occurring. The more negative the value of ΔG, the more "forceful" is the reaction in the postulated direction. (The most complete and modern values for ΔG of formation for the inorganic salts, over a wide temperature range, are available from the JANAF Tables, 1970.[80])

From the appropriate values of ΔG, several other thermodynamic quantities of importance to corrosion considerations can be derived. For example, the thermodynamic decomposition potential is directly related to ΔG (formation) and the redox potential of the salt to its ΔG(dissociation). The decomposition potential represents a measure of the stability of the salt (the more stable, the less corrosive, other things being equal), while the redox potential is a measure of its corrosion or oxidation aggressiveness (the lower the redox potential the lower the corrosiveness, other things being equal).

The free energy values are converted to the thermodynamic emf scale (as in aqueous solutions) by the expression:

$$E^o = - \frac{\Delta G^o}{nF}$$

but, in order to deal with any half reactions in specific fused salts, it is necessary to define the appropriate reference zero for <u>all</u> temperatures (comparable to the standard hydrogen electrode for aqueous solutions). While very many different types of reference electrodes have been used in molten salts, and some were proposed as suitable "universal" or "zero electrodes"[75], the most logical reference electrodes are obviously: Cl_2/Cl^-/(graphite or inert metal) for the chloride melts,[84] F_2/F^-/(graphite or inert metal) for the fluoride melts,[85] and $CO/CO_2/Au$[72,74] or $O_2/CO_2/Au$ [83,73,74] for the carbonate melts. While a reliable correlation of all the reference electrodes for different molten salts would be of great value to the corrosion and other electrochemical studies, so far, only the CO/CO_2 and the $O_2/CO_2/Au$ have been accurately correlated.[87,74]

The main variables which affect the degree (or amount) of corrosion in a given metal/molten salt system are as follows:

a. Nobility of Metal

More noble metals corrode less and more base metals more. For example, Ni is more noble than Cr in chloride melts and will, therefore, come to equilibrium with the melt at a lower contamination level (as determined by the value of the equilibrium constant K).

b. Stability of Melt

The larger its negative free energy of formation, $-\Delta G$, the more stable is the given salt melt and the lower is its corrosiveness, given that all the other conditions are the same. For this reason, for example, $MgCl_2$ is less corrosive than NaCl.

c. Initial Redox Potential of Melt

The more oxidizing is the original melt, the more corrosion will occur. However, since in many cases (especially in chloride melts), metals are soluble in their own halide melts,[82,83] the redox potential in the melt will fall as the melt gets saturated with its own metal. Thus, a salt which is reduced to an insoluble metal will be effectively less aggressive than a melt having a similar stability but in which the metal solubility is high.

d. Volatility of Corrosion Metal Products

If the volatility of the metal corrosion product is high, and if it cannot accumulate in the melt, the corrosion will proceed until an equilibrium is reached in the gas space above the melt.

e. Effect of Impurities

Impurity metals, etc., in the melt and certain metal alloy components contribute to additional corrosion effects. Of the most common corrosion-promoting impurities, oxide ion (resulting from the contact of the melt with air, or otherwise) and any traces of moisture are frequently the most serious, yet often not controlled sufficiently well, in many corrosion and electrochemical studies.

The effect of impurities in the chloride melts is fully discussed by Edeleanu and Littlewood,[88] that in the fluoride melts by Mamantov,[89] that in molten nitrates by Jordan, et. al.,[90] and that in alkali carbonates by Borucka.[74,91] From these and other publications, it is clear that in any molten salts, traces of foreign metals, or contamination by oxygen, or by trace quantities of water can each contribute to considerable inaccuracies in property measurements and that they affect the corrosion characteristics of the melt very considerably. Regretably, these effects were not known to the earlier experimenters in the field,and are still being overlooked by many people working in this field now. This, in turn, results in a volume of molten salt property data that are often not reliable and, in some instances, grossly inaccurate. The literature in this area must be, therefore, rather carefully scrutinized (with respect to the experimental apparatus and procedure involved) before the reported results are accepted as valid.

3.53 Apparatus and Experimental Procedure

Fully reliable apparatus and procedure, for molten salt property (and especially corrosion) studies should have the following features:

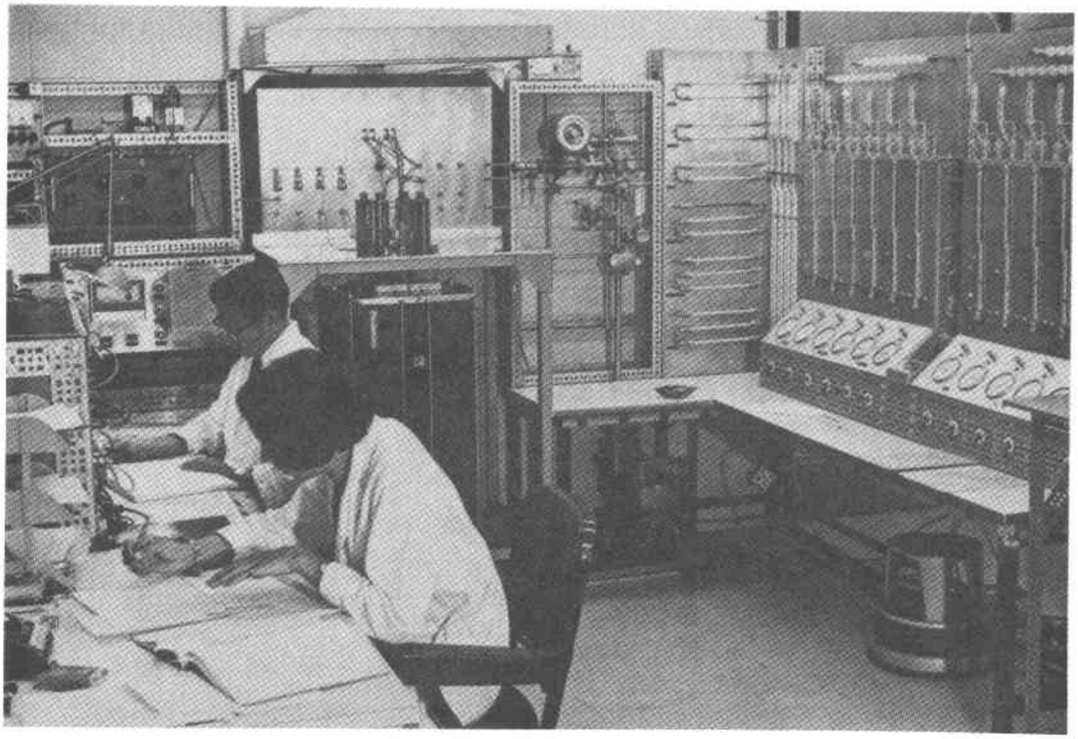
a. All materials (including the salt container, probes, etc.) in contact with the melt must be fully inert (and shown to be inert over the range of temperatures involved). This often poses a serious problem since the choice of such materials is very limited. Even the noble metals and their alloys, inert to highly pure melts, become oxidized or dissolve in melts with high $O^=$ ion concentration.[91] Caution must also be exercised in using glass containers for lower temperature studies (as practiced widely with nitrate and chloride melts) because, as shown by Edeleanu, et.al.,[92] glass contaminates chloride melts with $O^=$ ion and silica does the same thing though to a far lesser extent.[92] This apparently hopeless situation can be, however, resolved by initially insuring high purity of the melt and by monitoring accurately any subsequent oxide ion build-up or corrosion effects.

b. The apparatus enclosing the cell containing the molten salt must be fully air tight and vacuum tight. Glass apparatus of this type is generally common and widely used, but when glass cannot be considered, the apparatus constructed from ceramic and metal components is usually either fully or partially open to air (as in most of the early carbonate studies[93,94]).

For accurate gas electrode studies, up to 1000°C, in molten carbonates a fully reliable "O-ring" seal type of apparatus was fully described by Borucka, et. al.[72-74] and is shown here in Figures 3.1, 3.2 and 3.3. Such apparatus permits full control of the desired gas atmospheres over the melt and can give very accurate measurements of the oxide ion or moisture content whether these are introduced into the melt purposely or inadvertently.

c. The experimental procedure essential to all molten salt studies must involve the capability and effort to remove all impurities from the melt prior to experimentation, including even the smallest traces of water. When only the dissolved air and water are to be removed, prolonged evacuation up to 10^{-6} mm Hg of the (premelted) solid salt, melting under vacuum and repeating this cycle several times can be sufficient,[72-74] but better yet, any residual water (which is very strongly bound in most molten salts) should be electrolyzed out of the melt down to zero residual current. The latter practice

Fig. 3.1



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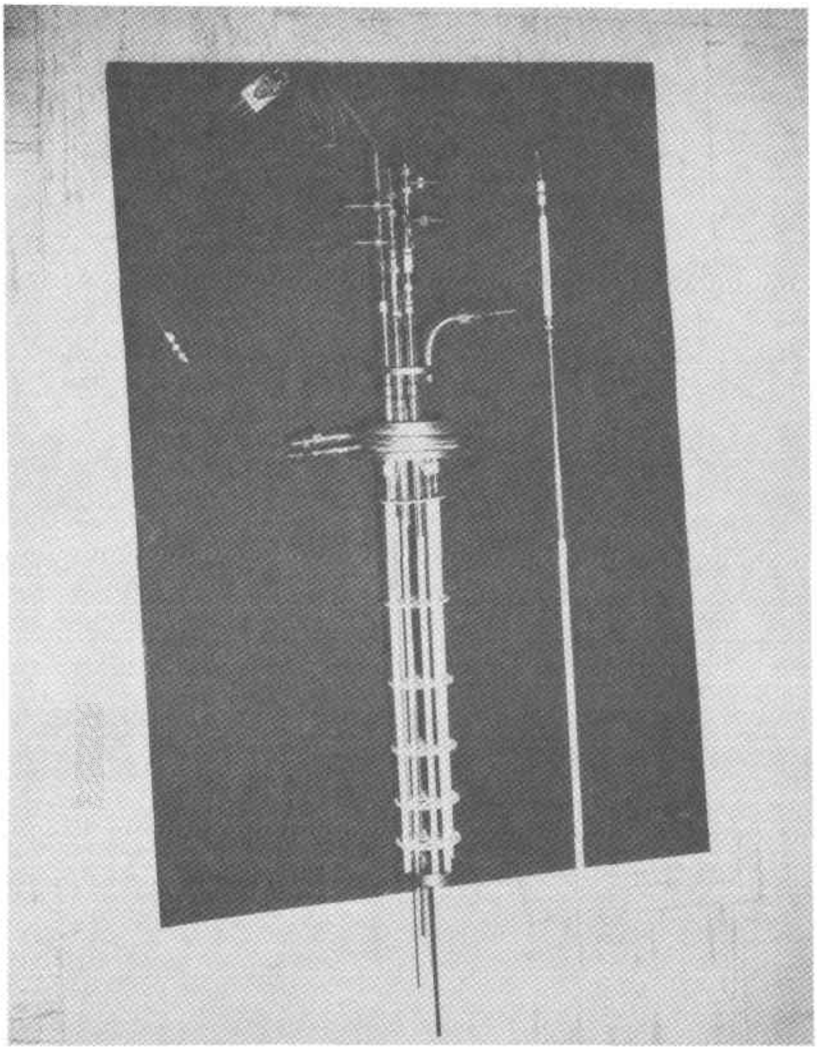
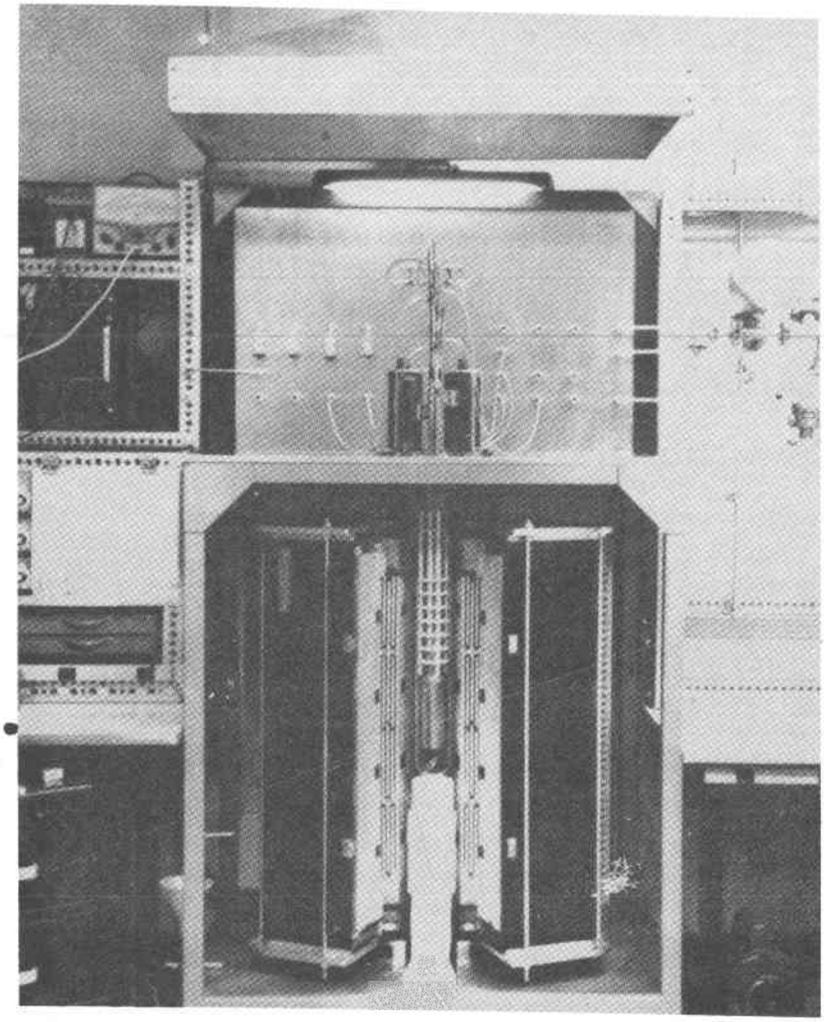
HIGH TEMPERATURE MOLTEN SALT STUDIES

Fig. 3.2



**GAS AND VACUUM TIGHT
O-RING-TYPE STAINLESS STEEL
HEADER AND PROBES
FOR MOLTEN SALT STUDIES**

Fig. 3.3



GAS AND VACUUM TIGHT FURNACE TUBE ASSEMBLY FOR MOLTEN STUDIES

was reported by Edeleanu, et. al.[88-92] and is definitely the safest and most complete.

In summary to this section, we must point out that the corrosion properties of various molten salts have, so far, not been always studied reliably, that the Pourbaix diagrams published for different molten salts[88,95,96,79] are far less practically useful than the equations on which they are based (since they cannot graphically yield, with any accuracy, the necessary data in the regions of practical importance), and that the actual practical corrosion of materials by molten salts is very much dependent on, if not governed by, the exact conditions prevailing in their use. However, many anti-corrosion procedures are possible, including that which involves proper selection of melt additives which can minimize or even fully eliminate the corrosiveness involved.

3.6 Discussion and Conclusions

Table 3.1 shows 36 selected single salts and their properties with melting points ranging from 246 to 1339°C. Some of these are suitable for a direct use in thermal energy storage application, whereas others form useful binary or ternary salts. A few salts of interest in Table 3.1 were included for comparison purposes, but proved not good enough in respect of their properties.

Examination of Table 3.1 shows that many of those salts which show the best thermal storage characteristics such as: MgF_2, NaCl, NaF, KCl, etc., all have the highest values of volume change upon fusion, as large as 20 to 40%. On the other hand, those few salts whose volume change on fusion is under 10% (as far as we can assess at present) are very few, and they do not show good thermal storage qualities except perhaps $CaCl_2$ (m.pt. 772°C, $\Delta V_{25^\circ - m.pt.} \simeq 4.1\%$, cal/\$=5,095).

It seems clear from the analysis of data in Table 3.1 that if single molten salts are to be used for thermal energy storage economically, their undesirable large volume change upon fusion must be tolerated and allowed for in the design of the equipment involved.

Table 3.1 was used as a guide for the selection of the binary and ternary salts presented in Tables 3.2 and 3.3 respectively.

Of the 32 binary salts listed in Table 3.2, with melting points from 220 to 1000°C, LiF/MgF_2 (m.pt. 741) is thermally the best and close to NaF/MgF_2, which is also thermally good, but even better in terms of its relative cost in calories/dollar. Experimentally measured properties for the binary salts are grossly lacking, but among the selection shown in Table 3.2, eleven salt mixtures show cal/gm >100, twenty six show cal/cc >100 (ten show cal/cc >200), and fifteen show the relative cost in cal/$ ≥10,000.

The list of twelve selected ternary salt mixtures shown in Table 3.3, with melting point range of 375 to 713°C, show that thermally and cost-wise, the best salts are KF/LiF/MgF_2 and NaF/KF/LiF.

While normally lithium salts are found to be considerably more corrosive than the salts of any other cations listed here,[91] they have been extensively studied and practically utilized in the nuclear reactor programs.[89] With the background of this important practical knowledge on the lithium and other fluoride melts, and their outstanding thermal characteristics, it seems that they should prove to be a good class of salts for thermal storage applications. Apart from these, and outstanding in its high thermal storage capability, coupled with low cost, is, of course, sodium chloride and also the sodium chloride-containing binaries and ternaries.

The selection of salts offered in this report is large and fully covers the melting point range from 220 to over 1000°C. Specific choice, however, must ultimately be made by the engineers who need to fulfill particular objectives of their task in this area.

4. CRITICAL SURVEY AND ASSESSMENT OF EXPERIMENTAL METHODS FOR DETERMINATION OF SALT PROPERTIES BELOW AND ABOVE MELTING TEMPERATURE

4.1 Physical Properties

4.11 Density, Partial Molar Volume and Thermal Expansivity

In addition to their use in the analysis of such properties as viscosity and conductivity, density studies are of considerable value in investigations of the salt structure ana permit the calculation of quantities such as partial molar volume and expansivity.

Densities of solid salts are most reliably measured by X-ray diffraction or linear dilatometry techniques which are reviewed in detail by Hindert and Sounder[97] and others.[98]

Liquid densitometry, fully reviewed by White,[99] can be accurate to ±0.1 or 0.2% at temperatures as high as 1950°C but requires considerable care in proper selection of the technique and apparatus as well as good experimental control of a number of limiting factors. The methods of measuring densities of molten salts are briefly summarized below together with data treatments.

The main factors affecting the precision of high temperature densitometry are as follows:

a) Temperature must be maintained uniform over the entire volume of the material studied as well as possible. (Typically, a non-uniformity of ±0.5°C contributes an error in density value of one part in 10^4). For precise work, temperature must be maintained constant to ±0.5°C over the period required to complete each determination. Thermal lag between the sample and the temperature sensing element must be eliminated.

b) With exception of the pyknometer technique (described below), all methods involve the measurement of a weight or length in the hot zone from a remote position at room temperature. Weighing can be performed accurately, but the balance must be protected from thermal effects. Direct optical observation of length is seldom possible while measurements by probes or electric contacts have the serious disadvantage that the entire device must come to thermal equilibrium.

c) Materials from which densitometers are constructed must be selected for their non-reactivity rather than ease of fabrication and thus methods involving complex or delicate apparatus are seldom practical.

d) Since most melts solidify with considerable shrinkage, serious manipulative problems of filling and emptying the apparatus, distortion of the containers, etc., must be overcome. In this respect, methods which depend on the volumetric calibration of these vessels are at a big disadvantage.

The four types of density measurement methods applicable to molten salts at high temperatures are as follows:

A. Archimedean Methods (direct or indirect)
B. Pyknometric Methods
C. Volumetric Methods
D. Pressure Methods

A. Archimedean Methods

This method is used most frequently and depends on the Archimedes' principle, which states that the buoyant force exerted on an object immersed in a fluid is equal to the weight of the displaced volume of the fluid. In the simplest direct Archimedean method a bob composed of an inert solid reference material is suspended in the melt by a wire from the arm of a balance (see Fig. 4.1). The density, ρ, is given by

$$\rho = \frac{B + S}{V^{o} + v'}$$

The bouyancy B is the difference in weights of the bob plus the immersed part of its suspension in vacuum and in the melt. V^{o} is the volume of the bob, v' is the volume of the immersed suspension and S is the surface tension effect.

The bob used must be made of a reference material of reproducible thermal properties and known to be inert to the melt studied. Often it is made of platinum, gold or noble metal alloys although some refractory metals such as tungsten, molybdenum and tantalum can be sometimes used. Otherwise, the bob can be made of a suitable non-porous ceramic material such as pure alumina or pure magnesia.

The indirect Archimedean method is used when the properties of the melt make the direct method unsuitable due to corrosion or other causes. Here the salt density ρ is measured in terms of the density ρ' of the buoyant liquid which must be calibrated against a reference solid. The crucible containing the melt studied is suspended in the reference melt contained by a larger crucible. The two melts must be however mutually insoluble and the smaller crucible must be inert to both the melts.

FIG. 4.1a Archimedian densitometer[61]

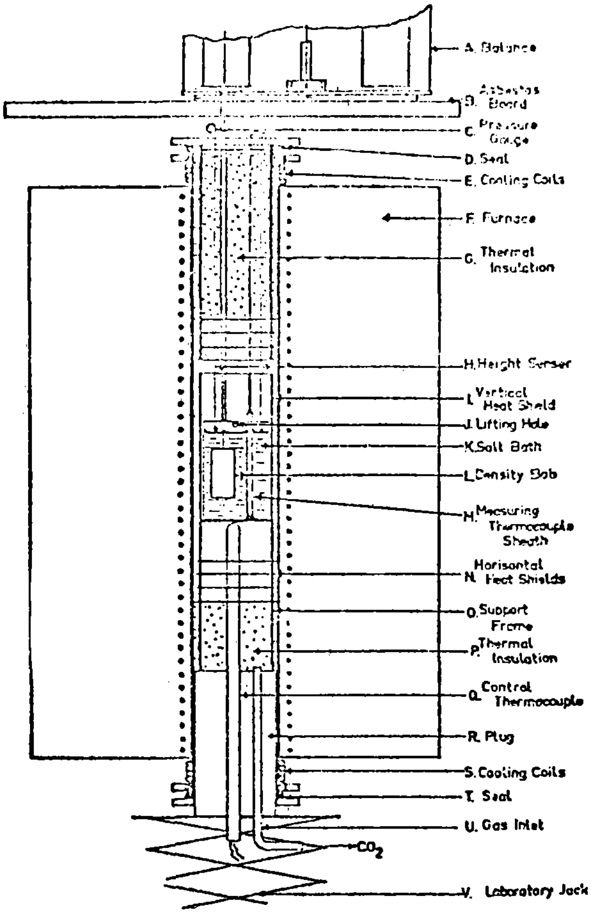
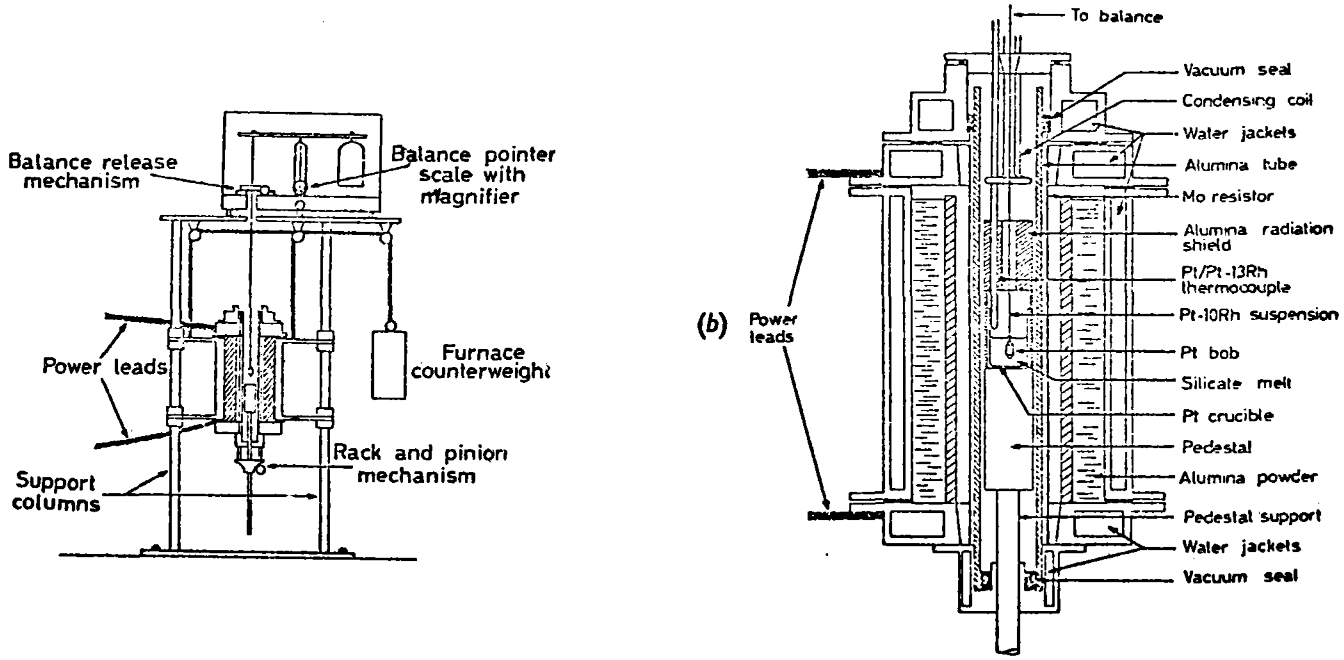


FIG. 4.1b An Archimedean densitometer for the study of molten silicates[61]


General view of apparatus

Section view of furnace and hot zone

With the first of the above methods, several difficulties arise if the melt studied has appreciable vapor pressures. Serious volatilization may lead to changes in melt composition (e.g., alkali carbonates), a lowering of the melt level and deterioration of the apparatus. While these problems can be fully eliminated by the use of the indirect Archimedean method, even in the direct method they can be considerably reduced by covering the crucible with a lid having a very small hole, just large enough to pass the balance wire. When no lid is used (as in the measurements of density and surface tension of molten carbonates, by Janz and Lorenz,[71]) the accuracy of results becomes uncertain especially at higher temperature.

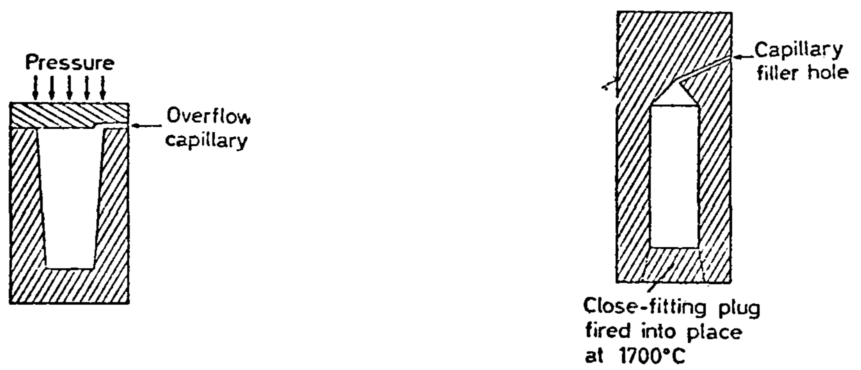
The basic apparatus, shown in Fig. 4.1, is sufficient for accurate density measurements on non-volatile molten salts but for any volatile salts and for the surface tension measurements, a more elaborate, gas and vacuum-tight apparatus (such as described by Borucka[72-74]) is mandatory.

In the situation where no adequate surface tension data are available, a modified two-bob densitometer can be used such as that described by Bockris, et.al.[100]

B. Pyknometric Methods

These methods define a volume in such a way that the filling and weighing of the vessel can be precise and convenient. Pyknometers, Fig. 4.2, have a particular advantage for the volatile liquids since the vessel involved has only one capillary size filler hole which restricts volati-

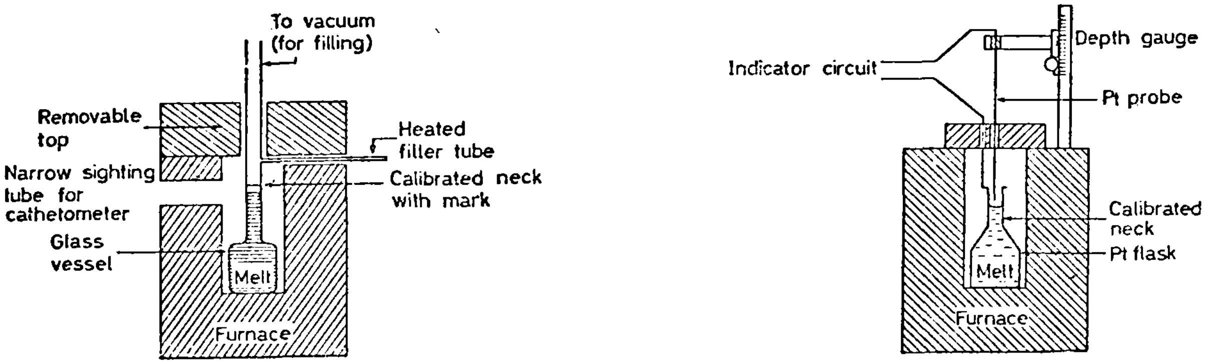
FIG. 4.2 Two types of high temperature pyknometers



(a) Graphite pyknometer

(b) Alumina pyknometer

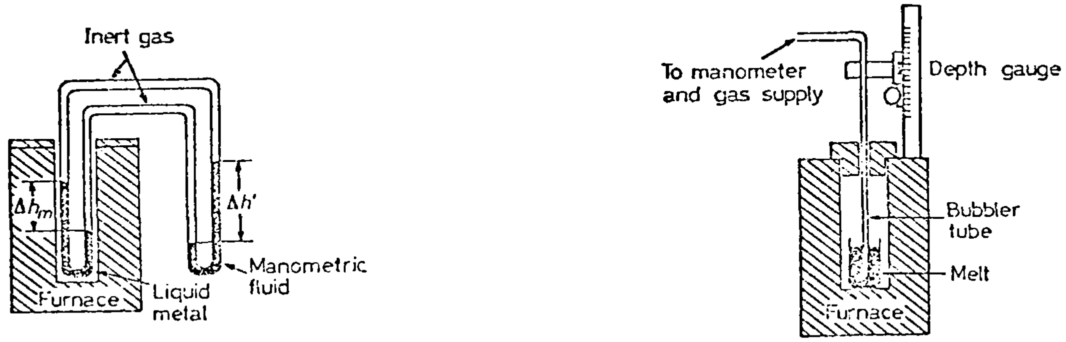
FIG. 4.3 Two types of liquid dilatometers



(a) Glass dilatometer

(b) Platinum dilatometer

FIG. 4.4 Methods based on pressure measurements



(a) Method of balanced columns

(b) Maximum bubble pressure method

lization. Nevertheless, these methods are seldom used in high temperature molten salt studies for the following reasons:

a) difficulty of construction of an accurate vessel from the refractory materials and tendency for distortion of the vessels made of metals such as platinum.

b) in most applications, the pyknometer, after each run, must be recalibrated, repaired or replaced.

c) each run yields the density value only for one particular temperature.

C. Volumetric Methods

A liquid dilatometer, Fig. 4.3, differs essentially from a pyknometer in that it serves to measure the volume of a given weight of liquid rather than the weight of a defined volume. Further, it measures the density over a range of temperatures during a single run. Furthermore, in the form of a large bulb with a narrow calibrated neck, the dilatometer is well suited for measurements of thermal expansivity and ρ for volatile liquids. While many precautions and corrections are necessary in using this method for high temperature molten salts, it is capable of a reproducibility of ±0.1%. It is certainly one of the most advantageous methods for use with volatile salts.

D. Pressure Methods

Two methods used at high temperatures to measure the pressure exerted by a column of liquid are: the method of balanced columns and the maximum bubble pressure method. The two systems, shown in Fig. 4.4, have the advantage of remote measurement of liquid levels and suitability for volatile salts. Of the two, the maximum bubble pressure method is simpler and suited also to the measurements of surface tension. The pressure P required to detach bubbles from an accurate standard bubbler tube is determined at two or more different depths of immersion in the melt, and the density simply calculated from the relation:

$$\rho = \frac{\Delta P}{\Delta h}$$

Discussion

While the density data reported usually in units of mass per volume are important for practical applications, in structural investigations where the attention is focused on the spatial requirements of various configurations of the constituent atoms, the atomic masses are less relevant, and the results of measurements must be treated in terms of molar or atomic volumes. This is also particularly important in the study of solutions where density isotherms can be misleading; even in ideal solutions the density and the specific volume are not always linear with molar concentration.

The molar volume v is defined by

$$v = \frac{V}{n} = \frac{M}{\rho} = \frac{\Sigma(NiMi)}{\rho}$$

where V is the total volume of n moles of substances 1, 2, etc., and M is the molecular weight of the liquid whose composition is defined by mol-fractions N_1, N_2, etc.

In terms of the partial molar volumes $\bar{v}_i$ the molar volume is given by

$$v = \Sigma(N_i\bar{v}_i)$$

Thus, $\bar{v}_i$ is the effective contribution of component i to the total volume of the solution.

The molar expansibility at constant pressure, $(\partial v/\partial T)_p$, which is related to density ρ and the expansivity α by

$$\left[\frac{\partial v}{\partial T}\right]_p = v\alpha = -\frac{v}{\rho}\left[\frac{\partial \rho}{\partial T}\right]_p$$

may be treated similarly, but it must be noted that the partial molar expansibility $(\partial\bar{v}_i/\partial T)_p$ is a second derivative and therefore requires correspondingly more precise density data for its calculation.

For precise calculation of $\bar{v}_i$ (by the method of intercepts[109]) it is desirable to make use of the volumetric deviation from ideality defined by

$$\Delta v = v - v^{ideal} = v - \Sigma(N_i v_i)$$

where v_i is the molar volume of pure component i. Since Δv is usually a small quantity, large scale plots can be used with advantage in evaluating the partial molar deviation $\Delta\bar{v}_i$ which is related to $\bar{v}_i$ by

$$\bar{v}_i = v_i + \Delta\bar{v}_i$$

In the case of fused binary systems, the variation of Δv with composition is usually very smooth; rapid changes in $\Delta\bar{v}_i$ seldom occur at compositions other than those corresponding to simple atom ratios.

On the other hand, the thermal expansibility is more sensitive to structure, e.g., in alkali silicate systems the expansibility increases by more than an order of magnitude on passing from a composition where strong Si-O-Si bonds dominate to a composition where the melt becomes ionic.[101]

4.12 Compressibility

The compressibility β for solid materials is usually determined by measuring the difference between the compressibility of the test substance and that of a reference substance of known compressibility, commonly iron or mercury.

β is defined by the equation:

$$\beta = -\frac{1}{V_o}\left[\frac{\partial V}{\partial P}\right]_t$$

in which (for a given temperature t) V is the volume at pressure P and V_o is the volume at P = 1 bar (1 bar = 0.987 atm).

The variation of β with temperature is:

$$A_P = \frac{1}{\beta_o}\left[\frac{\partial \beta}{\partial t}\right]_P$$

and with pressure it is:

$$A_t = \frac{1}{\beta_o}\left[\frac{\partial \beta}{\partial P}\right]_t$$

where β_o is the value of β at a specified temperature and usually at P = 1 bar, expressed in reciprocal bar units.

The change of α, the thermal expansibility, with pressure is readily calculated from the values of $1/\beta_o(\partial\beta/\partial t)$ for if

$$\alpha = \frac{1}{V_o}\left[\frac{\partial V}{\partial t}\right]_P$$

we have

$$\left[\frac{\partial\alpha}{\partial P}\right]_t = \left[\frac{\partial\beta}{\partial t}\right]_P$$

For most solids $1/\beta_o(\partial\beta/\partial P)_t$ is independent of temperature within the error of the experiment. It therefore follows that $1/\beta_o\ (\partial\beta/\partial t)_P$ is independent of pressure. It also happens that with most solids the variation of $1/\beta_o(\partial\beta/\partial P)_t$ with pressure is too small to be measurable.

The values of β for the solid salts of interest to this project, found in the literature[110] are based on:

$$\beta_{Hg} = 4.0 \times 10^{-6} \text{ and } \beta_{Fe} = 0.59 \times 10^{-6} \text{ at } 20^{\circ}C$$

and pressure of 1 bar, unless otherwise stated.

TABLE 4.1

The Isothermal Compressibilities of Solid Salts[110]

Salts	temp.°C	P(bars)	$10^6\beta$	-10^4A_t	10^4A_P
$MnCO_3$	0	125	1.3		
$CaCl_2$	20	300	4.36		
$CaBr_2$	20	300	4.84		
$CaCO_3$	25	1	1.36	0.06	4
$BaCl_2$	20	300	2.77		
LiCl	25	1	3.50	0.20	7
LiBr	25	1	4.30	0.25	8
NaCl	25	1	4.18	0.20	7
NaBr	25	1	5.09	0.26	8
KCl	25	1	5.65	0.27	5
KBr	25	1	6.68	0.32	6

At least for the solid alkali halides in the above table it seems that the compressibility β increases in the order Li<Na<K both for the chlorides and bromides.

The compressibilities of many molten alkali chlorides, bromides iodides and nitrates have been measured[56] by determination of the velocity of ultrasonic mechanical vibrations of about 10^6 cycle/sec in the melt. The velocity of ultrasound U_L in these liquids was found to be strictly proportional to the square root of absolute temperature, but over a temperature range of 200° - 500°C a linear relation with absolute temperature becomes applicable:

$$U_L = U_o - aT$$

where U_o and a are constants.

The isothermal compressibility (β_t) was found to increase, approximately linearly with the square of the mean radius of the ions of the salts (Figs. 4.5 and 4.6). β_t also increases with increase in temperature (Figs. 4.7 and 4.8).

Increase of the ratio of the specific heats C_p/C_v, and decrease of C_v occur upon increase of the size of X for a given M in a series MX and vice versa. The free volumes (V_f) increase with increasing particle size and increase of temperature.

From β_t, the internal pressures are calculated and these enable a satisfactory equation of state to be formulated.

Comparison of the free volumes with the changes in volume on melting ΔV, indicate the major role played by holes in the structure of these liquids. Some of the interesting data resulting from this work[56] are given in the Appendix.

The values of the adiabatic and isothermal compressibilities for these salts are shown in TABLE 4.2.

FIG. 4.5 Isothermal compressibility as a function of the cationic radius for liquid alkali-metal halides: O, chlorides; □, bromides; Δ, iodides.[56]

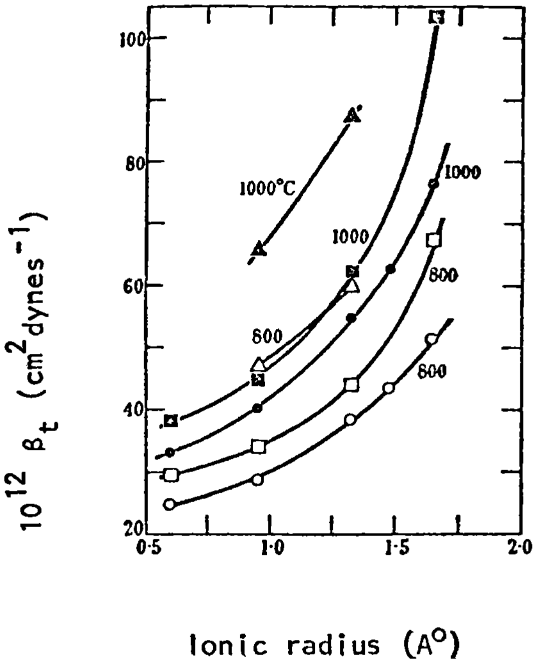


FIG. 4.6 Isothermal compressibility as a function of cationic radius for liquid alkali-metal nitrates.[56]

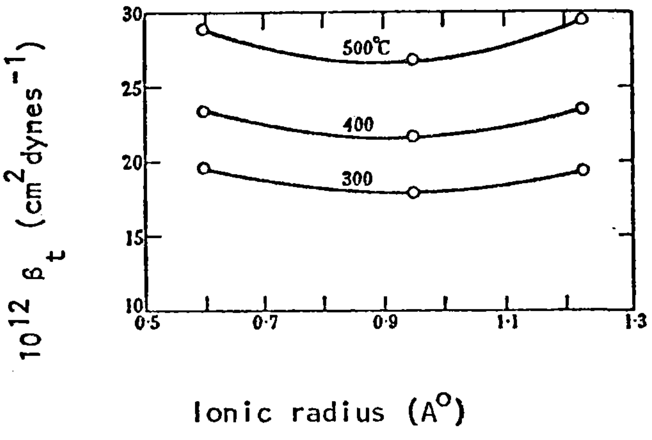


FIG. 4.7 Temperature dependence of the isothermal compressibility of liquid alkali-metal halides and cadmium chloride: 0, LiCl; △, NaCl; x, KCl; □, CsCl; ▽, NaI, ◑, $CdCl_2$; ◐, LiBr; ▲, NaBr; +, KBr; ▣, CsBr; ◓, KI.[56]

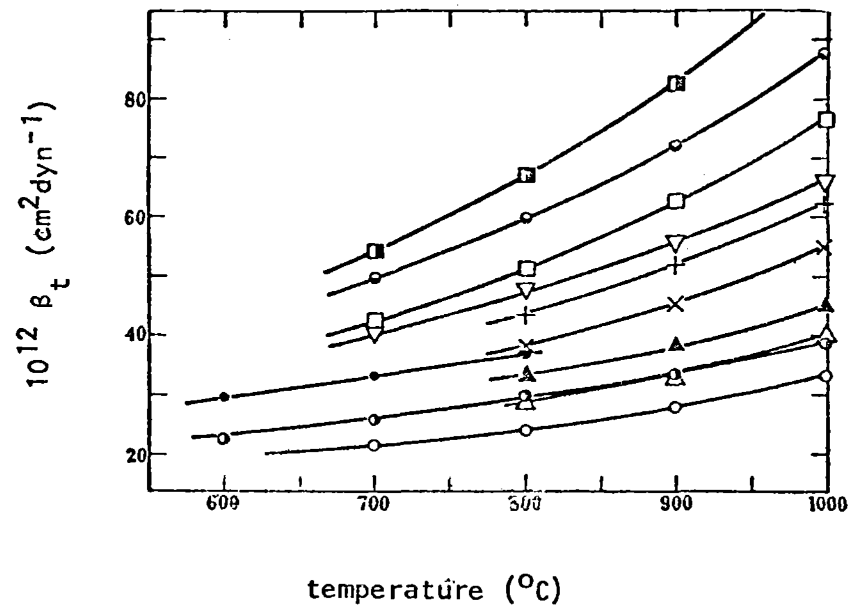


FIG. 4.8 Temperature dependence of the isothermal compressibility of liquid alkali-metal nitrates: ○, $LiNO_3$; x, $NaNO_3$; +, KNO_3.[56]

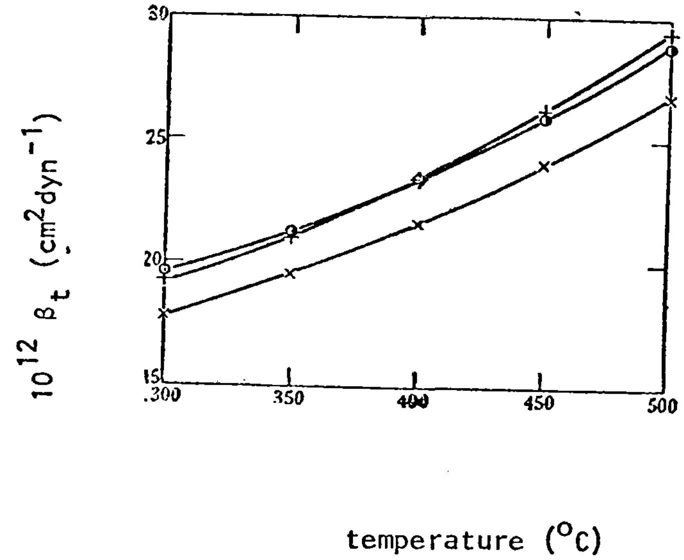


TABLE 4.2 The Adiabatic and Isothermal Compressibilities of Molten Electrolytes[56]

Salt	temperature (°C)	$10^{12}\ \beta_S$ (cm^2 dyn^{-1})	$10^{12}\ \beta_T$ (cm^2 dyn^{-1})	Salt	temperature (°C)	$10^{12}\ \beta_S$ (cm^2 dyn^{-1})	$10^{12}\ \beta_T$ (cm^2 dyn^{-1})
LiCl	700	17.7	21.7	LiBr	600	19.1	22.7
	800	20.0	24.7		700	21.4	25.8
	900	22.7	28.6		800	24.1	29.4
	1000	26.0	33.0		900	27.3	33.6
					1000	31.1	38.4
NaCl	800	20.9	28.7				
	900	24.2	33.8	NaBr	800	26.1	33.6
	1000	28.2	40.0		900	29.9	38.6
					1000	34.3	44.9
KCl	800	26.6	38.4				
	900	31.8	45.7	KBr	800	31.1	43.8
	1000	36.9	54.7		900	36.4	52.1
					1000	42.8	62.1
CsCl	700	28.7	42.9				
	800	33.8	51.2	CsBr	700	34.6	55.8
	900	40.4	62.7		800	41.5	67.1
	1000	48.7	76.3		900	50.5	82.7
					1000	62.2	103.1
$CdCl_2$	600	26.9	29.8				
	700	29.7	33.0	$LiNO_3$	300	17.7	19.6
	800	32.8	36.9		400	21.0	23.4
					500	25.4	28.9
NaI	700	29.2	40.0				
	800	33.4	47.3	$NaNO_3$	300	(15.6)†	(17.8)†
	900	38.4	55.6		400	18.7	21.6
	1000	44.6	65.6		500	22.6	26.8
KI	700	33.5	49.9	KNO_3	300	(16.1)†	(19.3)†
	800	39.4	59.9		400	19.3	23.4
	900	46.7	72.0		500	23.3	29.4
	1000	56.0	87.3				

† Hypothetical values for liquid state when substance solid.

4.13 Vapor Pressure

Vapor pressure is an important property which determines the thermal and composition stability of a given salt mixture. Ideally it should be as low as possible.

Experimental methods by which vapor pressures can be measured for molten salts fall into two categories: absolute and non-absolute. Absolute methods do not require the use of the gas law for calculation of vapor pressure while the non-absolute methods do and further depend on an assumption regarding the molecular weight of the salt vapor.

A. Absolute Methods

For molten salt studies, direct manometric measurement with the use of a Bourdon (spoon or sickle) gauge as a null detector is among the most useful methods.

Boiling and dew point methods.[111] The most accurate absolute method is the determination of boiling point at pressures that are held constant at various values between a few millimeters of Hg and 1 atm. The method was originated by Ruff and Bergdahl (1919) and was used in many early vapor pressure studies but the results were often uncertain due to superheating (up to 20°C).

The melt is held in a silica boiling tube in which is situated a silica "cold finger" condenser (cooled by compressed air). The temperature of boiling is determined by means of a noble metal thermocouple with the hot junction situated close to the surface of the melt to eliminate errors due to increase of measured temperature with increase of pressure (i.e., with depth of immersion). Experimentally the method is very straightforward. The temperature of the surrounding furnace as measured by another thermocouple is initially lower than the boiling point at the particular constant pressure which is applied and kept constant by means of a manostat. The furnace is allowed to heat slowly, the boiling point being the constant temperature registered by the thermocouple at the surface of the melt while the thermocouple that registers furnace temperature continues to rise steadily. Pressure is measured by means of a manometer. The experiment is repeated at various pressures, giving variation of boiling point with pressure. This method can be used to determine vapor pressure of a pure salt and total vapor pressure of a mixture.[111]

B. Nonabsolute Methods

Transpiration

This method is the most widely used indirect method and its use in molten salt systems originated with Rosner and Jellinek.[112]

An inert gas, such as Ar, is passed over silica boats containing the molten salt, becomes saturated with vapor, and enters a silica condenser tube situated very close to the thermocouple used for measuring temperature. The salt vapor condenses in the silica tube while the inert gas passes through to be collected and its volume measured. The weight of salt vapor collected is determined by analysis of the condenser contents. By assuming that the ideal gas law is obeyed (found to be a reasonable assumption at pressure below atmospheric), vapor pressure can be calculated if the molecular weight is known. Assumption that molecular weight is the same as formula weight is often made but is usually incorrect owing to polymerization

FIG. 4.9 Vapor pressure determination by measurement of boiling point.[111]

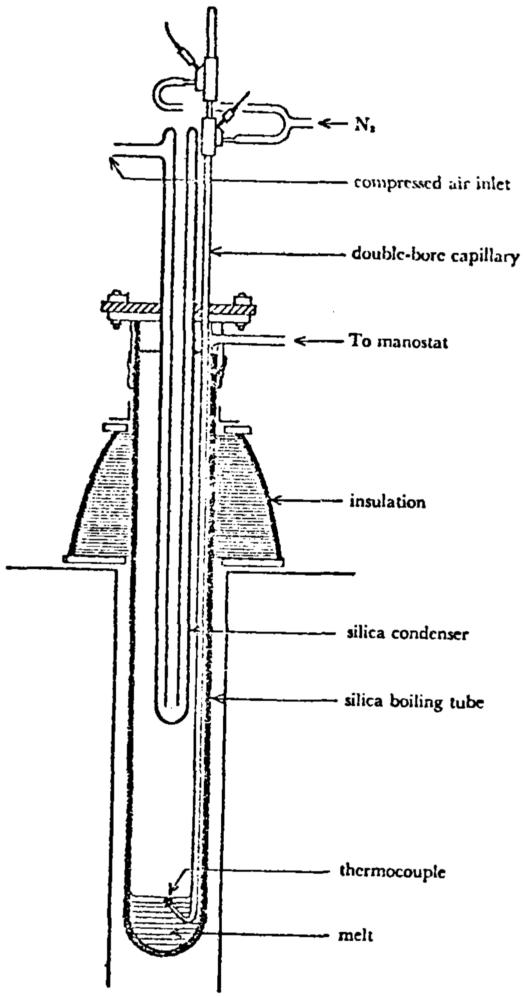
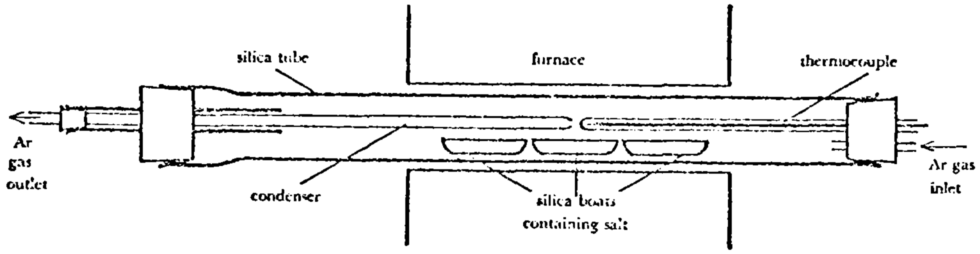


FIG. 4.10 Determination of vapor pressure by transpiration.[112]



of the vapor. The main advantage of the transpiration method is that it can be used to determine the partial pressures of components of a mixture.

Effusion

For high melting substances vapor pressure can be determined by Knudsen's formulas from weight of substance escaping into a vacuum from a small hole in a box.

4.14 Viscosity

The problems and limitations of high temperature viscometry are similar to those encountered with other physical property measurements. The primary limitation is the availability of suitable inert material from which the viscometer components, in contact with the melt at high temperature, can be accurately constructed. The difficulty of maintaining a large uniform temperature hot zone precludes the application of any method that involves long capillaries or bulky components.

In general, fused salts, as many molten metals, are highly fluid, having viscosities in the range of 0.5 to 5 centipoise.

In this section, only a brief account is given of the viscometric methods developed for molten salts, a more complete account being available in the review by Mackenzie[113] and the full details in the original papers.

The four principal groups of methods used for viscosity measurements at high temperatures, illustrated generally in Fig. 4.11, are as follows.

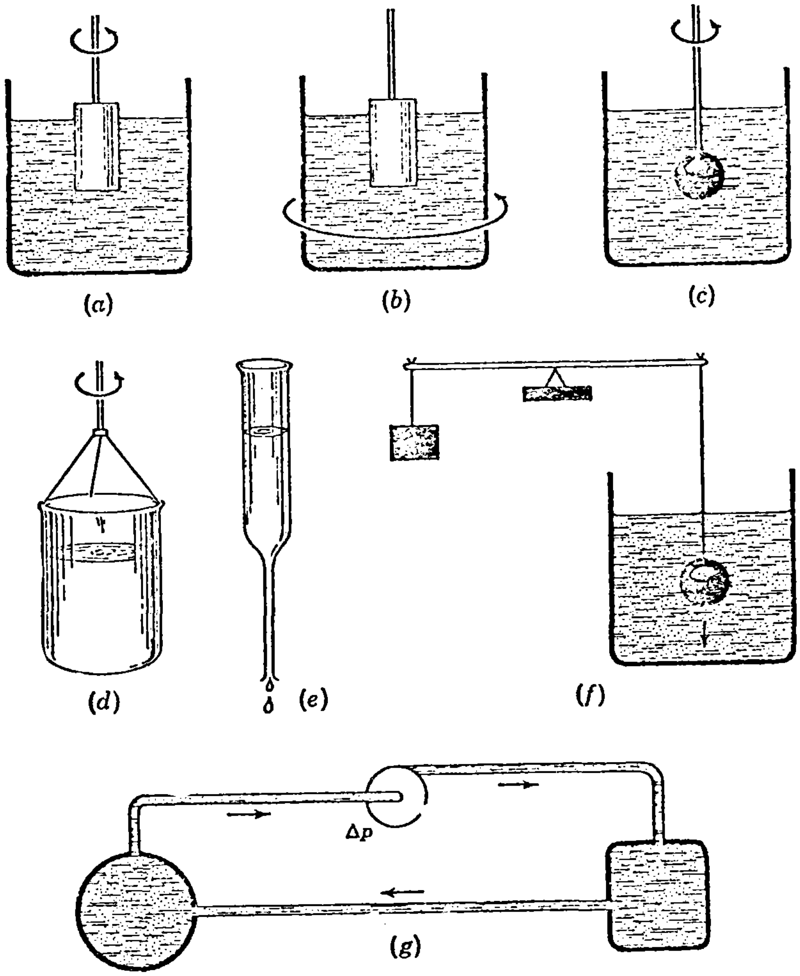
A. Concentric Cylinders Methods

In these methods the molten salt contained in the annulus between two concentric cylinders is maintained in a state of shear. The torque required to maintain a constant relative angular velocity is a measure of the viscosity. This involves either:

i. Rotation of Inner Cylinder while the outer cylindrical crucible containing the melt is kept stationary as in the apparatus of Rait and Hay,[114] shown in Fig. 4.12 or

ii Rotation of Outer Cylinder (crucible) while the inner

Fig. 4.11 Schematic diagrams of methods of determining viscosity.



(a) Measure velocity of cylinder for fixed torque, Rait and Hay, 1938.

(b) measure torque on cylinder for fixed velocity of crucible, Bockris and Lowe, 1953.

(c) measure damping of oscillating bob, Lorenz and Hochberg, 1916.

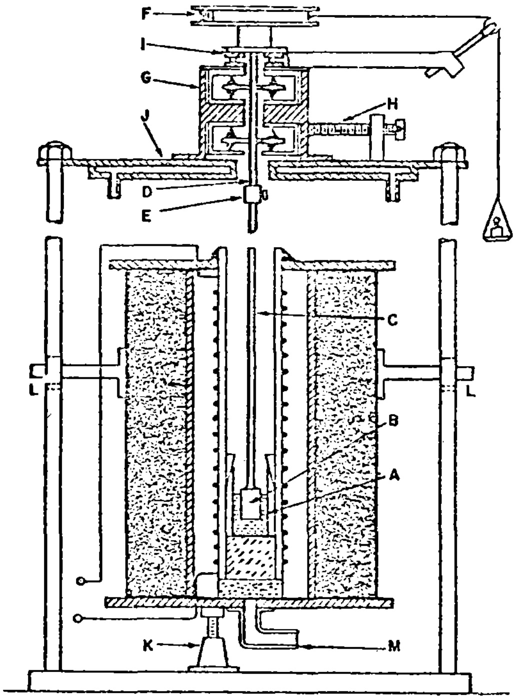
(d) measure damping of oscillating crucible, Barfield and Kitchener, 1954.

(e) measure velocity through capillary under gravity, Bloom, Harrap, and Heymann, 1948.

(f) measure velocity of partially couterbalanced falling body, MacKenzie, 1956.

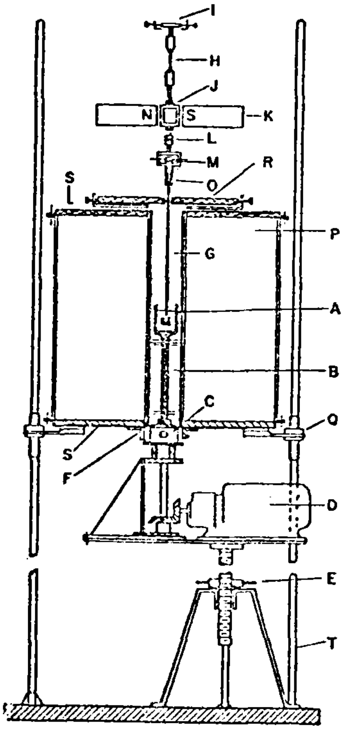
(g) measure flow through capillary under applied pressure, Spells, 1936.

Fig. 4.12 Concentric-cylinder viscometer with rotating inner cylinder (Rait & Hay)[114]



A, fixed crucible
B, rotating inner cylinder
C, alundum or graphite rod
D, silver steel spindle
E, multiple brass coupling
F, pulley wheel
G, special housing with alarm
balance movements
H, centering screw
I, ball-race
J, water-cooled plate
K, screw-jack
L, guide brackets
M, gas inlet

Fig. 4.13 Electromagnetic viscometer with rotating crucible (Bockris and Lowe)[115]



A, Mo crucible with graphite casing
B, graphite support with horizontal
radiation shields
C, self-centering chuck
D, ¼ h.p. 230 V d.c. shunt wound
motor
E, capstan screw-jack
F, chuck housing
G, hollow graphite connector
H, Be-Cu torsion wire
I, centering device for suspension
J, coil
K, permanent magnet
L, mirror
M, total reflecting prism
O, "Tufnol" insulating connector
P, Mo tube resistance furnace
Q, adjustable steel support
R, water-cooled 'D' plates
S, water-cooled furnace top and
bottom
T, rigid framework

concentric cylinder is kept stationary as in the apparatus of Bockris and Lowe,[115] shown in Fig. 4.13. Quantitative results for both these methods are given by Mackenzie.[113]

B. Oscillational Methods

Torsional oscillations performed by a solid bob suspended in a melt, or by a hollow vessel containing the melt, will experience a damping effect resulting in a progressive decrease of the amplitude of swing. The viscosity of the melt is evaluated from the resulting logarithmic decrement (defined as the logarithm of the ratio of two successive amplitudes of oscillation), the density of the melt, the dimensional constants of the apparatus, and (in some cases) the periods of oscillation. While with certain modifications of this method the absolute viscosity can be obtained, the mathematical expressions are complex, and the calculations involve tedious successive approximations. Instead, therefore, the apparatus is usually calibrated with liquids of known viscosity and then used for the measurement of the viscosity of the melt relative to the selected "standard".

Four main types of these methods involve either:

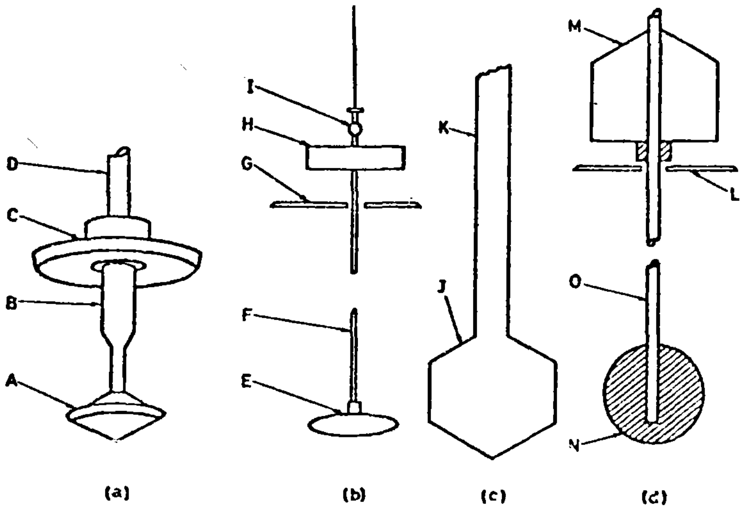
i. Oscillating Disc or Sphere[57,116-121] (different shapes and types shown in Fig. 4.14),

ii. Oscillating Cylinder,[114,122]

iii. Oscillating Crucible,[123-127]

iv. Oscillating Spherical Container.[128,129]

Fig. 4.14 Some typical oscillating bobs.[113]



(a) Stott1933 A, 1.8 in. diameter alumina disc; B, alumina stem; C, 3 in. diameter and ¼ in. thick steel disc; D, 3/16 in. steel rod;

(b) Lorenzo and Hochberg1916E, Pt-Ir disc of diameter 2.6 cm; F, Pt-Ir rod of diameter 0.15 cm and length 25 cm; G. furnace top; H. inertia bar; I, mirror

(c) Yao and Kondic 1952 J, graphite bob of diameter 4 cm; K, solid graphite connector

(d) Yao 1956 L, furnace top; M, Ni-Cr inertia weight; N, alumina sphere of diameter 3 cm; O, alumina tube and thermocouple sheath

C. Capillary Methods

These methods have been extensively used for liquid metals as well as fused salts up to 1,250°C mainly because of their simplicity and ease of measurements. At higher temperatures, however, their use is frequently precluded by the difficulties of obtaining refractories in the suitable tubular form and maintaining accurate uniformity of temperature in the hot zone of the furnace.

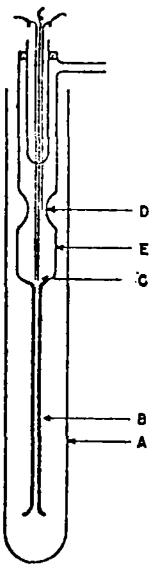
The capillary methods are based on the familiar Poiseuille principle which relates pressure drop across a given length of tube to the viscosity of the liquid flowing through it under laminar conditions (provided that a proper correction is applied for the loss of the kinetic energy at the tube entrance. Viscosity is evaluated from the following experimental data: pressure difference, time of flow, volume of flow, liquid density and dimensions of the capillary.

Details of the typical horizontal capillary[130,131] and vertical capillary[132,133] are shown in Figs. 4.15 and 4.16.

D. Falling Body Methods

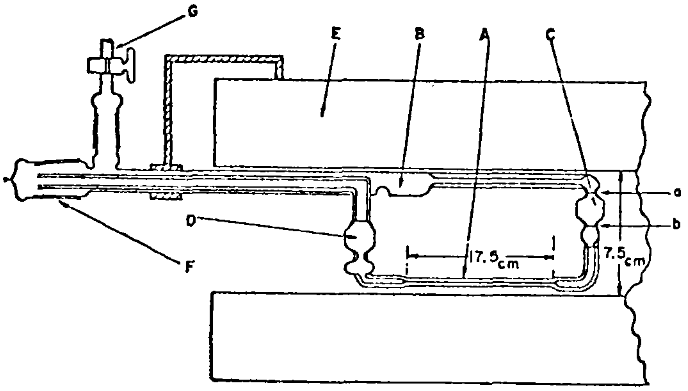
Both the free and the restrained sphere techniques are suitable only for relatively viscous liquids $\eta = 40$ poise). They are, therefore, not applicable to most fused salts[113] and will not be discussed here.

Fig. 4.15 Capillary viscometer (Bloom, Harrap and Heymann[130])



A, glass container, 3 cm internal diameter and 55 cm long
B, capillary of diameter 0.05 cm and length 12 cm
C, lower contact
D, upper contact
E, glass reservoir of 1.4 cm internal diameter and length 6 cm

Fig. 4.16 Horizontal capillary viscometer (Spells[131])



A, quartz capillary of diameter 0.04 cm
B, charging reservoir
C, bulb of standard flow volume
D, receiving reservoir
E, furnace
F, auxiliary opening for cleaning viscometer
G, vacuum line

According to Mackenzie,[113] for fused salts studies, the most suitable method of those described above is the vertical capillary method such as used by Bloom et.al.[130] This, however, is conditional upon the ability to maintain an accurately uniform temperature zone in the furnace and the availability of accurately dimensioned capillaries made of materials which are fully inert to the melt studied. Otherwise, it is clear that the oscillational methods should be considered as the next best alternative.

4.2 Phase Diagrams

The number of phases present and their composition at equilibrium under specified conditions are of great importance in studying high temperature molten salts. As the temperature increases and process rates become faster, equilibrium is more quickly reached. This fact is obviously advantageous in the phase diagram studies of molten salts at high temperatures yet, as with other property studies on these systems, it is offset by their corrosive nature and the necessity to ensure accurate temperature conditions and temperature measurements.

In general, the many methods developed for the determination of phase equilibria[62] can be divided into two main categories:

A. Static methods

B. Dynamic methods.

A. Static Methods

These methods employ the technique of holding a sample under specific conditions until equilibrium is reached, and then determining the number and composition of the phases present either by:

i. high temperature X-ray measurements[134-138] (Fig. 4.17) or microscopy[139-145] (Fig.4.18) directly in situ at the given temperature, or

ii quenching the salt so rapidly that the high temperature phases are frozen for a similar examination at room temperature[146-153] (Fig. 4.19).

In these methods it is necessary to ensure: that equilibrium is actually reached, that the final phases are properly identified, and that the high temperature state is correctly interpreted from the quenched samples.

Fig. 4.17 High temperature Debye-Scherrer X-ray camera employing resistance heating. Alcock, et.al.[135]

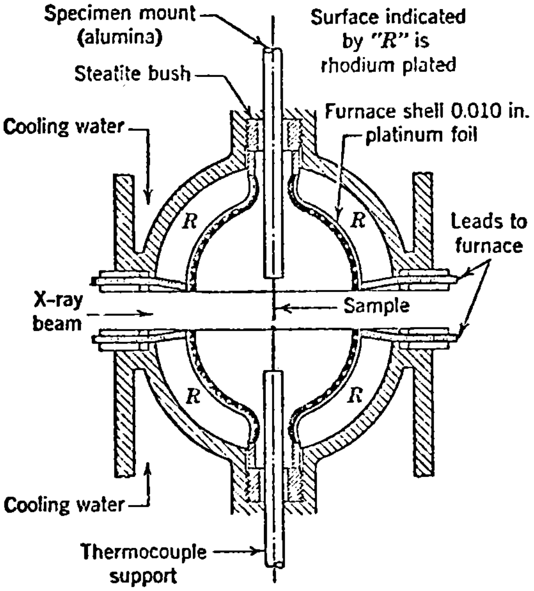


Fig. 4.18 Microscope furnace.[140-142]

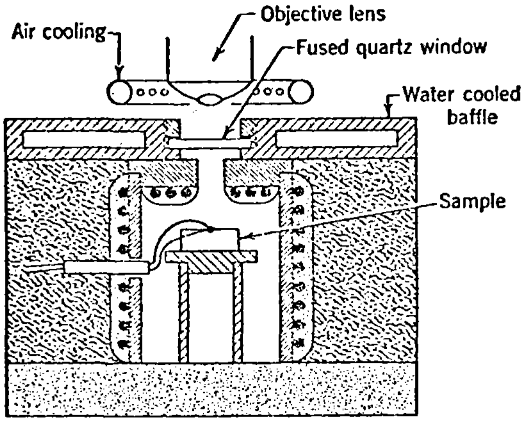
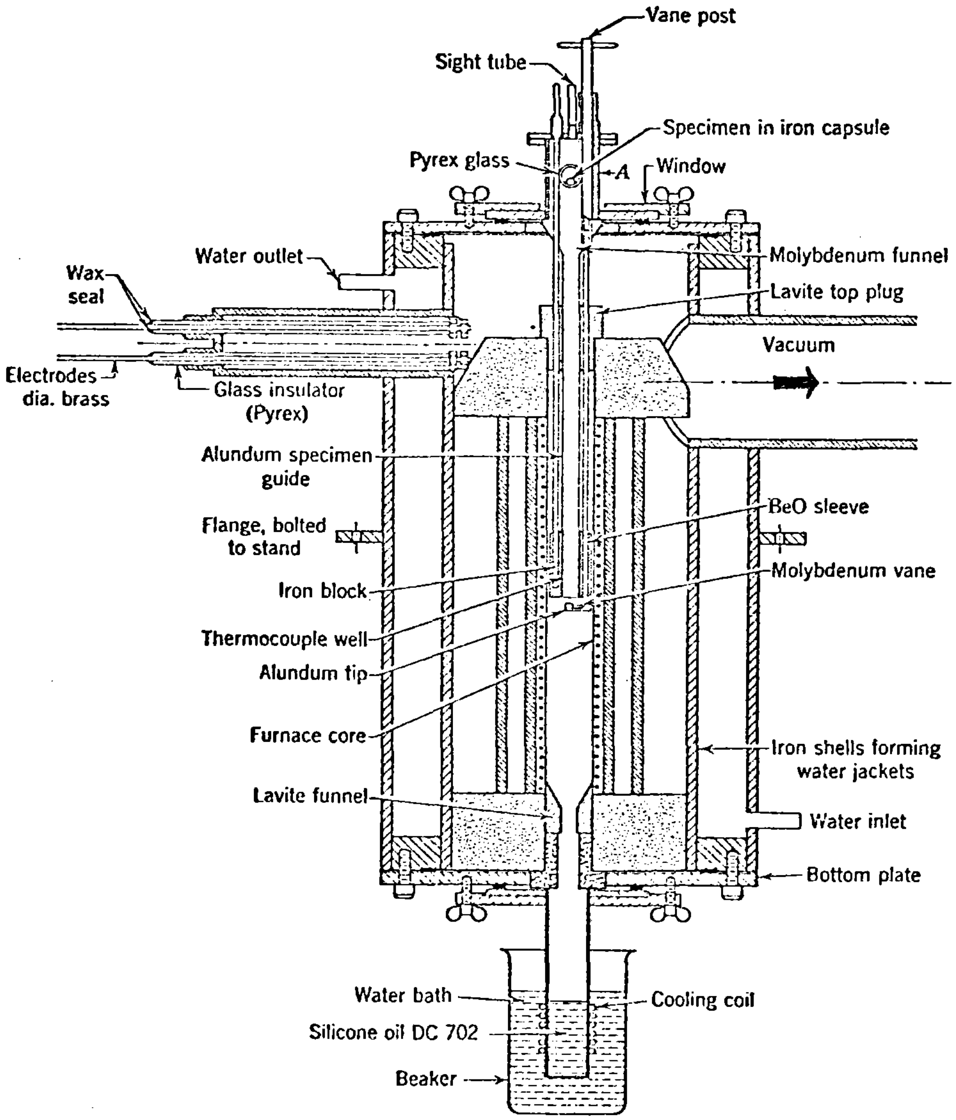


Fig. 4.19 Molybedunum resistor furnace for high temperature quenching.[153]



B. Dynamic Methods

These methods explore phase changes in the system while it is being cooled or heated. Typical of these methods is thermal analysis in which the temperature of a phase change is determined from changes in the rate of temperature rise or fall resulting from the heat of the reactions occurring. Here it is necessary to ensure that the temperature measurement corresponds to the point of inflection of the other properties during the phase change, and that the phase change takes place rapidly and reversibly at the equilibrium temperature without undercooling or segregation. In general, it is most convenient to heat (or cool) the sample surroundings at a constant rate. The relation between the observed cooling curve and the phase diagram as well as the magnitude of the heat effects are illustrated in Fig. 4.20. This type of cooling curve is satisfactory for determining phase relations, but not as sensitive as the derivative thermal curve shown in Fig. 4.21. The derivative curve can be derived from the direct thermal curve but in this case it cannot be any more accurate than the data used.

Depending on the system, either cooling or heating may be preferable. The cooling curve method is suitable for changes that take place at equilibrium temperatures under relatively rapid cooling. Liquidus and solidus temperatures of many ionic melts can be determined this way. However, when solid solutions and peritectic reactions occur, the solidus temperature on cooling curves may be doubtful because of segregation. In these cases, heating curves are preferable for the determination of the solidus while cooling can still be used for the determination of the liquidus.

Fig. 4.20 Phase diagram and cooling curves for two compositions. (Heat effects of phase changes are indicated by shaded areas in the upper diagram.)

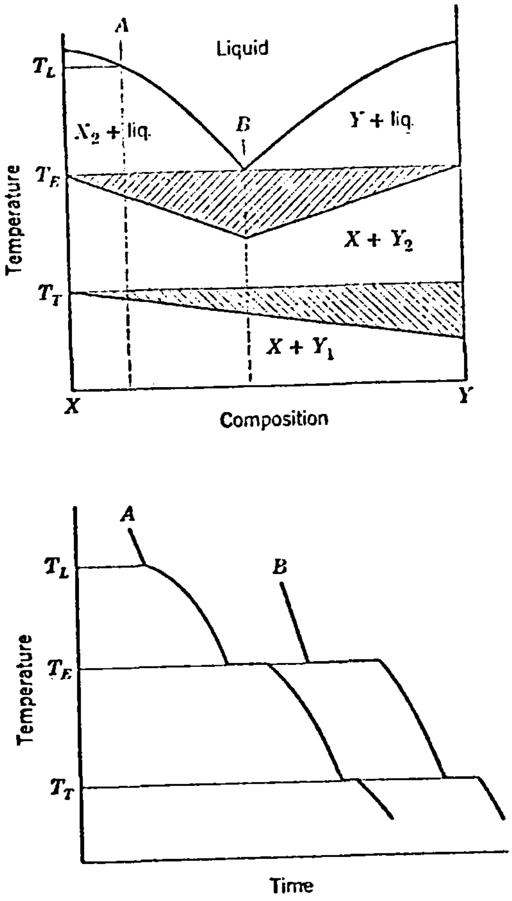


Fig. 4.21 (a) Direct and (b) derivative thermal curves.

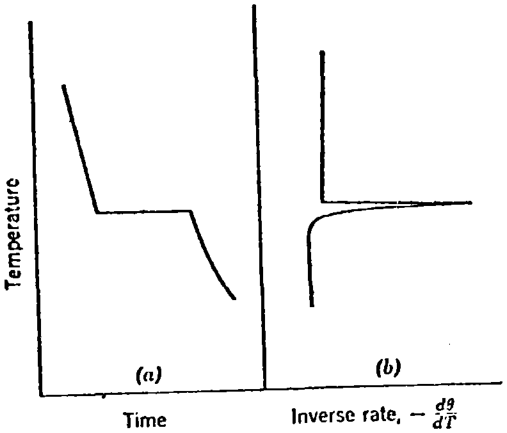


Fig. 4.22 Basic DTA system.

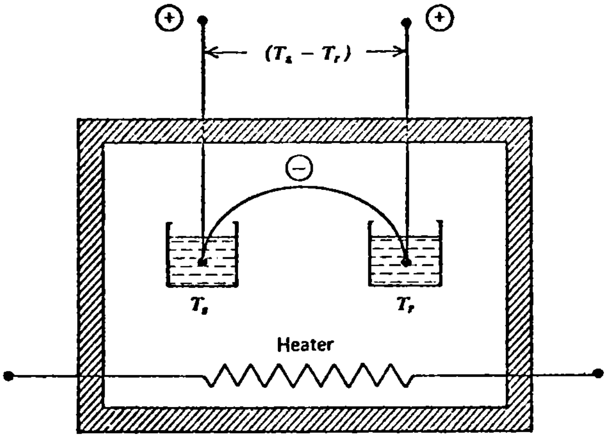
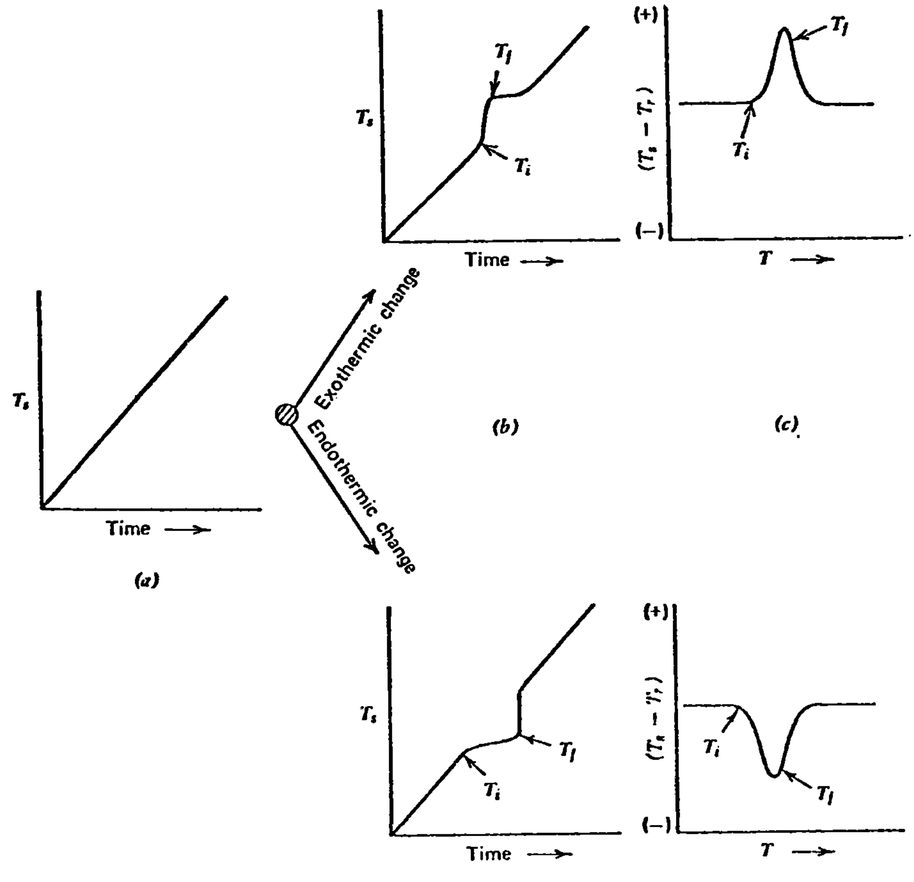


Fig. 4.23 Comparison between thermal analysis and differential thermal analysis.



The technique of differential thermal analysis, DTA,[154-159] is essentially a modification and refinement of thermal analysis. In this technique, the temperature of a sample is compared with the temperature of a thermally inert material and recorded as the sample is heated or cooled at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic enthalpic transitions such as those caused by: phase changes, fusion, crystalline structure inversions, vaporization, boiling, sublimation, dissociation or decomposition reactions, destruction of crystalline lattice structure, oxidation and reduction reactions and other chemical reactions. Generally, phase transitions, dehydration, reduction and some decomposition reactions produce endothermic effects, whereas crystallization, oxidation and some decomposition reactions produce exothermic effects.

The basic DTA system is illustrated in Fig. 4.22 while the comparison between thermal analysis and DTA is shown in Fig. 4.23.

In DTA, see also Fig. 4.24, the difference between the temperature of the sample T_s and that of the reference material, T_r, i.e., $T_s - T_r$, is the function recorded relative to time. Since the detection thermocouples are here opposed to each other, small differences between T_s and T_r can be detected with an appropriate voltage amplification device. Small samples, down to several micrograms in mass can be used in DTA studies and are, as a matter of fact, more desirable.

DTA is a simple and rapid technique well suited to, and widely used for molten salt phase studies. It is also very extensively discussed in books and other literature.[156-159]

4.3 Thermal Properties

4.31 Dynamic vs Static Techniques

In general, as with the phase diagram studies discussed above, most thermal properties of materials can now be studied by the more convenient, rapid and often more precise dynamic techniques which came to a wide use in relatively recent years[154-159] and often superseded the classical static methods. Nevertheless, many molten salt thermal studies are still conducted by the static methods which have not lost their importance in many cases.

The dynamic methods are very well described in many recent books[156-159] and journals.[160-162] For this reason, they are only briefly summarized here as to their applicability to the measurements of those thermal properties which are more fully described in this section in terms of the classical static techniques. In many cases, the complete thermal properties evaluation can only be achieved by supplementing the dynamic method of study with static measurements, or vice versa.

Table 4.3 summarizes the relevant dynamic techniques and Fig. 4.24 - the applicability of DTA and DSC to inorganic compounds.

4.32 Melting Point and Volume Change on Fusion

The volume change on fusion ΔV_f, as well as the volumetric characteristics in the immediate vicinity of the melting point are both of great importance in the application of salts to thermal energy storage. Additionally, they are of considerable importance in the study of the mechanism of melting and the structure of liquids.

TABLE 4.3 Relevant Thermal Analysis Techniques

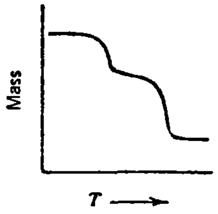
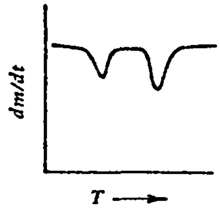
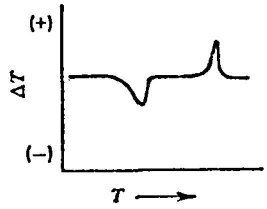
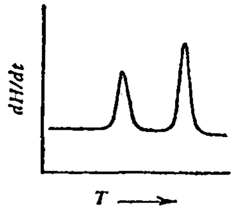
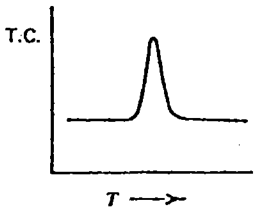
Technique	Parameter Measured	Instrument employed	Typical curve
Thermogravimetry	Mass	Thermobalance	
Derivative thermogravimetry (DTG)	dm/dt	Thermobalance	
Differential thermal analysis (DTA)	$T_s - T_r (\Delta T)$	DTA apparatus	
Differential scanning calorimetry (DSC)	Heat flow, dH/dt	Calorimeter	
Evolved gas detection (EGD)	Thermal conductivity	TC cell	

TABLE 4.3 (continued)

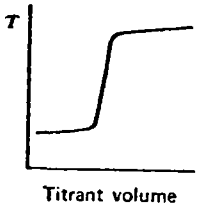
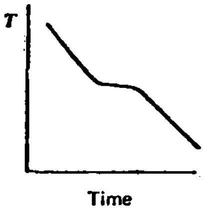
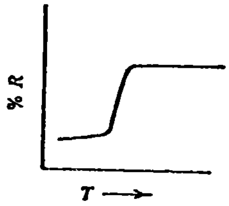
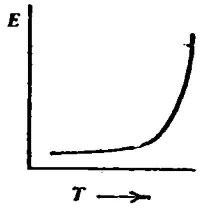
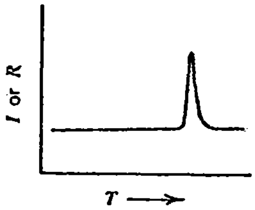
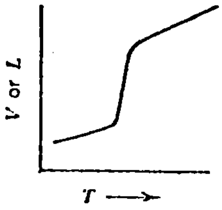
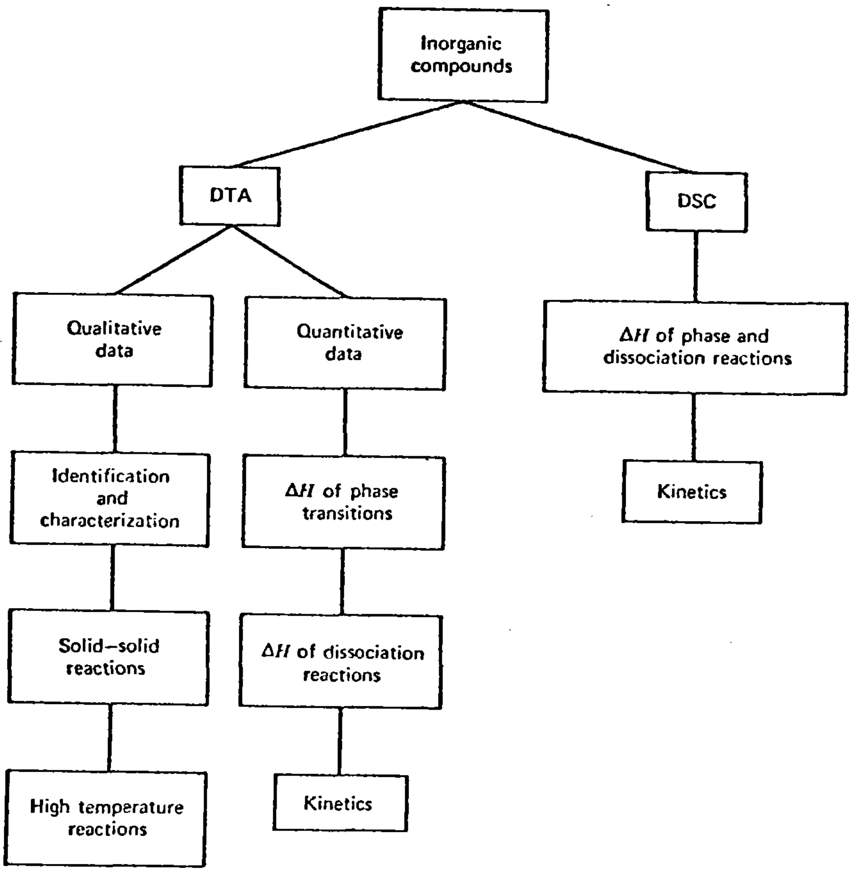
Technique	Parameter Measured	Instrument employed	Typical curve
Thermometric	Temperature	Calorimeter	
Thermal analysis	Temperature	Calorimeter	
Dynamic reflectance spectroscopy (DRS)	Reflectance	Spectrophotometer	
Emanation thermal analysis (ETA)	Radioactivity	ETA apparatus	
Electrical conductivity	Current or resistance	Electrometer or bridge	
Thermomechanical analysis (TMA) (dilatometry)	Volume or length	Dilatometer	

Fig. 4.24 Some applications of DTA and DSC to inorganic compounds



For many materials of interest, ΔV_f is only approximately known and, sometimes, even uncertain in sign.

The most common method of determining the value of ΔV_f depends on separate measurements on the solid and the liquid phases and extrapolation of the data to the melting point. Aside from the cumulative errors in making two independent measurements, the interesting regions of possible pre-melting or post-melting phenomena are passed over and thus the uncertainty in ΔV_f is correspondingly increased.

Since, in general, the ionic salts shrink on solidification, the method of "fed and unfed castings" offers some improved accuracy.

The "fed casting" is prepared by feeding a calibrated mould with sufficient liquid to fill the shrinkage voids formed during solidification. The weight, M_c, of this sound casting is then compared with the weight, M_u, of the "unfed casting" prepared by filling an identical mould with liquid just above the melting point but without feeding the mould during solidification. The fractional volume change on fusion is calculated from

$$\frac{\Delta V_f}{V_s} = \frac{M_c - M_u}{M_u}$$

Unfortunately, this "crystallzation pyknometry",[163] while measuring ΔV_f directly does not distinguish any volumetric effects in the vicinity of the melting point and hence cannot be fully accurate.

Better in this respect, at least in principle, is the indirect Archimedean technique such as used in the density measurements (see Fig. 4.11). The pre-melting and post-melting volumetric effects can be observed directly in a plot of buoyancy against temperature and may be converted to volumes by knowledge of the density of the buoyant liquid used. The most extensive exploitation of this method was made by Endo, et. al.[164] It seems likely that with great care the maximum bubble pressure method described in Sec. 4.11 could also be used to determine the volumetric effects near melting.

4.33 Specific Heat

Experimental methods for determining specific heats, C_p, and heat contents, H, at high temperatures may be grouped into three general categories.

1) The method of mixtures (used most frequently) consists of dropping the test sample from a furnace at a known, accurately measured temperature into a calorimeter operating at or near room temperature. This method determines the change in total heat content (enthalpy), H, of the substance between the temperature of the furnace and that of the calorimeter from which C_p is calculated by a process of differentiation:

$$C_p = \left[\frac{dh}{dT}\right]_p$$

Two disadvantages of this method are as follows:

a) If the heat of transition is small, the method is not very accurate.

b) If the sample tested undergoes a change of state on heating but does not revert to its original state on cooling, additional measurements of some other type become necessary to fix the heat content of the higher state with respect to the lower.

The advantages of the methods of mixtures are, on the other hand, important. Namely:

1) It is direct and reasonably rapid.
2) The results are accurate within the limits of reproducibility in the behavior of the substance.
3) It depends on now extraneous assumptions.

2) Methods depending upon heating or cooling rates have also been used widely but these produce less accurate results. They involve a comparison of the rate of heating and cooling of the test sample with the corresponding rate for a substance of known C_p under conditions which are supposed to be the same. However, differences in thermal conductivity and imperfectly reproducible heating and cooling conditions may sometimes lead to considerable errors.

Precise reproducibility of experimental conditions is especially important at high temperatures where, for example, a small displacement of the sample in the furnace may seriously alter the rate at which the radiant energy is received.

3) Numerous methods of direct measurement of specific heats are similar in that they involve measurement of the heat required to raise the temperature of the test sample by a relatively small step from a fraction of a degree to a few

degrees, depending upon the method and equipment.

4) Adiabatic methods for measuring specific heats offer apparently best accuracy. As originally devised,[165] and subsequently improved,[166,167] the sample is contained in an MgO sleeve with a Pt heater wound around it or a sample in the form of a hollow closed cylinder with the heating coil inside it to minimize the thermal lag. The electric input to the specimen is measured while it is otherwise thermally insulated from, but inside, a copper block maintained at temperature T_B. The temperatures of the sample T_s and of the block T_B are measured by thermocouples. Each of these temperatures is then varied at a rate of 1°C/min and plotted vs time. When the two curves cross and $T_s - T_B = 0$, no heat is being exchanged between the sample and the block so that at these points:

$$Q = mC_p \left[\frac{dT_s}{dt}\right]_{T_s=T_B}$$

where m is the mass of the specimen and Q is the power input to the internal heater. Accuracy for such measurements conducted by Sykes[167] in the temperature range of 30 to 600°C was ±0.6%.

According to the common practice in thermodynamic calculations, the specific heats of substances above room temperature are represented by equations in power series form:

$$C_p = a + bT + cT^2 + \ldots$$

where C_p is the molar specific heat at constant pressure, T is the absolute temperature and a, b, c, etc. are constants.

While the reason for adopting this expression is its mathematical convenience, in general, it is found that expressions of this type are not well adapted for fitting the high temperature specific heat experimental data and therefore a variety of other power-series equations have been proposed and used.[168]

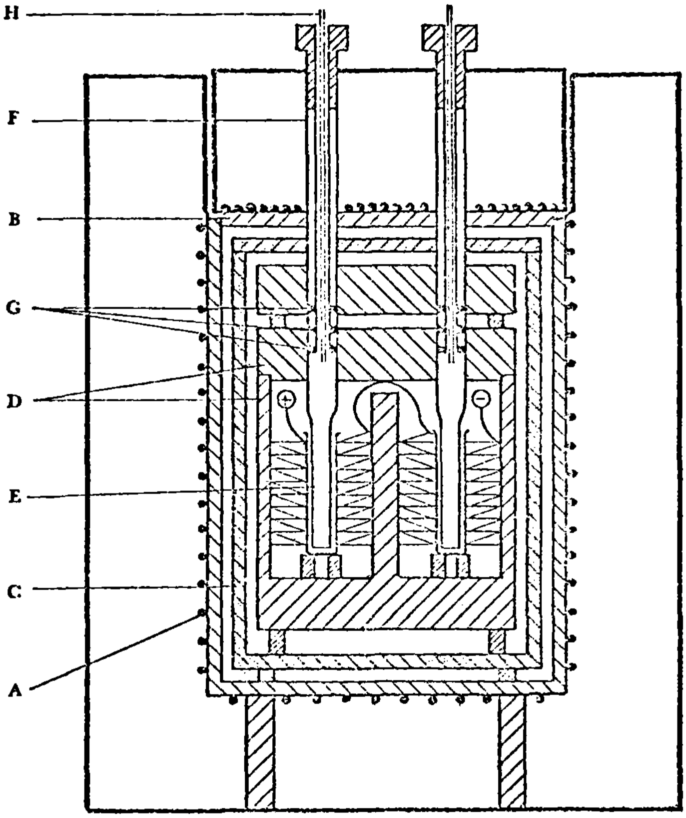
Available heat capacity data for the molten salts[36,51-53] indicates that $\left[C_{p(L)}/C_{p(s)}\right]$ m.pt. lies between the limits 1.04 and 1.20 with a mean value of 1.10 (for seventeen liquid metal halides and three liquid metal nitrates). Hence, in calculations for salts where $(C_{p(L)})$m.pt. has not been measured, the above mean empirical ratio was used.[51] Data for $C_{p(L)}$ of over 30 molten salts indicate a consistency of ±3% (the mean experimental error) over a temperature range 200 to 600°C. Consequently, $C_{p(L)}$ for the salts can be regarded as temperature independent.

4.34 Heat and Entropy of Mixing

For many molten salts, mixing involves evolution of considerable amount of heat.

Calorimetric investigations of molten salt systems have been carried out extensively by Kleppa,[169] who developed a twin differential reaction calorimeter capable of measuring the heat of mixing accurately below 500°C and with less accuracy up to 800°C. This is illustrated in Fig. 4.25. Two nearly identical differential calorimeters are located in cylindrical wells in a heavy aluminum jacket. In each of the twin units a temperature difference between the calorimeter and the surrounding jacket gives rise to a thermo-emf in a 96- junction thermopile. The two thermopiles are connected in series

Fig. 4.25 Twin calorimeter for measurement of heats of mixing of molten salts.



A, main heater; B, Top heater; C, heavy shield; D, aluminum jacket; E, calorimeter; F, protection tube; G, radiation shields; H, manipulation tube; ⊕——→⊖ thermopile in such a manner that the emf of one thermopile opposes the other. Hence, small drifts in temperature of the aluminum jacket will affect both emf's similarly but in the opposite sense, thus allowing an accurate determination of any very small temperature difference between the two calorimeters.

The whole assembly is heated to the required temperature. As long as no heat is generated in one or the other calorimeter, the difference emf remains zero. For measuring heats of mixing, known quantities of molten salt are mixed directly in one of the calorimeters while the other serves as a reference. The apparatus can be calibrated to measure the heat of mixing directly in terms of the temperature difference between the calorimeters after mixing. The experiment error of this method can be as low as ±0.5%.

Various other investigators used other methods. Bloom and Tricklebank[170] used a Bunsen fusion calorimeter to measure enthalpy change on cooling molten salt mixtures from known temperatures in excess of 800°C to room temperature. From the heat evolved on cooling (from different high temperatures to a fixed lower temperature) heat capacity of molten salts and their mixtures can be readily calculated as well as the heats and entropies of fusion, etc. The heats of mixing of molten salts can be calculated also from the enthalpies of cooling the mixture and the pure components to a fixed lower temperature, together with the heat of formation of the solid mixture (determined separately by solution calorimetry).

Obviously, the direct method of Kleppa is generally preferable except if the salt is volatile when in the direct method errors would arise from vaporization. This difficulty is avoided in the drop method by the use of sealed capsules.

Kleppa and co-workers[169] have utilized various empirical and semi-empirical expressions to obtain a relation between compositions and the heat of mixing per mole of different salt systems. Their early results were expressed in the form

$$\Delta H_{mix} = x(1-x)\ a + bx + cx(1-x)$$

where x is the mole fraction of the salt with the small cation. For any given system a, b and c are constants.

Theories of charge symmetrical molten salt mixtures, e.g. binary alkali nitrates, have been based on a modified conformal solution theory that relates ΔHmix with ionic dimensions and interionic forces of interaction. The extension of the theory by Davis and Rice[171] gives the following expression:

$$\Delta H_{mix} = x\ (1-x)(Uo + U_1\delta_{12} + V_2\delta^2_{12})$$

where $\delta = \dfrac{d_1-d_2}{d_1d_2}$

d_1 and d_2 are the sums of the ionic radii of the two component salts respectively, U_o, U_1 and U_2 are unevaluated coefficients that may be described qualitatively in terms of the type of interactions on which they depend.

The enthalpies of mixing per mole for the binary alkali halide systems can be represented approximately by the expression

$$H_{mix} = x(1-x)(U_o^{++} - 340\delta^2_{12})\text{kcal/mole}$$

However, for AgCl + alkali chloride for example, the inclusion of the $U_1\delta_{12}$ term as well as $U_2\delta_{12}$ term is necessary.

For many molten salts mixing involves evolution of considerable heat; for example for $MgCl_2$ + alkali chloride systems ΔH_{mix} is negative and $-\Delta H_{mix}$ increases sharply in the sequence Li<Na<K<Rb<Cs. $-\Delta H_{mix}$ plotted against mole fraction of the alkali chlorides shows maxima in all cases at about 0.6 mole fraction of each alkali chloride. This is explained as being due to the formation of complex anionic species of the form $MgCl_2^{2-}$ whose stability depends strongly on the alkali cation present.

4.35 Heat of Fusion

Heat of fusion is usually determined calorimetrically by one of the methods discussed above. For a solid melting at constant pressure ΔH_f is equal to the difference in enthalpy between liquid and solid. Per mole of substance

$$\Delta H_f = H_{liq} - H_{solid}$$

The latent heat at the melting point is necessarily a reversible heat, because the process of melting follows a path consisting of successive equilibrium steps. Thus, the entropy of fusion ΔS_f at the melting point is directly related to the heat of fusion by

$$S_{liquid} - S_{solid} = \Delta S_f = \frac{\Delta H_f}{T_f}$$

The values of the molecular heat of fusion for inorganic salts show no apparent regularities, not even in the case of salts which crystallize in the same system and class. For instance, silver nitrate and potassium nitrate, both of which crystallize in rhombic prisms, have practically identical molal heats of fusion, while sodium nitrate and lithium nitrate, which crystallize in the hexagonal form of the calcite type, show no such equality, nor is it apparent with chlorides or bromides of the same type.

Neither the latent heats of fusion of the salts themselves, nor the differences in them show any simple functional relationship to the atomic weights or the atomic volumes of their elements. The property is clearly not additive nor would one expect it to be.

Formal thermodynamic equations relating heat of fusion to other properties rely on the availability of accurate values for these properties which in the case of molten salts rarely applies. Additionally, most mixed molten salt systems of interest here do not represent ideal solutions. Blander[67] discusses the thermodynamic properties of molten salt solutions of different types, yet the resulting equations cannot be practically used in most cases due to the absence of the activity coefficient or other data.

For these reasons, accurate prediction of the heats of fusion for either the binary or the ternary salts from the values of the individual compounds is not presently possible.

4.36 Thermal Conductivity

Heat in solids is conducted by various carriers: electrons, lattice waves (or phonons), magnetic excitations and, in some cases, electromagnetic radiation. The total thermal conductivity is additively composed of contributions from each type of carrier.

In crystalline solids, the major factor controlling the intrinsic lattice conductivity is the Debye temperature: θ . Solids of high θ have generally higher conductivities. Another factor is the simplicity or complexity of the crystal lattice involved. Solids with simple crystal lattices have higher conductivities than those having complex structures. Since an excellent review of the experimental methods for measuring thermal conductivities in solids is presented by Touloukian et.al.;[54] (these methods being very many), they will not be discussed here.

The data presented in Ref. 14 for solid ionic salts of interest to this project are, unfortunately, very few and mostly cover the temperature range from near 0^{o}K to no higher than 450^{o}K.

In the case of liquids, it must be recognized that the measurement of thermal conductivity, even at room temperature, is difficult. Difficulties are multiplied for molten salts.

In liquids at high temperature, three modes of heat transfer exist: radiation, convection and conduction. Conduction is associated with transport of energy across the centers of the molecules on collision.

In fluids, as distinct from solids, molecules are not confined to fixed positions, but constantly move even if the fluid as a whole is in a state of rest.

Practically, this property is very important particularly when molten salts are used as heat transfer media e.g., under the designation HTS, $KNO_3 + NaNO_2 + NaNO_3$ eutectic.[36]

Thermal conductivities of molten salts are 2 to 5 times higher than those for common organic heat transfer media and their temperature coefficients are often small. Their thermal stability is also vastly superior to that of organic substances.

Thermal conductivity of molten salts has been measured by two main methods, steady state and transient.

Turnbull[172] used a transient method where a thin Pt wire, immersed in the molten salt, is heated by a constant current and its rate of temperature rise is measured. Under suitable conditions, the thermal conductivity may be evaluated from the rate of heat production and the temperature - time relation.

Bloom et.al.[173] used a steady state method where the transfer of heat (generated electrically) across a thin annulus of molten salt between two coaxial vertical silver cylinders gives the value of the conductivity k as

$$\kappa = Q\ln (r_2/r_1)/2\pi l(t_1-t_2)$$

Q is the quantity of heat flowing per sec., r_1, the external radius of the inner cylinder, r_2, the internal radius of the external cylinder, t_1 and t_2 are temperatures of inside and outside cylinders respectively, and l is the length of the molten salt annulus.

Kincaid and Eyring related the velocity of sound to thermal conductivity by the equation:

$$\kappa = 2.80\ k_B n^{2/3} \gamma^{-1/2} U_L$$

where

k_B is Boltzmann's constant, n the number of molecules per unit volume, $\gamma = Cp/Cv$ and U_L is the velocity of sound in the liquid.

The above equation can be combined with an equation used by Bockris and Richards[56] relating the free volume V_f with the velocity of sound:

$$V_f = \left[\frac{1}{U_L} \left\{ \frac{RT}{2(M_c M_a)^{1/2}} \right\}^{1/2} \right]^3 V$$

where M_c and M_a are the masses of cation and anion respectively and other symbols have the usual meaning.

Combination of the two above equations gives:

$$V_f = \left[\frac{2.80 k_B n^{2/3}}{\gamma^{1/2} k} \left\{ \frac{RT}{2(M_c M_a)^{1/2}} \right\}^{1/2} \right]^3 V$$

from which V_f can be calculated. For example, for $NaNO_3$ at 310°C, both the above formulae give the value of $V_f = 0.13$cc/mole.

III. APPENDIX

A-1 Additional Properties of Single Salts

TABLE A-1 Density of Single Salts[34]

Salt	$\rho = a - bT$		Temperature range °K	Uncertainty estimate (percent)
	a	$b \times 10^3$		
$NaNO_3$	2.320	.715	583 - 643	1.0
KNO_3	2.315	.729	620 - 880	0.2
NaOH	2.068	.4784	623 - 723	
KOH	2.013	.4396	673 - 873	
LiCl	1.8842	.4328	894 - 1054	0.2
NaCl	2.1393	.5430	1076 - 1301	.4
KCl	2.1359	.5831	1053 - 1212	.5
$MgCl_2$	1.976	.302	1021 - 1159	.2
$CaCl_2$	2.5261	.4225	1060 - 1223	.9
$SrCl_2$	3.3896	.5781	1167 - 1310	.7
$BaCl_2$	4.0152	.6813	1239 - 1354	5.0
$MnCl_2$	2.75701	.43766	923 - 1123	
$ZnCl_2$	2.7831	.448	593 - 673	.2
$CdCl_2$	4.078	.82	840 - 1080	.3
$SnCl_2$	4.016	1.253	580 - 753	1.3
LiBr	3.0658	.6520	825 - 1012	
NaBr	3.1748	.8169	1027 - 1218	1.0
KBr	2.9583	.8253	1014 - 1203	0.4
$MgBr_2$	3.087	.478	1040 - 1208	
$CaBr_2$	3.618	.500	1036 - 1064	
Li_2CO_3	2.2026	.3729	1012 - 1115	.2
Na_2CO_3	2.4797	.4487	1138 - 1277	.2
K_2CO_3	2.4141	.4421	1181 - 1283	.2
LiF	2.3581	.4902	1149 - 1320	.5
NaF	2.655	.54	1283 - 1819	
KF	2.6464	.6515	1154 - 1310	.6
MgF_2	3.235	.524	1650 - 2100	
CaF_2	3.179	.391	1640 - 2300	

Fig. A-1 Percent volume increase on fusion of alkali halides[40]

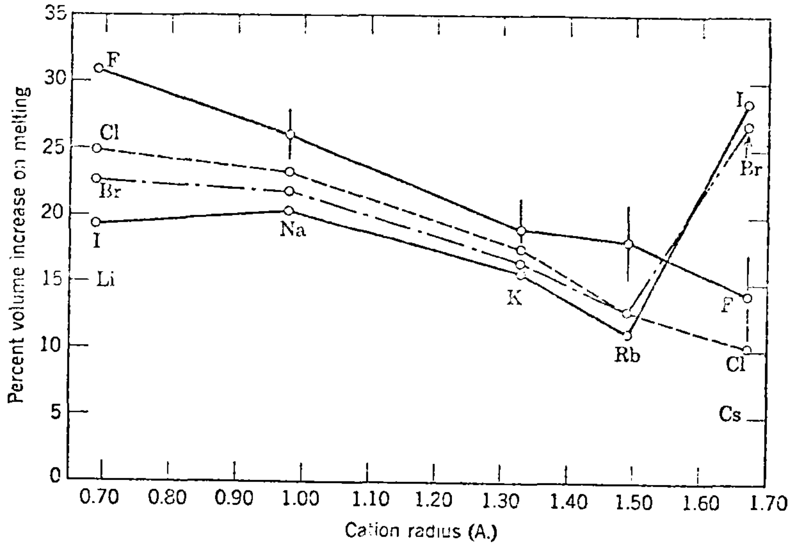


TABLE A-2 Molar Volume at 10% above m.p. for Pure Molten Salts[59]

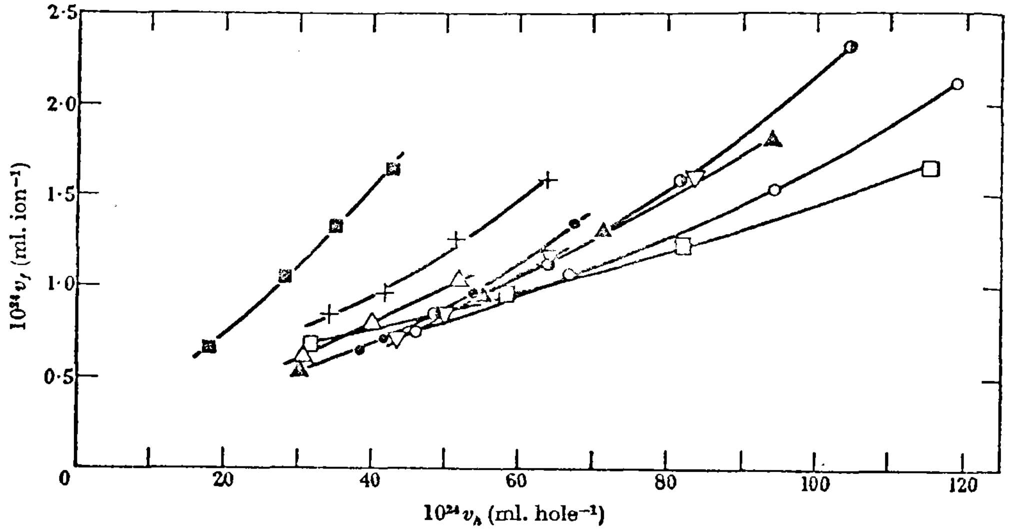
Salt	m.p. (°K)	V° (ml)
LiCl	883	28.96
NaCl	1074	39.02
KCl	1043	50.82
RbCl	995	56.10
CsCl	918	62.53
$ZnCl_2$	591	54.68
$CdCl_2$	841	55.24
$PbCl_2$	773	57.54

TABLE A-3 THE FREE VOLUMES OF CERTAIN ALKALI HALIDES AND NITRATES[56]

SALT	temp. (°C)	$10^8 \upsilon_o^{1/3}$ (cm)	V_f by (a) (ml mole^{-1})	V_f by (b) (ml mole^{-1})	SALT	temp. (°C)	$10^8 \upsilon_o^{1/3}$ (cm)	V_f by (a) (ml. mole^{-1})	V_f by (b) (ml. mole^{-1})
LiCl	700	2.27	1.01	0.49	LiBr	700	2.46	1.05	0.78
	800	2.26	1.26	0.72		800	2.43	1.29	1.06
	900	2.23	1.60	0.29		900	2.40	1.55	1.44
	1000	2.20	1.97	1.20		1000	2.35	2.13	1.95
NaCl	800	2.59	0.75	0.42	NaBr	800	2.68	1.15	0.74
	900	2.58	0.95	0.62		900	2.64	1.53	1.00
	1000	2.57	1.24	0.84		1000	2.60	1.87	1.40
KCl	800	2.88	0.85	0.51	KBr	800	3.01	1.02	0.68
	900	2.85	1.14	0.72		900	2.98	1.40	0.96
	1000	2.82	1.61	1.05		1000	2.95	1.90	1.34
CsCl	700	3.17	0.78	0.68	CsBr	700	3.29	0.86	0.59
	800	3.15	1.14	0.89		800	3.27	1.33	0.88
	900	3.12	1.55	1.45		900	3.24	1.90	1.30
	1000	3.09	2.16	1.85		1000	3.20	2.79	2.04
$CdCl_2$	600	2.52	0.71	0.63	$LiNO_3$	300	2.76	0.16	0.25
	700	2.51	0.85	0.84		400	2.73	0.25	0.41
	800	2.49	1.03	1.12		500	2.69	0.38	0.65
NaI	700	3.00	0.83	0.75	$NaNO_3$	307	3.01	0.18	0.13
	800	2.98	1.15	1.20		400	3.02	0.21	0.20
	900	2.96	1.47	1.65		500	3.01	0.32	0.33
	1000	2.94	1.98	2.31	KNO_3	333	3.25	0.10	0.13
KI	700	3.25	0.95	0.74		400	3.26	0.21	0.17
	800	3.23	1.29	1.04		500	3.26	0.31	0.26
	900	3.20	1.84	1.50					
	1000	3.17	2.53	2.20					

a,b: different methods of calculation (see ref. 56)

Fig. A-2 Plot of the free volume per ion against the average hole volume[56]



▣, LiCl; Δ,NaCl; O,KCl; ▲,CsCl; +,NaBr; ∇, KBr; ◑,CsBr; □,NaI; O, KI.

Fig. A-3 Entropy of fusion of the alkali halides[40]

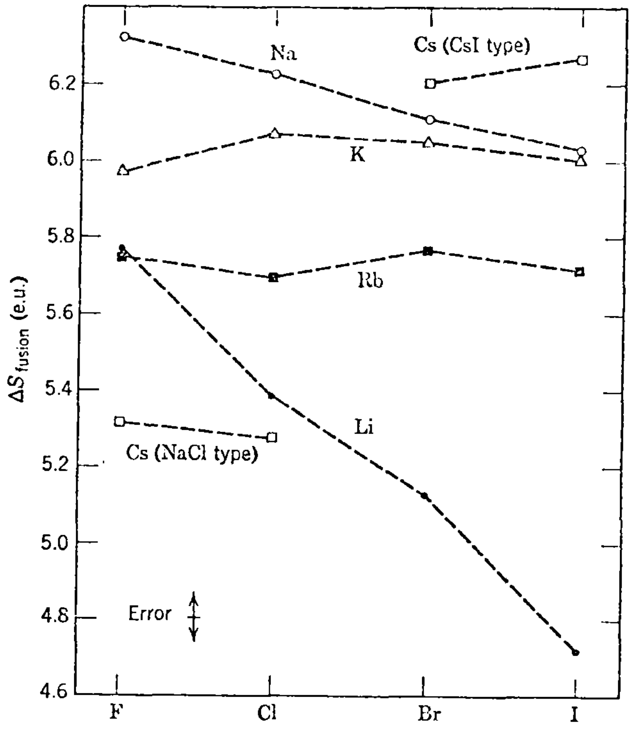


TABLE A-4 COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF THE ENTROPIES WITH REFERENCE TO THE ENTROPY AT THE MELTING POINT[56]

SALT	temperature (°C)	$S_T - S_o$ (calc.) (e.u.)	$S_T - S_o$ (expt.) (±10%) (e.u.)
LiCl	1000	1	8
NaCl	900	1	1
	1000	2	3
KCl	1000	2	3
CsCl	1000	6	6
NaBr	1000	4	3
KBr	800	1	1
	900	3	2
	1000	5	3
CsBr	1000	8	5
NaI	1000	5	5
KI	1000	6	4
$CdCl_2$	600	2	1
	800	7	5
$LiNO_3$	500	5	10
$NaNO_3$	500	4	10
KNO_3	500	5	8

TABLE A-5 THERMODYNAMIC PROPERTIES OF MOLTEN ELECTROLYTES[56]

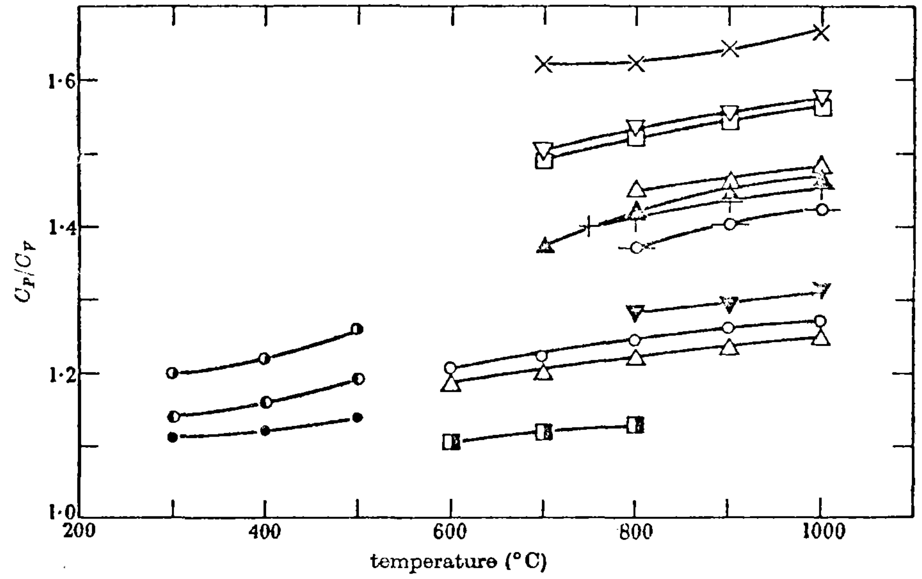
SALT	C_P (cal mole^{-1})	T (^{o}C)	γ	(C_P-C_V) (cal mole^{-1})	(cal mole^{-1})
LiCl	14.9†	700	1.22	2.6	12.3
		800	1.24	2.9	12.0
		900	1.26	3.1	11.8
		1000	1.27	3.1	11.8
NaCl	16.0	800	1.37	4.3	11.7
		900	1.40	4.6	11.4
		1000	1.42	4.7	11.3
KCl	16.0	800	1.45	4.9	11.1
		900	1.46	5.1	10.9
		1000	1.48	5.2	10.8
CsCl	15.5†	700	1.50	5.2	10.3
		800	1.53	5.4	10.1
		900	1.55	5.5	10.0
		1000	1.57	5.6	9.9
$CdCl_2$	22.4†	600	1.11	2.2	20.1
		700	1.11	2.4	20.0
		800	1.13	2.5	19.9
NaI	15.5†	700	1.37	4.4	11.1
		800	1.42	4.6	10.9
		900	1.45	4.8	10.7
		1000	1.47	5.0	10.5
KI	15.0†	700	1.49	4.9	10.1
		800	1.52	5.1	9.9
		900	1.54	5.3	9.7
		1000	1.56	5.4	9.6

SALT	C_P (cal mole^{-1})	T (^{o}C)	γ	(C_P-C_V) (cal mole^{-1})	(cal mole^{-1})
LiBr	15.5†	600	1.19	2.5	13.0
		700	1.20	2.6	12.9
		800	1.22	2.8	12.7
		900	1.23	2.9	12.6
		1000	1.24	3.0	12.5
NaBr	15.3†	800	1.28	3.4	11.9
		900	1.29	3.5	11.8
		1000	1.31	3.6	11.7
KBr	16.4†	800	1.41	4.8	11.6
		900	1.43	4.9	11.5
		1000	1.45	5.1	11.3
CsBr	15.5†	700	1.62	5.9	9.6
		800	1.62	5.9	9.6
		900	1.64	6.0	9.5
		1000	1.66	6.1	9.4
$LiNO_3$	26.9	300	1.11	2.6	24.3
		400	1.12	2.8	24.1
		500	1.14	3.3	23.6
$NaNO_3$	36.5	300	(1.14)‡	(4.5)‡	(32.0)‡
		400	1.16	4.9	31.6
		500	1.19	5.7	30.8
KNO_3	33.7	300	(1.20)‡	(5.6)‡	(28.1)‡
		400	1.22	6.0	27.7
		500	1.26	6.9	26.8

† Values calculated from data for the solid salt from the relation $(C_{P,L}/C_{P,S})=1.1$.

‡ Hypothetical values for liquid state when substance solid.

Fig. A-4 C_p/C_V as a function of temperature for certain liquid salts[56]



◐, LiNO$_3$; ◑, NaNO$_3$; O,KNO$_3$; O,LiCl; –O– , NaCl; Δ,KCl; ∇, CsCl; ▼,NaBr; +, KBr; X, CsBr; ▲, NaI; ◨, KI; □ , CdCl$_2$

TABLE A-6 Comparison of Calculated and Experimental Heat Capacities for Certain Halides[56]

salt	temperature (°C)	C_p (calc.) (cal mole^{-1})	C_p (expt.) (cal mole^{-1}
LiCl	1000	17	15
NaCl	1000	17	16
KCl	1000	8	16
CsCl	1000	12	15
NaBr	1000	15	15
KBr	1000	3	16
CsBr	800	16	15
NaI	1000	13	15
KI	1000	20	15
CdCl$_2$	800	23	22

TABLE A-7 VISCOSITIES OF SINGLE SALTS[34]

Salt	Best equation	Temperature range, °K	s Centipoise	Uncertainty estimate (percent)
$LiNO_3$	$\eta = 20.4645 + 1.34189 \times 10^{-2}T - 1.31061 \times 10^{-4}T^2 + 1.06106 \times 10^{-7}T^3$	533.2 - 702.2	.1143	8.5
$NaNO_3$	$\eta = 10.41 \times 10^{-2} \exp (3886/RT)$	589.2 - 731.2	.0282	1.5
KNO_3	$\eta = 50.1676 - 0.164572T + 1.86335 \times 10^{-4}T^2 - 7.12497 \times 10^{-8}T^3$	621.2 - 815.2	.0234	1.5
$LiNO_2$	$\eta = -14909.1 + 87.5812T - 0.171073T^2 + 1.11184 \times 10^{-4}T^3$	502.7 - 527.2	.0354	1.0
$NaNO_2$	$\eta = 187.118 - 0.876094T + 1.41024 \times 10^{-3}T^2 - 7.71608 \times 10^{-7}T^3$	563 - 613	.0187	1.0
KNO_2	$\eta - 864.798 - 3.61760T + 5.06274 \times 10^{-3}T^2 - 2.36530 \times 10^{-6}T^3$	686.8 - 725.4	.0055	(1.5)
NaOH	$\eta = 164.771 - 0.614833T + 7.80340 \times 10^{-4}T^2 - 3.33334 \times 10^{-7}T^3$	623.2 - 823.2	.0359	(1.5)
KOH	$\eta = 52.7561 - 0.166134T + 1.80314 \times 10^{-4}T^2 - 6.66494 \times 10^{-8}T^3$	673.2 - 873.2	.0120	(1.5)
LiCl	$\eta = 3.306 \times 10^{-2} \exp (7007/RT)$	902.9 - 1082.9	.0092	1.0
NaCl	$\eta = 81.9007 - 0.185538T + 1.42786 \times 10^{-3}T^2 - 3.70073 \times 10^{-8}T^3$	1085.9 - 1243.2	.0057	1.0
KCl	$\eta = 55.5632 - 0.127847T + 9.99580 \times 10^{-5}T^2 - 2.62035 \times 10^{-8}T^3$	1056.5 - 1202.0	.0132	1.5
$CaCl_2$	$\eta = 619.541 - 1.54489T + 1.29259 \times 10^{-3}T^2 - 3.61856 \times 10^{-7}T^3$	1058.7 - 1242.6	.0738	4.0
$SrCl_2$	$\eta - 4.401 \times 10^{-4} \exp (20555/RT)$	1150.5 - 1258.6	.0706	(4.0)
$BaCl_2$	$\eta = 1.643 \times 10^{-3} \exp (20029/RT)$	1261.4 - 1313.9	.0651	4.0
$SnCl_4$	$\eta = 3.187 \times 10^{-2} \exp (1928/RT)$	273 - 423	.0059	1.5
LiBr	$\eta = 6.868 \times 10^{-2} \exp (5355/RT)$	862.2 - 1046.2	.0180	2.0
NaBr	$\eta = 64.3240 - 0.152525T + 1.23215 \times 10^{-4}T^2 - 3.34241 \times 10^{-8}T^3$	1053.7 - 1212.7	.0040	1.0
KBr	$\eta = 128.339 - 0.334905T + 2.94450 \times 10^{-4}T^2 - 8.66540 \times 10^{-8}T^3$	1017.8 - 1181.2	.0056	1.0
Li_2CO_3	$\eta = -5259.12 + 14.8091T - 1.38581 \times 10^{-2}T^2 + 4.31294 \times 10^{-6}T^3$	1046.2 - 1122.2	.1022	3.0
Na_2CO_3	$\eta = 3.832 \times 10^{-5} \exp (26260/RT)$	1152.3 - 1245.2	.0112	3.0
K_2CO_3	$\eta = 1.161 \times 10^{-5} \exp (29487/RT)$	1186.2 - 1257.2	.0207	3.0

TABLE A-8 The Comparison of the Heat of Activation of Viscous Flow and the Quantity $-R\partial \ln V_f/\partial(1/T)$ $(=E_{V_f})^{56}$

SALT	E_{V_f} (kcal mole^{-1})	E_η (kcal mole^{-1})	SALT	E_{V_f} (kcal mole^{-1})	E_η (kcal mole^{-1})
LiCl	5.6	8.8	KBr	8.3	7.9
NaCl	6.6	9.4	NaI	7.3	7.4
KCl	8.6	7.8	KI	8.6	9.2
$CdCl_2$	4.1	4.0	$LiNO_3$	3.8	4.0
LiBr	6.8	6.0(?)	$NaNO_3$	4.5	3.9
NaBr	7.0	10.6	KNO_3	4.7	4.3

A-2 Additional Properties of Binary Salts

TABLE A-9 Densities of sodium-potassium carbonate binary mixtures

$$\rho = a - b\,T \text{ g/cc} \qquad (T = {}^{o}K)$$

Media. m,% Na_2CO_3	a	b x 10^3	t^oC range
100	2.4532±0.0064	0.4267±0.0054	868-973
90	2.4862±0.0013	0.4581±0.0011	844-973
80	2.4723±0.0018	0.4520±0.0016	796-963
75	2.4614+0.0026	0.4465+0.0022	811-980
70	2.4509±0.0019	0.4419±0.0016	792-976
60	2.4506±0.0015	0.4467±0.0007	767-959
58	2.4413±0.0006	0.4406±0.0005	773-966
50	2.4359±0.0015	0.4393±0.0014	730-952
40	2.42783±0.0019	0.4366±0.0017	739-956
30	2.4240±0.0019	0.4375±0.0016	802-977
25	2.4243±0.0013	0.4405±0.0012	810-951
20	2.4130±0.0019	0.4329±0.0016	851-980
10	2.4179±0.0037	0.4419±0.0030	893-987
K_2CO_3	2.4295±0.0085	0.4543±0.0694	907-981

Fig. A-5 Molar volume change of the alkali metal carbonate binary mixtures[61]

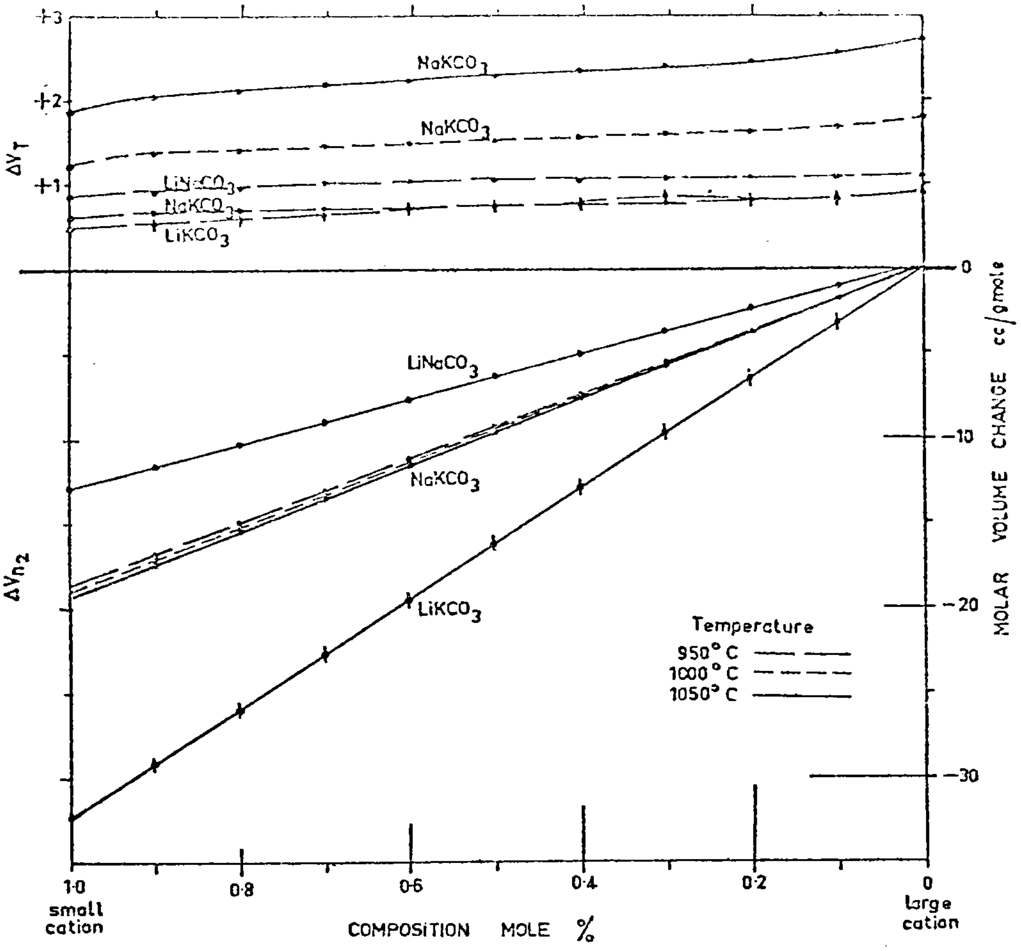


Fig. A-6 Densities and melting points of $NaKCO_3$ mixtures[61]

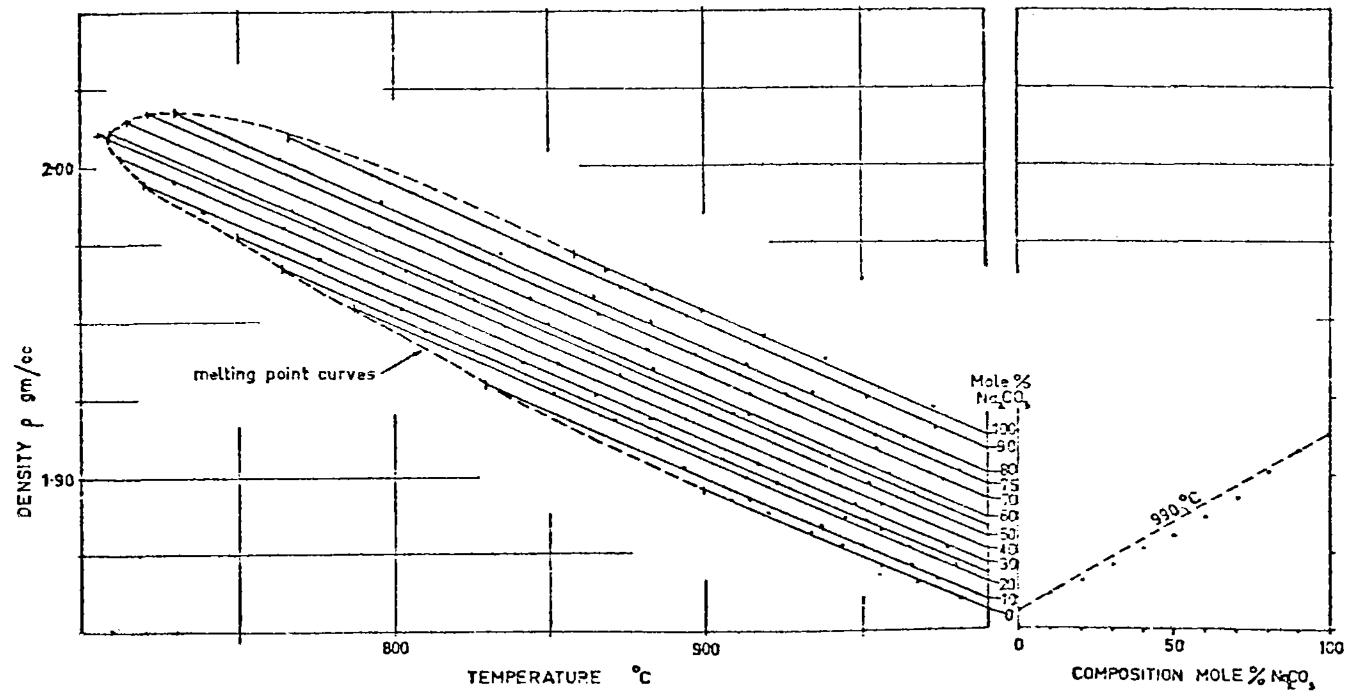
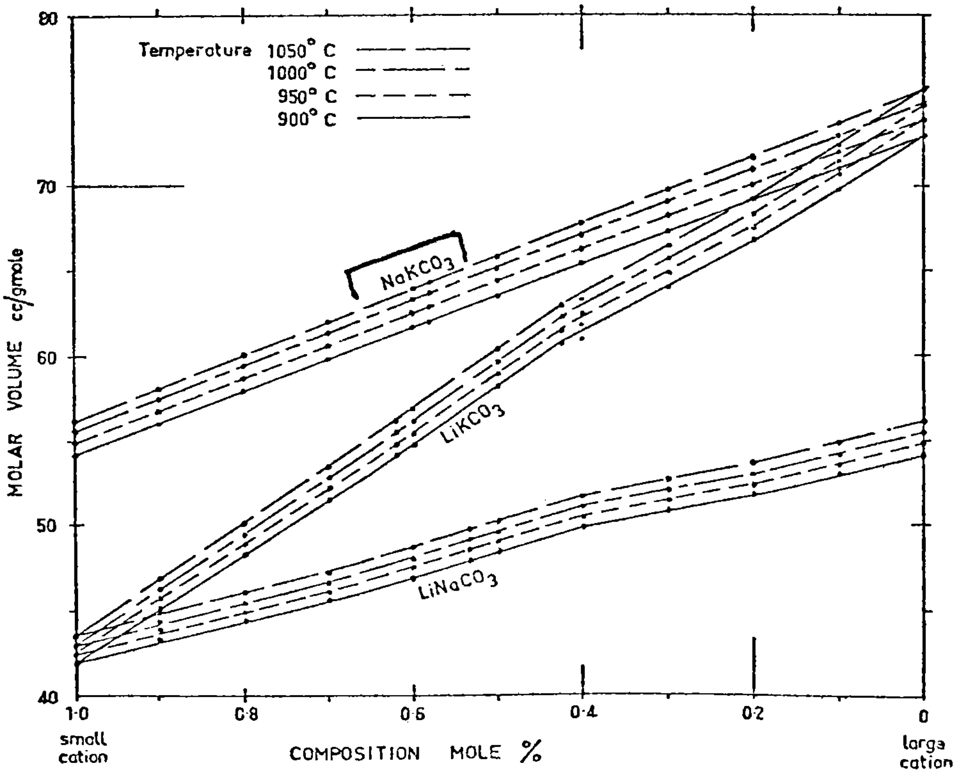
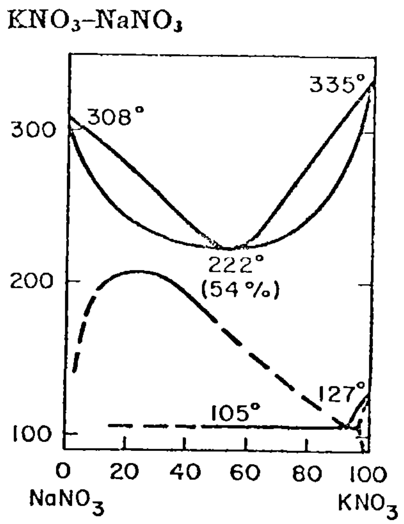


Fig. A-7 Molar volumes of the alkali metal carbonate binary mixtures[61]



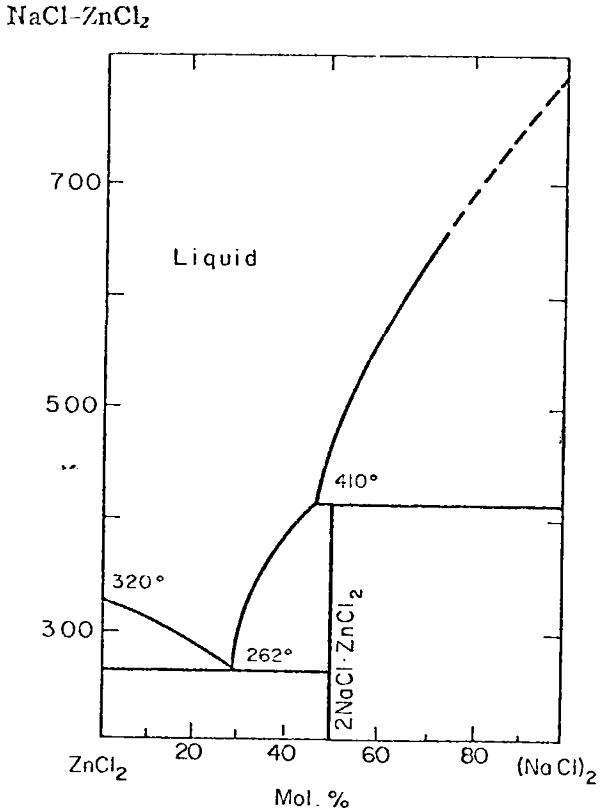
A.3 Phase Diagrams for Binary Salts(62)

Fig. A-8



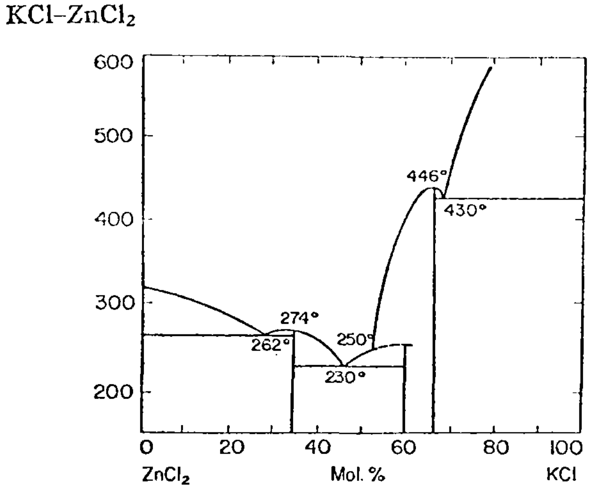
Adelheid Kofler, Monatsh. Chem., 86, 646 (1955).

Fig. A-10



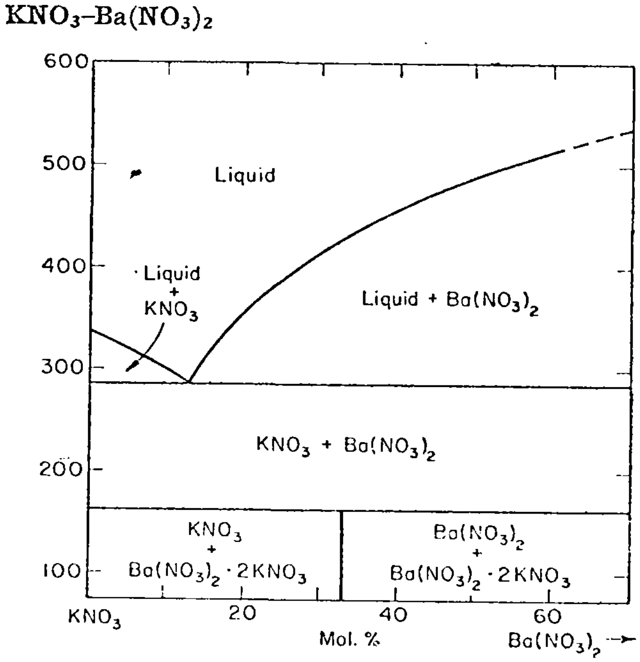
N. N. Evseeva and A. G. Bergman, Izv. Sektora Fiz.-Khim. Analiza, Inst. Obshch. Neorgan. Khim, Akad. Nauk SSSR, 21, 212 (1952)

Fig. A-9



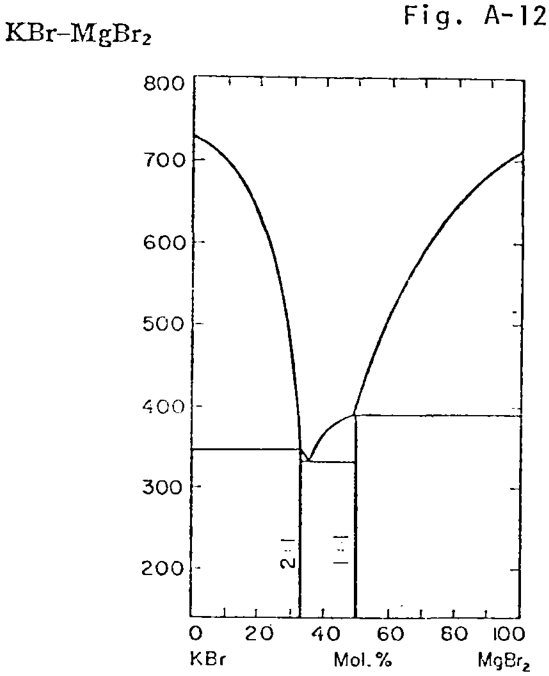
Ya A. Ugai and V. A. Shatillo, J. Phys. Chem. U.S.S.R., 23 (6) 745 (1949). See also F. R. Duke and R. A. Fleming, J. Electrochem. Soc., 104, 253 (1957).

Fig. A-11



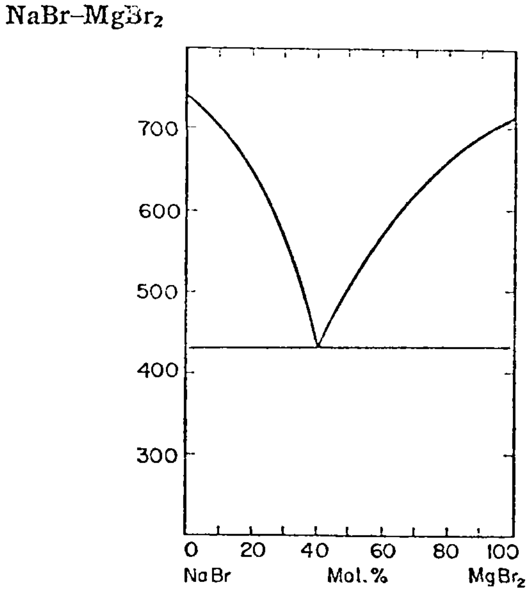
Meyer Markowitz, J. E. Ricci and P. F. Winternitz, J. Am. Chem. Soc., 77, 3484 (1955)

Fig. A-12



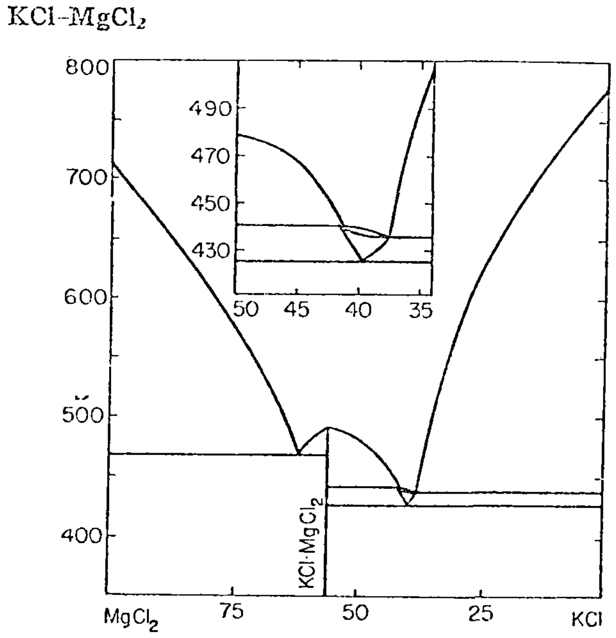
Georg Kellner, Z anorg. u. allgem. Chem., 99, 166 (1917).

Fig. A-13



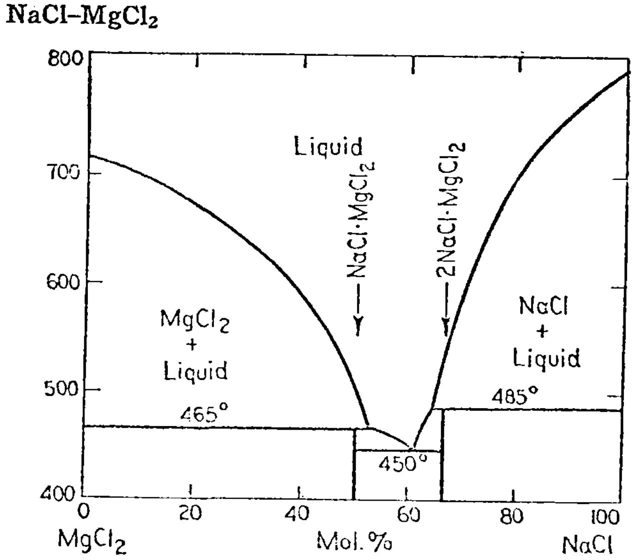
Georg Kellner, Z. anorg. u. allgem. Chem., 99, 158 (1917).

Fig. A-14



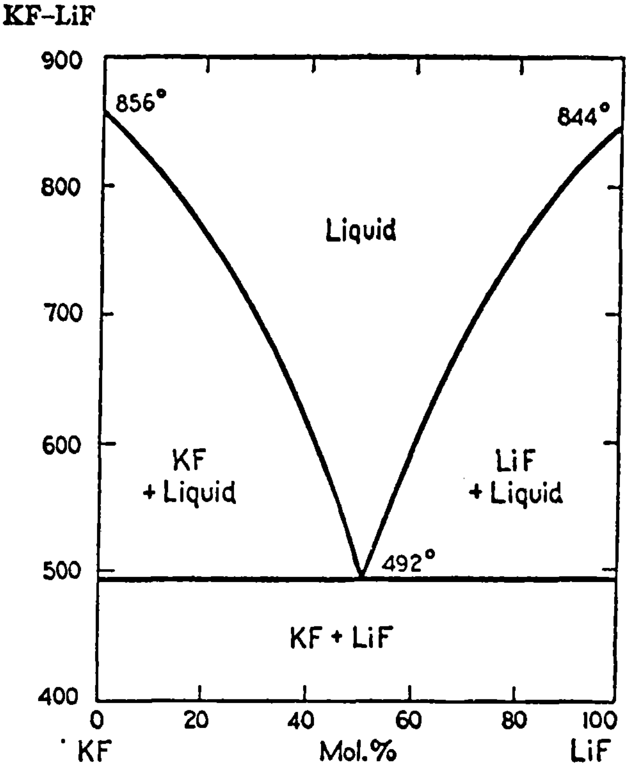
A. I. Icanov, Sbornik Statei Obshchei Khim, Akad. Nauk S.S.S.R., 1, (1953).

Fig. A-15



W. Klemm and P. Weiss, Z. anorg. u. allgem. Chem., 245, 281 (1940).

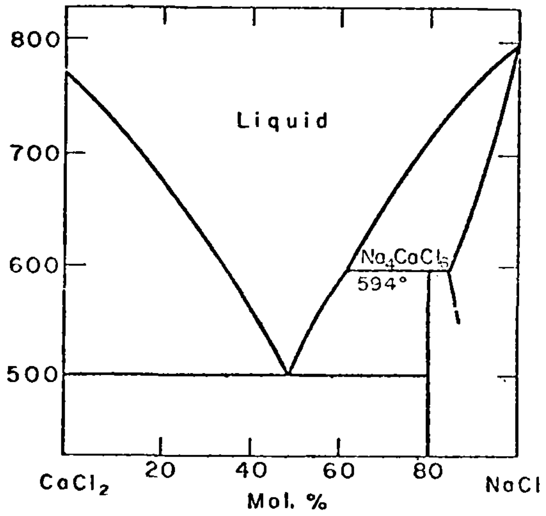
Fig. A-16



A. G. Bergman and E. P. Dergunov, Compt. rend. acad. sci., U.R.S.S., 31, 753 (1941)

Fig. A-17

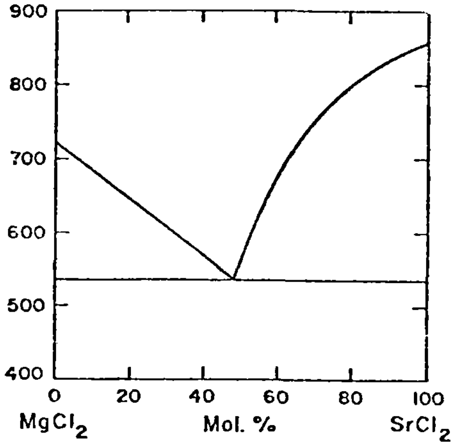
NaCl-CaCl$_2$



A Seltveit and H. Flood, Acta Chem. Scand., 12 (5) 1036 (1958).

Fig. A-18

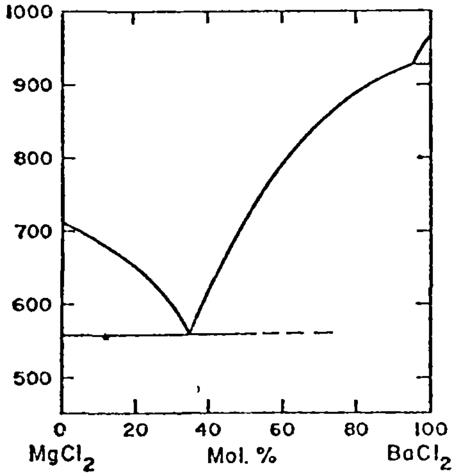
MgCl$_2$-SrCl$_2$



Carlo Sandonnini, Gazz. chim. ital., 44 I, 344 (1914).

Fig. A-19

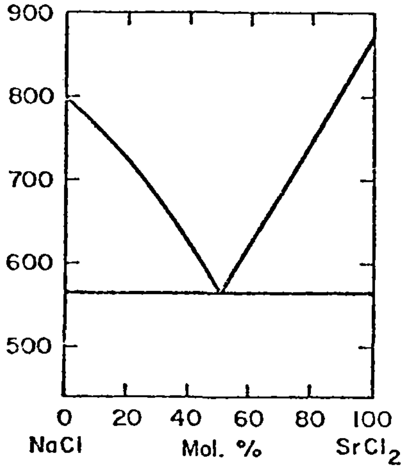
BaCl$_2$-MgCl$_2$



Carlo Sandonnini, Gazz. chim. ital. 44 I, 351 (1914).

Fig. A-20

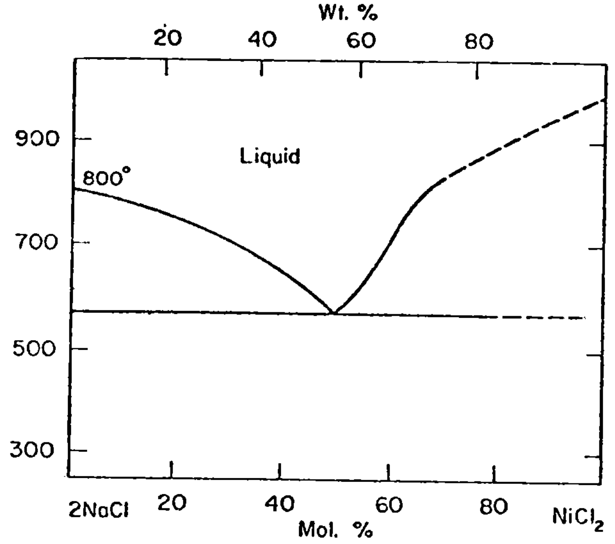
NaCl-SrCl$_2$



Erhard Vortisch, Neues Jahrb. Mineral., Geol., 38, 202, (1914).

Fig. A-21

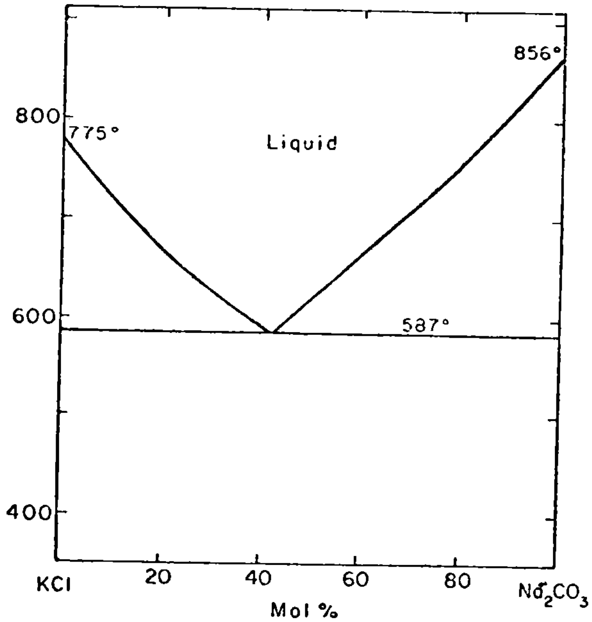
NaCl–NiCl₂



K. A. Bol'shakov and P. I. Fedorov, Zh. Neorgan. Khim., 5 (2) 469 (1960); Russ J. Inorg. Chem. (English Transl.), 224 (1960).

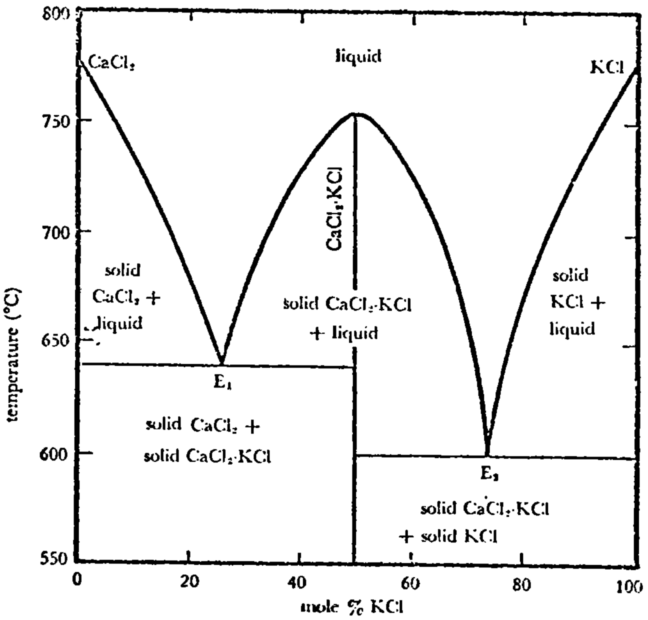
Fig. A-22

KCl–Na_2CO_3



Tomo-o Sato, Kinzoku-no-Kenkyu, 10, 453 (1933); see also N. N. Volkov and A. G. Bergman, Dokl. Akad. Nauk SSSR, 35, 50 (1942).

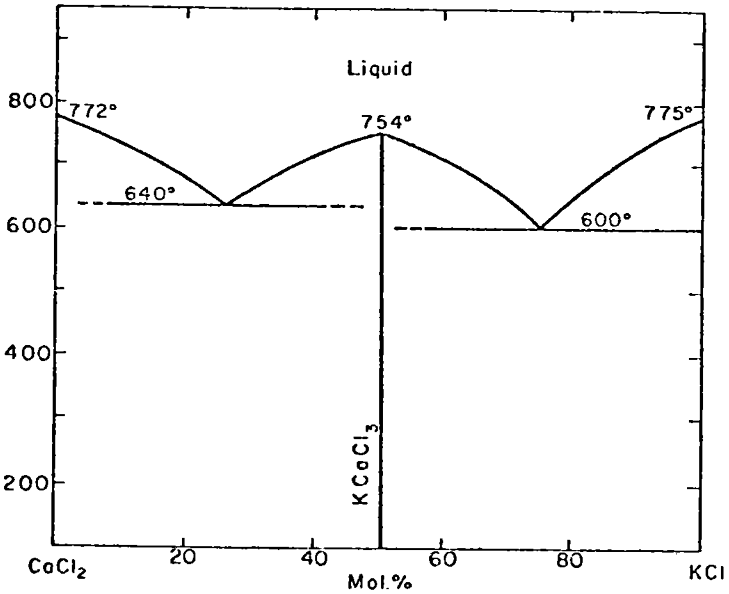
Fig. A-23a



(From data of K. Scholich, Neues Jahrb. Mineral, 43, 251 (1920).)

Fig. A-23b

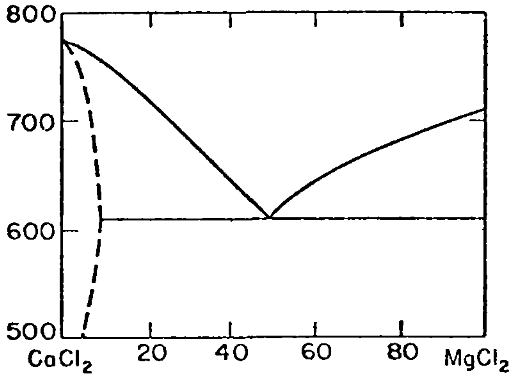
KCl–$CaCl_2$



V. E. Plyushchev, L. N. Komissarova, L. V. Meshchanmova, and L. M. Akukina, In Ah. Neorgan. Khim., 1 (4) 820(1956); Russ. J. Inorg. Chem. (Engl. Transl.) 220, (1956).

Fig. A-24

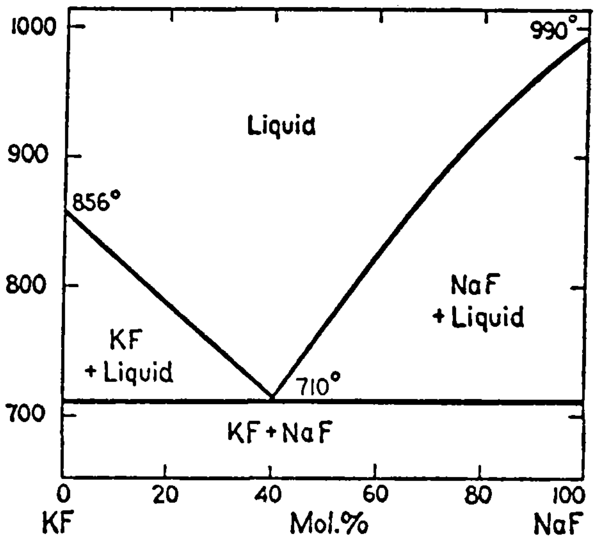
$CaCl_2$-$MgCl_2$



A. I. Ivanov. Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R., 1, 755 (1953).

Fig. A-25

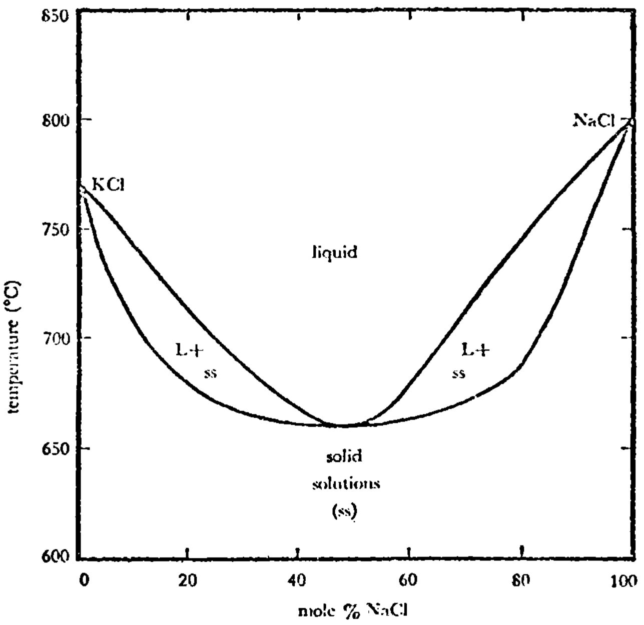
KF-NaF



A. G. Bergman and E. P. Dergunov, Compt. rend. acad. sci., U.R.S.S., 31, 753 (1941).

Fig. A-26

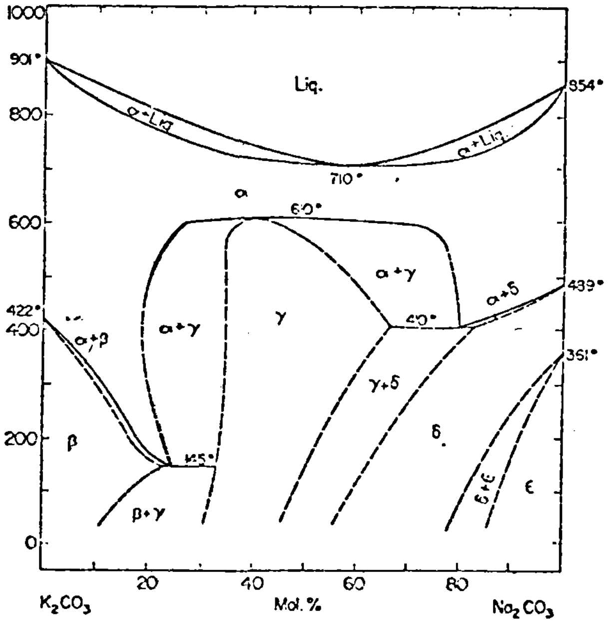
KCl-NaCl



(From data of W. P. Radischtschew, J. Gen. Chem. USSR, 5, 455 (1953).)

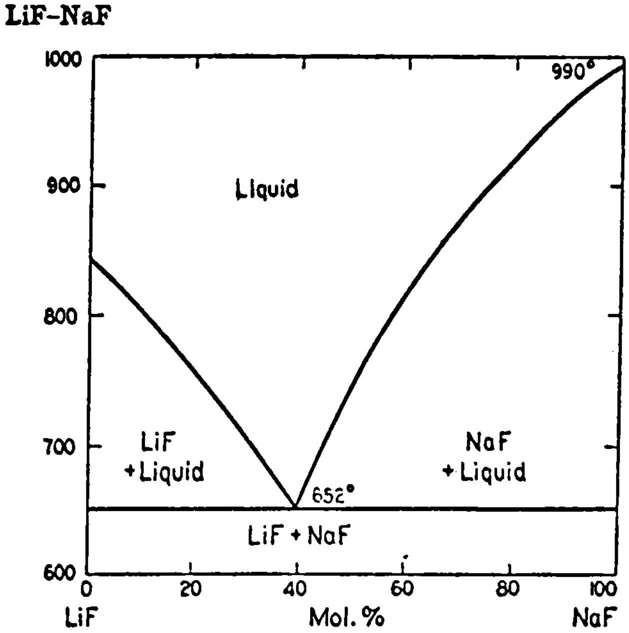
Fig. A.-27

K_2CO_3-Na_2CO_3



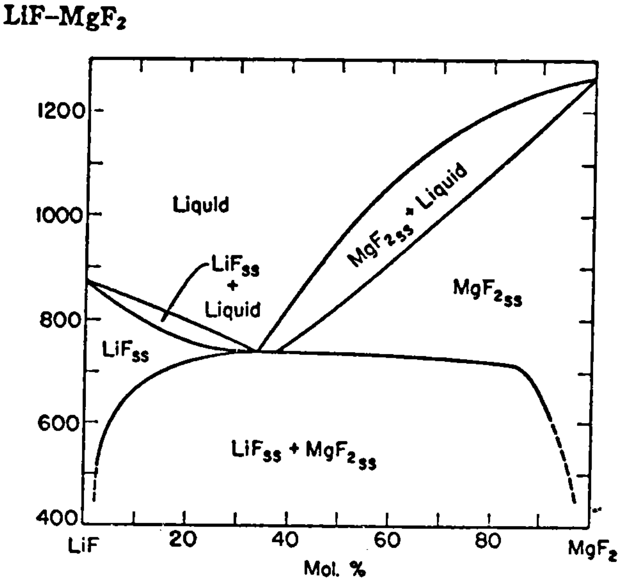
Arnold Reisman, J. Am. Chem. Soc. 81, 810 (1959).

Fig. A-28



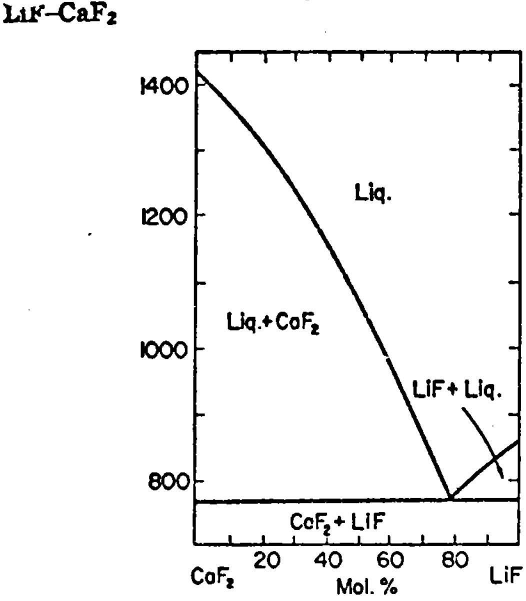
A. G. Bergman and E. P. Dergunov., Compt. rend. acad. sci., U.R.S.S., 31, 755 (1941).

Fig. A-29



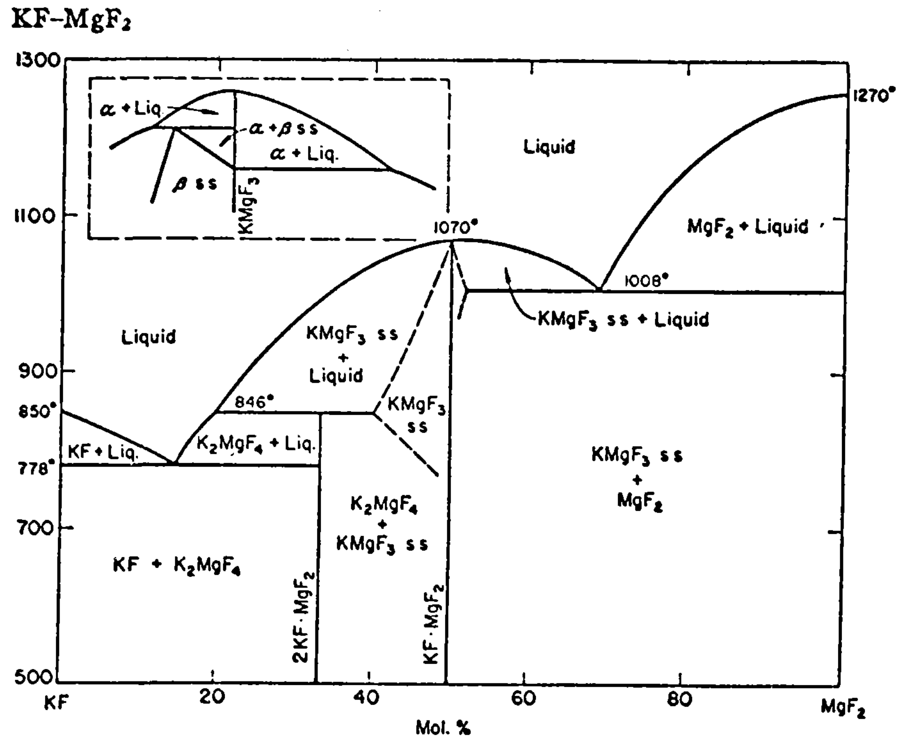
W. E. Counts, Rustum Roy, and E. F. Osborn, J. Am. Ceram. Soc. (1) 15 (1953).

Fig. A-30



W. E. Roake, J. Electrochem. Soc. 104, 661 (1957).

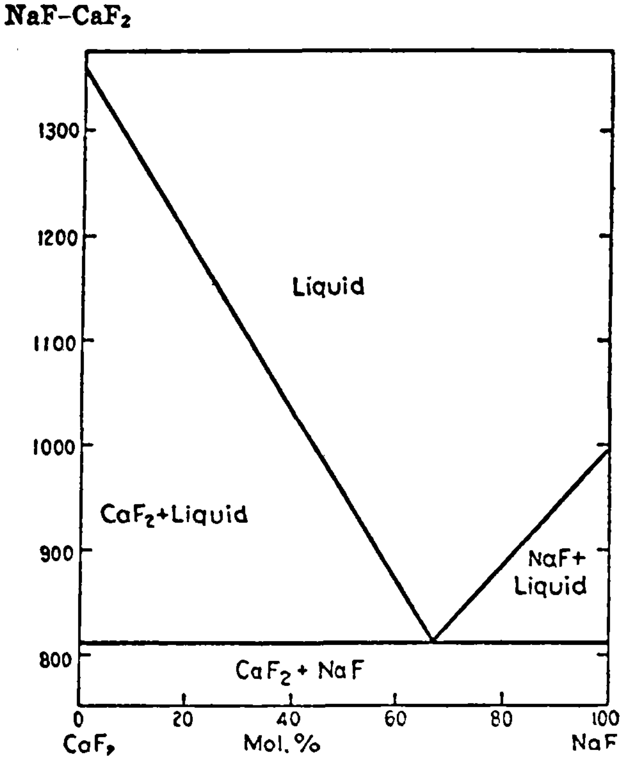
Fig. A-31



(Insert shows possible alternative for high-temperature region near KF-MgF_2.)

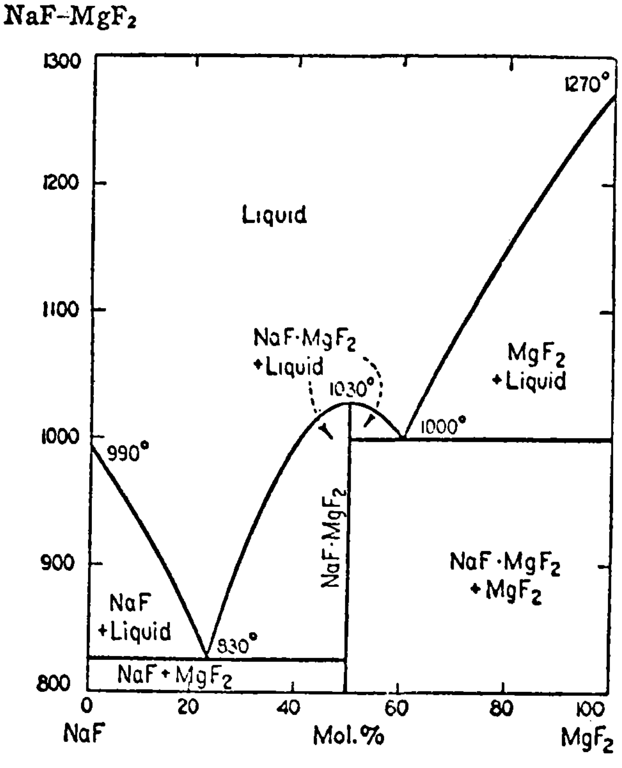
R. C. DeVries and Rustum Roy, J. Am. Chem. Soc., 75, 2481 (1953).

Fig. A.-32



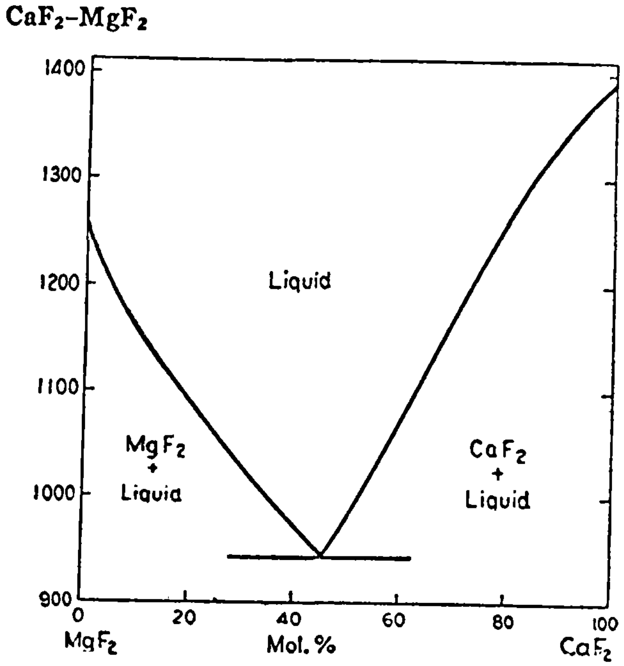
P. P. Fedotieff and W. P. Iljinskii, Z. anorg. u. allgem. Chem., 129, 101 (1923).

Fig. A-33



A. G. Bergman and E. P. Dergunov. Compt. rend. acad. sci., U.R.S.S., 31, 755 (1941).

Fig. A-34

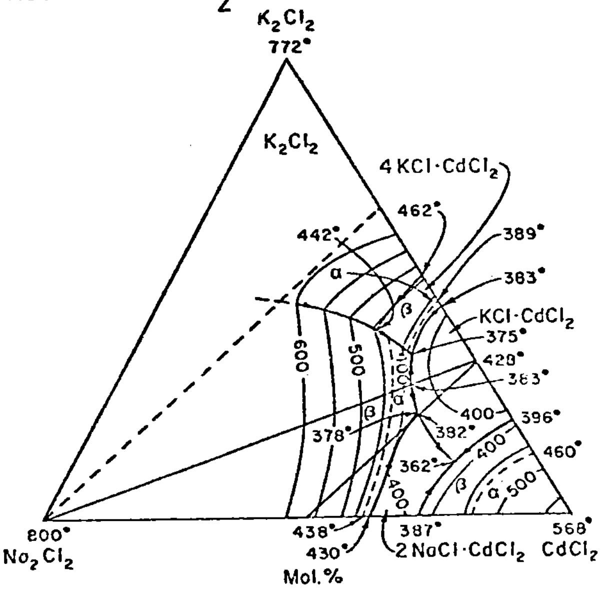


E. Beck, Metallurgie, 5, 504 (1908).

A.4 Phase Diagrams for Ternary Salts[62]

Fig. A-35

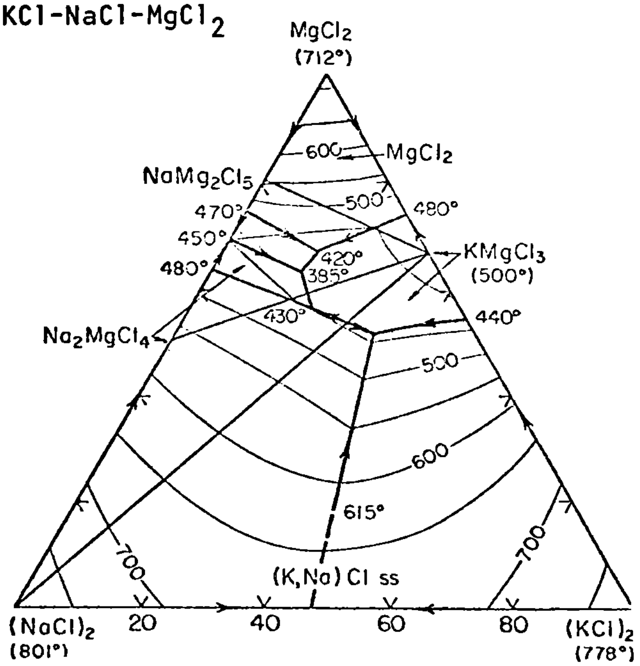
$KCl-NaCl-CdCl_2$



I. I. Il'yasov, A. K. Bostandzhiyan, and A. G. Bergman, Zhur. Neorg. Khim., 2, 177 (1957).

Fig. A-36

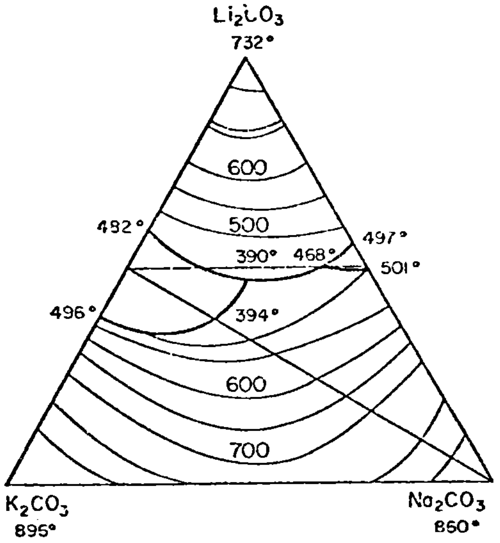
$KCl-NaCl-MgCl_2$



Ernst Janecke, Z. Anorg. Allgem. Chem., 261, 218 (1950).

Fig. A-37

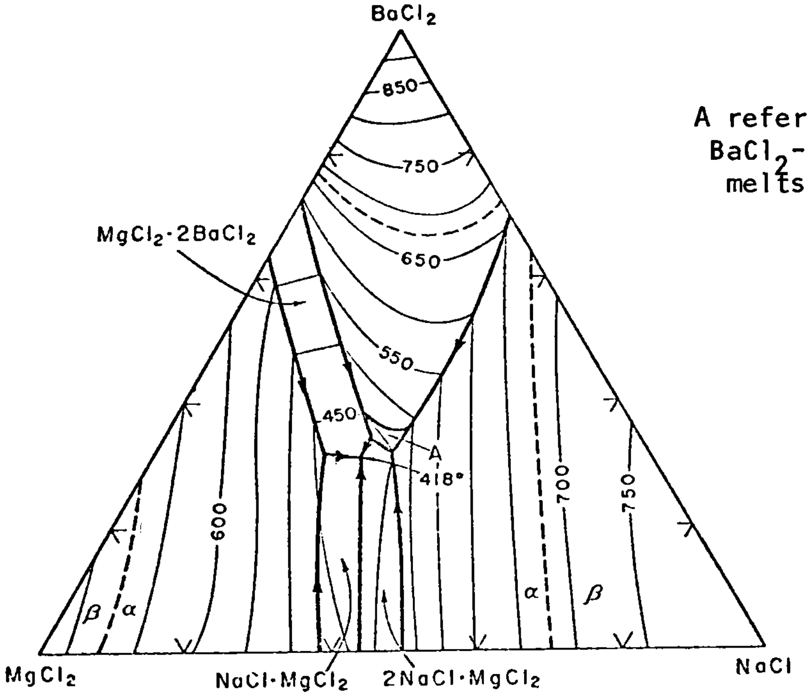
$K_2CO_3-Li_2CO_3-Na_2CO_3$



L. F. Volkova, Izvest. Sibirsk. Otdel. Akad. Nauk S.S.S.R., 1958, No. 7, p.34.

Fig. A-38

NaCl-BaCl$_2$-MgCl$_2$

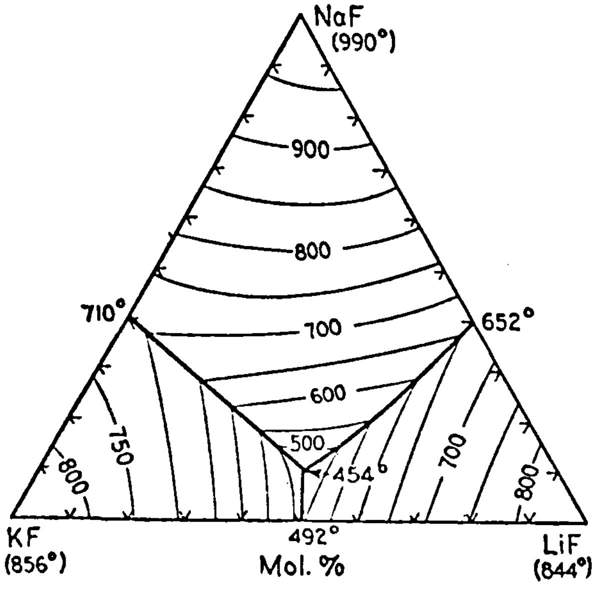


A refers to the compound BaCl$_2$-2MgCl$_2$-3NaCl which melts with decomposition

N. V. Bondarenko, Zh. Neorgan. Khim., 7, (6) 1387 (1962); Russ. J. Inorg. Chem. (English Transl.) 7, 717 (1962)

Fig. A-39

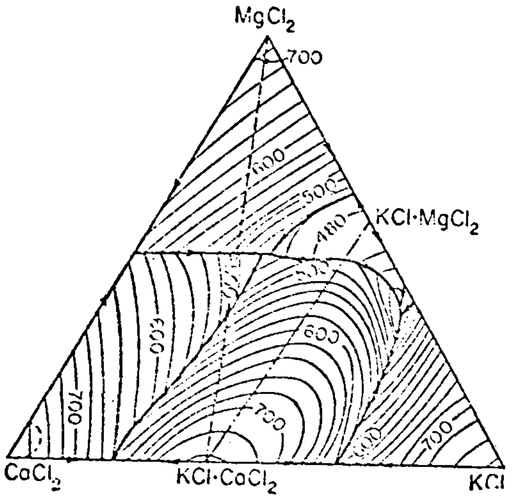
KF-LiF-NaF



A. G. Bergman and E. P. Dergunov. Compt. rend. acad. sci., U.R.S.S., 31, 754 (1941).

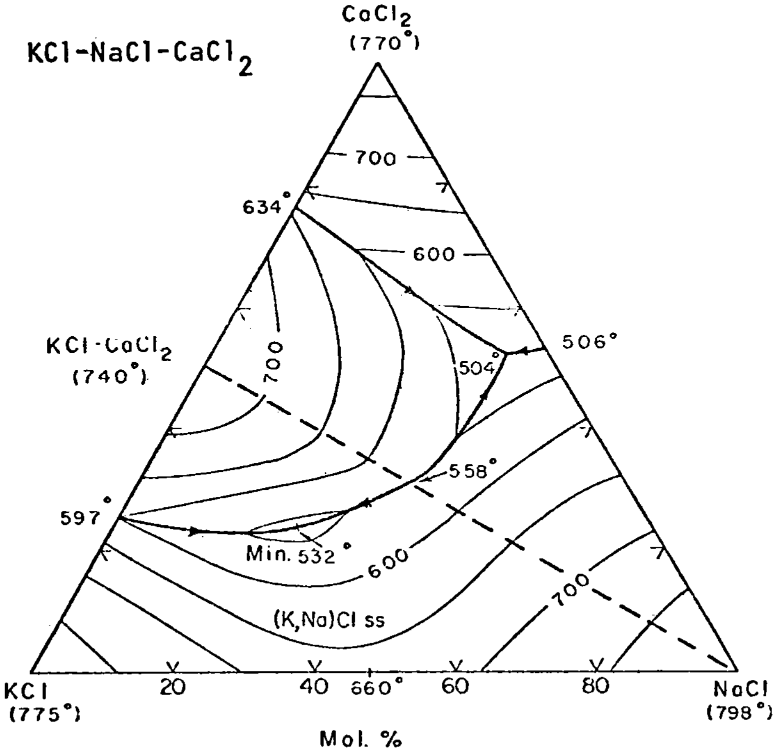
Fig. A-40

KCl-CaCl$_2$-MgCl$_2$



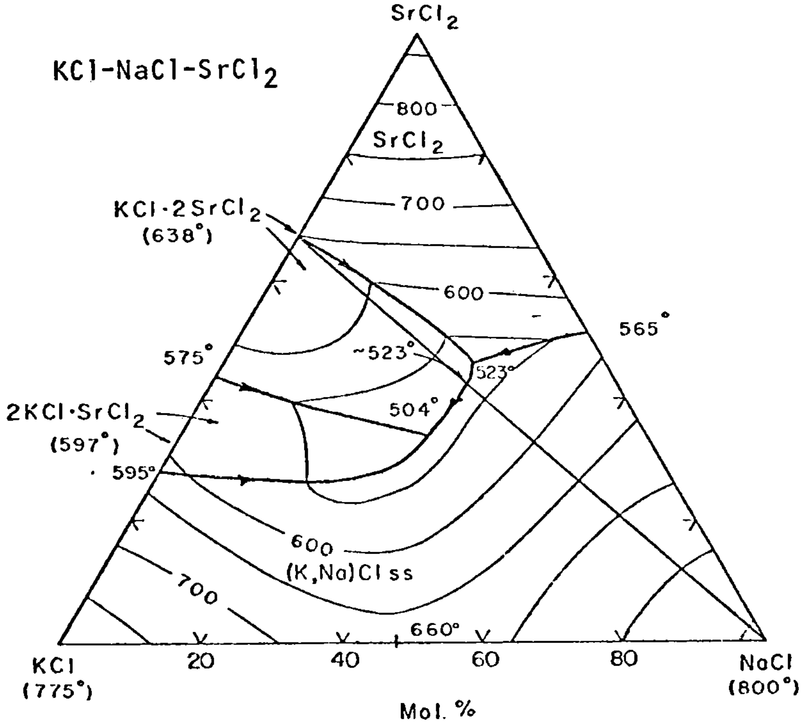
A. I. Ivanov, Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk S.S.S.R., 23, 197 (1953).

Fig. A-41



Kurt Scholich. Neues Jahrb. Mineral., Geol., 43, 262 (1920).

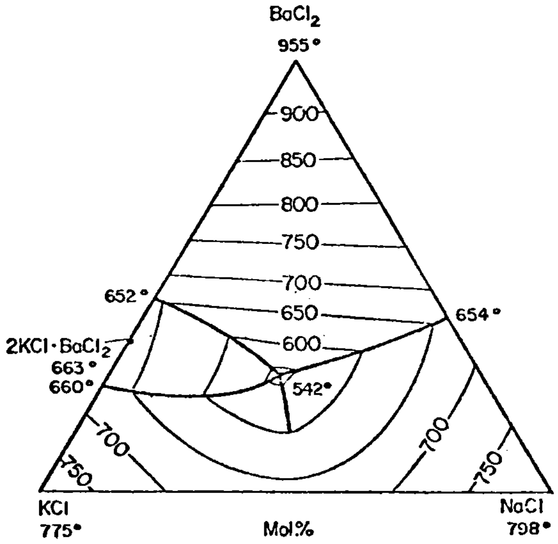
Fig. A-42



Kurt Scholich, Neues Jahrb. Mineral., Geol., 43, 269 (1920).

Fig. A-43

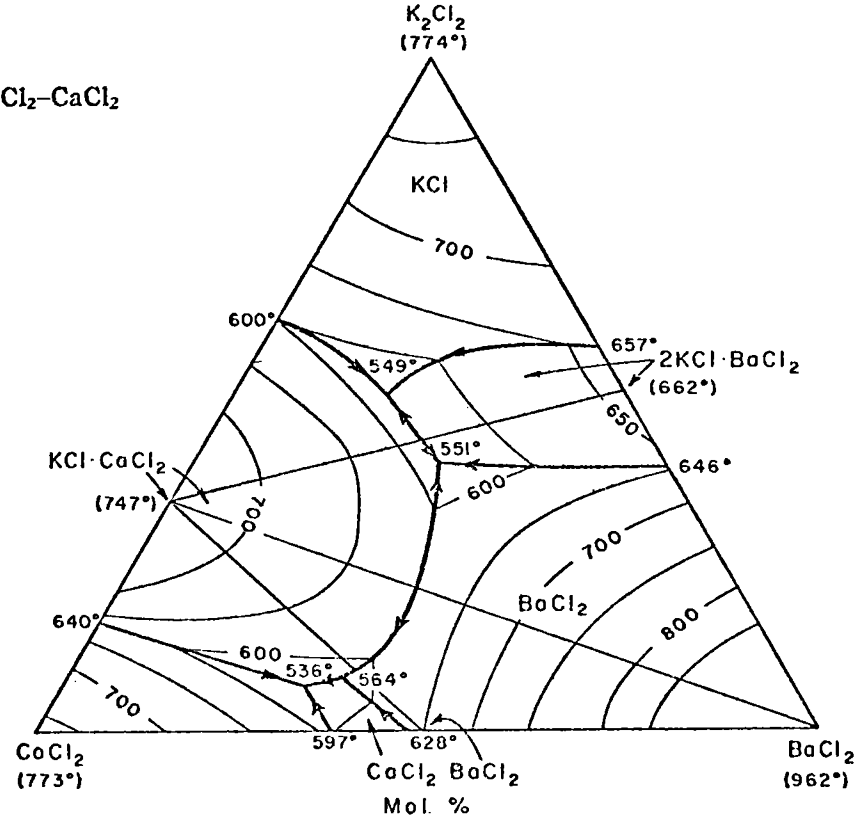
KCl–$NaCl$–$BaCl_2$



Erhard Vortisch, Neues Jahrb. Mineral., Geol., 38, 521 (1914).

Fig. A-44

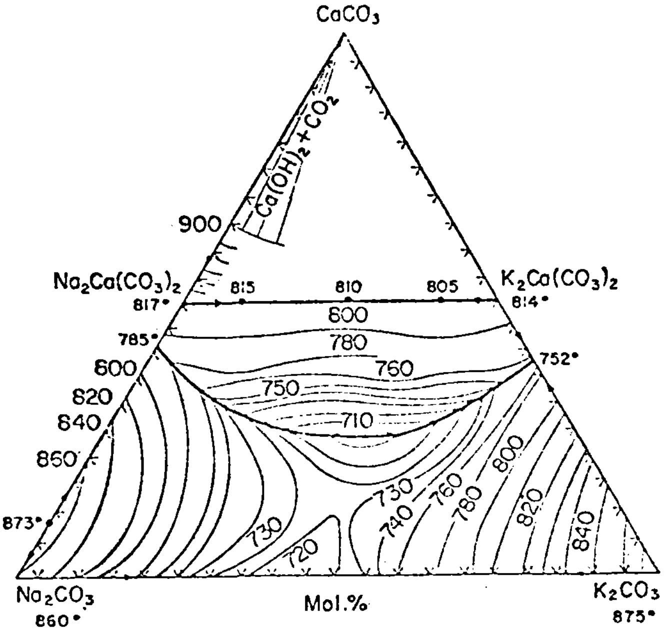
KCl–$BaCl_2$–$CaCl_2$



G. A. Bukhalova and V. T. Berezhnaya, Zh. Neorgan. Khim., 7 (6) 1399 (1962); Russ. J. Inorg. Chem. (English Transl.), 720 (1962).

Fig. A-45

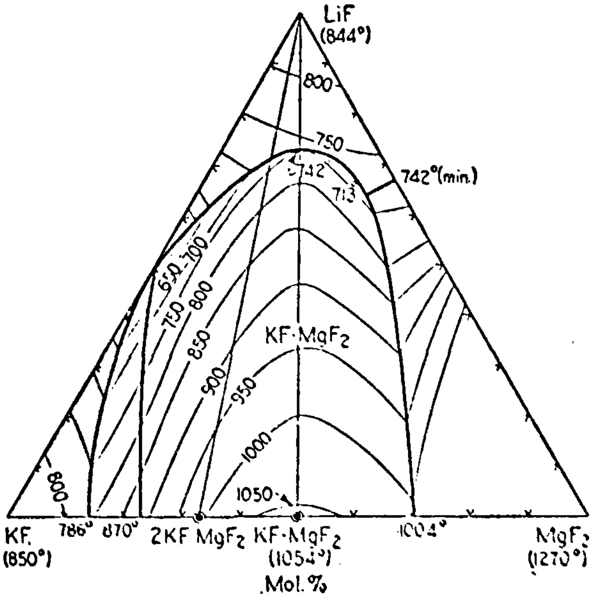
K_2CO_3-Na_2CO_3-$CaCO_3$



Paul Niggli, Z. Anorg. u. allgem. Chem., 106, 131 (1919).

Fig. A-46

KF-LiF-MgF_2



A. G. Bergman and S. P. Parlenko, Compt. rend. acad. sci., U.R.S.S., 31, 818-19 (1941).

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