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Thermodynamic properties of Ag_x-Au_{1-x} solid solution at 298–673K and pressure of 1 atm

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The most important work on the thermodynamics of gold – silver alloy is an article [*White, et al.,* 1957] and references therein. This remarkable work has not lost its significance and in the present. Suggested by the authors interpretation of uncoordinated and often conflicting literature data in combination with their own experimental data on the enthalpy of formation of alloys in the framework of the quasi-regular solid solution proved to be very persuasive. Resulting equations describe well the solution in the solid state from 273 K to melting temperatures and further in the liquid state. However, the scatter of literature data used is so large that the absolute values of the selected values of thermodynamic functions in the article [*White, et al.*, 1957] can be regarded as a talented predicted.

The purpose of this study was to find experimental methods to obtain data on activity in the alloys Ag-Au. It should be noted that the most common electrolyte (AgI, $RbAg_4I_5$), used for EMF measurements, contains iodine which reacts with the gold of the alloy that makes it impossible to interpret results. This reaction is described by [*White, et al.,* 1957]:

$$Au_{(alloy)} + Ag^+_{(\ electrolyte)} = Ag_{(alloy)} + Au^+_{(\ electrolyte)}$$

and which also observed in our experiments with iodine-containing solid electrolytes. Application of AgCl solid electrolyte allows to avoid this reaction.

Activity of silver for the five compositions Ag_x-Au_{1-x} solid solution $Ag_{0.1}Au_{0.9}$, $Ag_{0.3}Au_{0.7}$, $Ag_{0.5}Au_{0.5}$, $Ag_{0.7}Au_{0.3}$, $Ag_{0.9}Au_{0.1}$ were determined by solid-state galvanic cell in the temperature range 298–673K and atmospheric pressure of argon. Experiments used gold (99.9%) and silver (99.9%) foil. Alloys of the desired composition were obtained by melting a mixture of small pieces of gold and silver foil (~ $1mm^2$) in an evacuated ampoule in the gas flame. Fig.1. shows the scheme of a galvanic cell. Silver electrode (reference electrode) was made from a silver rod 3–4 mm in length and 6 mm in diameter. Solid electrolyte tablet was cut from a block of AgCl, obtained by zone melting. Elements of the cell (fig. 1) were placed in the cell holder (6.5 mm internal diameter) and pressed against a spring for better contact. Finally, the holder of the cell was placed in a container, cells body, made of quartz glass with pipes for input and output of the gas. The measurements were performed in a dry argon flow (flow rate 0.5–1 cm^3 per minute). Cell's design and methodology of the experiment are described in detail in the article [*Osadchi, Rappo,* 2004].

The measurements were made by temperature titration in increments of 50 K. Achieving equilibrium EMF takes from 10 hours to 10 days at different temperatures and compositions. Equilibrium was considered reached when the EMF remained constant within ± 0.003 V for several hours. Temperature dependence of the EMF determined in a reversible galvanic circuit

$$(+)\ Pt|C_{(graphite)}|Ag|AgCl|Ag_xAu_{1-x}|C_{(graphite)}|Pt\ (-)$$

with AgCl as a solid electrolyte. Activity of silver in the alloy is defined as:

$$\lg(a_{Ag}) = -nFE/RT\ln(10) \qquad (n=1),$$

where n – the number of electrons involved in the reaction, F – Faraday constant, E – EMF in volts, R – universal gase constant, T – temperature in Kelvin.

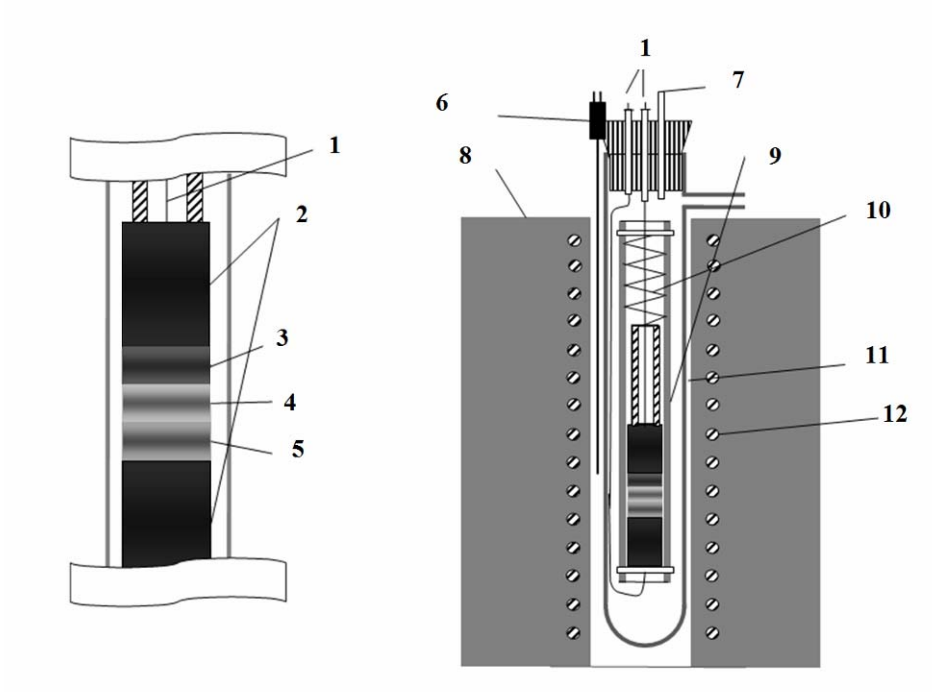

Fig. 1. The scheme of solid-state galvanic cell (1 – Au-wire, 2 – Graphite, 3 – sample system, 4 solid electrolyte (AgCl), 5 – reference system, 6 – thermocouple, 7 – gas input, 8 – resistance furnace, 9 – cell's holder 10 – spring, 11 – cell body, 12 – eating element)

The data obtained are well described by linear equations E = a + b (x) * T, which allowed us to refine the model [White, et al., 1957].

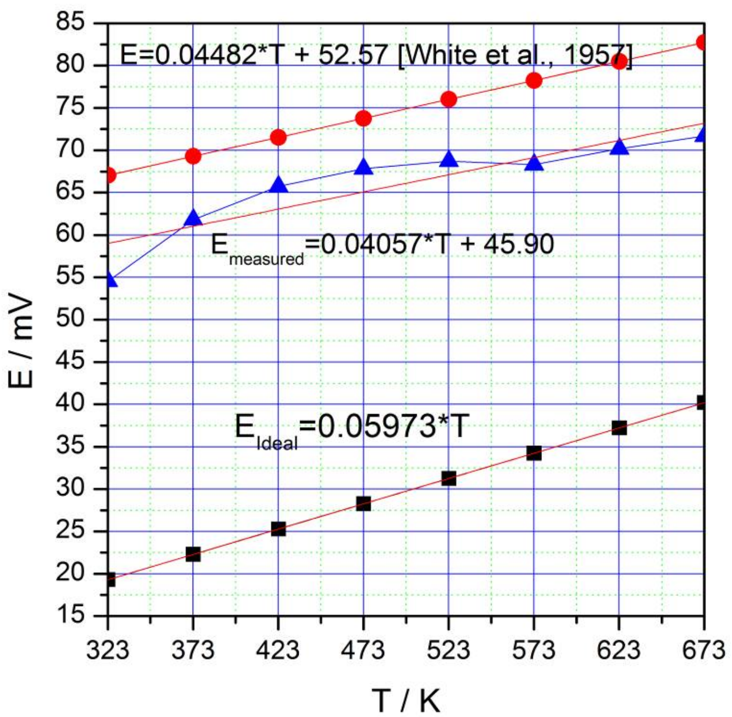

Fig.2. Comparison of the values of EMF of composition $Ag_{0.5}Au_{0.5}$, the experimental data, data [*White, et al.,* 1957] and for an ideal solid solution

The results of our measurements (fig. 2) show a systematic deviations in the EMF in the direction of decreasing compared with those calculated by the model [*White, et al.*, 1957] for all compositions. The experimental results describes in the terms of subregular model of solid solutions, borrowed from [*White, et* *al.,* 1957].Thermodynamic activity of components as a function of (x – mole fraction of silver) and the absolute temperature by the equations:

$$a_{Ag} = x\cdot\exp[-(2190-430(1-x)-0.873T)\cdot(1-x)^2/T] \quad (1)$$

$$a_{Au} = (1-x)\cdot\exp[-(1960-430x-0.873T)\cdot x^2/T] \quad (2)$$

The original model of [*White, et al.,* 1957] we have adopted formula expression look like:

$$a_{Ag} = x\cdot\exp[-(2840-810(1-x)-0.691T)\cdot(1-x)^2/T]$$

$$a_{Au} = (1-x)\cdot\exp[-(2440-810x-0.691T)\cdot x^2/T]$$

These equations (1) and (2) applicable in the temperature range 273–773K.

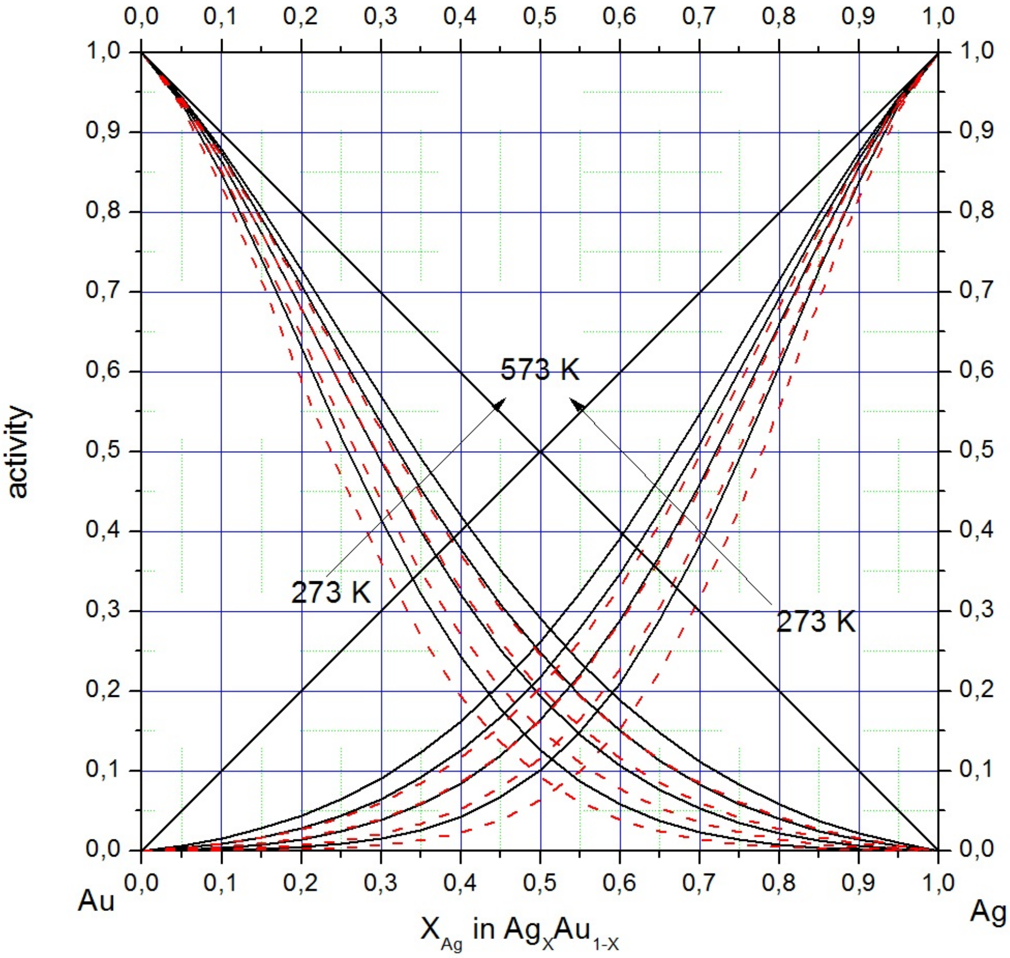

Fig. 3. Activity isotherms of silver and gold in the alloy (dashed lines denote the data [*White, et al.,* 1957], solid one experimental data)

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