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THERMODYNAMIC FUNCTIONS OF FORMATION OF LITHIUM TITANATES

U.N.Sharifova

*M.Nagiev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**demirtitan2015@gmail.com*

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By the method of electromotive forces measuring concentration chains: $\text{Pt} | \text{Li}_2\text{O} | \text{ZrO}_2 + 10 \text{ wt\% } \text{Y}_2\text{O}_3, \text{ lithium glass. } (\text{Li}_2\text{O})_x(\text{TiO}_2)_{1-x} | \text{Pt}$ in the temperature range $T=1000\text{--}1200\text{K}$ and concentrations $0.35\div 0.95$ mol fraction TiO_2 , the thermodynamic functions of the formation of the compounds Li_4TiO_4 , Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and phases based on $\text{Li}_2\text{TiO}_3\text{:Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$ were determined. With the exception of the compound Li_2TiO_3 , the thermodynamic functions of the formation of lithium titanates are determined for the first time. The thermodynamic functions of formation are calculated for the 1200 K and for the standard state at 298 K. The thermodynamic functions of the formation of lithium titanates are determined from simple substances and from binary compounds Li_2O and TiO_2 . In particular, for the free energy, enthalpy of formation and standard entropy we obtained: $\Delta G_{298}^0(\text{Li}_4\text{TiO}_4)=-2149 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta G_{298}^0(\text{Li}_2\text{TiO}_3)=-1565$; $\Delta G_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12})=-5923$; $\Delta H_{298}^0(\text{Li}_4\text{TiO}_4)=-2286 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{298}^0(\text{Li}_2\text{TiO}_3)=-1662$; $\Delta H_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12})=-6287$; $S_{298}^0(\text{Li}_4\text{TiO}_4)=119.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $S_{298}^0(\text{Li}_2\text{TiO}_3)=84$; $S_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12})=315.7$.

Keywords: lithium titanates, EMF method, free energy, enthalpy, entropy.

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Introduction

Alkali metal titanates are of interest for magneto-optical, ion-conducting and spintronic devices, ion batteries, for creating new highly efficient catalysts and functional nanoparticles [1, 2]. The most intensively studied are lithium titanates, composite nanostructured functional materials based on them to obtain an anode material with a high capacity, stability of the working potential during cycling with optimal electronic and ionic conductivity [3–7].

Lithium titanates

Lithium titanates are formed over the quasi-binary $\text{Li}_2\text{O}\text{--TiO}_2$ cross-section of the $\text{Li}\text{--Ti}\text{--O}$ ternary system [8]. In system $\text{Li}_2\text{O}\text{--TiO}_2$ compounds Li_4TiO_4 , Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_2\text{Ti}_3\text{O}_7$ are formed (Figure 1). The high-temperature form of Li_2TiO_3 forms a wide range of solid solutions between ~44 and 66% mol TiO_2 . The low-temperature form of Li_2TiO_3 forms solid solutions between ~47 and 51% TiO_2 . The spinel phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a upper stability limit at 1018°C , above which it decomposes to form Li_2TiO_3 and $\text{Li}_2\text{Ti}_3\text{O}_7$. $\text{Li}_2\text{Ti}_3\text{O}_7$ has a lower stability limit at $957\pm 20^\circ\text{C}$,

below which it decomposes into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rutile. During this decomposition, the metastable phase of unknown composition forms as an intermediate product $\text{Li}_2\text{Ti}_3\text{O}_7$ with a solubility region between ~74 and 76% TiO_2 . Each of the formed phases is of some interest for practice, in particular as an anode material for lithium-ion batteries (LIB). Graphite is usually used as an anode material, but changes in the structure during operation, rapid loss of power during cycling, and low thermal stability limit its widespread use [9]. Currently, one of the most promising anode materials for LIB is lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Thermodynamic parameters

Thermodynamic information is available for the compound Li_2TiO_3 . The enthalpy of stoichiometric Li_2TiO_3 was measured by drop calorimetry between 388 and 1856 K [8]. The heat capacity of stoichiometric $\beta\text{-Li}_2\text{TiO}_3$ was determined by the laser flash method up to 1000 K [10], by differential scanning calorimetry (DSC) up to 1100 K [11] and on non-stoichiometric material with $\text{Li/Ti}=1.9$ by DSC up to 1000 K [12, 13]. The enthalpy of $\text{Li}_{1.92}\text{Ti}_{1.02}\text{O}_3$ was further measured by

Fig. 1. Phase diagram of the $\text{Li}_2\text{O}-\text{TiO}_2$ system [8].

drop calorimetry between 397 and 1650 K which gives $H^0(T)-H^0(298\text{ K}) = -49181+131.876T+0.011097T^2+2651112T^{-1}\text{ J/mol}$ (298–1410 K) for the monoclinic phase and $H^0(T)-H^0(298\text{ K}) = 49729+50.517T+0.031679T^2-20143786T^{-1}\text{ J/mol}$ (1410–1700 K) for the cubic phase. The heat capacity of the phases was evaluated by differentiation. The value extrapolated to 298 K is $C_p(298\text{ K}) = (108.69) \pm 2.5\text{ J/K mol}$ [14]. The enthalpy of the $\beta \rightarrow \gamma$ transformation and melting of Li_2TiO_3 was evaluated from the enthalpy measurements of the modifications by drop calorimetry resulting in $\Delta_{\text{tr}}H = 11.5\text{ kJ/mol}$ and $\Delta_{\text{m}}H/110\text{ kJ/mol}$ [8]. The enthalpy of transformation of Li_2TiO_3 near its TiO_2 -rich boundary (51.3 mol% TiO_2) resulted from the enthalpies of the modifications at the interpolated transformation temperature in $\Delta_{\text{tr}}H = 8950\text{ J/mol}$ and directly by anisothermal calorimetry in $\Delta_{\text{tr}}H = 9390\text{ J/mol}$. This gives an average value $\Delta_{\text{tr}}H = (92009 \pm 300)\text{ J/mol}$ [14]. The reference book [15] contains the following thermodynamic parameters for the compound Li_2TiO_3 .

The values of the standard isobaric heat capacity, the heat of fusion, and the heat of the phase transition of the monoclinic $\leftrightarrow$ cubic com-

pound Li_2TiO_3 , given in Table 1, differ insignificantly from the data [8, 14].

Table 1. Thermodynamic functions of formation from simple substances and parameters of phase transitions of the compound Li_2TiO_3

Condition	Thermodynamic parameters	
κII , cubic	$\Delta H^\circ_{\text{f}0}$, kJ/mol	<u>-1657.596</u>
κII , cubic	$\Delta H^\circ_{\text{f}298.15}$, kJ/mol	<u>-1668.160 $\pm$ 9.204</u>
κII , cubic	$\Delta G^\circ_{\text{f}298.15}$, kJ/mol	-1577.321
κII , cubic	D_0 , kJ/mol	3184.396 $\pm$ 10.46
κII , cubic	$H^\circ_{298.15} - H^\circ_0$, J/mol	<u>16526.8 $\pm$ 83.68</u>
κII , cubic	$S^\circ_{298.15}$, J/mol.K	<u>91.755 $\pm$ 0.418</u>
κII , cubic	$C^\circ_{p298.15}$, J/mol.K	<u>111.043 $\pm$ 0.041</u>

Transition type	$T^\circ\text{C}$	ΔH , kJ/mol	ΔS , J/mol.K
κI (monoclinic) $\rightarrow$ κII (cubic)	<u>1213 $\pm$ 10</u>	<u>11.506 $\pm$ 0.836</u>	7.740
κII (cubic) $\rightarrow$ L	<u>1547 $\pm$ 20</u>	<u>110.164 $\pm$ 1.255</u>	60.542

However, in the literature, there are no thermodynamic parameters of the compounds Li_4TiO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Previously, the Li_2TiO_3 compound has not been studied by the method of electromotive forces (EMF).

The purpose of this work is to determine the thermodynamic parameters of lithium titanates by the EMF method.

Experiments and discussion of their results

Synthesis and physicochemical analysis

Lithium titanates are obtained by fusing a mixture of lithium carbonate and titanium dioxide in stoichiometric ratios according to the reaction:

For the synthesis, we used lithium carbonate, grade 554-13-2, 99.9% Li_2CO_3 , and titanium dioxide, grade ultrapure 9-2 TU 6-09-01-629-83, 99.98% TiO_2 . The results of the derivatographic analysis of reaction (1) at an equimolar ratio of lithium carbonate and titanium dioxide are shown in Figure 2.

TG and TGA curves in Figure 2 show that starting from about 709°C, the mass of the reactants decreases significantly. This is in agreement with the reference data that Li_2CO_3 decomposes into lithium oxide and carbon dioxide upon melting at 730°C [15]. A slight decrease in temperature is due to the fact that a mixture of Li_2CO_3 and TiO_2 powders is heated. At 1200°C, the weight loss is 17.24%. However, with the complete consumption of lithium carbonate and

titanium dioxide according to reaction (1), the weight loss should be 28.8%. For complete conversion of the starting materials, the mixture of substances was annealed at 1250°C for 5 hours.

From the TA and DTA curves in Figure 2. It also follows that at 153°C, an endothermic process occurs, associated with the dehydration of wet present in the mixture of reactants. The exothermic minimum is associated with the reaction between TiO_2 and Li_2O , obtained by the decomposition of Li_2CO_3 into Li_2O and CO_2 . Thermodynamic calculation of the enthalpy of the reaction $\text{Li}_2\text{O} + \text{TiO}_2 \rightarrow \text{Li}_2\text{TiO}_3$ shows that this reaction is exothermic. At the same time, the reinforcing reaction (1) is endothermic. This explains the endothermic effect following the exothermic effect at 725.6°C.

The results of derivatographic analysis, as well as measurements of electromotive forces (in the next section, EMF data will be presented), are in agreement with the results of the X-ray phase analysis of the authors [9].

From Figure 3 it follows that the reaction of obtaining $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is completed when the reaction products are kept for 5 hours at a temperature of 1080°C.

Fig. 2. Results of derivatographic analysis of reaction (1) at an equimolar ratio $\text{Li}_2\text{CO}_3:\text{TiO}_2 = 1:1$.

Fig. 3. X-ray diffraction patterns of powder mixtures of reaction products (1) at $\text{Li}_2\text{CO}_3:\text{TiO}_2$ 2:5, annealed for 5 h at 680 (1), 778 (2), 870 (3), 980 (4), and 1080 (5) according to [9].

Study lithium titanates by EMF

To determine the thermodynamic parameters of titanium lanthanides the EMF of concentration chains was measured:

The experimental technique described in [16] was used. The solid electrolyte of zirconium dioxide ZrO_2 , stabilized by yttrium oxide Y_2O_3 , has sufficient ionic conductivity, which is due to the migration of O^{2-} oxygen through anionic vacancies under the action of an electric field at temperatures above 800°C [17].

The measurements were carried out in the temperature range $T=1000\text{--}1200$ K and concentrations 0.35–0.95 mol fraction of TiO_2 . The EMF values were reproduced with an accuracy of ± 5 mV. The temperature dependences of the EMF were approximated by linear equations $E=(a \pm \Delta a)+(b \pm \Delta b) T$ using the OriginPro2021 computer program:

$$E, \text{ mV} = (961 \pm 10) - (3.106 \pm 0.03) \cdot 10^{-2} T, \quad \text{phase region } \text{Li}_4\text{Ti}_5\text{O}_{12} + \text{TiO}_2 \quad (3)$$

$$E, \text{ mV} = (430 \pm 4) - (1.520 \pm 0.02) \cdot 10^{-2} T, \quad \text{phase region } \text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04} + \text{Li}_4\text{Ti}_5\text{O}_{12} \quad (4)$$

$$E, \text{ mV} = (382 \pm 4) - (1.431 \pm 0.02) \cdot 10^{-2} T, \quad \text{homogeneous phase } \text{Li}_2\text{TiO}_3 \quad (5)$$

$$E, \text{ mV} = (134 \pm 2) - (1.380 \pm 0.02) \cdot 10^{-2} T, \quad \text{phase region } \text{Li}_4\text{TiO}_4 + \text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92} \quad (6)$$

According to the Gibbs-Helmholtz equation, the parameters of the linear equations are related to thermodynamic characteristics with the following relations:

$$\Delta G = -zFE, \Delta H = -zFa, \Delta S = zFb \quad (7)$$

where $z=2$ (oxygen charge in one mole of Li_2O), Faraday number $F=96.5$ J/mV.

The dependence of the EMF values for 1200 K on the composition is in accordance with the phase diagram of the $\text{Li}_2\text{O}\text{--TiO}_2$ system (Figure 1). According to Figure 4, schemes of potential-forming processes are drawn up diagrams. The potential-forming processes for dependencies (3–6) are, respectively, the following reactions:

Based on dependencies (3–11), the values of the thermodynamic functions of formation $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, Li_2TiO_3 , $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$ and Li_4TiO_4 were calculated. The dependence of the Gibbs free energy of formation of lithium titanates from one mole of a mixture of Li_2O and TiO_2 at 1200 K is shown in Figure 5.

The dependence of the EMF values for a temperature of 1200 K on the composition is shown in Figure 4.

The molar thermodynamic functions of the formation of lithium titanates of stoichio-

metric compositions $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 , and Li_4TiO_4 from Li_2O , TiO_2 , and simple substances are presented in Table 2.

Fig. 4. Dependence of the EMF values for 1200K on the composition in the Li_2O – TiO_2 system.

Table 2. The molar thermodynamic functions of the formation of lithium titanates from simple substances and from Li_2O , TiO_2 (denoted by *)

Compound	$-\Delta G_{1200\text{K}}^{0,*}$	$-\Delta H_{1200\text{K}}^{0,*}$	$-\Delta S_{1200\text{K}}^{0,*}$	$-\Delta G_{298}^0$	$-\Delta H_{298}^0$	S_{298}^0
	$\text{kJ}\cdot\text{mol}^{-1}$		$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$		$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	356.1 ± 4	371.1 ± 5	12.51 ± 0.2	5923 ± 30	6287 ± 40	315.7 ± 4
Li_2TiO_3	115.2 ± 1	120.2 ± 2	4.16 ± 0.2	1565 ± 10 1571 ± 10 [15]	1662 ± 20 1668 ± 20 [15]	84.0 ± 2 91.8 ± 2 [15]
Li_4TiO_4	137.9 ± 1	146.1 ± 3	8.82 ± 0.2	2149 ± 10	2286 ± 15	119.1 ± 3

Fig. 5. Dependence of the Gibbs free energy of formation of lithium titanates from one mole of a mixture of Li_2O and TiO_2 at 1200 K.

Comparison of the free energies of formation of lithium titanates of stoichiometric compositions $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, Li_2TiO_3 , $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$, Li_4TiO_4 from binary compounds Li_2O and TiO_2 shows that Li_2TiO_3 is characterized by the highest thermodynamic stability. At the same time, this compound, as well as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, and $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$, are relatively stable. $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$ and $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$ are boundary phases for the homogeneity region of Li_2TiO_3 .

Conclusion

Thus, for the first time, the free energies, enthalpies and entropies of formation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, and $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$ were determined both from simple substances and from binary compounds. The corresponding parameters for the Li_2TiO_3 compound obtained in this work by the electromotive force method are consistent with the reference data. The obtained thermodynamic information can be used to develop a technology for producing lithium-ion batteries.

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LİTİUM TİTANATLARIN ƏMƏLƏGƏLMƏ TERMODİNAMİKİ FUNKSIYALARI

Ü.N.Şərifova

Elektrik hərəkət qüvvəsi üsulu ilə $\text{Pt}|\text{Li}_2\text{O}|\text{ZrO}_2+10\% \text{ kütlə payı } \text{Y}_2\text{O}_3, \text{ litium. şüşə } |(\text{Li}_2\text{O})_x(\text{TiO}_2)_{1-x}|\text{Pt}$ elementlərinin $T=1000\text{--}1200\text{ K}$ temperatur intervalında və $0.35\div 0.95$ mol payı TiO_2 qatılıq intervalında ölçülməsi ilə Li_4TiO_4 , Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ birləşmələrinin və Li_2TiO_3 birləşməsi əsasında əmələ gələn $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$ fazalarının termodinamik parametrləri təyin edilmişdir. Li_2TiO_3 birləşməsi müstəsna olmaqla litium titanatların əmələgəlmə termodinamik funksiyaları ilk dəfə olaraq təyin edilir. $1000\text{--}1200\text{ K}$ intervalında təyin edilmiş qiymətlər

298 K temperaturuna ekstrapolyasiya olunmuşdur. Litium titanatların həm bəsit maddələrdən, həm də Li_2O və TiO_2 birləşmələrindən əmələgəlmə termodinamiki funksiyaları təyin edilmişdir. Litium titanatların əmələgəlmə sərbəst enerjisi, entalpiyası və standart entropiyası üçün bu kəmiyyətlər alınmışdır: $\Delta G_{298}^0(\text{Li}_4\text{TiO}_4) = -2149 \text{ kC}\cdot\text{mol}^{-1}$, $\Delta G_{298}^0(\text{Li}_2\text{TiO}_3) = -1565$, $\Delta G_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12}) = -5923$, $\Delta H_{298}^0(\text{Li}_4\text{TiO}_4) = -2286 \text{ kC}\cdot\text{mol}^{-1}$, $\Delta H_{298}^0(\text{Li}_2\text{TiO}_3) = -1662$, $\Delta H_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12}) = -6287$, $S_{298}^0(\text{Li}_4\text{TiO}_4) = 119.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $S_{298}^0(\text{Li}_2\text{TiO}_3) = 84$, $S_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12}) = 315.7$.

Açar sözlər: litium titanatları, EHQ üsulu, sərbəst enerji, entalpiya, entropiya.

ТЕРМОДИНАМИЧЕСКИЕ ФУНКЦИИ ОБРАЗОВАНИЯ ТИТАНАТОВ ЛИТИЯ

У.Н.Шарифова

Методом электродвижущих сил измерением концентрационных цепей: $\text{Pt} | \text{Li}_2\text{O} | \text{ZrO}_2 + 10 \text{ мас.}\% \text{Y}_2\text{O}_3$, литий.стекло $| (\text{Li}_2\text{O})_x(\text{TiO}_2)_{1-x} | \text{Pt}$ в интервале температур $T = 1000 - 1200 \text{ K}$ и концентраций $0.35 \div 0.95$ моль доля TiO_2 определены термодинамические функции образования соединений Li_4TiO_4 , Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ и фаз на основе Li_2TiO_3 : $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$. За исключением соединения Li_2TiO_3 термодинамические функции образования титанатов лития определяются впервые. Пересчитаны термодинамические функции образования на стандартное состояние при 298 K. Термодинамические функции образования титанатов лития определены как из простых, так и из двойных соединений Li_2O и TiO_2 . В частности, для свободной энергии, энтальпии образования и стандартной энтропии получены: $\Delta G_{298}^0(\text{Li}_4\text{TiO}_4) = -2149 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta G_{298}^0(\text{Li}_2\text{TiO}_3) = -1565$, $\Delta G_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12}) = -5923$, $\Delta H_{298}^0(\text{Li}_4\text{TiO}_4) = -2286 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H_{298}^0(\text{Li}_2\text{TiO}_3) = -1662$, $\Delta H_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12}) = -6287$, $S_{298}^0(\text{Li}_4\text{TiO}_4) = 119.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $S_{298}^0(\text{Li}_2\text{TiO}_3) = 84$, $S_{298}^0(\text{Li}_4\text{Ti}_5\text{O}_{12}) = 315.7$.

Ключевые слова: титанаты лития, метод ЭДС, свободной энергия, энтальпия, энтропия.