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# THERMOCHEMISTRY OF SELENATES OF SOME s-d-ELEMENTS

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**Abstract**

*The possibility of obtaining double selenates of cadmium' with the s-elements is showed. Isobaric heat capacity of the compounds was studied by the method of dynamic calorimetry in the range of 298.15 - 673 K. Abnormal jumps on the curves of the temperature dependence of the heat capacity of the compounds show phase transitions of the type II, due to the valuable physical properties of selenates. The results are of interest to inorganic materials engineering and for information banks on the thermodynamic constants of inorganic substances.*

**Key words**: *cadmium selenates, calorimetry, heat capacity, phase transitions of type II, the thermodynamic functions.*

The widespread introduction of electronic technology in various sectors of industry, science and inorganic chemistry confronts the task of finding new compounds with promising physical properties, such as semiconductor, ferroelectric, radioluminescent, piezoelectric, and pyroelectric and superconducting. In this regard, the study of a system consisting of oxides of alkali (alkaline earth), d-metals and selenium are important for inorganic materials engineering and forming them into new selenates can have both original and unique properties. Some semiconductor, ferroelectric, magnetic materials after special heat treatment transformed into a thermodynamically metastable state. That is, changing the original properties and parameters of these materials. These processes occur by desire for structure, formed under certain conditions, to move material in a thermodynamically stable state. To monitor changes in the temperature dependence of heat capacity of solid crystalline substances and the energy change in the exchange of cations, methods of calorimetric measurements of thermodynamic properties of crystalline compounds (Reznitskii 1981, Reznitskii 1978) are used. Thermodynamic and thermochemical properties of compounds are of interest for modeling the process of obtaining materials with desired properties.

At the Department of Inorganic and Technical Chemistry, Karaganda State University named after E.A.Buketov for several years a systematic study to find and develop the scientific foundations of the directed synthesis of new oxycompounds of selenium and tellurium with unique physical properties are carried out (Dyuseekeva 2008, Rustembekov 2009). In this paper we present the results of synthesis and calorimetric study of the specific heatscapacity, new selenates of some s-, d-elements. Studied double selenates were synthesized with a liquid-phase method. Alkali (alkaline earth) metals and d-elements (grade "chemically pure") and 68% probability selenic acid grade "chemically pure" in stoichiometric ratios were the initial components for synthesis. The formation of the equilibrium composition of the compounds and personality were controlled by X-ray and chemical analyzes (Dyuseekeva, Rustembekov 2007, Rustembekov, Dyuseekeva 2007, Rustembekov, Dyuseekeva 2008).

The heat capacity of the synthesized compounds was investigated in the temperature range 298.15 – 673 K on a series calorimeter ИТ-400. Experiments were carried out under monotonic

heating of the sample with an average speed of about 0.1 K per second for temperature differences between the sample and the medium 3 – 30 K. At such temperature changes the time lag of temperature on heat meters are measured. It should be noted that the value is determined by the temperature difference of heat flow. Measurement scheme of the device provides a measurement of temperature at fixed points in 25°C. Application of the device is limited to the volume specific heat $C_p = 10 \cdot 10^6$ J/K·m$^3$. Heat meters was the heat flux transducer, which provided flux measurements, leveled the surface temperature of the sample made it possible to carry out the grading directly in the thermal unit for accounting errors. Liquid nitrogen served as a refrigerant. The duration of the measurements over the entire temperature range with the processing of experimental data was less than 2.5 hours. Maximum permissible error of the instrument to passport data is ±10% (Technical description and operating instructions for the ИТ-400 1986). Calibration of the instrument was carried out on the basis of determining the thermal conductivity of heat meter $K_\tau$ (Platunov, Burawoy, Kurepin, Petrov 1986). To do this, several experiments were conducted with a copper sample and the empty ampoule. Thermal conductivity of the heat meter is determined by the formula:

$$\hat{E}_{\dot{O}} = \tilde{N}_{Cu} / (\bar{\tau}_{TCu} - \bar{\tau}^0), \quad (1)$$

where $C_{Cu}$ – total heat capacity of the copper sample, J/(mol·K);

$\bar{\tau}_{TCu}$ – the average time lag for heat meters in experiments with a copper sample, s;

$\bar{\tau}_T$ – the average delay time in the experiments with the empty ampoule, c.

Total heat capacity of the copper sample was calculated by the formula:

$$C_{Cu} = C_{s.h.} \cdot m_{Cu}, \quad (2)$$

where $C_{s.h.}$ – valued the specific heat capacity of copper, J/(mol·K);

$m_{Cu}$ – mass of the copper sample, kg.

The value of the specific heat capacity of the substance was calculated using the formula:

$$C_{s.h.} = K_т/m_0(\tau_т - \tau^0), \quad (3)$$

where $K_т$ – thermal conductivity of heat-flow meter;

$m_0$ – mass of the substance;

$\tau_т$ – the time lag of temperature on heat meters, s;

$\tau^0$ – the time lag of temperature on heat meters in the experiments with the empty ampoule, s.

Using the value of specific heat capacity, taking into account the molar mass value of molar heat capacity was calculated by the formula:

$$C_i = C_{s.h.} \cdot M, \quad (4)$$

where $C_{s.h.}$ – the specific heat capacity of a substance

M – molar mass of the substance.

At each temperature five parallel experiments were carried out, whose results were averaged and processed by methods of mathematical statistics.

At each temperature for the average values of specific heat capacity evaluated the standard deviation ( $\overline{\delta}$ ) of (Spiridonov, Lopatkin 1970):

$$\delta = \sqrt{\frac{\sum_{i=1}^{n}(C_i - \overline{C})^2}{n-1}}, \quad (5)$$

where n – is a number of experiments;

$C_i$ – is a measured value of specific heat capacity;

$\overline{C}$ – the arithmetic mean of the measured values of specific heatcapacity.

For the average values of molar heat capacity of (Dyuseekeva 2008, Rustembekov 2009) the random component of error was calculated:

$$\overset{0}{\Delta} = \frac{\delta \cdot t_p}{\overline{C}} \cdot 100, \quad (6)$$

where $\overset{0}{\Delta}$ – the random component of error in %;

$t_p$ – student's coefficient (for n = 5, $t_p$ = 2.75 with p = 0.95 confidence interval).

Systematic component of error was calculated by the formula:

$$\Delta_c = \frac{\overline{C} - C_0}{C_0} \cdot 100, \quad (7)$$

where $\Delta_c$ – the systematic component of error in %;

$C_0$ – the value of the heat capacity of the exemplary steps taken at the temperature at which heat is determined.

Determination of the maximum permissible error was carried out as follows:

$$\Delta = \Delta_{\tilde{n}} + \overset{o}{\Delta}. \quad (8)$$

In our studies we did not take into account the systematic errors and errors in temperature measurement, since they were negligible in comparison with the random component. According to the theory of errors, if random error is much larger bias error of the instrument scale, the accuracy of the instrument will be determined by random error (Dyuseekeva 2008, Rustembekov 2009), and random error is used instead of the limiting error.

The work was verified with the calorimeter to determine the specific heat of α-$Al_2O_3$. The resulting value (298.15) of α-$Al_2O_3$, equal to 76.0 J/(mol·K), agrees satisfactorily with its recommended value of 79.0 J/(mol·K). These data show not only the reliability of the results, but a negligible value of systematic error, such as the measurement error of temperature.

To determine the accuracy of the coefficients in the equations of the temperature dependences of heat capacity, values of the mean random errors for the considered temperature range were used.

Due to the fact that the technical characteristics of the device do not allow you to directly calculate the standard entropy of the selenates of the experimental data, it was determined by ion increments (Kumok 1987). Based on known relations with the experimental data on heat capacity and the, calculated values of entropy, temperature dependences of the functions $\tilde{N}_p^0(T)$ : f(T) were calculated. Calculations were carried out using the following formulas (Dyuseekeva 2008, Rustembekov 2009):

$$H^o(T) - H^o(298.15) = \int_{298.15}^{T} C_p^o dT , \quad (9)$$

$$S^o(T) = S^o(298.15) + \int_{298.15}^{T} \frac{\tilde{N}_p}{T} dT , \quad (10)$$

$$\hat{O}^{\tilde{o}\tilde{o}}(\grave{O}) = S^o(T) - \frac{H^o(T) - H^o(298.15)}{T} . \quad (11)$$

The errors in the temperature dependence of the enthalpy evaluated with an average error of the random component of the specific heat and the temperature dependence of the error and average error was calculated by summing the experimental determination of heat capacity and entropy calculation accuracy. The results of the calculations are defined within the accuracy of the calculation.

With the instrument of ИТ-400 in the range of 298.15 – 673 K the specific heats of compounds $Na_2Cd(SeO_4)_2$, $MgCd(SeO_4)_2$, $CaCd(SeO_4)_2$ were investigated, and then the molar heat capacity were calculated from the experimental values. The results are presented in Table 1.

Table 1. **The experimental values of heats $Na_2Cd(SeO_4)_2$, $MgCd(SeO_4)_2$, $CaCd(SeO_4)_2$**

| T, K | $C_p \pm \overline{\delta}$, J/(g·K) | $\tilde{N}_{\partial}^0 \pm \overset{o}{\Delta}$, J/(mol·K) |
|---|---|---|
| 1 | 2 | 3 |
| $Na_2Cd(SeO_4)_2$ | | |
| 298.15 | 0.3684±0.0130 | 164±16 |
| 323 | 0.5143±0.0081 | 229±10 |
| 348 | 0.6317±0.0069 | 281±9 |
| 373 | 0.7472±0.0084 | 332±10 |
| 398 | 0.8070±0.0102 | 359±13 |
| 423 | 0.8654±0.0033 | 385±4 |
| 448 | 0.7921±0.0085 | 352±10 |
| 473 | 0.7199±0.0076 | 320±9 |
| 498 | 0.6752±0.0076 | 300±9 |

| | | |
|---|---|---|
| 523 | 0.6155±0.0077 | 273±10 |
| 548 | 0.6055±0.0077 | 291±4 |
| 573 | 0.5627±0.0078 | 307±4 |
| 598 | 0.5428±0.0077 | 330±4 |
| 623 | 0.5865±0.0099 | 345±4 |
| 648 | 0.6415±0.0089 | 355±4 |
| 673 | 0.6668±0.0041 | 363±5 |
| | $MgCd(SeO_4)_2$ | |
| 298.15 | 0.5468±0.0168 | 231±20 |
| 323 | 0.6106±0.0066 | 258±8 |
| 348 | 0.7303±0.0069 | 309±8 |
| 373 | 0.5983±0.0058 | 253±7 |
| 398 | 0.7375±0.0056 | 312±7 |
| 423 | 0.8694±0.0060 | 367±7 |
| 448 | 0.9541±0.0069 | 403±8 |
| 473 | 1.0159±0.0076 | 429±9 |
| 498 | 0.9088±0.0062 | 384±7 |
| 523 | 0.8382±0.0063 | 354±7 |
| 548 | 0.7688±0.0063 | 325±7 |
| 573 | 0.7262±0.0101 | 307±12 |
| 598 | 0.9026±0.0077 | 381±9 |
| 623 | 0.9961±0.0066 | 421±8 |
| 648 | 1.1039±0.0073 | 467±9 |
| 673 | 1.1870±0.0074 | 502±9 |
| | $CaCd(SeO_4)_2$ | |
| 298.15 | 0.4896±0.0189 | 219±16 |
| 323 | 0.5122±0.0099 | 224±12 |
| 348 | 0.5750±0.0094 | 253±12 |
| 373 | 0.7665±0.0092 | 81±3 |
| 398 | 0.3851±0.0121 | 169±15 |
| 423 | 0.6047±0.0079 | 265±10 |
| 448 | 0.7346±0.0103 | 321±13 |
| 473 | 0.7741±0.0098 | 339±12 |
| 498 | 0.6733±0.0081 | 295±10 |
| 523 | 0.5865±0.0122 | 258±15 |

| | | |
|---|---|---|
| 548 | 0.4929±0.0072 | 217±9 |
| 1 | 2 | 3 |
| 573 | 0.3961±0.0083 | 173±10 |
| 598 | 0.4657±0.0053 | 205±6 |
| 623 | 0.4886±0.0100 | 215±12 |
| 648 | 0.5228±0.0154 | 229±19 |
| 673 | 0.5473±00132 | 241±16 |

From the results shown in Table 1, it is shown that over the entire temperature range of measurement error in the heats are stacked outside the error of the instrument of ИТ-400.

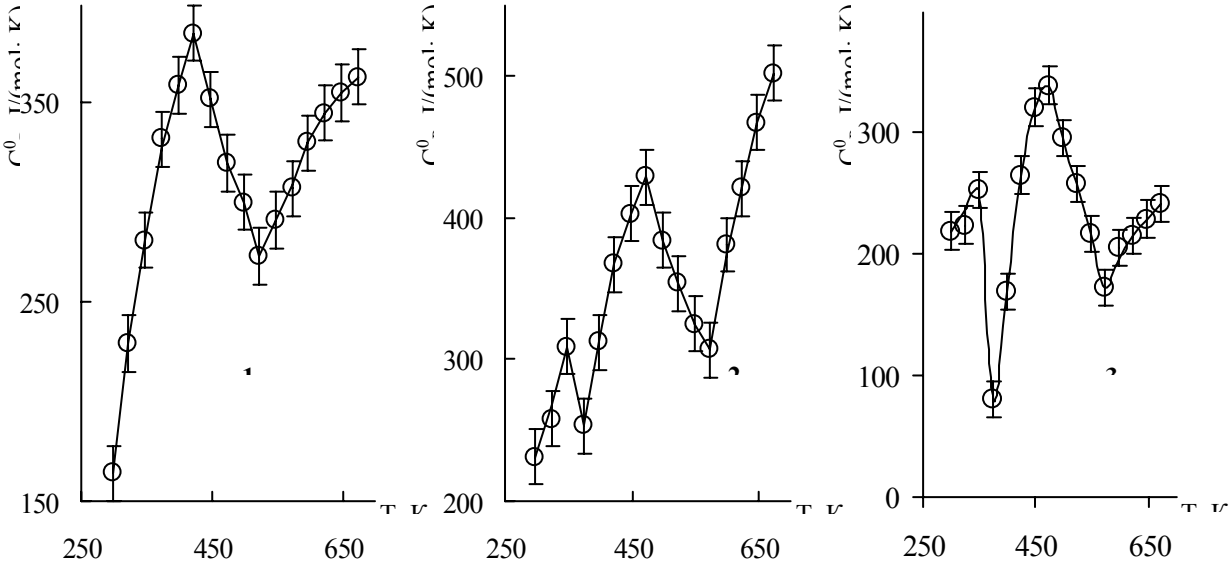
In the study of the specific heat $Na_2Cd(SeO_4)_2$, $MgCd(SeO_4)_2$, $CaCd(SeO_4)_2$ on the temperature at 423 K for $Na_2Cd(SeO_4)_2$ at 348 and 473 K in the two other compounds detected abnormal sharp discontinuities associated, probably, with phase transitions of type II. These transitions may be associated with cationredistribution, with changes in the coefficients of thermal expansion and changes of the magnetic moments of the synthesized compounds. Due to the presence of phase transitions, the dependence of $\tilde{N}^{o}_{p}(T): f(T)$ a few compounds was described by equations whose coefficients are given in Table 2.

Table 2. **The equations of the temperature dependence of specific heat $Na_2Cd(SeO_4)_2$, $MgCd(SeO_4)_2$, $CaCd(SeO_4)_2$ in the range of 298.15 – 673 K**

| Compound | The coefficients of the equation $\tilde{N}^{o}_{\delta} = a + bT + cT^{-2}$, J/(mol·K) | | | ΔT, K |
|---|---|---|---|---|
| | a | b·10$^{-3}$ | c·10$^{5}$ | |
| $Na_2Cd(SeO_4)_2$ | 603.3±22.3 | -2.3±0.1 | 389.8±14.4 | 298 – 423 |
| | 854.1±24.4 | -1110.2±31.8 | - | 423 – 598 |
| | 746.3±21.3 | -274.7±7.9 | -900.4±25.8 | 598 – 673 |
| $MgCd(SeO_4)_2$ | -231.1±6.2 | 1551.0±41.7 | - | 298 – 348 |
| | 1085.1±29.2 | -2231.2±60.0 | - | 348 – 373 |
| | 1495.7±40.2 | -1217.5±32.8 | -1097.3±29.5 | 373 – 473 |
| | -520.6±14.0 | 718.9±19.3 | 1364.6±36.7 | 473 – 573 |
| | 1792.6±48.2 | -830.6±22.3 | -3315.4±89.2 | 573 – 673 |
| $CaCd(SeO_4)_2$ | 14.6±0.7 | 685.4±32.5 | - | 298 – 348 |
| | 2641.9±125.2 | 6864.4±325.4 | - | 348 – 373 |
| | 3033.6±143.8 | -3561.3±168.8 | -2259.2±107.1 | 373 – 473 |
| | 1125.7±53.4 | -1662.5±78.8 | - | 473 – 573 |
| | 1113.2±52.8 | -741.8±35.2 | -1691.0 ±80.2 | 573 – 673 |

Graphical representation of heat depending on the temperature of the compounds is shown in the figure below.

Thus, in the range of 298.15 – 673 K specific heat capacityof double selenates were experimentally determined, equations of the temperature dependence of heat capacity are derived (Platunov, Burawoy, Kurepin, Petrov 1986, Spiridonov, Lopatkin 1970). In the study of the temperature dependence of the heat capacity of the synthesized compounds identified in the curves of $\tilde{N}_p^o(T)$ : f(T) λ-shape effects are probably related to the phase transition II-type: $Na_2Cd(SeO_4)_2$ (423 K), $MgCd(SeO_4)_2$ (348, 473 K), $CaCd(SeO_4)_2$ (348, 473 K).




Notation of curves: 1 – $Na_2Cd(SeO_4)_2$, 2 – $MgCd(SeO_4)_2$, 3 – $CaCd(SeO_4)_2$.

Fig. – Double selenates of cadmium of the heat capacity on the temperature

On the basis of known relationships, and values of the coefficients of the equations of the temperature dependence of the heat capacity of the compounds thermodynamic functions, $S^o(T)$, $H^o(T) - H^o(298.15)$ and $\hat{O}^{\delta\delta}(\grave{O})$ were calculated. The results are shown in Table 3. For all values of heat capacity and enthalpy over the entire range of temperatures average random error components were evaluated, and for the values of entropy and the reduced thermodynamic potential in the evaluation of error the accuracy of the calculation of the entropy was included (± 3%).

Table 3. **Thermodynamic functions $Na_2Cd(SeO_4)_2$, $MgCd(SeO_4)_2$, $CaCd(SeO_4)_2$ in the range 298.15 – 673 K**

| T, K | $\tilde{N}_{\delta}^{o}(T) \pm \Delta^{o}$, J/(mol·K) | $S^{o}(T) \pm \Delta^{o}$, J/(mol·K) | $H^{o}(T) - H^{o}(298.15) \pm \Delta^{o}$, J/mol | $\hat{O}^{\delta\delta}(T) \pm \Delta^{o}$, J/(mol·K) |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| $Na_2Cd(SeO_4)_2$ | | | | |
| 298.15 | 164±5 | 290±17 | - | 290±17 |
| 300 | 170±5 | 291±17 | 333±10 | 290±17 |
| 325 | 234±7 | 307±18 | 5404±155 | 290±17 |
| 350 | 284±8 | 326±19 | 11900±340 | 292±17 |
| 375 | 325±9 | 347±20 | 19538±559 | 295±17 |
| 400 | 359±10 | 369±22 | 28102±804 | 299±18 |
| 425 | 387±11 | 392±23 | 37429±1070 | 304±18 |
| 450 | 355±10 | 413±24 | 46642±1334 | 309±18 |
| 475 | 327±9 | 431±25 | 55160±1578 | 315±18 |
| 500 | 299±9 | 447±26 | 62985±1801 | 322±19 |
| 525 | 271±8 | 461±27 | 70115±2005 | 328±19 |
| 550 | 298±9 | 474±28 | 77286±2210 | 334±20 |
| 575 | 318±9 | 488±29 | 84963±2430 | 341±20 |
| 600 | 338±10 | 502±29 | 93061±2662 | 347±20 |
| 625 | 350±10 | 516±30 | 101509±2903 | 354±21 |
| 650 | 361±10 | 530±31 | 110248±3153 | 360±21 |
| 675 | 372±11 | 543±32 | 119225±3410 | 367±22 |
| $MgCd(SeO_4)_2$ | | | | |
| 1 | 2 | 3 | 4 | 5 |
| 298.15 | 231±6 | 237±7 | - | 237±13 |
| 300 | 234±6 | 238±14 | 465±13 | 237±13 |
| 325 | 273±7 | 259±15 | 6805±183 | 238±14 |
| 350 | 312±8 | 280±16 | 14114±380 | 240±14 |
| 375 | 248±7 | 299±17 | 21021±565 | 243±14 |
| 400 | 323±9 | 318±18 | 28330±762 | 247±14 |
| 425 | 371±10 | 339±19 | 37030±996 | 252±14 |
| 450 | 406±11 | 362±21 | 46762±1258 | 258±15 |

| | | | | |
|---|---|---|---|---|
| 475 | 431±12 | 384±22 | 57242±1540 | 264±15 |
| 500 | 385±10 | 405±23 | 67352±1812 | 270±15 |
| 525 | 352±9 | 423±24 | 76543±2059 | 277±16 |
| 550 | 326±9 | 439±25 | 85002±2287 | 284±16 |
| 575 | 305±8 | 453±26 | 92883±2499 | 291±17 |
| 600 | 373±10 | 467±27 | 101475±2730 | 298±17 |
| 625 | 425±11 | 484±28 | 111469±2999 | 305±17 |
| 650 | 468±13 | 501±29 | 122645±3299 | 313±18 |
| 675 | 504±14 | 520±30 | 134812±3626 | 320±18 |
| $CaCd(SeO_4)_2$ | | | | |
| 298.15 | 219±10 | 252±8 | - | 252±8 |
| 300 | 220±10 | 254±20 | 439±21 | 252±20 |
| 325 | 237±11 | 272±21 | 6158±292 | 253±20 |
| 350 | 254±12 | 290±22 | 12305±583 | 255±20 |
| 375 | 68±3 | 301±23 | 16143±765 | 258±20 |
| 400 | 197±9 | 311±24 | 19831±940 | 261±20 |
| 425 | 269±13 | 325±25 | 25723±1219 | 264±20 |
| 450 | 315±15 | 342±26 | 33080±1568 | 268±21 |
| 475 | 341±16 | 359±28 | 41321±1958 | 272±21 |
| 500 | 294±14 | 376±29 | 49202±2332 | 277±21 |
| 525 | 253±12 | 389±30 | 56044±2656 | 282±22 |
| 550 | 211±10 | 340±31 | 61847±2932 | 287±22 |
| 575 | 170±8 | 408±32 | 66610±3157 | 292±23 |
| 600 | 198±9 | 416±32 | 71292±3379 | 297±23 |
| 625 | 217±10 | 425±33 | 76490±3626 | 302±23 |
| 650 | 231±11 | 433±34 | 82091±3891 | 307±24 |
| 675 | 241±11 | 442±34 | 88000±4171 | 312±24 |

The values of standard entropies have been evaluated by the Kumokionic entropy increments (Kumok 1987) as follows:

$$S^o(298.15)\,Na_2Cd(SeO_4)_2 = 2S^i(298.15)\,Na^+ + S^i(298.15)\,Cd^{2+} + 2S^i(298.15)\,(SeO_4)^{2-} \quad (12)$$

$$S^o(298.15)\,MgCd(SeO_4)_2 = S^i(298.15)\,Mg^{2+} + S^i(298.15)\,Cd^{2+} + 2S^i(298.15)\,(SeO_4)^{2-} \quad (13)$$

$$S^o(298.15)\,CaCd(SeO_4)_2 = S^i(298.15)\,Ca^{2+} + S^i(298.15)\,Cd^{2+} + 2S^i(298.15)\,(SeO_4)^{2-} \quad (14)$$

Where $S^i(298.15)$ – ion entropy increment of the element.

Thus, by the method of dynamic calorimetry in the range of 298.15 – 673 K isobaric heat capacity of the synthesized double selenates s-elements and cadmium was studied, which are derived on the basis of the equation depending on the temperature of the heat capacity.On the curves of temperature dependences of heat capacity for all compounds detected λ-shaped effects related to the phase transition of type II. The presence of type II phase transition in the heat capacity curve suggests that these compounds may possess unique physical properties.On the basis of experimental data on heat capacity and entropy values calculated for the double selenates temperature dependences of thermodynamic functionswere determined. The research results may be of interest for the direct synthesis of halkogenates with desired properties, for chemical and metallurgical processes involving selenium compounds. In addition, they can serve as baseline data for basic reference and information banks on the thermodynamic constants of inorganic substances.

**REFERENCES**

Dyusekeeva A.T., Rustembekov K.T. The structure of the new dual-cadmium-sodium selenate //Actual problems of mining and metallurgical complex of Kazakhstan: proc. researcher.-practice. conference. (6 – 7 December 2007.). – Karaganda Univ KSTU, 2007. – P. 336 – 339. (Русский)

Dyuseekeva A.T. Synthesis and properties of double selenates, tellurites some d-elements: abstract. ... candidate. chem. science: – Karaganda: Karaganda State University named. E.A. Buketova, 2008. – 19 p. (Русский)

Kumok V.N. Direct and inverse problems of chemical thermodynamics. – Novosibirsk: Nauka, 1987. – P. 108 – 123. (Русский)

Platunov E.S., Burawoy S.E., Kurepin V.V., Petrov G.S. Thermophysical measurements and devices. – L.: Mechanical Engineering, 1986. – 256 p. (Русский)

Reznitskii L.A. Calorimetry solid. – Moscow: MGU, 1981. – 183 p. (Русский)

Reznitskii L.A. The study of metastable states of calorimetric methods //Results of Science and Technology: Chemical thermodynamics and equilibrium. – Moscow: VINITI. Issue 4. – 1978. – 43 p. (Русский)

Rustembekov K.T. Synthesis and properties of inorganic compounds based on chalcogens and their behavior in the hydrochemical processes: abstract. Doctor .... Chem. Science: – Karaganda: Karaganda State University named. E.A. Buketova, 2009. – 32 p. (Русский)

Rustembekov K.T., Dyusekeeva A.T. Synthesis, X-ray and IR spectroscopy $Na_2Cd(SeO_4)_2$ //Bulletin of KSU them. E.A. Buketova. Chemistry Series. – 2007. – №3 (47). – P. 72 – 74. (Русский)

Rustembekov K.T., Dyusekeeva A.T. Synthesis and structure of new double selenates of $Na_2Me^{II}(SeO_4)_2$ ($Me^{II}$ – Zn, Cu) //Complex processing of mineral raw materials: Materials intern. researcher.-practice. conference. devoted. 50th anniversary of their HMI. Zh. Abisheva and the 15th Anniversary of NC KPMS RK (25 – 26 September 2008.). – Karaganda: HMI 2008. – P. 442 – 446. (Русский)

Spiridonov V.P., Lopatkin L.V. Mathematical processing of experimental data. – Moscow: MGU, 1970. – 221 p. (Русский)

Technical description and operating instructions for the ИТ-400. – Aktobe: Aktobe plant "Etalon", 1986. – 48 p. (Русский)