THERMODYNAMIC PROPERTIES OF THE LIQUID Hg-Tl ALLOYS DETERMINED FROM VAPOUR PRESSURE MEASUREMENTS

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Abstract

The partial vapour pressure of mercury over liquid Hg-Tl liquid solutions were determined in the temperature range from 450 to 700 K by direct vapour pressure measurements carried out with the quartz gauge. From the measured $\ln p_{Hg}$ vs.T relationships activities of mercury were determined. Using Redlich-Kister formulas logarithms of the activity coefficients were described with the following equations:

$$\ln \gamma_{Hg} = A \cdot \left(1 - x_{Hg}\right)^2 + B \cdot \left(1 - x_{Hg}\right)^2 \left(4x_{Hg} + 1\right) +$$
$$+ C \cdot \left(1 - x_{Hg}\right)^2 \left(12x_{Hg}^2 - 8x_{Hg} + 1\right)$$
$$\ln \gamma_{Tl} = A \cdot \left(x_{Hg}\right)^2 + B \cdot \left(x_{Hg}\right)^2 \left(4x_{Hg} - 3\right) +$$
$$+ C \cdot \left(x_{Hg}\right)^2 \left(12x_{Hg}^2 - 16x_{Hg} + 5\right)$$

From which all thermodynamic functions in the solutions can be derived.

Keywords: mercury, thallium, pressure measurement, thermodynamic properties

1. Introduction

Binary Hg systems show many interesting physical properties. As a good example mercury tellurium system can be taken. Hg-Te system exibits HgTe intermetallic phase with the energy gap equal to zero. For thin films the energy gap of HgTe was found to be about 0,02 eV [1]. Due to proper addition of other components one can regulate the width of this gap. Element which is most often admixed with Hg-Te is Cd. In the ternary Hg-Te-Cd system the change of cadmium / tellurium ratio causes energy gap size to increase from 0 to about 1, 5 eV at 300 K [2]. Making layers of two semi-conductors alternatively one can produce a heterostructure, in which the width of the energy gap can change over a distance of several atomic diameters. This type of semi-conductors is used in devices working in the range of infra-red radiation [3].

There is a question if these interesting properties of HgTe phase can be modified due to the addition of other elements then Cd and can lead to the formation of the ternary phase. HgTl system shows the formation of nonstoichiometric low melting Hg_5Tl_2 phase and it is interesting to see if there is a range of solid solution between this phase and HgTe. However, before the investigation of the ternary system is attempted the properties of respective binaries must be known. In Fig. 1 the HgTl phase diagram is shown, while in Table 1 crystallographic information about phases existing in this system is gathered.
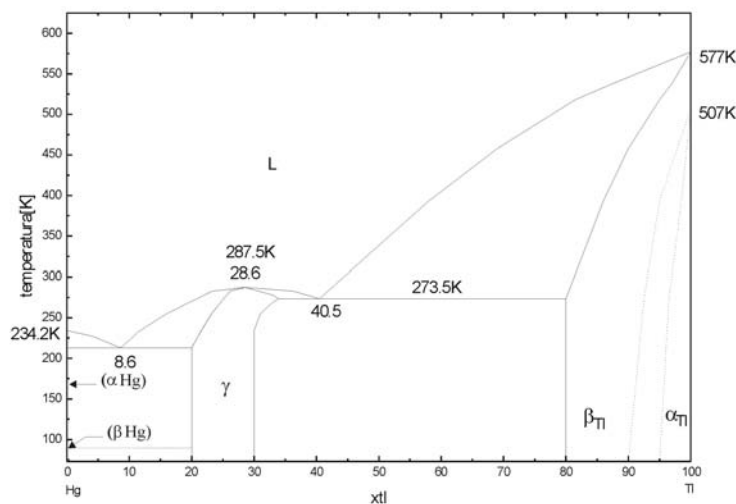

Figure 1. Phase diagram of binary system Hg-Tl.

Table 1. Crystallographic properties of phases of Hg-Tl system

Phase	Structure	Prototype
β^{Hg}	A6	α^{Pa}
α^{Hg}	A10	α^{Hg}
$\gamma\,(Hg_5Tl_2)$	A1(a)	Cu
α^{Tl}	A3	Mg
β^{Tl}	A2	W

Binary Hg-Tl system was investigated first time by Richard and Daniels[4] who used the concentration cells and a calorimeter. Then, Kleppa [5] and Predel [6] reported results of calorimetric investigations. Recently, a review of the thermodynamic data on HgTl system was given by Kozin [7].

Because of high mercury vapour pressure in the temperatures range from 500 to 700 and a negligible value of thallium vapour pressure in this temperature range, it was decided to examine the system Hg-Tl by means of the vapour pressure measurements

2. Experimental

2.1. Materials

Pure mercury (99.99%) obtained from Polish Chemical Reagents was additionally destillated in vacuum. Thallium of 99.999% purity was obtained from Merck. Samples of alloys were prepared separately by weighing appropriate amounts of metals and melting them in a silica chamber at temperature so high that the Hg vapour pressure reached about 0,9 bar. Under these conditions the system was kept for 2-3 h and then cooled. If the pressure in the reactor after cooling was greater than $1,5^{-5}$ bar, the reactor was opened and evacuated, and the whole procedure was repeated. Then, samples were used in further measurements of the vapour pressure over liquid phase.

2.2.Technique

The scheme of the apparatus is shown in Fig.2. The measurements of pressures of metal vapours consist in the use of a glass pressure gauge. This technique, developed years ago by Gibson [8], and used for the determination of dissociation pressure of cupric bromide by Jackson [9] , was also successfully applied to the determination of the parameters of ZnO reduction process [10,11], vapour pressure measurements over solid arsenic and arsenic oxide [12] as well as measurement of the vapour pressure of mercury over liquid Hg-In alloy [13]. Consequently, it can also be applied to the vapour pressure determination of mercury over liquid Hg-Tl alloy.
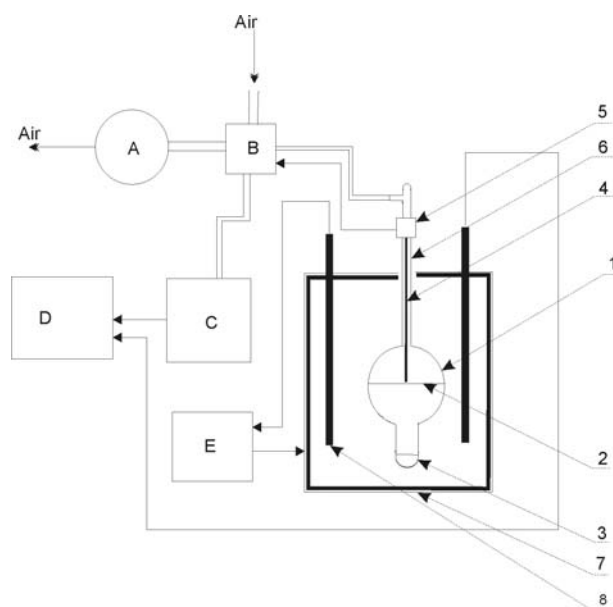

Figure 2. *Experimental arramgement. 1-silica vessel, 2 - silica membrane,*
3 - vaporization chamber, 4 - silica rod, 5 - transoptor, 6 - silica
tube, 7 - furnace, 8 - iron crucible, A - rotary pump, B - pressure
control, C - pressure measurement, E - furnace control,
D - computer

The main part of the apparatus consists of the silica vessel (1) which is divided into two parts by the silica membrane (2). A piece of prepared earlier Hg-Tl alloy (or pure mercury) of approximately 3 g was placed in the vaporization chamber (3) which was

evacuated and sealed under vacuum. In the upper part of the vessel a thin rod of silica was placed vertically on the membrane (4) in such a way that its upper end went through the transoptors' slit (5). The rotary pump was connected with the upper part of the vessel through the silica tube (6). The vessel was immersed in the resistant furnace (7). Additionally, a thick-walled iron crucible was placed in the furnace (8) to stabilize its thermal field.

At the beginning of the experiments the system was evacuated in order to equilibrate the initial pressure in both parts of the vessel (1) at room temperature. Zero position of the membrane was determined after cutting off the reactive space from the environment under vacuum on its both sides. Next, the temperature was increased and in about 1- 2 h reached constant value. Resulting deformation of the membrane under exerted pressure from the vaporization chamber pushed the silica rod through the transoptors slit and automatically opened the electromagnetic valve (B) equilibrating pressures on both sides of the membrane. Then, the pressure of the gas in the vaporization chamber was measured on the electronic manometer (C). Corresponding pressure and temperature values were recorded by the computer.

3. Results

Our experimental results are shown in Fig.3 and in Table 2. The vapour pressure over the liquid phase can be described by the Eq. (1):

$$\ln P_{Hg} = \frac{a}{T} + b\ln(T) + c \tag{1}$$

where: P – pressure [bar] and a, b, c – coefficients

Values of the coefficients a, b, c in Eq.(1) describing the pressure of Hg vapour for a given alloy concentration are given in Table 2. They were obtained by the Mathcad software fit of Eq.(1) to our experimental data.

Next, the activity of Hg in the alloy can be determined from the relation:

$$a_{Hg} = \frac{\overline{p}_{Hg}}{p_{Hg}^{0}} \tag{2}$$

$$\ln\left(a_{Hg}\right) = \ln\left(\overline{p}_{Hg}\right) - \ln\left(p_{Hg}^{0}\right) = \frac{a - a^{0}}{T} + \left(b - b^{0}\right)\ln(T) + \left(c - c^{0}\right) \tag{3}$$

where: $\overline{p}_{Hg}$ - pressure of Hg vapour over solution

p_{Hg}^{0} - pressure of Hg vapour over pure Hg

and consequently partial Gibbs energy of mercury, which can be derived as:

$$\Delta\bar{\mu}_{Hg} = RT \ln a_{Hg} = R\left(a - a^0\right) + RT\left(b - b^0\right)\ln(T) + RT\left(c - c^0\right) \tag{4}$$

the partial heat of mixing can now be obtained from Eq.(5):

$$\Delta\bar{H}_{Hg} = -RT^2 \ \frac{\partial \ln a_{Hg}}{\partial T} = -RT^2\left(-\frac{a - a^0}{T^2} + \frac{b - b^0}{T}\right) \tag{5}$$

as well as the partial entropy of mercury can be derived in the following way

$$\Delta\bar{S}_{Hg} = \left(-\Delta\bar{H}_{Hg} - \Delta\bar{\mu}_{Hg}\right)\frac{1}{T} = \left(R\left(b - b^0\right)\right)\left(1 + \ln T\right) - R\left(c - c^0\right) \tag{6}$$

Since $\ln(a_{Hg}) = \ln(x_{Hg}) + \ln(\gamma_{Hg})$, activity coefficients and excess partial functions of mercury can be easily derived:

$$\Delta\bar{S}_{Hg}^{ex} = -R \ln\gamma_{Hg} - RT\left(\frac{\partial \ln\gamma_{Hg}}{\partial T}\right)_P \tag{7}$$

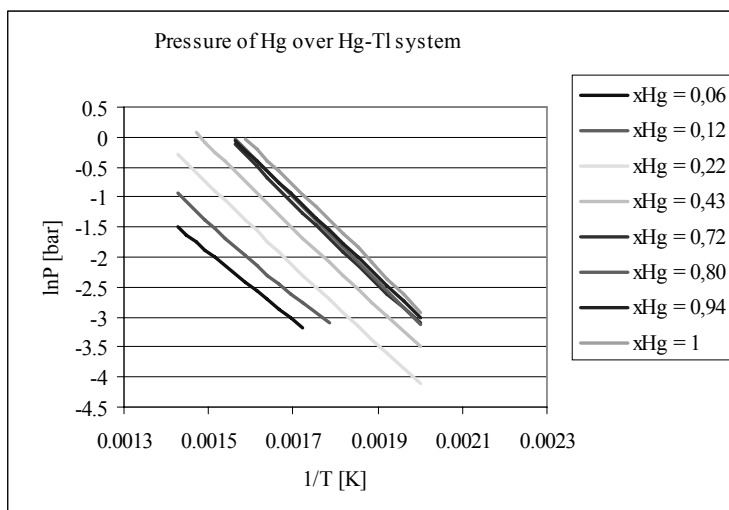$$\Delta\bar{\mu}_{Hg}^{ex} = RT \ln\gamma_{Hg} \tag{8}$$

Figure 3. Vapour pressure of Hg over alloy and pure mercury

In this way all partial functions of mercury can be obtained. It is clear now that all thermodynamic function can be derived if is known as function of temperature and the alloy concentration.

The values of mercury activity coefficients were approximated using Redlich-Kister equation [14]. Logarithms of the activity coefficients at 580K have been shown in Fig.4 while activities of both components at temperature 580K have been show in Fig.5. Redlich-Kister formulas obtained from presented experimental data are given by the following equations:

$$\ln \gamma_{Hg} = (-0.0031T + 2.1813) \cdot (1 - x_{Hg})^2 + (-0.0023T + 1.3526) \cdot (1 - x_{Hg})^2 (4 x_{Hg} + 1) + \qquad (8)$$
$$(-0.0035T + 1.9936) \cdot (1 - x_{Hg})^2 (12 x_{Hg}^2 - 8 x_{Hg} + 1)$$

$$\ln \gamma_{Tl} = (-0.0031T + 2.1813) \cdot (x_{Hg})^2 + (-0.0023T + 1.3526) \cdot (x_{Hg})^2 (4 x_{Hg} - 3) +$$
$$(-0.0035T + 1.9936) \cdot (x_{Hg})^2 (12 x_{Hg}^2 - 16 x_{Hg} + 5) \qquad (9)$$

Table 2. Equations describing the vapour pressure of Hg

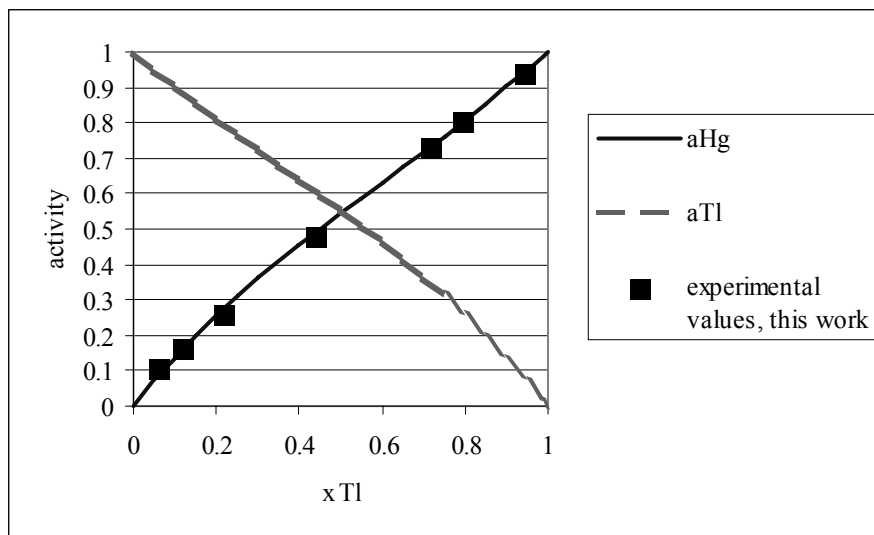| x_{Hg}	$\ln P_{Hg} = \dfrac{a}{T} + b \ln(T) + c$
0,01	$\ln P_{Hg} = \dfrac{2,547 \times 10^3}{T} + 13,647 \ln(T) - 96,422$
0,06	$\ln P_{Hg} = \dfrac{-3,083 \times 10^3}{T} + 4,114 \ln(T) - 24,046$
0,12	$\ln P_{Hg} = \dfrac{-2,173 \times 10^3}{T} + 6,341 \ln(T) - 39,356$
0,22	$\ln P_{Hg} = \dfrac{-4,703 \times 10^3}{T} + 3,33 \ln(T) - 15,384$
0,44	$\ln P_{Hg} = \dfrac{-4,611 \times 10^3}{T} + 3,647 \ln(T) - 16,936$
0,72	$\ln P_{Hg} = \dfrac{-3,376 \times 10^3}{T} + 6,137 \ln(T) - 34,494$
0,79	$\ln P_{Hg} = \dfrac{-1,104 \times 10^4}{T} - 7,482 \ln(T) + 65,573$
0,94	$\ln P_{Hg} = \dfrac{-6,706 \times 10^3}{T} + 0,438 \ln(T) + 7,761$
1	$\ln P_{Hg} = \dfrac{-1,106 \times 10^4}{T} - 7,317 \ln(T) + 64,673$

Fig 4. Activities of Hg and Tl at 580K and experimental values, this work
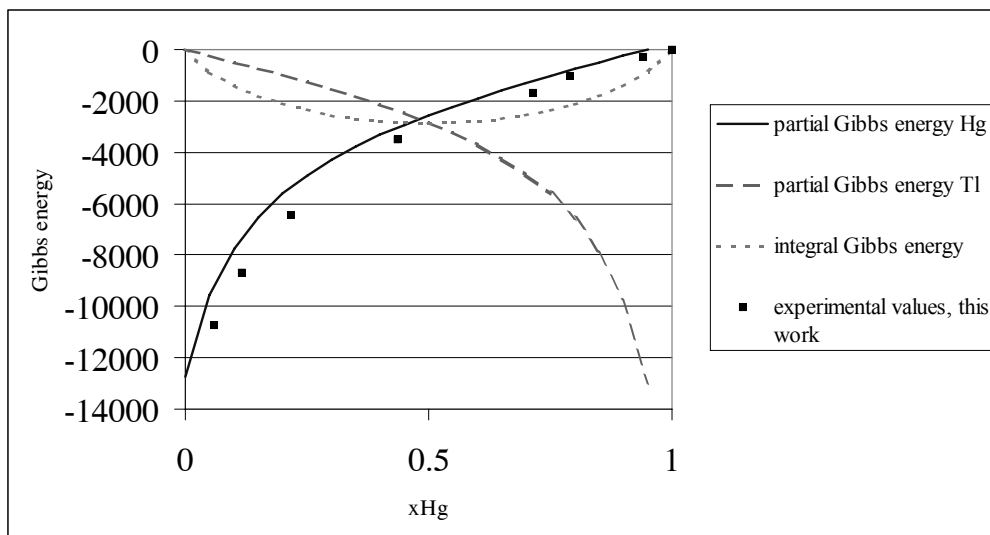

Fig 5. Partial and molar Gibbs energy functions at 580 K

Using equations (3) – (5) and derived Redlich-Kister formulas all thermodynamic functions for Hg-Tl liquid alloys were calculated and shown in Figures 3 through 8. In this way a full thermodynamic description of the liquid phase has been completed.
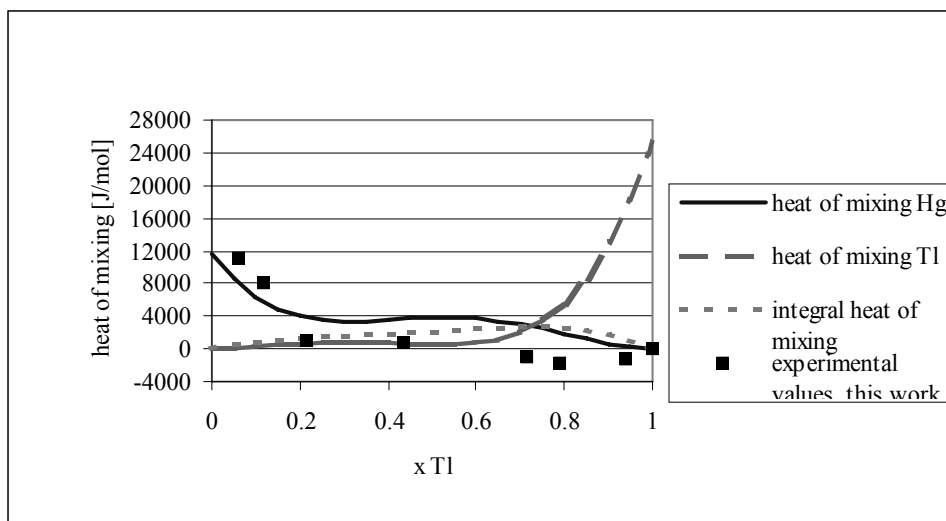

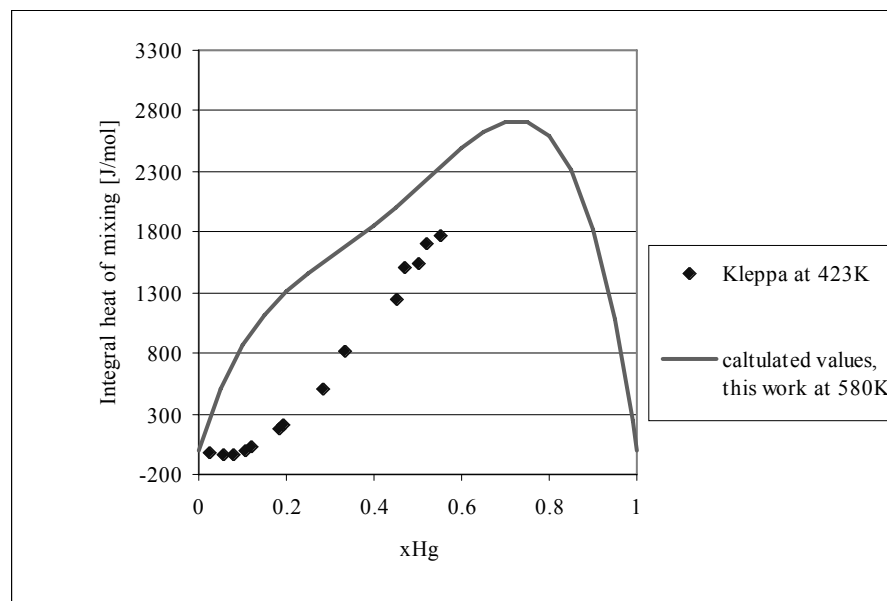*Fig 6. Heat of mixing functions at 580 K.*

Fig 7. Compared integral heat of mixing: Kleppa and this work

4. Conclusions

Using direct vapour pressure measurements with the arrangement based on the quartz gauge partial vapour pressures of mercury over liquid Hg-Tl solutions were determined. Applied experimental method seems to be sensitive enough to determine equilibrium vapour pressure properly. However, the question of the accuracy of this type of measurements is still open.
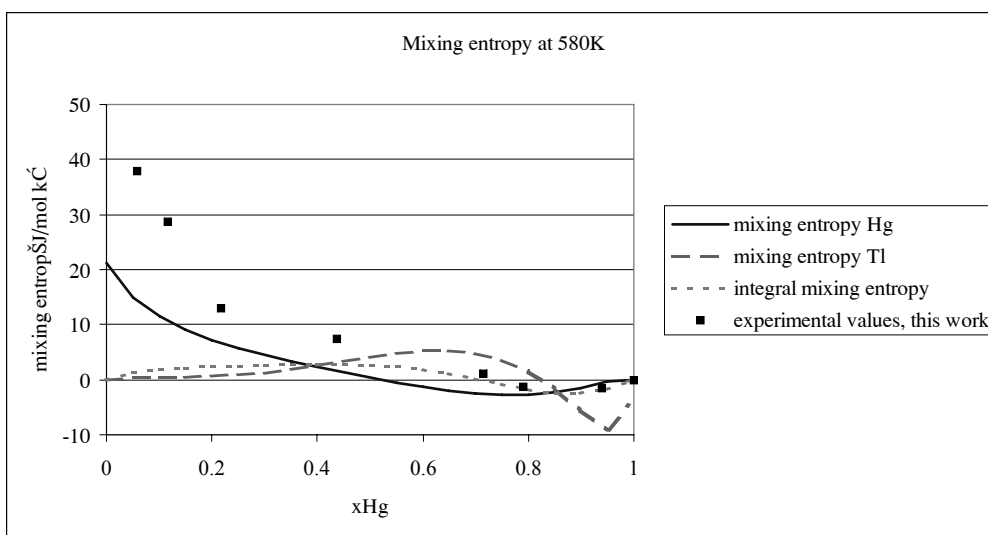

Fig 8. Entropy of mixing functions at 580 K

Equation (1) used for the interpretation of experimental data was obtained under the assumption that Δc_p between the liquid and the gas phase is constant. This assumption is reasonable. However, resulting fit of this equation to the experimental data suggests that at low temperature measured pressure was higher than the true equilibrium value. Thus, it seems that applied method may not be sensitive enough to detect vapour pressure changes at too low temperature.

From obtained experimental data the description of the thermodynamic properties of the liquid phase in the temperature range from 450 to 700 K was derived. Obtained results coupled with the information existing in the literature can be used for the future phase diagram calculation.

246

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