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THE INFLUENCE OF OXYGEN SOLUBILITY ON THE ELECTROCHEMICALLY MEASURED ACTIVITIES OF METALLIC COMPONENTS IN LIQUID Cu–Ag SOLUTIONS

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ABSTRACT

The activity of copper in the Cu–Ag liquid alloys was studied in a high temperature galvanic cell using calcia stabilized zirconia as a solid oxide electrolyte. Experiments were performed over the temperature range 1150–1300 K and in the range of X_{Cu} from 0.2 to 0.7 mole fraction. The activities were found to exhibit positive deviation from ideal behaviour and agreed well with those reported in literature. The influence of oxygen on the electrochemically measured thermodynamic functions of metallic components was estimated at 1373 K, using previously determined solubility data.

INTRODUCTION

Solid state electrochemical methods become a reliable tool for the determination of the thermodynamic properties of liquid alloys[1–6]. Accurate results can be obtained, provided the following conditions are satisfied:

(a) the solid electrolyte has complete ionic conductivity in the range of P_{O_2} provided by the experiment;

(b) the oxide used for saturation of the liquid alloy is much more stable compared to the oxide of the other component;

(c) there are no side reactions running in the cell;

(d) the solubility of oxygen in the liquid alloy is small.

The thermodynamic properties of liquid copper–silver alloys have been determined by the vapour pressure method by Edwards and Downing[7] and Golonka[8]; calorimetrically by Oriani and Murphy[9] and Dokken and Elliot[10]; and electrochemically by Choudary and Ghosh[6]. However, in a subsequent study, an assumption was made that the solubility of oxygen in liquid copper–silver alloys is below 1 at.%. As pure copper and pure silver exhibit a large oxygen solubility range at elevated temperatures, one may expect a similar effect to take place in the case of the alloy. The solubilities of oxygen in liquid copper–silver alloys were determined in the previous paper[11]. The present work, in which a solid electrolyte galvanic cell was used to determine the copper activity in the Cu–Ag liquid alloy, was undertaken to study the influence of oxygen solubility on the electrochemically determined activities of metallic components.

EXPERIMENTAL

Principle

The cell used in this study was

$$Cu_{(s)}, Cu_2O_{(s)}/ZrO_2 + CaO/Cu + Ag_{alloy(l)}, Cu_2O_{(s)} \tag{1}$$

giving the electromotive force equal to

$$E = \frac{RT}{4F} \ln \left(\frac{P''_{O_2}}{P'_{O_2}}\right) \tag{2}$$

where P'_{O_2} and P''_{O_2} are the partial pressures of oxygen on the right- and left-hand side of the cell, respectively, and they are fixed by the reaction

$$4\ Cu(\text{solid or in alloy}) + O_{2(g)} = 2\ Cu_2O_{(s)} \tag{3}$$

In both cases, the equilibrium constant K is equal to

$$K = \frac{a^2_{Cu_2O}}{a^4_{Cu} P_{O_2}} \tag{4}$$

Choosing pure liquid copper as the reference state and taking into account that Cu_2O remains solid under experimental conditions on both sides of the cell, the equilibrium constant K is equal to

$$K = \frac{1}{P''_{O_2}} \tag{5}$$

in the case of the Cu_2O formation from pure components and consequently

$$K = \frac{1}{a^4_{Cu} P'_{O_2}} \tag{6}$$

in the case of the Cu_2O formation from the alloy.

Combining eqns. (2), (5) and (6) one obtains

$$-FE = RT \ln a_{Cu} = \Delta\bar{\mu}_{Cu} \tag{7}$$

The activity of copper can now be calculated from the measured e.m.f. of the cell at constant T. Under experimental temperature and oxygen partial pressure ranges a zirconia based electrolyte has been reported to be a pure ionic conductor[1 2]. Also, since the difference in the standard free energy of the formation of Cu_2O and Ag_2O oxides is large in the range of temperatures and concentrations employed in this study, any exchange reaction of the type

$$2\ \underline{Ag} + Cu_2O \rightarrow 2\ \underline{Cu} + Ag_2O \tag{8}$$

is not likely to occur.

Materials

Pure copper MOOB and pure silver were obtained from Polskie Odczynniki Chemiczne, Poland, and were 99.99% and 99.2% pure, respectively. The solid electrolyte tubes, fully stabilized, were obtained from Yamari Trading Co., Japan, while cuprous oxide obtained from Baker's Chemical Co. was 99.2% pure. Argon gas was 99.998% pure. Chromium cermet was supplied by Morgan Refractories Ltd., England.

Apparatus and measurements

Experiments were performed in a resistant furnace obtained from Metals Research Ltd., England. The cell was kept in the mullite tube of the furnace. The internal cell arrangement is shown in Fig. 1. About 50 g of the Cu–Ag alloy was held in an alumina crucible, which was placed in the constant temperature zone of the furnace about 10 cm long. Both ends of the tube were closed with water-cooled brass heads. The brass head on the top held different tubes going into the cell and permitted electrical connections. The metal–metal oxide mixture for the reference electrode was prepared by mixing equimolar fractions of Cu and Cu_2O powders, and then packing them into the bottom of the electrolyte tube. The Cu + O phase diagram[13] shows that the solubility of oxygen in solid copper in equilibrium with Cu_2O is negligibly small in the temperature range under investigation. A platinum lead wire was inserted into the powder. The electrolyte tube was attached to a tight-fitting alumina tube by

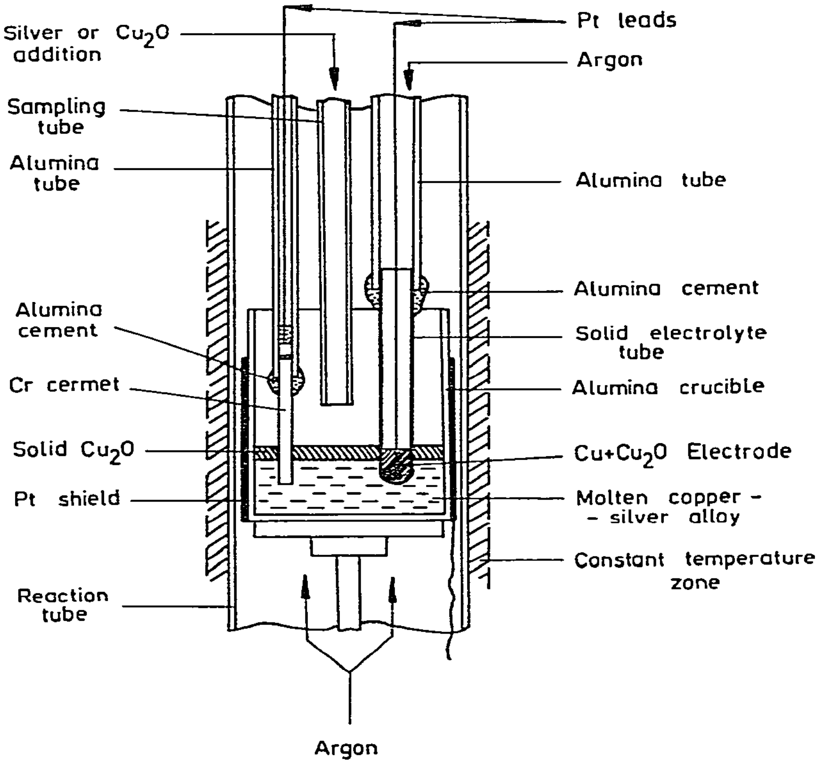

Fig. 1. Cell used to measure e.m.f. in liquid alloys.

means of alumina cement. This tube was suspended on a brass head. The conducting lead, made of chromium cermet, was arranged in a similar manner. It was about 35 mm long and was pre-oxidized before experiments in air at 1200°C. An inert atmosphere was maintained by flushing the furnace tube with argon which had been purified by passing it over copper and titanium chips at 450 and 800°C, respectively.

After the alloy charge had been melted at constant temperature, the liquid alloy was saturated with oxygen by the addition of Cu_2O pellets. The steady e.m.f. value was obtained about 2 h after addition. The reversibility of the cell was checked by passing a small current through the cell. Then, the e.m.f. value was recorded and the temperature was changed. The temperature cycling was done up and down in the range 1150–1300 K. E.m.f.s were recorded at intervals of 1 h by means of the V 534 digital voltmeter obtained from Elwro, Poland and after a full cycle had been

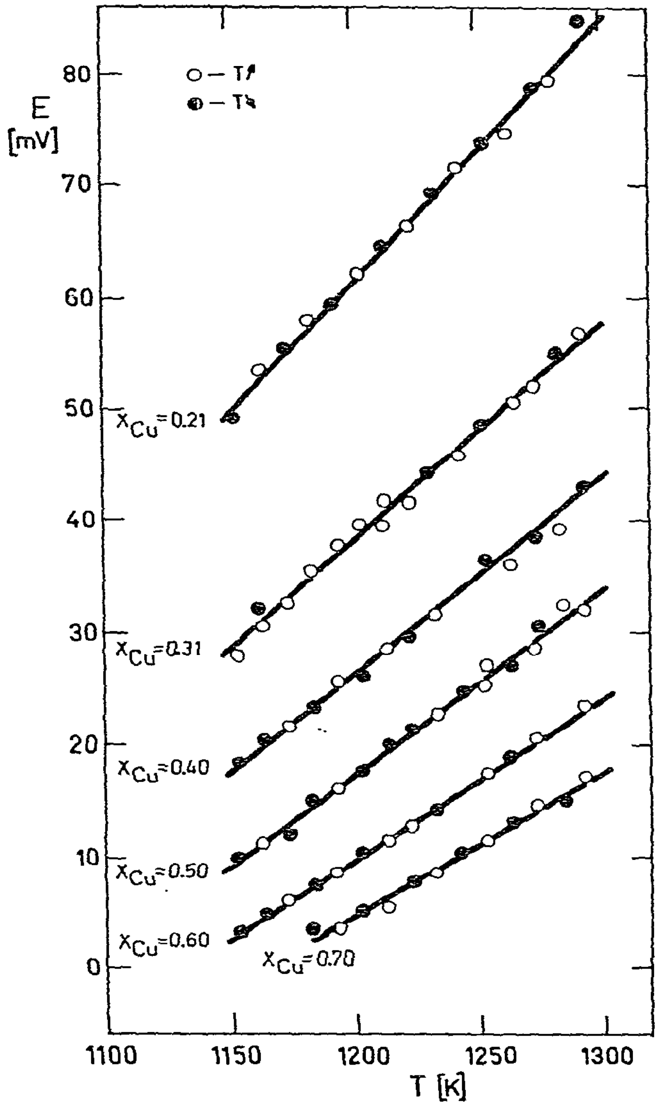

Fig. 2. The experimentally measured Cu–Ag cell e.m.f.'s as a function of temperature.

completed, the sample was withdrawn from the bath and the composition of the alloy was changed by the addition of silver. The procedure was then repeated.

RESULTS

The e.m.f., measured for investigated compositions as a function of temperature in the Cu–Ag system, is plotted in Fig. 2. It was found to be a linear function of temperature and equations of the type $E = A + BT$ representing these lines obtained by the least squares method along with standard deviations are presented in Table 1. The cell e.m.f.s gave partial quantities for copper by making appropriate corrections for fusion values of copper, as shown below

$$\Delta\bar{\mu}_{\mathrm{Cu}} = -EF - \Delta\mu_{\mathrm{f}} \tag{9}$$

$$= -F(A + BT) - (\Delta H_{\mathrm{f}} - T\Delta S_{\mathrm{f}})$$

$$= (-FA - \Delta H_{\mathrm{f}}) - T(FB - \Delta S_{\mathrm{f}})$$

Consequently

$$\Delta\bar{H}_{\mathrm{Cu}} = -FA - \Delta H_{\mathrm{f}} \tag{10}$$

$$\Delta\bar{S}_{\mathrm{Cu}} = FB - \Delta S_{\mathrm{f}} \tag{11}$$

where $\Delta\bar{\mu}_{\mathrm{Cu}}$, $\Delta\bar{S}_{\mathrm{Cu}}$ and $\Delta\bar{H}_{\mathrm{Cu}}$ are partial free energy, entropy and heat of solution, respectively. Fusion values for copper were taken from Hultgren's et al. compilation[14] and the free energy change of the reaction

$$\mathrm{Cu}_{(s)} \rightarrow \mathrm{Cu}_{(l)} \tag{12}$$

is equal to

$$\Delta\mu_{\mathrm{f}} = 3120 - 2.3\,T \text{ cal mole}^{-1} \tag{13}$$

TABLE 1

EXPERIMENTAL DATA ON LIQUID Cu–Ag ALLOYS IN THE RANGE 1150–1300 K

X_{Cu}	$E = A + BT$ (mV)
0.21	$E = -221.3 + 0.2355\,T \pm 0.4$
0.31	$E = -193.7 + 0.1933\,T \pm 0.1$
0.40	$E = -183.8 + 0.1751\,T \pm 0.5$
0.50	$E = -180.6 + 0.1650\,T \pm 1.0$
0.60	$E = -163.9 + 0.1447\,T \pm 0.6$
0.70	$E = -152.7 + 0.1311\,T \pm 1.1$

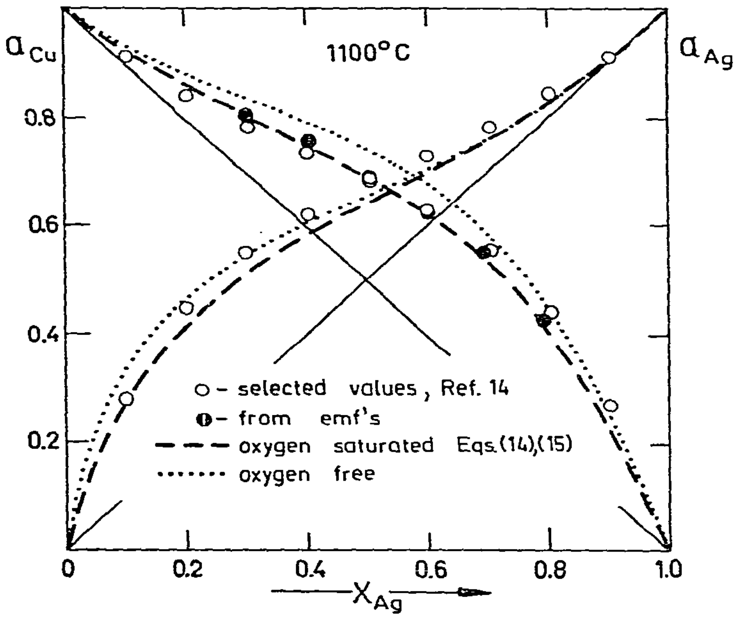

Fig. 3. Activities of silver and copper as functions of the alloy composition at 1100°C.

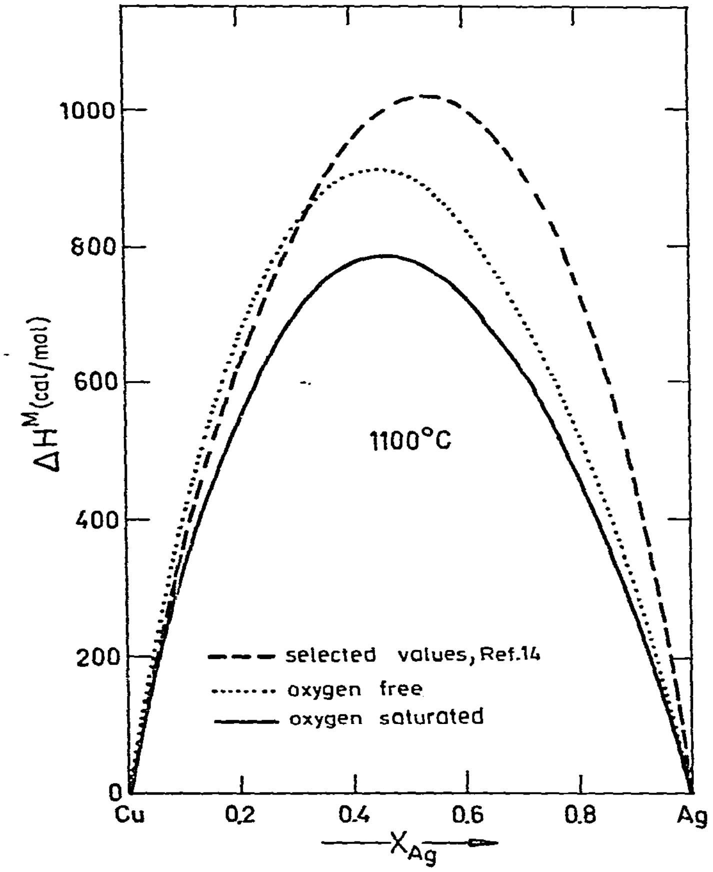

Fig. 4. Integral molar heats of mixing of Cu–Ag alloys at 1100°C.

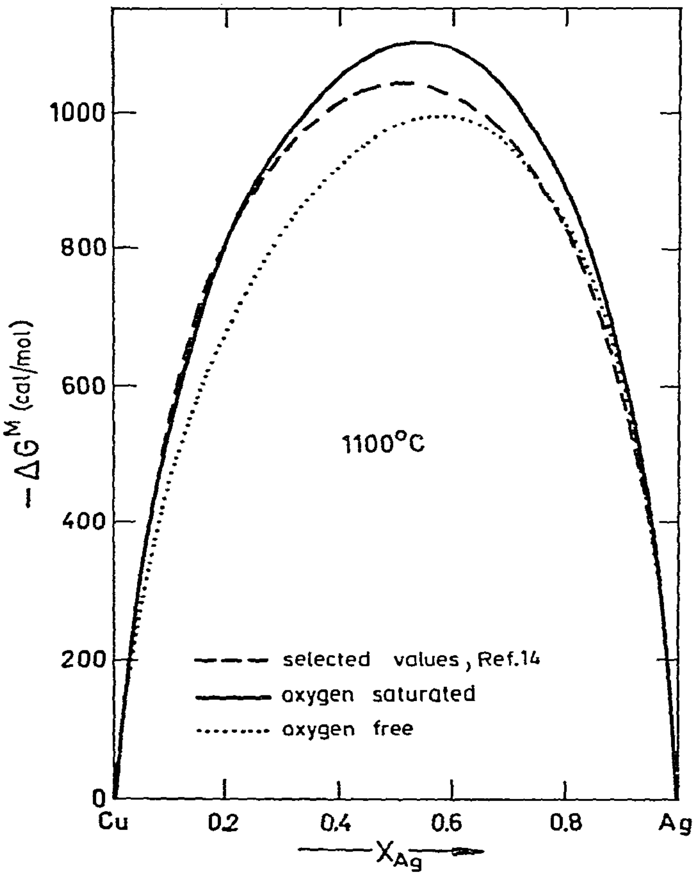

Fig. 5. Integral molar free energies of mixing of Cu–Ag alloys at 1100°C.

The activities of Cu at 1373 K were calculated from eqns. (7) and (9), and presented graphically in Fig. 3 in comparison with those evaluated by Hultgren et al.[14]. It is clear from Fig. 3, that they exhibit positive deviation from Raoult's law. Partial thermodynamic quantities for silver were determined using Krupkowski's method[15]*. It was shown previously[16, 17] that this method describes thermodynamic properties of metallic solutions adequately if they exhibit positive deviation from the ideal solution model. Moreover, it was shown by Krupkowski[18] that application of this equation does not require investigation performed over the whole range of compositions of the alloy. Using the usual procedure[15], expressions for the logarithm of the activity coefficient of copper and silver were established as follows

$$\ln \gamma_{Cu} = \left(\frac{1416}{T} + 0.016\right) X_{Ag}^{1.67} \tag{14}$$

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* A general form of Krupkowski's equations for a binary solution is as follows

$$\ln \gamma_i = \omega(T)\, X_j^m;\ \ln \gamma_j = \omega(T) \left(X_j^m - \frac{m}{m-1} X_j^{m-1} + \frac{1}{m-1} \right)$$

where $\omega(T) = (\alpha/T) \pm \beta$.

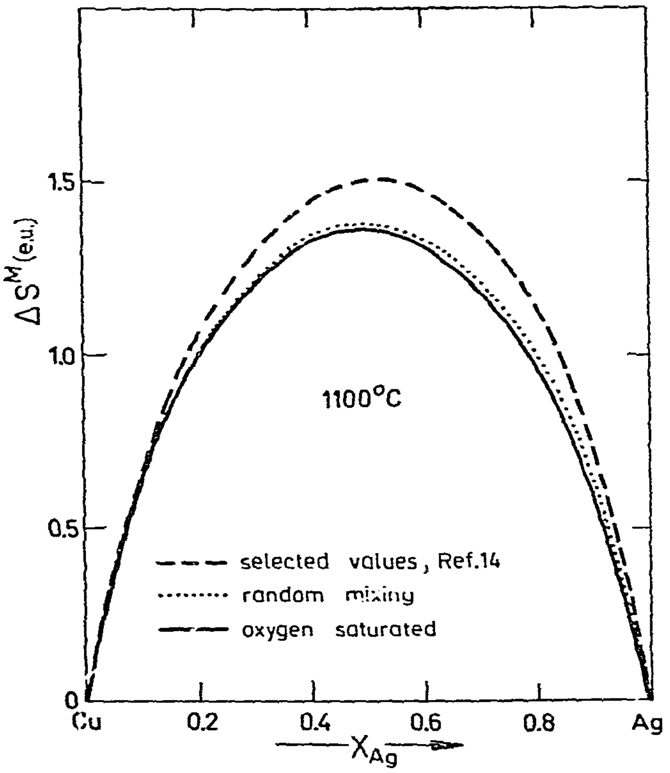

Fig. 6. Integral molar entropies of mixing of Cu–Ag alloys at 1100°C.

$$\ln \gamma_{Ag} = \left(\frac{1416}{T} + 0.016\right)\left(X_{Ag}^{1.67} - 2.4925\, X_{Ag}^{0.67} + 1.4925\right) \qquad (15)$$

Equations (14 and 15) enabled us to calculate all thermodynamic quantities of liquid Cu–Ag alloys. An integral heat of mixing, free energy of mixing, entropy of mixing and activities at 1100°C are shown by solid line and compared with those selected by Hultgren et al.[14] in Figs. 3–6.

ESTIMATION OF THE OXYGEN INFLUENCE

A comparison of the results obtained with those selected by Hultgren et al.[14] reveals that thermodynamic functions differ from calculated values on the basis of e.m.f. measurements. It was shown previously[19] that oxygen may affect the value of the activity coefficient of the metallic component in dilute solution.

Choudary and Chang[20] derived a general relation that incorporated the effect of oxygen solubility on the logarithm of the activity coefficients of metallic components in the alloy over the whole composition range. In the case of the Cu–Ag system it takes the form

$$\ln \left(\frac{\gamma_{Ag}}{\gamma_{Cu}}\right)_{\substack{X_{Ag} \\ X_O = X_O^*}} = \ln \left(\frac{\gamma_{Ag}}{\gamma_{Cu}}\right)_{\substack{X_{Ag} \\ X_O = 0}} + X_O^* \left(\frac{\partial \ln \gamma_O^{Ag}}{\partial X_{Ag}}\right)_{X_{Ag}} \qquad (16)$$

where X_0^* denotes the mole fraction of oxygen in a saturated Cu–Ag alloy.

Since eqns. (14 and 15) represent a saturated solution, it is possible to establish a similar expression for an oxygen-free alloy.

After rearrangement of eqn. (16) and insertion of the functional dependences of types (14) and (15) into eqn. (16) one may obtain

$$\omega^0(T)\left(\frac{1}{m^0-1}-\frac{m^0}{m^0-1}X_{\mathrm{Ag}}^{m^0-1}\right)=\omega(T)\left\{\mathrm{F}\left(X_{\mathrm{Ag}}\right)\right\}-\Delta \tag{17}$$

Both parameters $\omega^0(T)$ and m^0 at the left hand side of eqn. (17) characterize an oxygen-free metallic solution and it is obvious that they changed simultaneously due to the presence of oxygen in the melt. However, the problem may be solved as follows:

To begin with, the right-hand side of eqn. (17) is determined because terms

$$\omega(T)=\frac{1416}{T}+0.016$$

$$\mathrm{F}\left(X_{\mathrm{Ag}}\right)=\left(\frac{1}{m-1}-\frac{m}{m-1}X_{\mathrm{Ag}}^{m-1}\right)\text{ for } m=1.67,$$

and

$$\Delta=X_0^*\left(\frac{\partial\ln\gamma_0^{\mathrm{Ag}}}{\partial X_{\mathrm{Ag}}}\right)_{X_{\mathrm{Ag}}}$$

can be calculated at constant temperature and X_{Ag}. Next, one may avoid the unknown parameter $\omega^0(T)$ in eqn. (17) by dividing the eqns. one by another for different alloy compositions at constant T, e.g.

$$\left(\frac{\dfrac{1}{m^0-1}-\dfrac{m^0}{m^0-1}(0.7)^{m^0-1}}{\dfrac{1}{m^0-1}-\dfrac{m^0}{m^0-1}(0.6)^{m^0-1}}\right)=\frac{\omega(T)\{\mathrm{F}(0.7)\}-\Delta}{\omega(T)\{\mathrm{F}(0.6)\}-\Delta} \tag{18}$$

Finally, parameter m^0 can be established numerically as the right-hand side of expression (18) is a known constant value. Then, coming back to eqn. (17), parameter $\omega^0(T)$ can be calculated for a previously established value of m^0.

Calculations have been performed at 1100 °C for $X_{\mathrm{Ag}}=0.7$; 0.6; 0.5 and 0.4. At this temperature $\omega(1373)=1.047$ and m being independent of temperature is equal to 1.67. The term Δ has been calculated using saturation solubility determined previously[11], while a derivative $(\partial\ln\gamma_0^{\mathrm{Ag}}/\partial X_{\mathrm{Ag}})_{X_{\mathrm{Ag}}}$ has been calculated graphically from the results of Fruehan and Richardson's[21] and Jacob and Jeffes'[22]. Mean values of m^0 and $\omega^0(1373)$, obtained in this way, are equal to 1.51 and 1.145, respectively.

Using these parameters, activities of copper and silver have been recalculated and are shown by dotted lines in Fig. 3, as well as ΔG^{M} (Fig. 5). As calculations were restricted to only one temperature, 1100 °C, it is difficult to follow the change of parameters α and β of the $\omega(T)$ function affecting the variation of heat and entropy change with composition. Fortunately, the integral entropy change does not differ significantly from a random mixing value. The excess entropy is small (i.e. small value of β) and it seems reasonable to assume that $\beta^0 - \beta \simeq 0$. Consequently

$$\omega^0(T) - \omega(T) = \frac{\alpha^0 - \alpha}{T} \tag{19}$$

(a situation that corresponds to regular solution model) and the recalculated value of α^0 at 1100°C is equal to

$$\alpha^0 = \alpha + [\omega^0(T) - \omega(T)]T = 1550 \tag{20}$$

An estimated change of the heat of mixing shown by the dotted line in Fig. 4 resulted from the change of α to α^0, as well as from the change of the asymmetry parameter m to m^0.

DISCUSSION

The determined values of thermodynamic functions in the liquid Cu–Ag system are found to be in reasonable agreement with those selected by Hultgren et al.[14]. The change in values under the influence of oxygen is visible. Deviation of the activity curve is similar to that obtained by Choudary and Chang[20] in the case of the Cu–Pb alloy. It is seen from Fig. 3 that due to the presence of oxygen, the behaviour of metallic components becomes more ideal. As thermodynamic properties of metallic alloys have been linked with the free electron theory since Varley's work[23] one may seek the answer to the problem in the oxygen–electron gas interaction. It was demonstrated that the heat effect of oxygen dissolution in the liquid alkali metals may be estimated under assumption that oxygen dissolves as the negative ion due to its interaction with the outer shell electrons of metallic ions[24, 25]. Probably the same process takes place in the case of the liquid alloy. When more and more oxygen negative ions enter the solution during the dissolution process they will influence the charge transfer between metallic bands affecting the resulting heat of mixing.

It was shown that in the saturated metallic solutions the presence of oxygen (and probably the other non-metals) may influence activities of metallic components. Therefore, carrying on e.m.f. measurements by means of the solid oxide galvanic cell one should take this effect into account.

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