Russian Chemical Reviews **69** (2) 179 – 186 (2000) © 2000 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2000v069n02ABEH000490

Heat-accumulating properties of melts

A M Gasanaliev, B Yu Gamataeva

Contents

I.	Introduction	179
II.	Methods of the thermal energy accumulation with the use of melts	180
III.	Criteria for the estimation of the heat-accumulating properties of melts	183
IV.	Principles for the development of heat-accumulating materials based on multi-component systems	184
V.	Conclusion	185

Abstract. Data on the heat-accumulating properties of melts are generalised. The principles and methods of thermal energy accumulation with the use of melts are considered. The problem of search for heat-accumulating materials with the required properties based on multi-component systems of anhydrous inorganic compounds is discussed. The bibliography includes 57 references.

I. Introduction

One of the major problems of the national economy, *viz*., decreasing power consumption of production, can be solved by two methods. The first one is more efficient transformation of primary energy into electrical and thermal energy. This can be done by increasing the efficiency factor of power stations, by using cheaper fuel types or renewable energy sources, such as wind, geothermal sources, tides, sea waves, *etc*.

The second method of ever-growing importance involves increasing the efficiency of the energy utilisation by the consumer. The expenses for saving fuel and electric power are two to three times lower than those required for expanding the fuel and energy base. The following measures for improving the efficiency of energy usage by the consumers can be listed: transition to more perfect and less power-consuming technologies; use of secondary power resources; smoothing the time differences between the energy generation and energy demand schedules by means of accumulation.

Accumulation of electric energy is a difficult problem. The capacities of the existing electrochemical accumulators are insufficient for their use on an industrial scale. The promising superconducting electric power accumulators are still under development. The hydraulic methods for energy storage make it possible to accumulate significant amounts of energy; however, this involves large capital investment and impact on the environment (not always favourable).

Methods for the thermal energy accumulation have been developed in detail and tested under various conditions. The world energy crisis of the 1970s has confirmed once again the urgency of the problem of the thermal energy accumulation followed by heat recovery and transformation into useful work.[1]

Studies along these lines include two aspects, namely, the chemical-technological and technical-physical ones.[2, 3] The chemical-technological aspect includes choosing the heat-accumulating materials (HAM), studying their properties and selecting the accumulation method. The thermal energy accumulation and recovery methods involving melts are based on the following processes: heating compounds to a high temperature followed by heat release on cooling (heat accumulation due to the heat capacity of the solid and liquid phases); reversible first-order phase transitions (accumulation due to latent heat of phase transitions); reversible chemical reactions (chemical accumulation). The technical-physical aspect examines selection of the processes for the transformation and use of the stored energy.

National programmes on the thermal energy accumulation with the use of reliable and inexpensive accumulators have been developed in different countries and are now being implemented. The use of such accumulators enables one to replace the traditional fuel types (coal, natural gas) by non-traditional renewable energy sources[4, 5] as well as allows one to use the spent heat in chemical-technological processes or for heat supply.

However, an important drawback of heat accumulators is the high cost of accumulated energy, mainly because of the cost of the HAM. For this reason, the development of heat accumulators starts from the search for cheap HAM with high heat capacity and predetermined properties.

Synthesis of novel inorganic materials with predetermined properties requires complex studies of fusibility diagrams and physicochemical properties of multi-component systems by modern physicochemical methods, primarily those using computer 3D simulation methods.[2, 6 – 8]

Recent studies on HAM mostly deal with crystal hydrates of inorganic salts, salt eutectics and metal alloys traditionally used in this field. The present review generalises the data regarding the methods and principles of the thermal energy accumulation using melts of anhydrous inorganic compounds as the HAM. Criteria for the estimation of the heat-accumulating ability of melts and a new methodological approach to the development of HAM based on multi-component systems and study of their physicochemical properties are considered. Special attention is given to the systematisation of experimental data on the fusibility diagrams of multi-component systems.

A M Gasanaliev, B Yu Gamataeva Dagestan State Pedagogical University, ul. 26 Bakinskikh Komissarov 57, 360219 Makhachkala, Russian Federation. Fax (7-872) 267 06 03. Tel. (7-872) 268 44 80

Received 19 March 1999
Uspekhi Khimii **69** (2) 192 – 200 (2000); translated by S S Veselyi

II. Methods of the thermal energy accumulation with the use of melts

The most popular heat accumulators use melts as the HAM. They can accumulate thermal energy either due to the heat capacity of solid or liquid media or due to the latent heat of phase transitions and chemical reactions. Non-isothermal and isothermal accumulators are distinguished, depending on the mode of heat storage.

1. Heat accumulation due to the heat capacity of solid and liquid media

The most popular method of heat accumulation is that due to the heat capacity of liquid and solid media. A compound which accumulates heat due to the heat capacity of its different phases is called a heat-capacity compound. Heat accumulators with such a compound as the working medium are non-isothermal. They are used for the heat accumulation over a broad temperature range (several hundred degrees). The allowed temperature variation in an accumulator is normally specified (it is determined by the temperature of the heat source, the temperature of the heat-carrier, the temperature required by the consumer, and the temperature differences controlling the intensity of heat exchange during the accumulator charge and discharge phases). Water (for temperatures up to 100 °C), air, noble gases, melts of simple and complex inorganic compounds and technical oils can serve as heat-carriers.

If melts are used as heat-capacity HAM, it has to be taken into account that the specific heat is generally independent of temperature and is a constant. The specific energy stored by a heat-capacity heat accumulator is determined by the formula

$$Q = C_p \Delta T,$$

where C_p is the specific heat of the accumulator working medium at constant pressure; ΔT is the difference between the starting and final accumulation temperatures.

It is known from thermodynamics that the specific heat is the higher the smaller the relative molecular mass of the compound. Therefore, compounds with small molecular masses are used as working media for heat-capacity accumulators.

Of anhydrous inorganic compounds, systems based on oxides, the so-called refractory compounds, are used as the HAM most commonly. The properties of the most promising oxide-based HAM are analysed in Ref. 9. A great many experimental studies relate to the determination of the dependences of C_p, thermal conductivity factor (λ) and apparent density (ρ) on temperature and open porosity (O_p). In some cases, natural minerals and anhydrous inorganic compounds obtained from them are used, *e.g.* granite, sand, pebbles, gravel, cobble-stone, macadam, sand–pebble mixture, *etc*. Such heat-capacity HAM are inexpensive and readily accessible, are not corrosive with respect to construction materials, but have low effectiveness in terms of their thermal properties, which results in the low density of the accumulated energy.

The increase in the specific density of the heat-capacity HAM increases the specific heat, and hence the amount of accumulated heat in the bulk material. The materials based on magnesia have the highest heat capacity; these materials have sufficient thermal conductivity in the temperature range 100–900 °C to be used as heat-capacity HAM (Table 1).

As the proportion of magnesia and the material apparent density increase, the thermal conductivity increases. The thermal conductivity of hyperdense heat-capacity HAM (3.55–3.97 kg m^{-3}) exceeds 30 W m^{-1} K^{-1} at 100 °C, while it is less than 5 W m^{-1} K^{-1} for dense (3.00–3.50 kg m^{-3}) and medium-density ones (1.83–2.96 kg m^{-3}).[9] Medium-density materials containing mixtures of magnesia with SiO_2, Al_2O_3, Cr_2O_3, or CaO and having an open porosity of 20%–30% are most efficient in terms of thermal conductivity (λ changes from 0.74–3.93 at 100 °C to 1.07–1.80 at 900 °C). Magnesia-based materials containing chromium oxide are the most heat-resistant (see Table 1).

2. Heat accumulation owing to the latent heat of phase transitions

The accumulation of heat with the use of the latent heat of phase transitions of anhydrous inorganic compounds is possible in the following changes in the state of aggregation:[3,8] melting ⇄ crystallisation, vapourisation ⇄ condensation, sublimation and decomposition.

The heat-accumulating materials which accumulate heat due to phase transitions are called phase-transition HAM. The accumulators with such materials as the working media are isothermal.

The accumulators in which the latent heat of the melting ⇄ crystallisation phase transition is used have good energetic characteristics. The principle of such an accumulator is based on the thermal energy absorption accompanying the crystal lattice destruction upon heating of a compound and energy liberation upon crystallisation of the melt on cooling.

In many technological processes, the only useful thermal energy is that accumulated due to the heat of phase transitions and due to the heat capacity of the material in the liquid phase.[10–14] These processes include: maintaining the given operating temperature of steam at thermal and nuclear power plants; transformation of thermal energy into electrical energy through the Brighton cycle; thermal energy accumulation and transfer with the use of molten phase-transition HAM as heat-carriers; increasing the efficiency of non-traditional systems by compensating for the intermittent and non-steady nature of renewable energy sources (solar, wind, geothermal, *etc*.).

The type of the thermodynamic cycle and the nature of the HAM are determined by the operating temperature range of the heat accumulator. This primarily assumes a relationship between the characteristics of the main power system, the accumulator and the parameters of the cycle in which the mass and heat transfer occur. For example, Table 2 lists the efficiency values of three cycles. Yet another example: the maximum temperature of the hot source at a solar power station without radiation concentrating by local concentrators is about 100 °C. In this case, it is only possible to speak about a cycle with evaporation of the working media such as freons. However, these working media cause ecological problems if they leak. In this case, a perfect HAM would consist of eutectic compositions based on *n*-component mixtures of hydrates and anhydrous compounds with m.p. $\leqslant$ 100 °C.

The thermal characteristics of the most promising systems based on aluminium chloride and alkali metals with the heat-accumulating ability above 0.3 GJ m^{-3} are presented in Table 3.

Table 1. Heat-accumulating properties of oxide heat-capacity HAM in the temperature range 100–900 °C.

Refractory compounds (mass %)	O_p (%)	ρ /kg m^{-3}	C_p /MJ m^{-3} K^{-1}	λ/W m^{-1} K^{-1}
Chamotte, 28 $\leqslant$ Al_2O_3 $\leqslant$ 45	20–24	2.05–1.85	1.5874–2.4232	0.74–1.07
Periclase-chromite, 65.5 MgO–14.2 Cr_2O_3	24–30	2.81–2.52	2.3575–3.5011	2.42–2.08
Forsterite, 58.3 MgO–38.9 SiO_2	20–30	2.69–2.29	2.2115–3.5409	3.93–1.80
Periclase-spinel, 75.6 MgO–18.2 Al_2O_3	3–10	3.15	3.1617–4.0219	2.04–3.33
Periclase	0–3	3.55–3.37	3.6954–4.5683	34.82–7.52
Magnesian limestone, 70 MgO–26.2 CaO	18–21	2.80–2.68	3.2217–3.4232	1.74–2.72

Table 2. Characteristics of thermodynamic cycles.

Cycle	Characteristic cycle parameter	Efficiency
Temperature range 40 – 268 °C		
Carnot	–	0.420
Rankin	steam under a pressure of 5 MPa	0.365
Temperature range 40 – 450 °C		
Chirn	evaporation at 268 °C	0.380
Carnot	–	0.567

Table 3. Characteristics of phase-transition HAM for accumulation of low-potential thermal energy (m.p. ⩽ 100 °C).

System (mass %)	M.p. /°C	ρ /kg m^{-3}	ΔH_m (see [a])	
			I	II
77 $AlCl_3$ – 5 $BaCl_2$ – 18 NaCl	50	1786	168.5	0.3009
88.5 $AlCl_3$ – 11.5 LiCl	80	1645	199	0.3274
22.2 $LiNO_3$ – 10.9 $NaNO_3$ – 66.9 NH_4NO_3	81	–	127	–
26.4 $LiNO_3$ – 58.7 NH_4NO_3 – 14.9 KNO_3	81.5	–	–	0.234
78.1 $AlCl_3$ – 5.5 KCl – 16.4 LiCl	85	1631	196	0.3207
77.9 $AlCl_3$ – 11.3 KCl – 10.8 NaCl	88	1653	191	0.3185
73.8 $AlCl_3$ – 21.8 NaCl – 4.4 $TlCl_3$	98	1659	192	0.3185
73.7 $AlCl_3$ – 22.2 KCl – 4.1 $TlCl_3$	100	1650	184.2	0.3039
63.8 $AlCl_3$ – 18.1 KCl – 18.1 $TlCl_3$	100	1743	156.1	0.2756

[a] The accumulated energy is usually expressed as enthalpy/weight ratio $\Delta H/M$ or enthalpy/volume ratio $\Delta H/V$, therefore the dimensionalities are: (I) kJ kg^{-1}; (II) GJ m^{-3}.

Judging by the data listed, the choice of phase-transition HAM for the accumulation of low-potential thermal energy is limited, particularly if one takes the cost of the accumulated energy into account.[7]

Studies of movement of the solidification (melting) frontier of HAM on a planar unit cell model of a heat accumulator [15] were carried out using an eutectic three-metal alloy with composition (mass %) 50 Bi – 31 Pb – 19 Sn and the parameters: $T = 94.5$ °C, $\rho = 9590$ kg m^{-3}, $\Delta H_m = 26.4$ kJ kg^{-1}, $C_p = 0.138$ kJ kg^{-1} K^{-1}, $\lambda = 16.5$ W m^{-1} K^{-1} as a phase-transfer heat-accumulating material.

The heat-accumulating ability of metal alloys (> 0.2 GJ m^{-3}) is ensured by their high densities, unlike the case of salt melts where this ability is ensured by the enthalpy of melting (see Table 3).

It has been shown (see, *e.g.*, Refs 8 and 16) that an efficient short-term accumulator of average-potential thermal energy can be represented by an accumulator that uses the heat of phase transitions (melting ⇄ crystallisation) of mixtures of anhydrous inorganic compounds. These mixtures represent mainly *n*-component eutectic compositions of molten alkaline and alkaline-earth metal salts with melting points of 100 – 500 °C. The ranges of the melting points (m.p.) and ΔH_m for the recommended phase-transition HAM and the most promising eutectic compositions are given in Table 4.

Thermodynamic analysis of such systems shows [8, 19] that the highest heat-accumulating ability is characteristic of salt eutectics based on lithium nitrate possessing high heats of phase transition (370 kJ kg^{-1}) and thermal stability up to 500 °C and a melting point of 256 °C; in addition, these are not corrosive with respect to many structural materials and their alloys. Eutectic compositions containing only alkali and alkaline-earth metal nitrates (except for $LiNO_3$) can be used at operating temperatures only 30 – 50 °C higher than their melting points (due to decomposition).

Table 4. Characteristics of phase-transition HAM for accumulation of medium-potential (100 < m.p. < 500 °C) thermal energy.[6, 16 – 18]

System (mass %)	M.p. /°C	ρ /kg m^{-3}	ΔH_m (see [a])	
			I	II
29 $LiNO_3$ – 17 $NaNO_3$ – 49.4 KNO_3 – 4.6 $Sr(NO_3)_2$	105	2087	110	229.6
17.5 LiCl – 82.5 $AlCl_3$	114	2376	251	596
21.6 KCl – 78.4 $AlCl_3$	128	2343	254	595
31.7 $LiNO_3$ – 68.3 KNO_3	135	1780	135.6	241.4
55.4 $LiNO_3$ – 4.5 $NaNO_3$ – 40.1 KCl	160	1905	266	507
58.1 $LiNO_3$ – 41.9 KCl	166	1918	272	522
47.9 $LiNO_3$ – 1.4 LiCl – 50.7 $NaNO_3$	180	1986	267	530
57 $LiNO_3$ – 43 $NaNO_3$	193	1880	248.3	467
45 $LiNO_3$ – 47 $NaNO_3$ – 8 $Sr(NO_3)_2$	200	1993	199	397
87 $LiNO_3$ – 13 NaCl	208	1889	369	697
93.6 $LiNO_3$ – 6.4 NaCl	220	1850	363	675
98 $LiNO_3$ – 2 Li_2SO_4	255	2357	354	834.4
1.8 LiF – 39.9 LiCl – 8.3 NaCl – 50 KCl	368	2048	523	1071
29 LiCl – 24 LiF – 21 Li_2CO_3 – 26 Li_2SO_4	419	2252	387	871.4
29.6 KCl – 53.8 Li_2SO_4 – 16.6 NaCl	420	2062	586.2	1209
26.9 NaCl – 73.1 $Sr(NO_3)_2$	424	2152	244	252

[a] The dimensionalities are: (I) kJ kg^{-1}; (II) MJ m^{-3}.

High ΔH_m values are characteristic of alkali metal chlorides and sulfates, and hence intense heat liberation is observed on the DTA (or DSK) cooling curves for eutectic mixtures with lithium nitrate.[16] Addition of alkali metal nitrates to halide-, sulfate- and carbonate-containing mixtures of alkali and alkaline-earth metals allows not only reduction of the operating temperature but also an increase in the heat-accumulating ability, as well as a decrease in the corrosive effect of these mixtures on structural materials.

The number of components in promising eutectic systems (*n*) ranges from 1 to 4. If $n > 4$, degeneration with respect to both the melting points and the physicochemical properties occurs; this increases the cost of the accumulated energy with the heat-accumulating ability being the same.

Technical and economic analysis showed that accumulators with high-temperature phase-transition HAM (m.p. > 500 °C) as the heat-carriers, particularly eutectic compositions of salt and metal multi-component systems, are most suitable for non-traditional energy sources.[5] However, the development of such accumulators entails the solution of a number of complex technical problems (for example, the corrosion compatibility of the HAM with structural materials, intensification of heat exchange in the charge and discharge modes, regeneration of the HAM, *etc.*).

Of the phase-transition HAM used for the thermal energy accumulation, eutectic metal alloys possess the best thermal conductivities and stabilities. Analysis of published data on thermodynamic parameters of metal-based multi-component systems [17, 19] made it possible to single out the most promising ones for use as the working materials in heat accumulators (Table 5).

Of ionic compounds, alkali and alkaline-earth metal fluorides, chlorides, carbonates, and sulfates have the best thermal properties for the accumulation of high-potential thermal energy. Salt eutectics are the most power-intensive (due to the enthalpy of melting, see Table 6). The ΔH_m values were found experimentally or calculated using the additivity principle. The experimental studies of heat capacity were carried out using a continuous-heating calorimeter.[17]

Table 5. The characteristics of phase-transition HAM from metal alloys.

System (mass %)	M.p. /°C	ρ /kg m^{-3}	ΔH_m (see [a])	
			I	II
78.55 Ga – 21.45 In	15.7	6197	69.7	0.4429
86.5 Ga – 13.5 Sn	20.55	5885	81.9	0.4942
96.5 Ga – 3.5 Zn	25.0	5946	88.5	0.5415
67 Ga – 20.5 In – 12.5 Zn	10.7	6170	67.2	0.4185
82 Ga – 12 Sn – 6 Zn	18.8	5961	86.5	0.5255
74 Ga – 22 Sn – 4 Cd	20.2	5983	75.2	0.4571
93 Ga – 5 Zn – 2 Cd	24.6	6020	85.03	0.5246
13.3 Sn – 50 Bi – 10 Sd – 26.7 Pb	70	8974	45.8	0.412
46.3 Mg – 53.7 Zn	340	4600	185	0.851
96 Zn – 4 Al	381	6630	138	0.916
34.65 Mg – 65.35 Al	497	2155	285	0.615
60.8 Al – 33.2 Cu – 6.0 Mg	506	3050	365	1.113
64.6 Al – 5.2 Si – 28 Cu – 2.2 Mg	507	4400	374	1.644
68.5 Al – 5.0 Si – 26.5 Cu	525	2938	364	1.069
64.3 Al – 34.0 Cu – 1.7 Sb	545	4000	331	1.324
66.92 Al – 33.08 Cu	548	3600	372	1.339
83.14 Al – 11.7 Si – 5.16 Mg	555	2500	485	1.213
87.76 Al – 12.24 Si	557	2540	498	1.265
46.3Al – 4.6 Si – 49.1 Cu	571	5560	406	2.260
86.4 Al – 9.4 Si – 4.2 Sb	575	2700	471	1.272

[a] The dimensionalities are: (I) kJ kg^{-1}; (II) GJ m^{-3}.

Table 6. Enthalpy of melting of salt eutectics with m.p. > 500 °C.[16, 17, 20, 21]

System (mass %)	M.p. /°C	ΔH_m /kJ m^{-3}
50 Li_2CO_3 – 50 K_2CO_3	505	335
64.25 LiCl – 35.75 Li_2CO_3	510	339.7
56.4 Na_2SO_4 – 12.9 NaCl – 30.7 KCl	528	410
56.7 Li_2SO_4 – 10.3 Na_2SO_4 – 33 KCl	536	514.6
26.2 LiF – 73.8 Li_2SO_4	540	348.9
64.5 LiCl – 35.5 NaCl	556	414.5
25.7 LiF – 36.5 NaF – 10.6 MgF_2 – 27.2 CaF_2	593	510
24.8 LiF – 75.2 Li_2CO_3	595	594.5
10.4 NaF – 39.4 NaCl – 50.2 KCl	602	370.3
32.6 LiF – 50.4 NaF – 17 MgF_2	622	625
34.7 LiF – 3.3 NaF – 37.5 MgF_2 – 24.5 CaF_2	651	470
48 LiF – 52 NaF	652	711
24 LiF – 76 NaCl	680	476.9
67 LiF – 33 MgF_2	746	708
46 LiF – 54 MgF_2	750	847
75 NaF – 25 MgF_2	832	649
31 NaF – 69 MgF_2	996	710
29.5 KF – 70.5 MgF_2	1006	770

From the viewpoint of thermal accumulation, salt systems have drawbacks such as rather low thermal conductivities and undesirable volume increase by 10% – 30% upon melting; because of this, it is necessary to provide free volume for thermal expansion of the melt in the accumulators.

Prediction of the properties of ionic systems without experimental studies was carried out using the equation[17]

$$\Delta H_m = \Delta H_m^{add} + \Delta\Delta H_m ,$$

where $\Delta H_m^{add} = \Sigma x_i \Delta H_{m\,i}\,(T_e)$; x_i is the mole fraction of the ith component; $\Delta H_{m\,i}\,(T_e)$ is the enthalpy of melting of the ith component referred to the temperature of the eutectic.

Comparison of the $\Delta\Delta H_m$ values and the enthalpy of mixing of melts ΔH_{mix} showed [17] that

$$\Delta\Delta H_m = \Delta H_{mix} .$$

Eutectic mixtures containing salts of stable intersecting elements of mutual systems have the highest heat content.[16] Several papers report on the finding of stable intersecting elements in three-, four- and five-component mutual systems and studying their heat-accumulating properties.[20, 22]

3. Chemical accumulation

Chemical accumulation implies the energy accumulation and release by virtue of chemical reactions. The accumulated energy can be released as heat, electrical energy, light, or mechanical energy.

Depending on the type of the accumulated energy, one distinguishes thermochemical (energy is accumulated as heat) and electrochemical accumulators (energy is accumulated as electrical energy sometimes supplemented with some heat).

Both natural organic (coal, oil products, natural gas, *etc*.) and synthetic fuels (organic and inorganic) can serve as chemical accumulators. A special place among the compounds used as heat accumulators in thermochemical accumulators belongs to melts and alloys of naturally abundant compounds, such as metals, oxides, hydroxides, salts, *etc*. Simulation of the thermodynamics and thermochemistry of reactions involving these compounds facilitates essentially the selection of the HAM and the calculation of parameters of chemical accumulators.

The state-of-the-art in this field was considered in Ref. 8. Accumulation can be based on three main reaction types involving melts of inorganic compounds: (1) synthesis of complex coordination compounds,[23–25] inclusion compounds [26] and ammonia complexes,[27, 28] hydration of alkaline-earth metal oxides (CaO, MgO);[29, 30] (2) decomposition of carbonates,[31] sulfates,[32] alkaline-earth metal hydroxides, ammonium hydrogensulfate (NH_4HSO_4),[33] metal hydrides;[34] (3) exchange decomposition in full conversion points in mutual multi-component systems formed by ionic melts of inorganic compounds (hydroxides, salts).[4] Of interest are chemical reactions that involve ionic compounds [35] capable of reversible accumulation (Table 7).

The following scheme of exchange reactions in mutual multicomponent systems serves as the basis of heat accumulation:

$$n\mathrm{AX} + m\mathrm{BY} + \ldots = c\mathrm{AY} + d\mathrm{BX} + \ldots + Q ,$$

where AX, BY, AY, and BX are ionic compounds; n, m, c, d are the stoichiometric factors in the exchange reaction; Q is the heat effect of the reaction.

This type of processes is also used for the synthesis of diverse compounds. For instance, exchange decomposition occurring to the full conversion point of ternary mutual system Na,Ca/F,Cl is, on the one hand, the most efficient method to obtain calcium fluoride; on the other hand, this is a process that can be used in thermochemical accumulators (Q = 519.72 kJ mol^{-1}).[36]

It is recommended to use a powder mixture of equivalent quantities of calcium chloride and sodium fluoride for reversible accumulation.[37] The thermochemical equation of the reaction is

$$CaCl_2 + 2NaF = CaF_2 + 2NaCl - 101.28\ \mathrm{kJ\ mol^{-1}}.$$

The reaction starts at 490 °C. The mixture can be heated to a maximum temperature of 600 °C.

If the specific heat effect of the exchange reaction is within $30 \leqslant Q < 250$ kJ kg^{-1}, accumulation of thermal energy is an efficient side process to save energy in chemical technology. If $Q > 250$ kJ kg^{-1}, the reaction is applicable as a working process in thermochemical accumulators.

The major problem in the development of chemical heat accumulators is the choice of chemical reactions that meet the following requirements:[3] the heat effects of the reaction should be

Table 7. Thermodynamic characteristics of some exchange decomposition reactions in ternary mutual systems.[35]

Reaction	M.p. /K (see[a])	$-\Delta H$ /kJ mol^{-1}		$-\Delta G$ /kJ mol^{-1}	
		ΔH°_{298}	ΔH_T	ΔG°_{298}	ΔG_T
$2\,NaOH + CaCl_2 = 2\,NaCl + Ca(OH)_2$	320	162.5	175.6	163.4	157.9
$2\,NaOH + CaSO_4 = Na_2SO_4 + Ca(OH)_2$	320	83.5	138.6	89.9	76.4
$Na_2CO_3 + CaCl_2 = 2\,NaCl + CaCO_3$	782	104.6	108.8	100.8	89.5
$Na_2CO_3 + Ca(NO_3)_2 = 2\,NaNO_3 + CaCO_3$	310	74.3	64.3	73.1	67.6
$Na_2SO_4 + CaCl_2 = 2\,NaCl + CaSO_4$	782	77.3	76.4	73.5	62.2
$Na_2SO_4 + Ca(NO_3)_2 = 2\,NaNO_3 + CaSO_4$	310	47.0	40.3	45.8	45.7
$Na_2S + CaCl_2 = 2\,NaCl + CaS$	782	138.6	141.5	136.5	124.7
$Na_2S + CaSO_4 = Na_2SO_4 + CaS$	890	61.3	65.1	62.6	59.6
$2\,(KOH + NaCl = KCl + NaOH)$	320	53.3	55.9	43.7	31.1

[a] The melting point of the lowest-melting reaction component.

no less than *ca.* 250 kJ kg^{-1} or *ca.* 1800 kJ litre^{-1} if gaseous products are taken into account; the volume density of the accumulated energy should be as high as possible at a minimum possible volume of the reaction products.

4. Comparative analysis of the properties of heat-accumulating materials

The prospects of the development of heat accumulators in which accumulation and liberation of energy occur due to the heat-accumulating properties of melts of inorganic compounds are estimated using the following HAM parameters: specific volume, heat capacity, heat and phase transition temperature (in chemical reactions, in solid and liquid phases).

The heat-capacity heat accumulators are less thermally efficient in comparison with phase-transfer and thermochemical ones, because the considerable 'heat storage capacities' needed despite the HAM temperature increase in them requires a minimum quantity of thermal energy consumed.[1] However, heat-capacity heat accumulators are characterised by low cost and simplicity and hence they have found wide use.

The accumulators with the use of the heat effects of reversible phase transitions are characterised by high energy density, small HAM mass and virtually constant operating temperature; the temperature difference of the heat-carrier transferring heat to the consumer and the heat source charging the accumulator is determined only by the required heat transfer intensity. In heat-capacity accumulators, in most cases this difference also depends on the change in the working medium temperature.

The drawback of the isothermal phase-transfer accumulators is that one has to use a different working medium with a specific phase transition (melting) temperature for each required temperature. In practice, phase-transfer heat accumulation is partially combined with accumulation of physical heat, *i.e.* with heat-capacity accumulation. These are called hybrid accumulators; they are most popular for high-temperature short-term accumulation.[20]

The thermochemical heat accumulators ensure the compactness of the accumulator for long-term heat storage and the absence of losses, as well as the possibility of accumulation at ambient temperature without recourse to thermal insulation. However, the limited number of cheap chemical compounds that meet the requirements for HAM is the main obstacle for the development of such accumulators.[38]

Comparative analysis shows that phase-transition HAM accumulate an order of magnitude more heat than materials that do not undergo phase transitions. This stems from the fact that the phase transition enthalpies of many compounds are much higher than the heat-capacity effect, particularly upon accumulation of medium- and low-potential thermal energy where the operating temperature range is not very wide. The evaporating and sublimating HAM accumulate 3 – 5 times more heat than the melting ones, while the HAM in thermochemical accumulators accumulate an order of magnitude more than the evaporating ones.[18]

The basic obstacles preventing the wide use of heat accumulators include insufficient development of problems regarding good thermal insulation from the environment, the absence of well-developed models for the calculation of heat and mass transfer in heterogeneous systems and for increasing the efficiency of electric power reproduction and accumulator power rating. In view of this, studies of the thermal, thermodynamic and technological characteristics of the available HAM as well as development of novel power-intensive materials with a wide operating temperature range are required. Solution of the above problems would ensure the effectiveness, high performance and low cost of energy accumulation. The hybrid (phase-transition and thermochemical) heat accumulators with melts of inorganic compounds as the HAM can prove to be the most promising for the development of durable heat-accumulating systems. The increase in the efficiency of power system can amount from 15% – 25% (with heat-capacity accumulators) to 80% – 85% (with thermochemical accumulators); in these cases, the cost of the heat accumulator is about 5% of the total power system cost.[39]

For each power system, the choice of particular methods for the thermal energy accumulation is determined by both local conditions and the results of actual technical and economic calculations.

III. Criteria for the estimation of the heat-accumulating properties of melts

When choosing the accumulator type, one has to consider such factors as the methods for the supply and removal of energy, the amount of the stored energy, the operating temperature levels, the storage period, the heat transfer intensity, the investment and working costs, and the requirements for operational reliability and safety.

In the design of a heat accumulator, the prime thing is the search for a HAM the properties of which affect the majority of the above-mentioned factors. The choice of the material is primarily determined by the operating temperature level and the amount of the thermal energy to be accumulated. The basic requirements for the melts which can be used as the HAM are as follows: an acceptable melting point determining the accumulator operating temperature; high values of such specific quantities as the heat effect (which eventually determines the volume of the material used, and hence, the accumulator compactness and cost), the heat capacity, the thermal conductivity, the density; low viscosity in liquid phase and low thermal expansion coefficient; stability of the physicochemical parameters in the operating temperature range, *i.e.* the absence of chemical transformations; stability of the thermal and thermodynamic characteristics of the HAM; low vapour density; abundance in nature; low cost.[2, 17]

There are also a number of operational requirements for melts, such as operating safety (the absence of explosion hazard or the presence of gaseous products easy to detect, environmental safety, the absence of hazardous pollution), easy heat absorption and liberation (the absence of supercooling and segregation), stability of physicochemical properties in multiple duty cycles, low corrosivity toward structural materials.

The performance of accumulators employing melts of inorganic compounds as the phase-transition HAM much depends on the extent of their supercooling (below the phase transition temperature) and on whether phase stratification occurs. In order that the heat of phase transition are used more completely, it is necessary to ensure minimum overcooling when the HAM crystallises.[1] This means that liberation of the accumulated energy occurs at a lower temperature than the HAM melting point; as a result, the accumulator may fail to operate at this temperature. Therefore, one of the major requirements for phase-transition HAM is that they should have an equilibrium crystallisation point where the fluid phase is transformed into solid one, avoiding a metastable supercooled state. This requires creating conditions where crystallisation occurs quickly, for example, by using an additive that accelerates this process.[40] Supercooling in the crystallisation is a minimum if the difference between the HAM melting points and the heat source temperature is 5–10 °C. This temperature range makes it possible to reduce thermal losses and the extent of supercooling of the melt; on the other hand, it is sufficient to provide good heat transfer when withdrawing heat from the HAM. If the supercooling of the melt is 5–10 °C, heat dissipation virtually stops, hence increasing the crystallisation rate is of importance.

Of anhydrous inorganic compounds that can be utilised for heat accumulation, only certain chlorides and nitrates (*e.g.*, calcium chloride and nitrate) and eutectic compositions containing more than 40 mass % of these compounds crystallise with supercooling. Borax, sodium silicate, and strontium and barium fluorides and chlorides can be used as the crystallisation stabilisers.

Segregation decreases the heat exchange between the solid and liquid phases, which necessitates continuous stirring of the HAM during crystallisation.[17]

When designing heat-accumulating systems, a comprehensive approach is required, including the development of a procedure for numerical solution of multi-parameter heat exchange problems with the use of thermodynamic analysis methods, theoretical and experimental simulation for optimisation and studies of the thermal and thermodynamic properties of HAM and operating parameters of the accumulators.

The final stage of studies involves the development of methods for optimisation of the design of heat-accumulating systems as regards the thermal and economic efficiencies and environmental safety.

IV. Principles for the development of heat-accumulating materials based on multi-component systems

Development of promising HAM calls for search for specific compounds or eutectic compositions that combine the above-mentioned properties in the optimum way. The search for such compounds is a complex problem, as certain properties can be combined in a material, while others cannot. Therefore, preliminary estimation of the thermal characteristics of the known HAM and the selection of physicochemical systems which can serve as a basis for creating new materials should be carried out with regard to the most important thermal accumulation parameters, such as temperature, specific enthalpy (heat capacity) and density.

Pure anhydrous inorganic compounds and their eutectic mixtures are promising as the HAM.[23] Unlike crystal hydrates, eutectic mixtures undergo melting and crystallisation at constant temperature, irrespective of the number of components. The search for eutectic compositions is carried out with the use of reference data bases on the physicochemical properties of compounds and the fusibility diagrams. The starting components of eutectics include metals, alkali and alkaline-earth metal oxides, hydroxides, nitrites, nitrates, halides, carbonates, sulfates and phosphates, which belong to traditional HAM, as well as transition metal compounds.

At present, the choice of compositions that meet the requirements for the HAM is limited, especially from the viewpoint of the accumulated energy cost. Therefore, directed development of HAM and study of their properties and technological characteristics are topics of current interest.[41]

Novel materials can be created using the results of studies of the phase diagrams and composition–property diagrams for various physicochemical systems as their theoretical base. The trend of an increase in the information output with minimisation of experiment is characteristic of modern research in the field of multi-component systems. This is achieved by using: (1) experiment planning with the use of modern rapid methods;[42] (2) computer simulations with modern solid modelling methods;[42–50] (3) development of fast methods and measuring instruments for studying the composition–property diagrams that require the use of automatic recording systems, systems for data collection and processing and those for controlling the experiment.[51,52] The development of methods and measuring instruments that enable the study of a set of properties in one experiment improves not only the information output but also the quality of the experimental data, since the results of measuring the different properties refer to the same sample in the same state.[53,54]

The above ways of optimisation in the study of the composition–property diagrams can be used independently of each other, but combining them is the most efficient. This is taken into account in the development of algorithms for computer programs required for the simulation and automation of the physicochemical analysis of multi-component systems.[55–57]

Algorithmisation and programming imply the wide use of modern methods for the calculation, prediction and analysis, both for preliminary estimation of the physicochemical properties and composition–property diagrams and for subsequent processing of experimental data with the use of computer programs. Then the confirming experiments performed on the basis of complex methodology for the study of multi-component systems are minimised.[40]

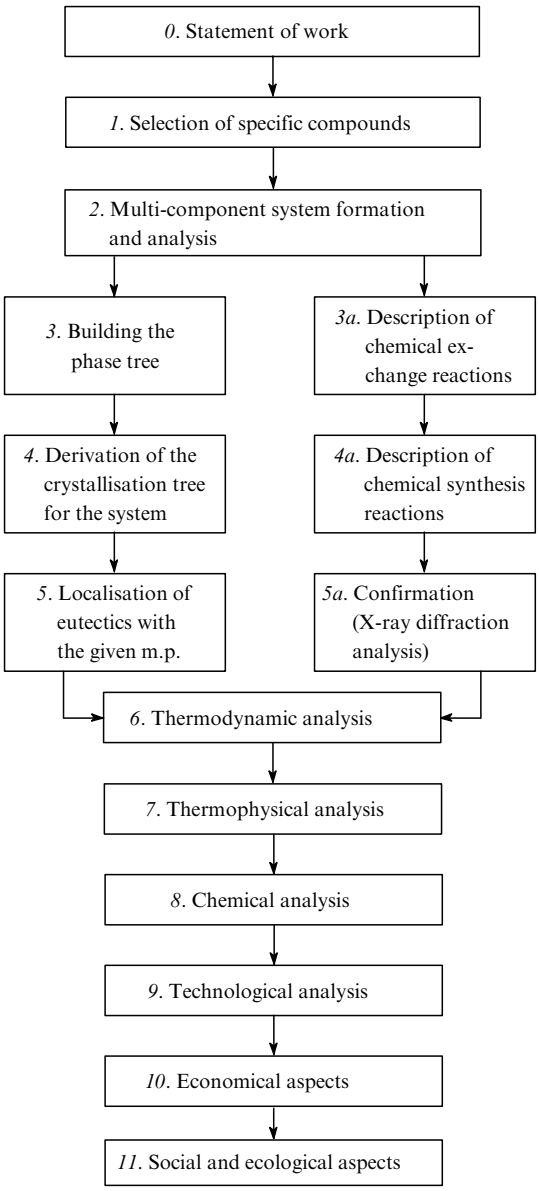
This approach allows one to establish the logical sequence of steps (from the choice of the starting components to the development of recommendations on the design of heat accumulators), to reduce the laboriousness of experimental studies, and to carry out directed, efficient and cost-effective choice of systems with predetermined properties applicable as multi-purpose HAM.

A five-level algorithm has been suggested (Scheme 1) as a methodological basis for HAM development from melts [2] consisting of: zero level, statement of work (stage *0*); first level, data analysis (stages *1* and *2*); mathematical analysis level (stages *3* and *3a*); experimental and theoretical level (stages *4–9*); analytical level (stages *10* and *11*).

The results of studies are presented graphically as the composition–property and property–property fusibility diagrams and in tabulated form.

The three basic rules should be observed in studies with the use of the algorithm suggested: (1) first, theoretical analysis as thorough as possible should be performed in each of the eleven stages; (2) a computer is used for work optimisation; (3) justified choice of compositions for subsequent studies is made in each level.

Scheme 1



V. Conclusion

Power plants used in various branches of industry are expensive, hence the increase in their efficiencies is a problem of vital importance. This problem can partially be solved by using accumulated energy. Presently, directed development and perfection of both heat accumulators and power-intensive working materials for them are under way.

The development of HAM implies not only the estimation of their chemical (corrosion activity), thermal (heat and mass transfer) properties and environmental safety but also the search for the optimum heat accumulator design with the use of simulation methods, calculation of its technical and cost efficiency and selection of structural materials.[22–35]

The basic directions of chemical research on cost-effective HAM based on melts and their efficient operations include development of new and perfection of the existing methods of energy transformation and storage, search for new materials with controlled properties capable of serving as structural materials, heat accumulators and heat-carriers of heat accumulators, development of computerised methods for the simulation of the thermodynamics of heat and mass transfer in accumulators of particular design, optimisation of research and development efforts with the use of computers.

Depending on the required energy storage time period, buffer (15–60 min), short-term (up to 2–3 days) and long-term (week, month, season) accumulation types are distinguished. Accumulation of this duration is used in production of energy during 'peak hours' (hydroelectric, nuclear power plants), during cloudy hours (solar power plants), for supply of heat to stand-alone consumers and so on. It cannot be ruled out that development of power-intense heat-accumulating systems using direct chemical transformation methods will result in considerable progress in heat and energy supply.

In order to select energetically and economically advantageous HAM, one has to know their thermal characteristics. Since an experimental study on the complex of properties that is required for estimating the heat-accumulating ability of a melt is commonly a complex task (in particular, reference equipment operated by skilled personnel and long measurements are necessary), it is very important to have methods for the prediction of the heat-accumulating properties of melts based on incomplete or indirect data.

An important place in obtaining the required information on the properties of HAM belongs to approximate calculation methods and prediction with the use of the system approach for discovering the relationship between the thermal properties (reaction heats) and the nature of the components.

The most efficient methods of HAM research are the calculation-experimental ones which combine theoretical calculations with experimental studies. In particular, the HAM properties can be determined with the use of the experimentally studied phase diagrams of multi-component systems. It is this methodological approach that is implied by algorithm considered above (see Scheme 1).

References

1. G Beckmann, P V Gilli *Thermal Energy Storage* (Translated into Russian; Moscow: Mir, 1987)
2. A M Gasanaliev, B Yu Gamataeva *Metodologicheskie Osnovy Teplovogo Akkumulirovaniya s Ispol'zovaniem Rasplavov, S.-Peterburg, 1999* (Methodological Foundation of Thermal Storage with the Use of Melts, St. Petersburg, 1999); article deposited at the VINITI 1969-V (Moscow, 1999)
3. L A Reznitskii *Zh. Neorg. Khim.* **43** 1288 (1998) [a]
4. R K Rokhas, Candidate Thesis in Technical Sciences, Moscow Energy Institute, Moscow, 1993
5. A M Magomedov *Netraditsionnye Istochniki Energii* (Non-Traditional Sources of Energy) (Makhachkala: Yupiter, 1996)
6. *Teplofizicheskie Svoistva Teploakkumuliruyushchikh Materialov. Kristallogidraty* (Thermal Properties of Heat-Storage Materials. Crystal Hydrates) (Moscow: Institute of High-Temperature of Academy of Sciences of the USSR, Scientific Information Centre on Thermal Properties of Pure Substances, 1990)
7. M A Dibirov, in *Fiziko-Khimicheskii Analiz Mnogokomponentnykh Sistem (Tez. Dokl. Vseros. Konf.)* [Physicochemical Analysis of Multi-Component Systems (Abstracts of Reports of All-Russian Conference)] (Makhachkala: Dagestan State Pedagogical University, 1997) p. 19
8. B Yu Gamataeva, Candidate Thesis in Chemical Sciences, Dagestan State Pedagogical University, Makhachkala, 1995
9. V I Dauknis, A I Kuklyauskas, in *Akkumulirovanie Energii i Puti, Povysheniya Effektivnosti Raboty Elektrostantsii i Ekonomii Energii. Akkumuliruyushchie Energoustanovki, Teplovye Protsessy i Teploakkumuliruyushchie Materialy* (Energy Storage and Ways of Increasing the Efficiency of Operation of Power Plants and Economy of Energy. Stored Power Plants, Thermal Processes and Heat-Storage Materials) (Moscow: Khimiya, 1986) Pt. 2, p. 182
10. C Etievant, J L Peube,A Vialarou, J P Allard, J Bounin, F Pharabod, in *Solar Electricity (Proceedings of International Conference), Toulouse, 1976*
11. L J Radosevich, C E Wyman *J. Sol. Energy Eng.* **105** 111 (1983)
12. R H Carthy, W L Conger *Int. J. Hydrogen Energy* **5** 7 (1980)

13. R J Copeland, R E West, F Kreith, in *Proc. Intersoc. Energy Convers. Eng. Conf. 19th* Vol. 2 (Golden: Sol. Energy Res. Inst., 1984) p. 1171; *Chem. Abstr.* **101** 233 183 (1984)
14. R B Akhmedov *Energiya* **4** 22 (1985)
15. T B Voronina, V I Gudkov, O V Shimanskii, in *Akkumulirovanie Energii i Puti, Povysheniya Effektivnosti Raboty Elektrostantsii i Ekonomii Energii. Akkumuliruyushchie Energoustanovki, Teplovye Protsessy i Teploakkumuliruyushchie Materialy* (Energy Storage and Ways of Increasing the Efficiency of Operation of Power Plants and Economy of Energy. Stored Power Plants, Thermal Processes and Heat-Storage Materials) (Moscow: Khimiya, 1986) Pt. 2, p. 151
16. N A Vasina, E S Gryzlova, S G Shaposhnikova *Teploakkumuliruyushchie Svoistva Mnogokomponentnykh Solevykh Sistem* (Heat-Storage Properties of Multi-Component Salt Systems) (Moscow: Khimiya, 1984)
17. N M Martynova, E K Rodionova, T A Tishura, L I Cherneeva, in *Akkumulirovanie Energii i Puti, Povysheniya Effektivnosti Raboty Elektrostantsii i Ekonomii Energii. Akkumuliruyushchie Energoustanovki, Teplovye Protsessy i Teploakkumuliruyushchie Materialy* (Energy Storage and Ways of Increasing the Efficiency of Operation of Power Plants and Economy of Energy. Stored Power Plants, Thermal Processes and Heat-Storage Materials) (Moscow: Khimiya, 1986) Pt. 2, p. 167
18. Y Takahashi , M Kamimoto , Y Abe, K Sakamoto *Thermochim. Acta*, **123** 233 (1988)
19. V N Danilin, P E Shurai I T Sryvalin *Tr. Krasnodar. Politekh. In-ta* 65 (1969)
20. M A Dibirov, A M Gasanaliev, B Yu Gamataeva, M M Magomedov, in *Fiziko-Khimicheskii Analiz Mnogokomponentnykh Sistem (Tez. Dokl. Vseros. Konf.)* [Physicochemical Analysis of Multi-Component Systems (Abstracts of Reports of All-Russian Conference)] (Makhachkala: Dagestan State Pedagogical University, 1997) p. 19
21. A S Trunin *Kompleksnaya Metodologiya Issledovaniya Mnogokomponentnykh Sistem* (Complex Methodology of Investigation of Multi-Component Systems) (Samara: Samara State Technological University, 1997)
22. I K Garkushin, A S Trunin, A I Sechnoi, M A Dibirov, N N Verdiev *Eksperimental'noe Opredelenie Oblastei Sostavov na Diagrammakh Sostoyaniya pri Poiske Teploakkumuliruyushchikh Sostavov, Moskva, 1988* (Experimental Determination of Regions of Composition on State Diagram in Search for Heat-Storage Compositions, Moscow, 1988); article deposited at the VINITI 1029-V (1988)
23. L A Reznitskii, S E Filippova *Usp. Khim.* **62**. 474 (1993) [*Russ. Chem. Rev.* **62** 437 (1993)]
24. L A Reznitskii *Zh. Fiz. Khim.* **67** 2379 (1993) [b]
25. L A Reznitskii, S E Filippova *Vest. Mosk. Univ., Ser. 2, Khim.* **38** 132 (1997) [c]
26. P Touzain, J Michel, P Blum *Synth. Met.* **8** 313 (1983)
27. J Villermaux *Recherche* **14** 1346 (1983)
28. I Fujiwara, Y Nakashima, T Goro *Energy Convers. Manage.* **21** 157 (1981)
29. M Tmar, C Bernard, M Ducaroir *Sol. Energy* **26** 529 (1981)
30. G Flamant, D Herlandez, C Bonet, J P Traverse *Sol. Energy* **24** 385 (1980)
31. O Abu Leiych *Ber. Kernforshungsanlage Juelich, Juel-1847* 157 (1983); *Chem. Abstr.* **99** 91 062 (1983)
32. N El Ghandour, R Valls, M Ducaroir *Bull. Soc. Chim. Fr.* (5-6, Pt. 1) 133 (1983)
33. S M Ranade, M Ch Lee, H W Prengle Jr *Sol. Energy* **37** 375 (1986)
34. H Buchner *Energy Storage, Trans. Int. Assem., 1st* (Oxford: Pergamon Press, 1980) p. 327; *Chem. Abstr.* **94** 194 868 (1981)
35. A P Protsyuk *O Nekotorykh Zakonomernostyakh Napravlenii Reaktsii v Solevykh i Okisno-Solevykh Sistemakh pri Nagrevanii, Moskva, 1977* (Some Regularities of Reaction Routes in Salt and Oxide Salt Systems at Heating, Moscow, 1977); article deposited at the VINITI 2492-77 (1977)
36. V N Danilin *Fizicheskaya Khimiya Teplovykh Akkumulyatorov* (Physical Chemistry of Heat Accumulators) (Krasnodar: Krasnodar Polytechnic Institute, 1981)
37. I K Garkushin, B V Anipchenko, in *Ftoridnye Materialy (Tez. Dokl. X Simp. po Khimii Ftoridov)* [Fluoride Materials (Abstracts of Reports of the Xth Symposium on Chemistry of Fluorides)] (Moscow: Moscow State University, 1998) p. 36
38. V V Ershevich, V Ya Peisakhovich, A N Kir'yanova *Elektr. Stantsii* **4** 37 (1985)
39. A G Chukaev, A M Kuks *Izv. Vyssh. Uchebn. Zaved., Mashinostroenie* (1) 67 (1984)
40. A M Gasanaliev, Doctoral Thesis in Chemical Sciences, Institute of Chemistry, Academy of Sciences, Uzb. SSR, Tashkent, 1989
41. Zh A Koshkarov, A M Gasanaliev, M V Mokhosoev *Zh. Neorg. Khim.* **35** 1254 (1990) [a]
42. A M Gasanaliev, K D Kurbanmagomedov, A S Trunin, G E Shter *Modelirovanie Khimicheskikh Reaktsii v Mnogokomponentnykh Sistemakh na Personal'noi EVM, Cherkassy, 1988* (Modelling of Chemical Reactions in Multi-Component Systems on a Personal Computer, Cherkassy, 1988); article deposited at the ONIITEKhIM 01154-88 (1988)
43. Zh A Koshkarov, M V Mokhosoev , A M Gasanaliev *Dokl. Akad. Nauk SSSR* **308** 889 (1989) [d]
44. A M Gasanaliev, Zh A Koshkarov *Dokl. Akad. Nauk SSSR* **311** 892 (1990) [d]
45. V I Posypaiko, S A Tarasevich, E A Alekseeva *Prognozirovanie Khimicheskikh Vzaimodeistvii v Sistemakh iz Mnogikh Komponentov* (Prediction of Chemical Interaction in Multi-Component Systems) (Moscow: Nauka, 1984)
46. Ya L Kharif *Metody Teoreticheskogo Analiza i Rascheta Diagramm Sostoyaniya* (Methods of Theoretical Analysis and Calculation of State Diagrams) (Moscow: Moscow Chemical Technological Institute, 1986)
47. P L Kapitsa *Eksperiment, Teoriya, Praktika* (Experiment, Theory and Practice) (Moscow: Nauka, 1987)
48. A G Morachevskii, I B Sladkov *Fiziko-Khimicheskie Svoistva Molekulyarnykh Neorganicheskikh Soedinenii* (Physicochemical Properties of Molecular Inorganic Compounds) (St Petersburg: Khimiya, 1996)
49. Zh A Koshkarov, S M Lok'yaeva, in *Fiziko-Khimicheskii Analiz Mnogokomponentnykh Sistem (Tez. Dokl. Vseros. Konf.)* [Physicochemical Analysis of Multi-Component Systems (Abstracts of Reports of All-Russian Conference)] (Makhachkala: Dagestan State Pedagogical University, 1997) p. 21
50. A M Gasanaliev, K D Kurbanmagomedov, in *Vseros. Konf. po Termicheskomu Analizu i Kalorimetrii (Tez. Dokl.)* [All-Russian Conference on Thermal Analysis and Calorimetry (Abstracts of Reports)] (Kazan': Kazan' State University, 1996) p. 53
51. V P Meshalkin *Ekspertnye Sistemy v Khimicheskoi Tekhnologii. Osnovy Teorii, Opyt Razrabotki i Primenenie* (Expert Systems in Chemical Technology. Foundations of Theory, Experience in the Development and Application) (Moscow: Khimiya, 1995)
52. A M Gasanaliev, K D Kurbanmagomedov, in *Fiziko-Khimicheskii Analiz Mnogokomponentnykh Sistem (Tez. Dokl. Vseros. Konf.)* [Physicochemical Analysis of Multi-Component Systems (Abstracts of Reports of All-Russian Conference)] (Makhachkala: Dagestan State Pedagogical University, 1997) p. 68
53. V P Egunov *Vvedenie v Termicheskii Analiz* (Introduction in Thermal Analysis) (Samara: Samara State Technology University, 1996)
54. T G Lupeiko, S P Vydrenok, in *Vseros. Konf. po Termicheskomu Analizu i Kalorimetrii (Tez. Dokl.)* [All-Russian Conference on Thermal Analysis and Calorimetry (Abstracts of Reports)] (Kazan': Kazan' State University, 1996) p. 46
55. V I Lutsyk, Doctoral Thesis in Chemical Sciences, Irkutsk State University, Irkutsk, 1997
56. A E Rozhanskaya, Candidate Thesis in Chemical Sciences, Samara State Technology University, Samara, 1995
57. A M Gasanaliev, N N Verdiev, A S Trunin, G E Shter, Yu I Sultanov *Algoritm Opisaniya Khimizma v Mnogokomponentnykh Vzaimnykh Solevykh Sistemakh s Razvitym Kompleksoobrazovaniem, Cherkassy, 1988* (Algorithm of Description of Chemism in Multi-Component Mutual Salt Systems with Extensive Complex Formation, Cherkassy, 1988); article deposited at the ONIITEKhIM 834-KhP88 (1988)

[a] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[b] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[c] — *Moscow Univ. Bull. (Engl. Transl.)*
[d] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*