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Sh.K.Amerkhanova, R.M.Shlyapov, A.S.Uali

Ye.A.Buketov Karaganda State University
(E-mail: amerkhanova_sh@mail.ru)

Evaluation of interrelation of electrochemical properties and thermal storage capacity of the melt of crystal hydrates of inorganic substances on the basis of $Na_2S_2O_3{\cdot}5H_2O$

Research of conductivity of concentrated salt solutions are of great interest in connection with the structural changes in electrolytes. The heat storage properties of the mixture of sodium thiosulfate pentahydrate and sodium tellurate dihydrate were calculated. Firstly the coefficients of temperature dependence of heat capacity of sodium tellurate were calculated. Melting temperature of mixtures at ratios (50:1, 25:1, 10:1), which are equal to 349 K, 307 K, 326 K, were determined. The specific melting heat of mixtures was calculated. It was shown, that heat of fusion of mixture $Na_2S_2O_3{\cdot}5H_2O$ — $Na_2TeO_4{\cdot}2H_2O$ (10:1) is maximal and equals to 238.5 $kJ{\cdot}kg^{-1}$. An analysis of the temperature dependence of the electrical conductivity was carried out. It showed the presence of high activity and mobility of tellurate-ions. It was shown that crystallization process is changed from quasi-equilibrium to the «explosive» at low temperatures ranging from T=318 K.

Key words: heat storage properties, sodium thiosulfate pentahydrate, electrical conductivity, specific melting heat, kinetic characteristics, sodium tellurate.

Researches on the conductivity of concentrated salt solutions became the subject of great interest in connection with the structural changes in electrolytes. It is known that concentrated and saturated solutions of electrolytes refer to the third type of liquids organization with the lack of water structure according to the classification formed by the results of measurement of the dielectric permittivity [1].

At the same time a number of theories were suggested for the mechanism of electrical conductivity: hydrodynamic, where ions are presented in the form of balls moving in a viscous medium [2], theory of Debye-Hückel-Onsager in which the movement of ions is caused by electrostatic forces under the influence of an electric field, and braking is caused due to the formation and disappearance of the ion atmosphere [3], in Eyring's theory ion is hopping from one equilibrium position to another [4], Ivashkevich theory, where the electrical conductivity is determined by the equation of communication between the concentration of ions and the medium viscosity. On the other hand, inorganic compounds containing some crystallized water show the ability to store heat, as a result of *solid – liquid* phase transition, which is then released into the environment during crystallization. In most cases the heat storage based on phase transition is understood as the accumulation of fusion heat.

The heat content (internal energy) of a liquid or solid phase is often used as an addition to the heat of the phase transition. It increases the capacity of the battery, but makes it impossible to take advantage of heating at constant temperature [5].

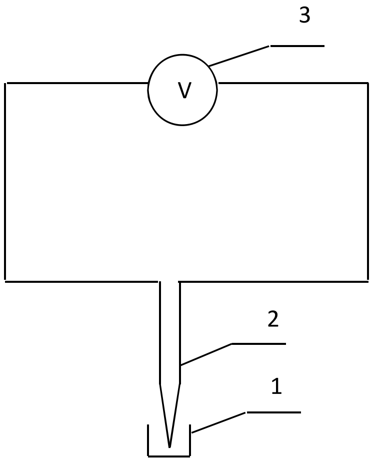
It is known from the literature sources that the enthalpy of melting of sodium thiosulfate crystalline is higher than the one of anhydrous salt, i.e. in the reverse process of crystallization into the environment more heat will be generated, therefore the substance may have been selected as a material having some heat storage properties, and on the basis of their costs, the storage capacity and reliability of heat during repeated thermal cycling [6]. Furthermore, the effect of adding the sodium sulfate decahydrate on the process of crystallization of sodium thiosulfate pentahydrate is also marked [7].

In connection with this the evaluation of the electrochemical properties of heat storage materials based on mixtures of crystal hydrates $Na_2S_2O_3.5H_2O$ — $Na_2TeO_4{\cdot}2H_2O$ is the task of the theoretical and practical plan which gives the opportunity to perform the modification of the base crystal hydrates. The aim is to determine the heat storage capacity and electrochemical properties of mixtures of crystal hydrates $Na_2S_2O_3{\cdot}5H_2O$ — $Na_2TeO_4{\cdot}2H_2O$.

Sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) chemically pure, telluric acidic sodium dihydrate ($Na_2TeO_4{\cdot}2H_2O$) analytical grade have been used as the starting materials for heat storage materials.

Inorganic mixtures are obtained by mixing sodium thiosulfate pentahydrate and sodium tellurate dihydrate in various proportions by weight of (50:1, 25:1, 10:1), weight 5 g sodium thiosulfate, from which the weight of sodium tellurate dihydrate additives is calculated.

After mixing, the mixtures were heated up to a temperature at which solids are dissolved in the crystallized water. Method for determining the specific heat of fusion [8]. The samples were heated by convection. Temperature control was performed by a thermometer, which was immersed in the sample at a visual and thermal analysis and thermocouple (chromel-alumel (298–1073 K)) during measuring thermal emf. The thermo-emf. was recorded using a voltmeter brand EV2265–1 with divisions of 0.1 mV (Fig. 1).



1 — Sample; 2 — Thermocouple chromel-alumel; 3 — Voltmeter

Figure 1. Apparatus for measuring thermal emf.

A method for determining the heat release rate is as follows. After the material in the crucible has melted and reached the temperature higher than the melting temperature, the furnace is turned off, and at regular intervals millivoltmeter readings are fixed.

Conductivity studies were carried out in a thermostated vessel with the capacity of 50 ml. The electrical conductivity was measured in mark OK-102 conductivity meter. The working electrode was made of a pair of platinum plates of 1 cm^2. To recalculate the values of specific conductivity from Sim·cm^{-1} to Ohm·cm^{-1} the instrument constant has been determined by measuring the χ 0.001 M KCl at standard temperature [9].

According to the graph of the thermocouple (chromel-alumel) capacity dependence on the temperature the graph of temperature dependence on time is made, an exemplary form of which is shown in Figure 2.

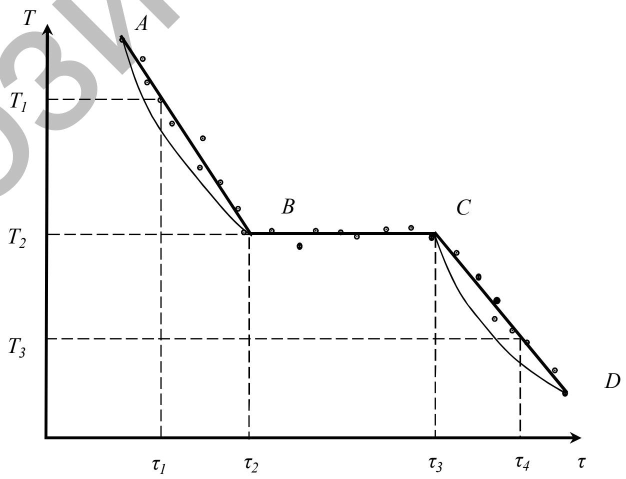


Figure 2. Thermocouple temperature dependence on time

On the graph AB area corresponds to a cooling of the molten metal before the start of crystallization, BC area — to metal crystallization, and CD area — to solid metal cooling (T_2 is the melting point). Replace the resulting graph with the idealized one by connecting points A and B, C and D with straight lines. The amount of heat delivered per time unit by average liquid metal with the crucible during cooling:

$$\frac{Q_1}{\tau}=\frac{(MC_1+mC_2)\cdot(T_1-T_2)}{\tau_2-\tau_1}, \qquad (1)$$

where M — melting pot; m — mass of metal; C_1 — specific heat capacity of the melting pot (C_1 =1090 J× ×kg^{-1}·K^{-1}); C_2 — the specific heat of the test liquid metal (for tin — C_2 = 266 J·kg^{-1}·K^{-1}).

When cooling solid metal per unit of time the amount of heat is given:

$$\frac{Q_2}{\tau}=\frac{(MC_1+mC_2^{'})\cdot(T_2-T_3)}{\tau_4-\tau_3}, \qquad (2)$$

where $C_2^{'}$ — the specific heat capacity of the investigated solid metal ($C_2^{'}$ = 230 J·kg^{-1}·K^{-1}).

Since during crystallization temperature of the metal does not change, the rate of heat transfer during this period can not be measured directly. The rate of heat transfer, all other things being equal, depends on the temperature difference between the heated body and the environment, so the average speed of cooling before and after crystallization process will be approximately equal to the rate of heat transfer during solidification.

Using this, you can write:

$$\frac{Q_0}{\Delta\tau}=\frac{1}{2}\left(\frac{Q_1}{\Delta\tau}+\frac{Q_2}{\Delta\tau}\right). \qquad (3)$$

Using the equations (1), (2) and (3), we have found:

$$\frac{Q_0}{\Delta\tau}=\frac{1}{2}\left((MC_1+mC_2)\frac{T_1-T_2}{\tau_2-\tau_1}+(MC_1+mC_2^{'})\frac{T_2-T_3}{\tau_4-\tau_3}\right). \qquad (4)$$

In the graph the times τ_1 and τ_2 are chosen so that:

$$\tau_2-\tau_1=\tau_3-\tau_2;$$
$$\tau_4-\tau_3=\tau_3-\tau_2. \qquad (5)$$

We have placed the equation (4) in the expression (2). Taking into account (5), we have obtained:

$$\lambda=\frac{1}{2m}\Big((MC_1+mC_2)\big(T_1-T_2\big)+(MC_1+mC_2^{'})\big(T_2-T_3\big)\Big). \qquad (6)$$

To calculate the kinetic parameters the Arrhenius equation has been used, in which the rate constant was replaced with the specific conductivity. Activation energy of the electrical conductivity has been calculated graphically according to the equation:

$$\lg\chi=\lg A_0-E_a/2.303RT. \qquad (7)$$

Calculation of kinetic parameters was performed according to the formulas [4]

$$\Delta H^{\#}=E_a-2RT. \qquad (8)$$

Then we have found the value of $\Delta S^{\#}$ according to the equation:

$$\Delta S^{\#}=R\,[2{,}303\lg A_0-2{,}303\lg(\frac{kT}{h})-1]; \qquad (9)$$

$$\Delta G^{\#}=\Delta H^{\#}-T\Delta S^{\#}. \qquad (10)$$

In this scientific work heat-storage properties have been calculated for example, inorganic salts, sodium thiosulfate and modified salts of elements of (VI) group. It has been shown that sodium thiosulfate is a solvent with respect to the additive, since the melting point of the second component is significantly higher. In this regard, the melt mixture is a solution, the heat capacity of which is different from the heat capacity of the solvent (basic salt). Also for the first time coefficients of the temperature dependence of heat capacity for sodium tellurate were determined by Landia's method [10] in the range 298 K – T_m (Table 1).

Table 1

The coefficients of the temperature dependence of sodium tellurate heat capacity

Compound	C_p, cal·mol^{-1}·K^{-1}			298 – T$_m$
	a	b·10^3	c·10^5	
Na_2TeO_4	36.04	4.84	0.37	298–1009 K

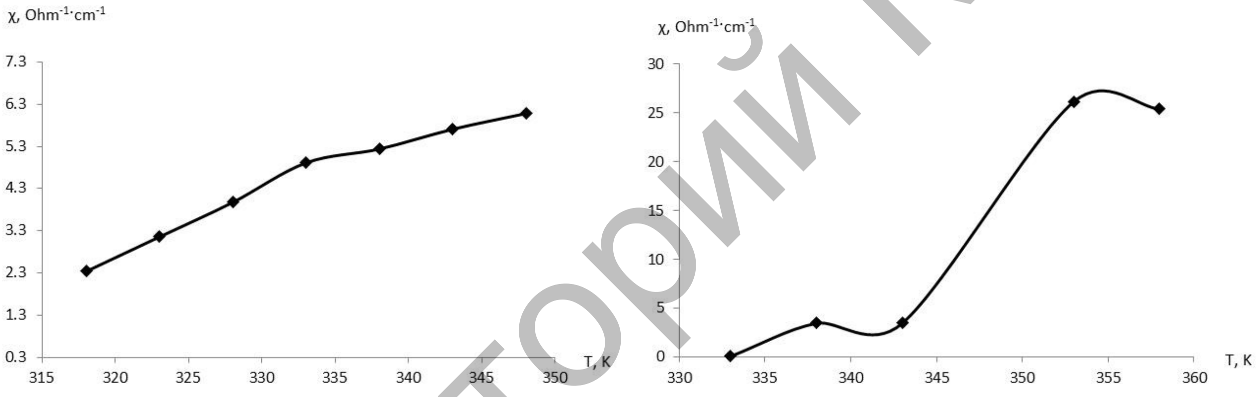
The indicated coefficients of temperature dependence of sodium tellurate heat capacity (Table 1) can be used for the calculation of heat capacity of the mixture of sodium thiosulfate pentahydrate — sodium tellurate dihydrate. Next, on the base of the kinetic curves of cooling, the melting temperature of mixture, and the fusion heat of the mixtures of sodium thiosulfate pentahydrate with sodium tellurate have been calculated (Table 2).

Table 2

The thermodynamic characteristics of melting mixtures of sodium thiosulfate pentahydrate with sodium tellurate dihydrate

Mixture	T_m, K	C_p(solid), $J \cdot kg^{-1} \cdot K^{-1}$	C_p(melt), $J \cdot kg^{-1} \cdot K^{-1}$	λ, kJ·kg
$Na_2S_2O_3 \cdot 5H_2O$-$Na_2TeO_4 \cdot 2H_2O$ (10:1)	326	885.3	92.25	269.3
$Na_2S_2O_3 \cdot 5H_2O$-$Na_2TeO_4 \cdot 2H_2O$ (25:1)	307	883.2	46.4	60.3
$Na_2S_2O_3 \cdot 5H_2O$-$Na_2TeO_4 \cdot 2H_2O$ (50:1)	349	885.1	30.0	32.9
$Na_2S_2O_3 \cdot 5H_2O$	321	1451.6	12.9	94

Effect of temperature on the conductivity of mixtures of sodium thiosulfate pentahydrate — sodium tellurate dihydrate in a weight ratio (25:1; 50:1) has been investigated. However, high consumption of sodium tellurate dihydrate restricts the use of the mixture as a heat storage material, so it is necessary to evaluate the electrochemical properties providing maximum heat output. The results determining the electrical conductivity for mixtures of sodium thiosulfate pentahydrate – sodium tellurate dihydrate are shown in Figure 3.



$Na_2S_2O_3 \cdot 5H_2O$ – $Na_2TeO_4 \cdot 2H_2O$ (25:1)

$Na_2S_2O_3 \cdot 5H_2O$ – $Na_2TeO_4 \cdot 2H_2O$ (50:1)

Figure 3. The temperature dependence of the electrical conductivity for the mixture $Na_2S_2O_3 \cdot 5H_2O$ – $Na_2TeO_4 \cdot 2H_2O$

The data in the table show that adding sodium tellurate dihydrate leads to lower specific heat of fusion. The lower mixture melting point compared to a basic salt of sodium thiosulfate pentahydrate is associated with the coordination of tellurate — ions with water molecules.

On the other hand the addition of sodium tellurate dihydrate increases not only the melting point but also the specific heat of melting, due to the formation of the eutectic mixture while removing water. The melting point and fusion heat of these mixtures have been identified, it is shown that the addition of sodium tellurate dihydrate in 10: 1 ratio increases the specific heat of melting to 238.7 $kJ \cdot kg^{-1}$. Thus the mixture of the composition of 90.9 % of sodium thiosulfate, 9.1 % sodium tellurate dihydrate can be used as heat-storage material.

Data given in Figure 3 make it possible to judge about the presence of high activity and mobility of ions due to the absence or reduction of solvents. These conductivity data are in accord with those for the pure molten nitrate salts, alkali metal chlorides, but they are characterized by high melting points.

Figure 4 shows that the change in conductivity and temperature is exponential, which is due to an increase in the ionic contribution to the overall conductivity of the melt. Furthermore, energy characteristics of the melt mixture conduction have been defined, since the fundamental period contributing to the process of heat transfer is cooling (Table 3).

Table 3

Changes in the kinetic characteristics of the electrical conductivity of melts $Na_2S_2O_3 \cdot 5H_2O - Na_2TeO_4 \cdot 2H_2O$ (C_1:C_2)

C_1:C_2	T_1–T_2 (heating), K	E_a, kJ·mol^{-1}	lg$A$	T_2–T_1 (cooling), K	E_a, kJ·mol^{-1}	lg$A$	$\Delta S^{\#}$, J·mol^{-1} K^{-1}	$\Delta H^{\#}$, kJ·mol^{-1}	$\Delta G^{\#}$, kJ·mol^{-1}
25:1	318–333	43.30	7.49	343–323	27.11	4.83	60.99	21.41	0.48
							61.01	21.49	0.86
							61.02	21.57	1.25
							61.04	21.65	1.63
							61.05	21.74	2.02
	333–348	14.00	2.97	323–303	48.93	6.64	95.75	43.64	13.19
							95.76	43.72	13.74
							95.78	43.81	14.30
							95.79	43.89	14.86
50:1	323–343	403.49	62.25	353–323	16.06	3.94	43.96	10.19	–5.33
							43.97	10.27	–5.03
							43.99	10.35	–4.73
							44.01	10.44	–4.43
							44.02	10.52	–4.14
	343–348	457.10	70.14				44.04	10.60	–3.84
							44.05	10.69	–3.54
	348–358	–31.50	–3.21	318– 298	40.84	7.85	118.96	35.56	–2.27
							118.97	35.64	–1.60
							118.99	35.72	–0.93
							119.00	35.81	–0.25
							119.02	35.89	0.42

In this case, the activation energy is the minimum kinetic energy required so that an ion could perform a translational motion and for the appearance of electric current. Therefore, heating up to 333 K allows to decrease the activation energy as the melts almost do not contain any crystallized impurities and the process of transferring the atomic charge is flowing in the diffusion mode. On the other hand the activation energy is the sum of the true activation energy, which active ions have and the excess energy needed to perform a jump from one quasi-equilibrium position with the oscillation frequency of the ion ν_1 to the state with the oscillation frequency ν_2 during τ [11].

Since this mixture consists of sodium salts, the common ion is sodium ion, and the center of the quasi-equilibrium state are anions (thiosulfate ion and tellurate ion). Low enough positive pre-exponential factor suggests low values of the relaxation times of ions with respect to the equilibrium position, which are increased when heated and are reduced upon cooling. I.e. in the cooling process there is the destruction of crystal lattice by ions having a high kinetic energy, which they transmit in a collision with the formed lattice sites. Hence the collision of an ion with a lattice site can be viewed as a reaction between a mobile cation and static anion the product of which is the activated complex, i.e., this bimolecular reaction [12]. Therefore, all the kinetic parameters can be applied to the cooling process which relate to bimolecular reactions in condensed matter, namely the activation enthalpy and entropy of activation. The data on the Gibbs energy of activation show that at low temperatures ranging from T = 318 K, the crystallization process proceeds from a quasi-equilibrium and «explosive,» which promotes rearrangement of the crystal lattice, the release of excessive kinetic and potential energy into the environment.

Similar calculations were made for 1:50 ratio, it is shown that the heating process takes place in the diffusion mode, and high values of pre-exponential factor enable us to judge about fairly high mobility of ions. At the same time cooling is accompanied by a decrease in the activation energy and pre-exponential factor, and the crystal lattice is stabilized. This fact is confirmed by the values of Gibbs energy of activation. From the temperature of 318 K cooling is followed by a slight increase in the activation entropy, change of the structure, but it does not lead to a significant change in the amount of heat released into the environment. Therefore, one of the main criteria for the selection of heat-retaining materials is the increment of the Gibbs energy of activation when the temperature changes from T to T_0.

Thus, the value of the electrical conductivity of molten mixture of sodium thiosulfate crystalline — sodium tellurate dihydrate of different composition have been determined. Coefficients of the temperature dependence of the heat capacity of sodium tellurate dihydrate have been calculated. It is shown that the addition of sodium tellurate dihydrate in an amount of 2 % by the weight of sodium thiosulfate pentahydrate increases the heat output. The values of activation entropy, the Gibbs energy of activation, which indicate the electrochemical nature of the transition from a quasi-equilibrium to «explosive» which facilitates the rearrangement of the crystal lattice, the release of excessive kinetic and potential energy into the environment.

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Ш.К.Амерханова, Р.М.Шляпов, А.С.Уәли

$Na_2S_2O_3 \cdot 5H_2O$ негізінде бейорганикалық заттар кристаллогидраттары қоспаларының электрохимиялық қасиеттері және жылужинағыш қабілеттілігі арасындағы өзара байланысты бағалау

Концентрацияланған тұз ерітінділерін зерттеу өткізгіштік электролиттерде құрылымдық өзгерістерге байланысты үлкен қызығушылық тудыруда. Мұнда натрий тиосульфатының пентагидраты және натрий теллуратының дигидрат қоспасының жылу сақтау қасиеттері есептелген. Алғаш рет Ландийдың әдісі мен натрий теллуратының жылу жинағыш қасиетіне температуралық тәуелділік коэффициенттері анықталды. (50:1, 25:1, 10:1) қатынастағы 349 K, 307 K, 326 K тең болатын қоспалардың балқу температуралары есептелді. Қоспалардың ерекше жылулық балқу температуралары белгіленді. Қоспалардың $Na_2S_2O_3 \cdot 5H_2O$ – $Na_2TeO_4 \cdot 2H_2O$ жасырын жылулық балқуы (10:1) максималды және 238,5 кДж/кг тең екені көрсетілді. Электр өткізгіштігінің температура тәуелділігіне талдау жүргізілді. Ол жоғары белсенділігі мен теллурат-ионының қозғалғыштығына негізделген. Кристалдану процесі T = 318 K төмен температурада квазитепе-теңдіктен жарылғышқа дейін өзгереді деп көрсетілген.

Ш.К.Амерханова, Р.М.Шляпов, А.С.Уали

Оценка взаимосвязи электрохимических свойств и теплоаккумулирующей способности расплавов кристаллогидратов неорганических веществ на основе $Na_2S_2O_3 \cdot 5H_2O$

Исследования электропроводности концентрированных растворов солей представляют большой интерес в связи со структурными изменениями в электролитах. Были рассчитаны теплоаккумулирующие свойства смеси пентагидрата тиосульфата натрия и дигидрата теллурата натрия. Впервые методом Ландия были найдены коэффициенты температурной зависимости теплоемкости для теллурата натрия. Определены температуры плавления смесей при соотношениях (50:1, 25:1, 10:1), которые равны 349 K, 307 K, 326 K. Была рассчитана удельная теплота плавления смесей. Показано, что скрытая теплота плавления смеси $Na_2S_2O_3 \cdot 5H_2O$ – $Na_2TeO_4 \cdot 2H_2O$ (10:1) максимальна и равна 238,5 кДж/кг. Проведен анализ температурной зависимости электропроводности. Это обусловлено высокой активностью и подвижностью теллурат-ионов. Показано, что процесс кристаллизации изменяется от квазиравновесного к взрывному при низких температурах от T = 318 K.