Structure and properties of dental casting gold alloys

II. Emf-measurements using stabilized ZrO_2 as solid electrolyte as a means of studying cluster formation in gold-copper alloys

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The existence of complexes (clusters) in the alloy system Au-Cu was studied through determination of the copper activity for 14 different compositions at temperatures around 1100 K. The experimental data were obtained from emf measurements using stabilized ZrO_2 as the solid electrolyte. Using an equilibrium calculation method the relative amounts of »free» gold, of »free» copper and of complexes were indicated. The best fit to experimental data was obtained with a model assuming the existence of the complexes Cu_3Au, CuAu, $CuAu_3$ and $CuAu_9$.

Key-words: Gold; copper; alloys

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A previous study (*Bergman, Holmlund & Ingri*, 1972) determined the face-centered cubic unit cell length of solid solutions of gold, silver and copper within a composition range of interest for dentistry. To be able to explain the experimentally determined cell length as a function of the alloy composition, the existence of clusters (complexes) was suggested. Their compositions and relative amounts could be indicated using an equilibrium method. As concerns the binary Au-Cu alloy system a model with the three complexes Au_3Cu, AuCu and $AuCu_3$ was found to give the best fit to the experimental data. To explain experimental data obtained for the ternary Au-Ag-Cu system, a fourth complex Au_3Ag had to be introduced.

In the same study, some property data from this proposed model were compared with results from other types of measurements. Among these the data of activity measurements in solid solutions were of particular interest. *Wagner & Engelhardt* (1932) measured the potential of the cell Cu/CuCl, KCl(l)/(Cu, Au) for different compositions of the alloy electrode at different temperatures. *Trondsen & Bolsaitis* (1970) used the cell

Pt, O_2(g), Cu (in alloy), Cu_2O ||ZrO_2(CaO)||Cu_2O, Cu (pure), O_2 (g), Pt

and measured the potential, mainly in the copper-rich part of the alloy system at temperatures between 720° C and 920° C. The agreement indicated by the results of these two emf studies and

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corresponding calculated data from the proposed cluster model was an inducement to undertake further studies. In the present work further measurements of the activity of copper in Au-Cu alloys have been carried out to obtain reliable data over a broad composition range for testing the proposed cluster model. The activity determinations were based upon the emf measurement method using stabilized ZrO_2 as the solid electrolyte, which method was considered as the most suitable one.

The measurements were carried out at temperatures around 1100 K because this temperature range is of particular interest as regards the heat treatment of dental casting gold alloys.

As cluster formation may influence many of the physical properties of an alloy, *e.g.* conductivity, hardness, tensile strength, a detailed knowledge of the cluster formation in a dental casting gold alloy is of great importance. (Au, Cu) is one of the basic alloy systems in these alloys and any cluster formation within this system is of interest. Among the phases which have been suggested in the Au-Cu alloy system at temperatures below about 400° C, Cu_3Au and CuAu can be regarded as well established from many previous studies (*Hansen & Anderko* 1958). The existence of ordered phases such as $CuAu_3$ and Cu_3Au_2 are also suggested, although with less evidence. From several works (*e.g. Germer et al.*, 1942; *Ogawa & Watanabe*, 1952; *Greenholz & Kidron*, 1970; *Bergman et al.*, 1972) there are indications of short-range ordering also at higher temperatures.

It has already been pointed out in a previous study (*Wagner & Engelhardt*, 1932) that in the Au-Cu alloy system certain difficulties arise in the gold-rich region of the system, for which consequently few measurements have been carried out. However, as this region is of particular interest as regards the dental gold alloys, the present study aimed to obtain measuring points from this part of the alloy system.

MATERIALS AND METHODS

Metals and metal oxides used. Binary gold-copper alloys with the compositions given in Table I were prepared using metal wires with a diameter of 0.5 mm; the purity for gold was 99.95 % (*Nyström & Matthey*, England) and for copper 99.90 % (Cu, type SM-0010-02 Svenska Metallverken, Sweden). Copper powder and Copper (I) oxide (Merck p.a., Germany) and Copper (II) oxide (Fisher p.a., U.S.A.) were used in testing the reference systems $Cu\text{-}Cu_2O$ and $CuO\text{-}Cu_2O$. Platinum foils and wires were delivered from Platinaverken, Sweden.

Specimen preparation. The metals were weighed and melted together in an inert atmosphere as described in a previous paper (*Bergman, Holmlund & Ingri*, 1972). The melt was kept at 1100° C for fifteen minutes, slowly cooled to 800° C in the furnace and then quenched in water.

Immediately before a run the solid solutions were heat treated for six hours at 800° C in an argon atmosphere and then quenched in water at room temperature. Powder specimens were prepared using an air-cooled dental coromant bur. Most of the specimens were checked by X-ray powder diffraction ($CuK\alpha$ radiation, Guinier-Hägg camera) and no extra lines besides those from the fcc (Au, Cu) alloy could be detected.

Emf measurements. In order to determine the activity of Cu in Cu-Au alloys the following cell was used:

$Pt,O_2(g)$, Cu(in alloy), $Cu_2O||ZrO_2(CaO)||O_2$(air), Pt

The solid electrolyte which provides pure oxygen anion conduction consists of a solid solution of 10 mole per cent CaO in ZrO_2. In the ZrO_2 structure, Ca^{2+} ions can replace Zr^{4+} ions and as a result O^{2-} ion vacancies are formed, which easily become mobile at higher temperatures (*e.g. Kiukkola & Wagner*, 1957; *Sato*, 1971).

In the cell there are two platinum electrodes situated on each side of the solid electrolyte tube. If the partial pressures of the oxygen are the same at both electrodes no reaction can occur. However, if the partial pressure of oxygen is higher at one electrode, O^{2-} ions will move from this electrode to the other one. The electrode reactions for this concentration cell can be written:

+ pole: $O_2(air) + 4e^- \rightarrow 2O^{2-}$

electrolyte: O^{2-} migration

— pole: $2O^{2-} \rightarrow O_2$ (sample) $+ 4e^-$

Electrode process: $O_2(air) \rightarrow O_2$ (sample)

By connecting the electrodes with a potentiometer which has a high input resistance the existing potential difference, E, can be measured. This measured value, E, is related to the partial pressures of oxygen as follows:

$$E = -\frac{RT}{4F}\ln\frac{p_{O_2}}{p^*_{O_2}} \qquad (1)$$

where R is the gas constant, T the absolute temperature, F the Faraday constant, p_{O_2} the oxygen partial pressure of the sample and $p^*_{O_2}$ the oxygen partial pressure in air (= 21.23 kPa).

Cell arrangement and operation. In the present study the cell arrangement shown in Fig. 1 was used. The ceramic tubes and crucibles were Degussit AL 23 quality containing more than 99.5 % Al_2O_3. The zirconium tube was of the type Degussit ZR 23 (Degussa, Germany) with an outer diameter of 6 mm, inner diameter of 3 mm and, 600 mm in length. A Pt-Pt (10 mass % Rh) thermocouple was used for the temperature measurements. The pure Pt-wire of the thermocouple was used as one of the cell electrodes, see Fig. 1. The high input resistance potentiometer sensitive to 1 μV (Data Precision, series 2000 Digital Multimeter; Model 2520) was connected to the cell by shielded cables to avoid picking up stray potentials.

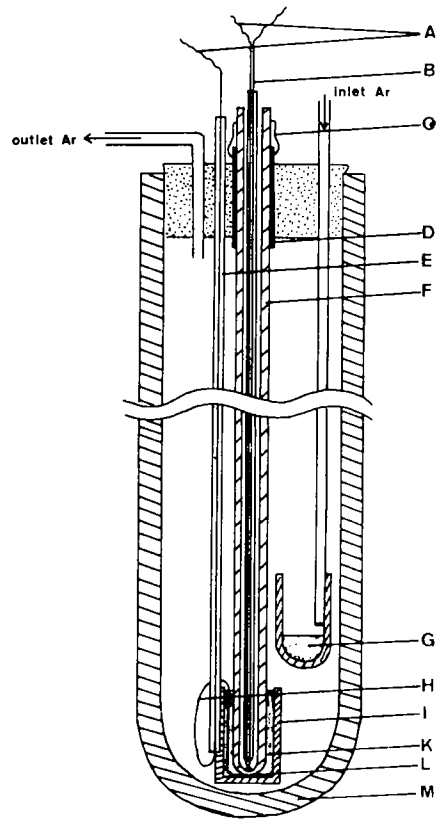

Fig. 1. The experimental set-up
A = Pt wires. B = Pt(10 mass % Rh) wire. C = teflon tape. D = glass tube. E = suspending Al_2O_3 capillary. F = ZrO_2(CaO) tube. G = pre-reactor with sample. H = Pt electrode wire. I = Al_2O_3 crucible. K = sample mixture. L = Pt foil. M = external Al_2O_3 tube; the bottom is kept in the centre of the furnace.

The reaction temperature of the electrically heated vertical tube furnace was regulated by a variable voltage transformer. At the bottom of the crucible (10 mm in diameter and 15 mm high) containing the sample was placed a Pt foil with an average weight of 6 mg in close contact with the second Pt electrode. The outer side of the closed end of the ZrO_2-tube was ground from the original thickness of 1.5 mm to about 0.8 mm. In this way the diffusion distance for oxygen ions across the electrolyte was reduced which contributed to a shortening of the time needed to reach equilibrium. The same tube end was then platinized using chloro-platinic acid. A very small coil of Pt-wire (diameter 0.1 mm) was put into the ZrO_2 tube in close contact with the joint of the termocouple at the bottom. These steps reduced to a large extent the resistence within the cell which in the region 1100 K was $2 - 30$ kΩ.

The cell was assembled by inserting the zirconium tube into the cell crucible in close contact with the platinum electrode at the bottom. The remaining free volume of the crucible was then carefully packed with a mixture of about one gram of the (Au, Cu) alloy powder and Cu_2O. The cell was then put into the cold furnace.

The ZrO_2 tube passed freely inside a glass tube through the rubber stopper at the top of the furnace tube. The use of Teflon-tape provided a gas-tight seal between the glass tube and the ZrO_2 tube. The capillary tube suspending the emf Pt wire was sealed in the same way.

During each run a continuous stream of inert gas (argon, AGA quality SR) passed through the furnace tube. The gas was purified by passing it over active copper at about 180° C and dried by passing it through concentrated sulphuric acid before it was led into a prereactor situated immediately above the cell, see Fig. 1. A powder mixture of the same type as in the cell was put into this prereactor. In this way the gas was pre-equilibriated before reaching the sample within the cell.

This procedure was undertaken because some tentative measurements had indicated creep in the emf-values due to oxygen pressure gradients due to the fact that the oxygen pressure level of the inflowing inert gas deviates from the equilibrium level. The gas flow during a run was about 10 ml per minute. At the end of the gas outlet the gas was bubbled through sulphuric acid to keep the system under a small positive pressure and prevent back diffusion.

A typical run was started by allowing the gas to flush into the furnace tube for at least six hours at room temperature before the heating of the furnace was begun. The gas stream was then reduced to about 10 ml per minute and the temperature of the furnace was slowly raised over 16—18 hours to about 50 K below the solidus temperature of the alloy in question. When the cell had reached a steady potential at this temperature readings of the emf and temperature were started. Emf readings were continuously taken down to about 1050 K during a period which was extended to about ten hours. Between each reading enough time was left to reach equilibrium. Stable potentials were in general attained more rapidly at higher temperatures than at lower temperatures. The reproducibility of the emf values was $\pm$ 2 mV or better. If the cell was also allowed to work the following day a constant drift in the emf readings was sometimes observed and therefore emf values from the first day only were used.

The reference system Cu—Cu_2O was measured several times during the progress

of the present study. The value of E for pure Cu was needed for the calculations but was also used for testing the experimental set-up after changes or replacements of parts of the equipment. In addition the set-up was tested by emf measurements of the system CuO-Cu_2O. The equipment had also been tested by measurements against air, giving an emf equal to zero, as expected.

CALCULATIONS

Relation between copper activity and emf values

In the present study the equilibrium reaction

$$2\ Cu\ (\text{in alloy}) + 1/2\ O_2(g) \rightleftharpoons Cu_2O(s) \quad (I)$$

was studied by determination of p_{O_2} for various alloy compositions. The law of mass action gives the following relationship

$$a_{Cu}^{-2} \cdot p_{O_2}^{-1/2} = K$$

or, in logarithmic form

$$\log a_{Cu} = -1/4 \log p_{O_2} - \tfrac{1}{2} \log K \quad (2)$$

where a_{Cu} is the activity of Cu in the (Au, Cu) alloy, and K the equilibrium constant for reaction (I). From measurements with pure Cu ($a_{Cu} = 1$), the value of $\log K$ can be determined according to the expression

$$\log K = -\tfrac{1}{2} \log p'_{O_2} \quad (3)$$

where p'_{O_2} is the equilibrium oxygen pressure in the case of pure Cu. By inserting equation (3) into equation (2), the following relationship will be obtained:

$$\log a_{Cu} = 1/4\ [\log p'_{O_2} - \log p_{O_2}] \quad (4)$$

The following relationships are valid for the cell, cf. equation (1):

$$E\ (\text{pure Cu}) = -\frac{RT \ln 10}{4\ F}\ [\log p'_{O_2} - \log p^*_{O_2}] \quad (5a)$$

$$E\ (\text{alloy}) = -\frac{RT \ln 10}{4\ F}\ [\log p_{O_2} - \log p^*_{O_2}] \quad (5b)$$

giving

$$\Delta E = E\ (\text{pure Cu}) - E\ (\text{alloy}) = -\frac{RT \ln 10}{4\ F} (\log p'_{O_2} - \log p_{O_2}) \quad (6)$$

By use of equations (4) and (6), the following equation is derived:

$$\log a_{Cu} = -F\,(RT \ln 10)^{-1} \cdot \Delta E \quad (7)$$

The alloy is considered to behave as an *ideal* mixture of »free» copper, »free» gold and the complexes Cu_pAu_q and hence $a_{Cu} = x_{Cu}$. Thus, the E-values measured permit determination of the content of »free» copper, x_{Cu}.

Calculation of the equilibrium constants β_{pq}

To obtain a structural explanation of activity data determined, a least squares treatment including various structural models was used. The general assumptions for these calculations will be outlined:

The mass balances can be written

$$n^*_{Cu} = n_{Cu} + \Sigma p \cdot n_{pq} \quad (8)$$

$$n^*_{Au} = n_{Au} + \Sigma q \cdot n_{pq} \quad (9)$$

where n^*_{Cu} and n^*_{Au} represent the original weighed amounts of copper and gold; n_{Cu}, n_{Au} and n_{pq} represent the amounts at equilibrium of free copper, free gold and complexes; p and q are the integers indicating the atomic composition of the complex Cu_pAu_q.

By dividing the terms in equations (8) — (9) with the total number of moles Σn_i, the following equations are obtained:

$$\frac{n^*_{Cu}}{\Sigma n_i} = x_{Cu} + \Sigma p \cdot x_{pq} = X_{Cu} \quad (10)$$

$$\frac{n^*_{Au}}{\Sigma n_i} = x_{Au} + \Sigma q \cdot x_{pq} = X_{Au} \quad (11)$$

where X_{Cu} and X_{Au} are the mole fractions of total Cu and Au, x_{Cu} and x_{Au} repre-

sent the mole fractions of free copper and free gold and x_{pq} the mole fraction of a complex. The value x_{pq} is related to x_{Cu} and x_{Au} according to the expression

$$x_{pq} = \beta_{pq} \cdot x_{Cu}^{p} \cdot x_{Au}^{q} \quad (12)$$

where β_{pq} is the equilibrium constant for the formation of the complex Cu_pAu_q. Equation (12) is based upon the law of mass action and assuming the alloy to be an ideal solution with Cu, Au and various Cu_pAu_q complexes as constituents. By use of equation (12), equations (10) and (11) can be written

$$X_{Cu} = x_{Cu} + \Sigma p \cdot \beta_{pq} \cdot x_{Cu}^{p} \cdot x_{Au}^{q} \quad (13)$$

$$X_{Au} = x_{Au} + \Sigma q \cdot \beta_{pq} \cdot x_{Cu}^{p} \cdot x_{Au}^{q} \quad (14)$$

By systematic search, the model (i.e. set of (p, q) values) giving the best fit to experimental data could be indicated. This systematic calculation procedure was carried out using the computer program LETAGROP (*Ingri & Sillén*, 1964; *Arnek et al.*, 1969; *Brauner et al.*, 1969). The best model was the one that gave the lowest error squares sum $U = \Sigma(Z(\text{calc}) - Z(\text{exp}))^2$, where Z indicates the average number of »bound» Cu (Cu existing in the complexes) per Au. The two Z quantities used are defined

$$Z(\text{calc}) = \frac{X_{Cu}(\text{calc}) - x_{Cu}}{X_{Au}}$$

$$Z(\text{exp}) = \frac{X_{Cu} - x_{Cu}}{X_{Au}}$$

where $X_{Cu}(\text{calc})$ is calculated according to equation (13).

In the present study, the calculation procedure had to be somewhat modified, due to adjustments necessary for the total amounts of Cu and Au. As the quantity $\Sigma n_i = n_{Cu} + n_{Au} + \Sigma n_{pq}$ is an unknown parameter, which depends on the degree of the complex formation in the alloy, it follows from equations (10) and (11) that X_{Cu} and X_{Au} have to be corrected. For a definite set of (p, q) values »true» values of X_{Cu} and X_{Au} could be obtained from an iterative procedure as follows:

1. As a first step Σn_i was put equal to $(n_{Cu}^{*} + n_{Au}^{*})$ and approximate values $X_{Cu} = n_{Cu}^{*}/\Sigma n_i$ and $X_{Au} = n_{Au}^{*}/\Sigma n_i$ were used in the Letagrop input and, as usual, guessed β_{pq} values. The Letagrop calculations then give improved values of β_{pq}, say β'_{pq}.

2. At this stage the value of Σn_i will be adjusted to correspond to the β'_{pq} values. This can be done using the computer program HALTAFALL (*Ingri et al.*, 1967). This procedure implies that the actual values of β'_{pq}, X_{Au} and x_{Cu} are put into the program and the values of x_{Au} and the various x_{pq} will be calculated.

3. With a knowledge of all the x_i values, an improved value Σn_i can be determined according to equation (10) for each alloy composition. Finally, modified values X_{Cu} and X_{Au} are calculated, which are used in the next iteration cycle, starting at point 1.

It was found that 2—3 iteration cycles were sufficient to reach the »true» conditions.

RESULTS

The emf values measured are plotted as a function of temperature for different alloy compositions, see Fig. 2. For each composition, the emf was measured at several (7—15) temperatures, and the data obtained fitted quite well, within 1—2 mV, to a straight line. At 1100 K a value was obtained for the reference system $Cu—Cu_2O$, $E = 418.5 \pm 2$ mV, and for the system $CuO—Cu_2O$, a value $E = 104.4 \pm 2$ mV. These values are in acceptable agreement with those reported by *Charette & Flengas* (1968) which were

Table I. *Basic experimental data at 1100 K and calculated values for Z(exp) and Z (calc)—Z(exp)*

X_{Cu}	E/mV	a_{Cu}	$Z(\text{exp}) \times 10^2$	$(Z(\text{calc})-Z(\text{exp})) \times 10^2$
0.10	171.3	0.07	10.3	6.1
0.20	172.1	0.07	23.2	— 1.6
0.25	189.0	0.09	30.5	— 4.0
0.30	232.0	0.14	36.8	1.5
0.40	265.1	0.20	53.4	7.3
0.45	256.9	0.18	67.3	— 2.9
0.50	269.7	0.21	79.6	— 3.3
0.55	284.0	0.24	93.7	— 5.3
0.60	317.9	0.35	99.1	5.9
0.70	356.0	0.52	121.9	4.6
0.75	370.6	0.60	134.2	1.8
0.80	387.5	0.72	140.3	8.4
0.85	396.2	0.79	157.7	— 1.7
0.90	403.3	0.85	173.5	—11.1
(0.95	409.1	0.91)		

X_{Cu} = mole fraction of copper in the gold-copper alloy;
E/mV = emf obtained at 1100 K; a_{Cu} = the activity of copper in the alloy;

$$Z(\text{calc}) = \frac{X_{Cu}(\text{calc}) - x_{Cu}}{X_{Au}} \text{ and}$$

$$Z(\text{exp}) = \frac{X_{Cu} - x_{Cu}}{X_{Au}}$$

420.6 mV and 102.5 mV respectively. As can be seen from Fig. 2, the slopes of the straight lines are approximately the same except for the compositions $X_{Cu} = 0.30$ and $X_{Cu} = 0.40$ which show a steeper slope.

Table I shows the emf values obtained at 1100 K together with the corresponding values of a_{Cu}, the activity of copper in the alloy. The values of Z(exp) and of Z(calc) — Z(exp) were obtained from the proposed model giving the least error squares sum $U = \Sigma(Z(\text{calc}) - Z(\text{exp}))^2$. As the uncertainty of a calculated value of a_{Cu} is rather large if ΔE is in the region of about 10 mV or less, see equation (7), the measuring point for the Cu alloy with $X_{Cu} = 0.95$ was not included in the calculations. In Fig. 3 are plotted a_{Cu}-values obtained at 1100 K for

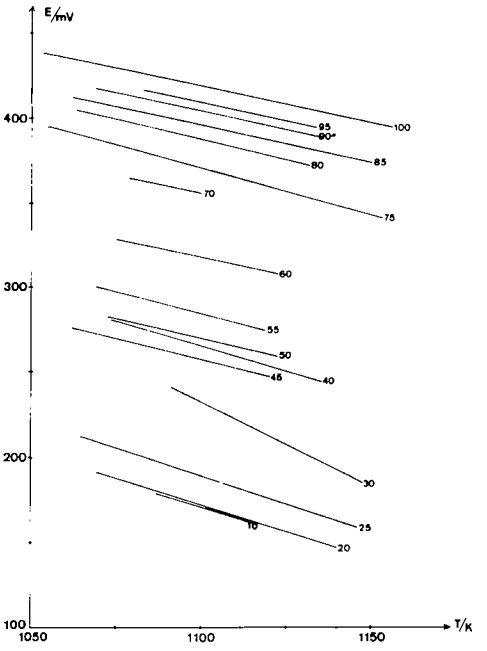

Fig. 2. The emf (E/mV) measured against temperature (T/K) for different mole per cent of copper (X_{Cu}) in the alloy.

various alloy compositions, X_{Cu}. Corresponding results from a previous study (*Trondsen & Bolsaitis*, 1970) are also indicated and their values agree well. However, for alloy compositions with $X_{Cu} < 0.80$ only two values were given in that study.

A great number of models, sets of (p, q) values, were systematically tested. Among these the very best models, *i.e.* those giving the least error squares sums are given in Table II together with corresponding equilibrium constants, as defined by expression (12), and standard deviations $\sigma(\beta_{pq})$. The quantity $\sigma(Z(\text{exp}))$ is the standard deviation of Z in the experimental material.

DISCUSSION

A steady emf of the cell can be reached after equilibrium at all interfaces between the solid electrolyte and the adjacent

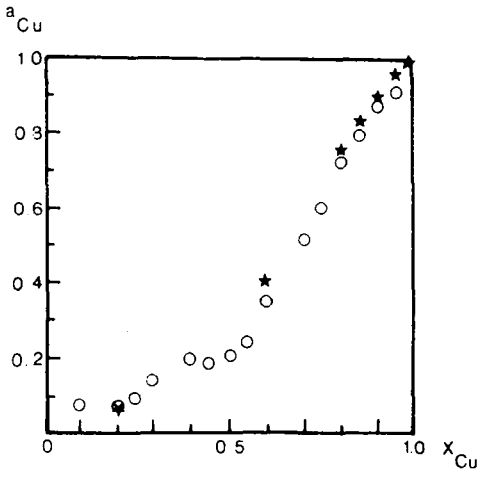

Fig. 3. The activity of copper, a_{Cu}, as a function of the mole fraction of copper, X_{Cu}, at 1100 K. O present study, ★ *Trondsen & Bolsaitis, loc. cit.*

Table II. *Some of the models tested, and the corresponding »best» equilibrium constants*

p	q tested	Error squares sum × 10	$\sigma(Z(\text{exp}))$ $\times 10^3$	β_{pq}	$\sigma(\beta_{pq})$
0	3	1.9	120	$3.0 \cdot 10^7$	$1.1 \cdot 10^7$
1	1			2048	341
3	1			1704	308
1	3	2.1	139	$5.6 \cdot 10^7$	$3.0 \cdot 10^7$
1	1			984	53
3	1			660	80
1	9	0.42	57	$4.3 \cdot 10^{24}$	$2.7 \cdot 10^{24}$
1	3			$1.8 \cdot 10^8$	$0.8 \cdot 10^8$
1	1			2251	150
3	1			1408	29

p, q are the integers indicating the atomic composition of the complex Cu_pAu_q; Error squares sum, $U = \Sigma\ (Z(\text{calc}) - Z(\text{exp}))^2$; β_{pq} are the equilibrium constants, defined by the expression (12), and standard deviations $\sigma(\beta_{pq})$. The quantity $\sigma(Z(\text{exp}))$ is the standard deviation of Z in the experimental material.

phases. With an increasing amount of gold the equilibrium pressure of oxygen will increase (c.f. reaction (I)) and thus the dissociation of the oxide Cu_2O will become more pronounced. Hence the alloy becomes richer in copper, and a drift of the alloy composition will occur. In the present study, a prereactor was used to overcome these problems by pre-equilibriating the inflowing gas. However, a small potential drift could not be avoided if the cell was allowed to work for a couple of days. The emf values for $X_{Cu} = 0.40$ and 0.45 are probably somewhat in error, presumably caused by such a drift. Errors of this type could probably be greatly reduced using a closed system, from which no oxygen could be transferred out of system.

A drift in the emf readings during a particular experiment could also be due to the presence of an oxidizing or reducing impurity in the gas stream. Thermal segregation of the gas phase at stagnation areas can cause the same kind of error. Local temperature differences within the cell could be a source of thermoelectric forces influencing measuring data. However, these sources of error were judged to be minor disturbances in the present study.

After testing a lot of models with various sets of (p, q) values, it was found that models containing only two complexes did not explain experimental data well. As regards three complexes, it turned out that a better fit was obtained, especially for both of the models ((0,3), (1,1), (3,1)) and ((1,3), (1,1), (3,1)). However, there remained some effects located to the points at lower X_{Cu} values. These effects could be explained by introducing a fourth complex with a high Au-content. The very best fit to the total experimental data, including the »best» determination of the complex constants, was obtained for the model with a fourth complex, $CuAu_9$, added to the three complexes Cu_3Au, CuAu and $CuAu_3$. Values for the error squares sum and the complex constants for these models discussed are

given in Table II. A more detailed discussion of these calculations and some structural aspects will be set out in a forthcoming paper (*Bergman et al.*, 1976).

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