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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

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MEASUREMENT OF THE VAPOR PRESSURE OF SOLID SOLUTIONS Au–Ag AND Au–Cu

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In the present work, the partial vapor pressure of gold, copper, and silver over solid solutions that these elements form with one another was measured. The measurements were carried out by the Knudsen effusion method, using the apparatus shown in Fig. 1. It is a somewhat modified version of an apparatus developed in our laboratory by Yu. A. Priselkov.

Fig. 1. Apparatus for measuring the vapor pressure of metals:
1 –water-cooling jacket; 2 –receiver; 3 –quartz cup, fixing the beginning and end of exposure; 4 –effusion chamber; 5 –shielding casing made of quartz; 6 –thermocouple; 7 –place where the quartz tube is fastened to the apparatus; 8 –armature of the fixing device; 9 –armature of the lifting mechanism of quartz cup 3; 10 –device for fixing the position of quartz cup 3; 11 –connection of the apparatus with the vacuum system; 12 –inductor for heating; 13 –glass rods of the lifting mechanism; 14 –ground joint for introducing the thermocouple into the apparatus; 15 –ground joint connecting the receiver with the apparatus; 16 –shock absorber.

Fig. 2. Partial vapor pressure of gold (a) and silver (b) in the Au–Ag system:
1 –pure gold; 2–6 –systems with different gold contents (at. %): 2 –81.3; 3 –68; 4 –60; 5 –29; 6 –15; 7 –pure silver; 8–11 –systems with different silver contents (at. %): 8 –79.5; 9 –71; 10 –44; 11 –18.7.

The effusion chamber was made entirely of molybdenum, which

does not react with any of the metals studied. The area of the effusion orifice did not exceed $1 \cdot 10^{-3}$ cm^2, which ensured the equilibrium vapor pressure inside the chamber. The chamber was heated by an inductor connected to the circuit of a high-frequency generator. The temperature was measured with a Pt/PtRh

Figure 3

Figure 2: Figure 3

thermocouple, calibrated in the apparatus by the melting points of silver and gold. The accuracy of temperature regulation was ±1°.

In the work we used gold, silver, and copper containing the radioactive isotopes Au^{198}, Ag^{110}, and Cu^{65}.

After washing the condensate from the receiver and precipitating the corresponding element with a carrier (as a sulfide in the case of gold, as a bromide in the case of silver, and as 8-oxyquinoline in the case of copper), the amount of evaporated metal was determined from the activity of the preparation. The activity was determined on apparatus "B" using AMM-4 counter tubes for silver and AS-1 and AS-2 for gold and copper, and was compared with the activity of standards. The standards were prepared by dissolving a weighed portion of the active metal and precipitating, by the method described above, the radioactive metal from an aliquot part of the solution.

For a more accurate determination of the amount of evaporated metal, a decay curve was recorded for each sample and standard in the case of gold and copper.

The saturated vapor pressure, or the partial vapor pressure of a metal over its alloy, was calculated from the formula:

$$P = \frac{17.14 \cdot m}{t \cdot s \cdot K} \sqrt{\frac{M}{T}},$$

where P is the vapor pressure in mm Hg, m is the amount of evaporated metal in g, t is the evaporation time in sec, s is the area of the effusion orifice in cm^2, T is the absolute temperature, M is the molecular weight of the metal, and K is the dimensionless Clausing coefficient, taking into account the resistance of the effusion orifice to the molecular beam of the evaporating metal.

Fig. 3. Partial vapor pressure of gold (a) and copper (b) in the Au–Cu system: 1 –pure gold; 2-5 –systems with different gold contents (at. %): (2 –94; 3 –74.7; 4 –34.7; 5 –10.13); 6 –pure copper; 7-11 –systems with different copper contents (at. %): (7 –83.8; 8 –70.4; 9 –50; 10 –29.6; 11 –10.34)

From the data obtained, the following equations were found for the curves of the saturated vapor pressure of gold, silver, and copper.

For gold in the temperature interval from 800 to 1000°:

$$\log P_{\text{mm}} = -18016/T + 8.683.$$

For silver in the temperature interval from 760 to 960°:

$$\log P_{\mathrm{mm}} = -14058/T + 8.855.$$

For copper in the temperature interval from 900 to 1070°:

$$\log P_{\mathrm{mm}} = -17320/T + 9.320.$$

Using the data obtained for the saturated vapor pressure and the values of

$$\left(\frac{F_0 - H_0^0}{T}\right)_{\mathrm{tv}} \quad \text{and} \quad \left(\frac{F_0 - H_0^0}{T}\right)_{\mathrm{gas}} \tag{2}$$

we calculated the latent heats

of sublimation of gold, silver, and copper at absolute zero ΔH_0^0, and also the latent heats of sublimation of these metals ΔH_T for the middle of the temperature interval in which the vapor-pressure measurements were carried out.

The data obtained for the partial vapor pressure of gold, silver, and copper in gold-silver and gold-copper alloys are given in Figs. 2 and 3, which show the dependence of $\lg P$ on $\frac{1}{T}$.

An attempt was made to determine simultaneously the partial vapor pressures of silver and gold in gold-silver alloys. For this purpose, alloys containing radioactive isotopes of silver and gold were prepared. The partial vapor pressure of gold and silver in these alloys is shown in Fig. 2 (alloys with 28.9 and 81.3 at.% gold and alloys with 71.1 and 18.7 at.% silver).

Table 1

	Au	Ag	Cu
ΔH_T, kcal/g · mol	82.4	64.4	79.3
ΔH_0^0, kcal/g · mol	86.8	67.7	80.9

From the values obtained for the partial vapor pressures and saturated-vapor pressures, the activities of gold, silver, and copper in gold-copper and gold-silver alloys were calculated.

Figure 4 shows the dependence of the activities of gold and copper on their concentration in gold-copper alloys (A), and the behavior of the activity of gold in gold-

Fig. 4. Activities of gold and copper in the Au-Cu system (A) and of gold and silver in the Au-Ag system (B): 1 –gold; 2 –copper; 3-6 –silver (3 –original data; 4 –data from work (^{1}); 5 –data from work (^{3}); 6 –data from work (^{4})).

Fig. 4. Activities of gold and copper in the Au–Cu system (A) and of gold and silver in the Au–Ag system (B).

Figure 3: Fig. 4. Activities of gold and copper in the Au–Cu system (A) and of gold and silver in the Au–Ag system (B).

silver alloys and of silver in gold–silver alloys (B), obtained in the present work and in the works of other authors. As can be seen from the curves, the activities of silver in the gold–silver alloys studied are in good agreement with the values of the activity of silver found in the works of other authors ([1,3,4]). From all the diagrams presented it is evident that negative deviations from Raoult' s law are observed in the gold–silver and gold–copper systems.

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CITED LITERATURE

1. C. L. McCabe, H. M. Schadel, C. E. Birchenall, *J. Metals*, **5** (1953).
2. K. K. Kelley, *Bur. Mines Bull.*, No. 383 (1935).
3. A. A. Zhukhovitskii, S. N. Kryukov, M. E. Yanitskaya, A. G. Golitsyn, DAN, **102**, No. 1 (1955).
4. V. V. Kornev, DAN, **107**, No. 5 (1956).

Note: Figure translations are in progress. See original paper for figures.