DETERMINATION OF STANDART THERMODYNAMIC PROPERTIES OF BOGDANOVITE (Au_3Cu) BY SOLID STATE GALVANIC CELL METHOD

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Three minerals are known in Au-Cu system. They are Au_3Cu, AuCu and $AuCu_3$. But Au_3Cu (bogdanovit) was discovered not long ago relatively and its thermodynamic properties were not studied until now.

Bogdanovit was received with alloying of elementary Au and Cu at Au excess at T=1300 K (in ratio $Au:Au_3Cu=1:1$). The drop of alloy was pressing in the form of tablet.

Thermodynamic properties of the following reaction

$$3Au(cr)+Cu(cr) = Au_3Cu(cr)$$

were determined in galvanic cell

$$(-)\ Pt \mid Cu \mid RbCu_4Cl_3I_2 \mid Au,\ Au_3Cu \mid Pt\ (+) \qquad (A)$$

which represents at the fig.1.

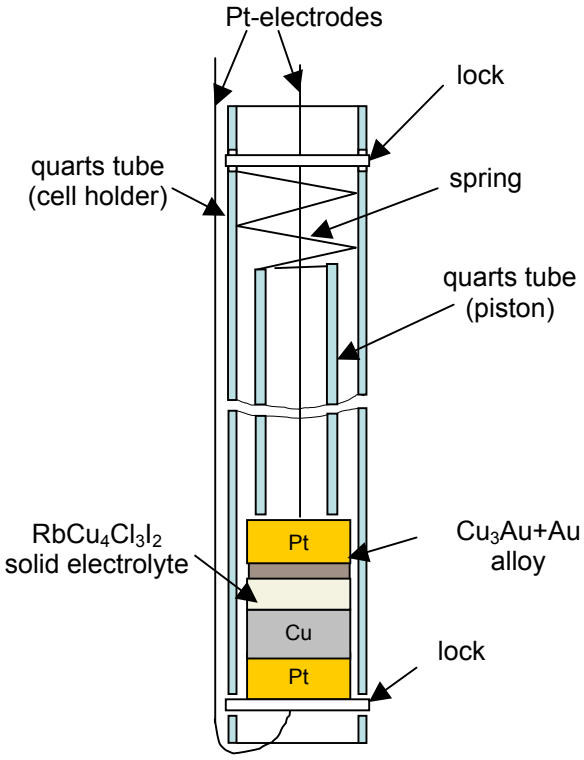

Fig.1. Principal sketch of the cell

The $RbCu_4Cl_3I_2$ (cr) conducting Cu^+ ions was used as solid electrolyte. The measurements were realized at 369-443 K temperature range and at atmospheric pressure of dry argon current.

The cell was heated in vertical resistance furnace (at constant current). Constant temperature (±0,1 K accuracy) was measured in the middle of the cell and support with help of electronic thermoregulator «PROTERM-00». Both temperature and EMF (electromotive force) were automatic measured with (± 0,005) mV accuracy with multi-channel millivoltmeter. Channels with $\sim 10^{13}$ Ω entrance resistance were used for EMF measurements.

Measurements were realized with «temperature titration» method. It consists of changing the temperature with 5-20°C step and expecting of EMF equilibrium values. A temperature-EMF (E, mV) dependence of the cell (A) (in supposition that $\Delta_r C_p=0$) was found as linear equation:

$$E(A)=(375{,}0\pm7{,}1)+(0{,}260\pm0{,}01)\cdot T/K,\ (369<T/K<443),\ R^2=0{,}9523 \qquad (1)$$

Table 1. Experimental EMF and temperature values

T, K	E, mV	ΔE=E-Ecalc, mV
371.3	473.20	1.58
371.0	470.00	-1.54
380.7	475.00	0.93
381.8	473.55	-0.80
392.8	478.80	1.58
392.8	476.10	-1.12
392.8	477.96	0.74
403.7	479.13	-0.92
414.4	483.00	0.16
425.0	488.00	2.40
425.0	483.20	-2.40
445.2	492.27	1.42
435.0	488.10	-0.10
425.0	484.18	-1.42
424.9	485.10	-0.47

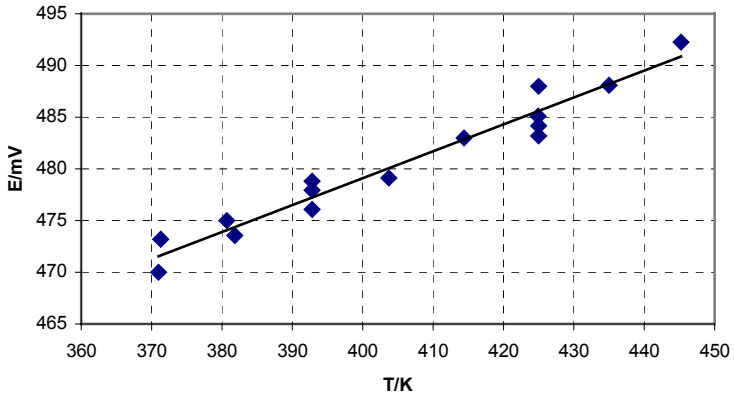

Fig. 2. Experimental EMF-temperature dependence

Using fundamental thermodynamic equations:

ΔG=-nFE, $(G/T)_p$=-S, ΔG=ΔH-$T\Delta S$, (2,3,4) where

n=1 – electron quantity in electrode process $Cu=Cu^{+}+e$;

F=96484, 56 $C \cdot mol^{-1}$ – Faraday constant;

E – EMF, V.

And also with the aid of auxiliary data for Au and Cu [1] (S^0(Au) =47.497 e.u.; S^0(Cu) =33.164 e.u.) standard thermodynamic properties of bogdanovit Au_3Cu (cr, 298.15 K) were calculated and located at the table 2.

Table 2. Standard thermodynamic properties of bogdanovit (Au_3Cu)

$\Delta_f G^0$(J·mol^{-1})	$\Delta_f S^0$(J·mol^{-1}·K^{-1})	$\Delta_f H^0$(J·mol^{-1})	S^0(J·mol^{-1}·K^{-1})
-(43661±1300)	25.09±1.50	-(36182±1300)	175.66±1.50

References

1. *Ihsan Barin*. Thermochemical Data of Pure Substances. – VCH, Weinheim, 1995.

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