THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF GOLD AND SILVER

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In a study of the thermal equilibrium relationships of alloy systems it is frequently found that the customary thermometric methods employed are not sufficiently sensitive to detect transformations of a physical or chemical nature in the solid state when the thermal changes involved are small. When it is suspected that such a change has escaped observation it becomes necessary to complete the investigation by a study of other properties of the alloys. Of the properties suitable for this purpose the electric potential assumed by an alloy in contact with an electrolyte has been promiscuously employed. The disagreement between individual observers and the lack of a critical observance of the limitations of this method have cast it into disrepute as a precise research tool in this field.

In order to obtain electromotive force measurements which will permit of reliable thermodynamic calculations the following very important factors must be considered in determining the choice of materials and in planning the procedure. The alloy electrode must consist of a homogeneous solid solution. If the alloy be heterogeneous in structure local electrolytic actions take place between the micrographic constituents at the surface, resulting in an alteration of the effective composition of the alloy and consequently in a variation of the potential. Unless the precaution is taken of annealing the solid solution for a sufficiently long time just below its melting point, the fractional crystallization which accompanies the solidification of a molten solution will result in an electrode with a surface richer in the higher melting constituent. In this connection it is important to remember that the greater the separation of the liquidus and solidus curves in the equilibrium diagram the longer and more careful an annealing process is required. Perhaps the first effect of annealing is to remove strains produced by unequal velocities of cooling at different parts of the specimen, causing contraction to take place unequally. This factor is of major importance when potential measurements are to be made at room temperature. Even in the case of pure metal electrodes errors of the order of several centivolts may occur.[2] Due to the extremely small diffusion coefficients of metals at low temperatures, e. m. f. measurements must be made by means of small capacity electrostatic instruments such as the quadrant or string electrometer in order to avoid serious polarization effects. An electrolyte should be chosen which will not react with the

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[2] Lewis, THIS JOURNAL, **28**, 158 (1906).

electrodes and containing a sufficiently large concentration of ions of the more electropositive metal. If these precautions are taken and a cell is set up containing a metallic solid solution electrode and a pure metal electrode both immersed in an electrolyte containing ions of the latter, then accurate and reliable potential measurements are possible from which precise thermodynamic calculations can be made.

In this research solid solutions of gold and silver were investigated electrochemically by means of the cell Ag(s)/AgCl(s)/Ag + Au(s. soln.) in the temperature range from 200 to 400° and at mole fractions of silver varying from 1.000 to 0.150. There have been three earlier electrochemical investigations of the gold–silver solid solutions. Tammann[3] studied these alloys in aqueous and molten silver nitrate. His methods are open to criticism on many of the points mentioned above. Ölander[4] made a careful investigation of the cell Ag(s)/AgCl + KCl(l)/Ag + Au(s. soln.) from 400 to 625° over a wide composition range. Wagner and Englehardt,[5] employing the experimental technique described by Ölander, have measured the potentials of the same cells from mole fraction 1.000 to 0.0825 of silver and from 410 to 1085°. Reference will be made later to the results of these last two investigations.

Experimental Part

In the preliminary experimental work the electrodes were immersed in several different electrolytes at widely different temperatures. Among those tried were silver nitrate in aqueous and alcoholic solution at room temperature, pure fused silver nitrate, molten solutions of silver nitrate in a mixture of potassium and sodium nitrates, and pure fused silver chloride. The nitrate electrolytes were especially unsatisfactory, probably due to their reaction with the electrodes. While fused silver chloride was much better it was found that the e. m. f. of the cells changed slowly with time. This can be ascribed to the formation of a pyrosol of silver in the fused salt since a gradual darkening of the melt was noticed.[6] Solid silver chloride proved to be most satisfactory and permitted reproducible measurements to be made down to 200° over a long period of time. Previous use of solid silver chloride has proved it to be entirely satisfactory in galvanic cells at these temperatures.[7]

Silver and gold of the highest purity obtainable from commercial sources were employed, no attempt at further purification being made. Silver chloride was prepared as previously described. Weighed quantities of the two metals were melted together in a small graphite crucible. The button

[3] Tammann, *Z. anorg. allgem. Chem.*, **107**, 1 (1919).

[4] Ölander, THIS JOURNAL, **53**, 3577 (1931).

[5] Wagner and Englehardt, *Z. physik. Chem.*, [A] **159**, 241 (1932).

[6] *Cf.* Lorenz and Helfenstein, *Z. anorg. allgem. Chem.*, **23**, 255 (1900).

[7] Wachter, THIS JOURNAL, **54**, 919, 2271 (1932).

thus obtained was hammered into the form of a rod about 2 cm. long and 2 mm. in diameter. The rods were then annealed for at least twenty-four hours at 850°. The electrodes, both alloy and pure silver, having been spot-welded to 25 cm. lengths of nichrome wire, were dipped into the electrolyte of molten silver chloride contained in a large Pyrex test-tube. When the fused salt had solidified the cell was put into an air-stirred electric furnace the temperature of which was hand-controlled with suitable rheostats. Since the nichrome lead-wires went deeply within the furnace no trouble was experienced with thermopotentials. With the electrolyte always kept in the solid state no creeping along the electrodes occurred. Temperatures were measured by means of a chromel–alumel thermocouple calibrated at the freezing points of tin, zinc and lead. The potentials of the cells were measured by a Leeds and Northrup type K potentiometer in conjunction with a sensitive galvanometer. With this apparatus the e. m. f. of a cell could be read to 0.1 mv. at 200°. Whatever polarization was produced during a measurement must have been negligible since the cells remained constant and reproducible over a period of several days. One cell was short-circuited for several minutes with the result that its e. m. f. immediately dropped; however, within a few hours the cell potential returned to its normal value. This would indicate that at these temperatures diffusion processes are quite rapid in gold–silver alloys.[8]

The cells responded very rapidly to changes in temperature. In general, however, care was taken to avoid changes greater than 5° an hour at the higher and much less at the lower temperatures. No attempt was made to thermostat the furnace, simultaneous readings of temperature and e. m. f. proving very satisfactory. Occasionally the furnace was left with a given rheostat setting for ten or more hours during which the fluctuations in temperature did not exceed 1 or 2° and the e. m. f. of the cells remained constant. No trouble was experienced with gold, in the alloys richer in that constituent, reducing silver from silver chloride.

A few alloys, especially those at the lower concentrations of gold, gave potential readings at first which were very much higher than could reasonably be expected. These were removed, re-annealed, and then replaced in the cells. Their e. m. f. readings after the additional heat treatment were very much lower. Further heat treatment produced no further changes in potential. Two silver wires immersed in an electrolyte of solid silver chloride did not differ by more than ±0.01 millivolt at the furnace temperatures employed in this research. Obviously the difficulties of reproducibility and unstable phases which are so frequently encountered in low temperature work with bulk metal electrodes become negligibly small at elevated temperatures.

[8] Braune, *Z. physik. Chem.*, **110**, 147 (1924), gives the diffusion coefficient of gold into silver the value of 0.0002 sq. cm./day at 847°.

Results

The electromotive force readings with their corresponding temperatures for the seven cells measured are given in Table I and plotted in Fig. 1. The data for all of the cells can be plotted as straight lines within the limits of the experimental error of ± 0.3 millivolt. From a very large scale plot of Fig. 1 the potentials corresponding to the temperatures of 200 and 400° were read off for each cell. The isothermal curves at these two temperatures of e. m. f. against composition were plotted from these values and are reproduced in Fig. 2. The manner in which the points fall along smooth curves in Figs. 1 and 2 predisposes one toward confidence in the validity of these measurements.

TABLE I

E. M. F. IN VOLTS OF CELLS CONTAINING SILVER OF VARIOUS MOLE FRACTIONS, N_1, DILUTED WITH GOLD

t, °C.	E. m. f.	t, °C.	E. m. f.	t, °C.	E. m. f.	t, °C.	E. m. f.
$N_1 = 0.863$		300.0	0.0393	236.5	0.0598	$N_1 = 0.285$	
		304.2	.0393	267.3	.0618		
199.2	0.0120	321.6	.0403	281.0	.0614	189.3	0.1205
213.0	.0124	327.4	.0415	290.0	.0623	197.3	.1208
233.5	.0128	358.3	.0417	308.7	.0634	228.2	.1235
238.3	.0123	368.1	.0413	334.1	.0650	238.0	.1242
244.1	.0130	376.7	.0415		.0666	254.8	.1255
248.6	.0131			359.2	.0673	309.0	.1290
271.7	.0132	$N_1 = 0.605$		373.3	.0675	337.0	.1311
277.0	.0128	192.4	0.0468	420.9	.0692	360.2	.1324
292.9	.0143	208.5	.0473	438.3	.0702	381.3	.1340
303.3	.0148	229.8	.0482			407.2	.1358
332.0	.0152	271.3	.0489	$N_1 = 0.414$		417.6	.1366
369.0	.0152	275.0	.0499	210.0	0.0822		
384.3	.0151	322.0	.0515	224.5	.0835	$N_1 = 0.150$	
		325.6	.0520	229.3	.0838	193.7	0.1836
$N_1 = 0.650$		359.9	.0525	252.6	.0844	224.1	.1867
208.5	0.0356	376.2	.0533	269.7	.0853	253.0	.1902
229.9	.0372			294.4	.0865	275.5	.1935
238.0	.0371	$N_1 = 0.526$		309.2	.0871	315.8	.1983
268.4	.0388	194.0	0.0576	327.0	.0879	346.3	.2029
283.0	.0379	195.9	.0581	343.3	.0885	374.4	.2064
290.2	.0387	208.3	.0582	395.6	.0907	415.1	.2121
		218.2	.0584	407.0	.0913		

In order to facilitate the thermodynamic calculations and to make their results more useful, the e. m. f.'s at the two temperatures mentioned above were taken at equal intervals of 10 mole per cent. from mole fraction 1.000 to 0.200 of silver. In all which follows the subscript 1 refers to silver and 2 to gold.

The partial molal free energy of dilution, $\Delta \bar{F}_1$, was calculated by means of the relation $\Delta \bar{F}_1 = -23,074 \Delta E$, where E is the electromotive force in volts. The partial molal entropy of dilution, $\Delta \bar{S}_1$, was obtained from the

expression $23,074\ dE/dT = \Delta\bar{s}_1$.   From these two the partial molal heat of dilution, $\Delta\bar{H}_1$, was easily calculated from the equation $\Delta\bar{H}_1 = \Delta\bar{F}_1 + T\Delta\bar{s}_1$.   The activity, a_1, is given by $\Delta E = -RT/23,074\ \ln a_1$.   In all of the above calculations pure silver was taken as the standard state.   In order to calculate the corresponding partial molal quantities for gold in these solid solutions, the Duhem equation was employed in the integrated
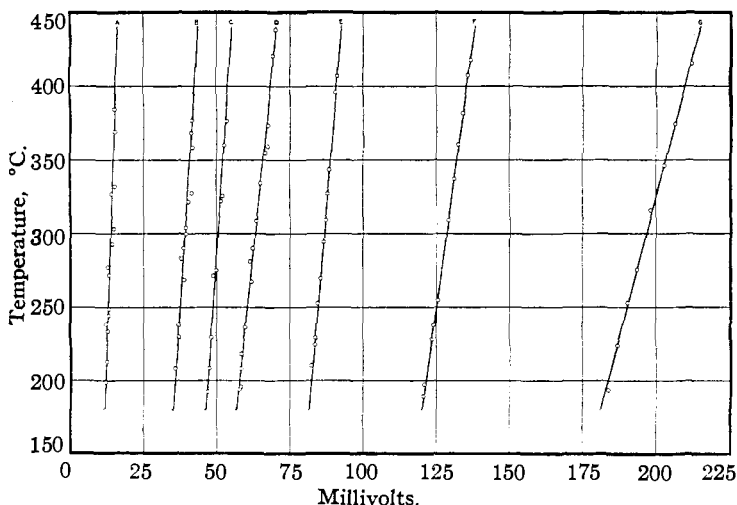

Fig. 1.—Temperature variation of e. m. f. of cells containing different gold–silver solid solutions.   Mole fraction of silver in A is 0.863, B is 0.650, C is 0.605, D is 0.526, E is 0.414, F is 0.285 and G is 0.150.

form, performing a graphical integration and taking pure gold as the standard state.   For a_2, the equation was $\log a_2/N_2 = -\int_0^{N_1} N_1/N_2\ d \log a_1/N_1$; for $\Delta\bar{s}_2$ it took the form $\Delta\bar{s}_2 = -\int_0^{N_1} N_1/N_2\ d\ \Delta\bar{s}_1$; and for $\Delta\bar{H}_2$ it was $\Delta\bar{H}_2 = -\int_0^{N_1} N_1/N_2\ d\ \Delta\bar{H}_1$.   The partial molal free energy of dilution for gold, $\Delta\bar{F}_2$, was obtained from a_2 by means of the equation $\Delta\bar{F}_2 = RT\ \ln a_2$.   The total thermodynamic quantities, ΔF, ΔH, and Δs, for the process of solution as represented by the equation

$$N_1Ag(s) + N_2Au(s) = N_1Ag\cdot N_2Au(s.\ soln.)$$
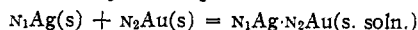
were easily obtained from the corresponding partial molal quantities. For example, for the total free energy change of dilution, $\Delta\bar{F} = N_1\Delta\bar{F}_1 + N_2\Delta\bar{F}_2$, and similarly for the others.   The results of all these computations are given in Table II.

Discussion of Results

   For the purpose of comparison the observed e. m. f.'s at 400° of Ölander[4] are plotted as triangles and of Wagner and Englehardt[5] as squares in Fig. 2.

TABLE II
### THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF GOLD IN SILVER

N_1	dE/dT mv./deg.	$\Delta \bar{S}_1$ cal./deg.	$\Delta \bar{S}_2$ cal./deg.	$-\Delta \bar{H}_1$ cal.	$-\Delta \bar{H}_2$ cal.
1.000	0	0		0	
0.900	0.0100	0.231	3.794	98	2895
.800	.0215	.496	2.130	199	2339
.700	.0305	.704	1.471	373	1793
.600	.0405	.935	1.036	587	1391
.500	.0475	1.096	0.832	935	958
.400	.0495	1.142	.793	1453	540
.300	.0665	1.534	.589	1948	263
.200	.109	2.515	.282	2418	96

200°

N_1	E volts	$-\Delta \bar{F}_1$ cal.	$-\Delta \bar{F}_2$ cal.	a_1	a_2
1.000	0	0		1.000	0
0.900	0.0090	208	4733	0.802	0.0065
.800	.0188	434	3386	.631	.0273
.700	.0306	706	2570	.472	.0649
.600	.0446	1029	1980	.335	.122
.500	.0639	1453	1459	.213	.212
.400	.0864	1993	1024	.120	.337
.300	.1159	2674	654	.058	.499
.200	.1564	3608	342	.022	.696

400°   200°
N_1 Ag(s) $+$ N_2 Au(s) $=$ N_1Ag·N_2Au (s. soln.)
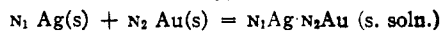
N_1	E volts	$-\Delta \bar{F}_1$ cal.	$-\Delta F$ cal.	$-\Delta H$ cal.	Δs cal.
1.000	0	0	0	0	0
0.900	0.0110	254	660	377	0.587
.800	.0231	533	1024	627	.823
.700	.0367	847	1266	799	.934
.600	.0527	1216	1409	909	.975
.500	.0725	1673	1456	947	.964
.400	.0963	2222	1412	905	.933
.300	.1292	2981	1260	769	.873
.200	.1782	4112	995	561	.729

In his thermodynamic calculations and conclusions therefrom Ölander has apparently placed too much stress on the minor variations from the regular smooth curve which may be drawn through his points. It is highly improbable that so many abrupt thermodynamic discontinuities would present themselves in this simple series of solid solutions. The thermal equilibrium diagram gives no indication of them, the micrographic and x-ray analyses do not reveal them, and the chemical as well as physical similarities of the two constituents would not lead us to expect them. It is not sufficient to establish the reproducibility with temperature of the individual cells employed. They must also be reproducible with respect

to composition. There are two serious sources of error in Ölander's experimental methods. It is highly probable that his alloys were insufficiently annealed. He allowed only two hours at 930° for this important treatment which should have been especially prolonged since the alloys were in the form of rather long wires 1 mm. in diameter. The fractional crystallization which would occur upon solidification of the molten alloy would result in a casting whose outer portion would be richer in gold.
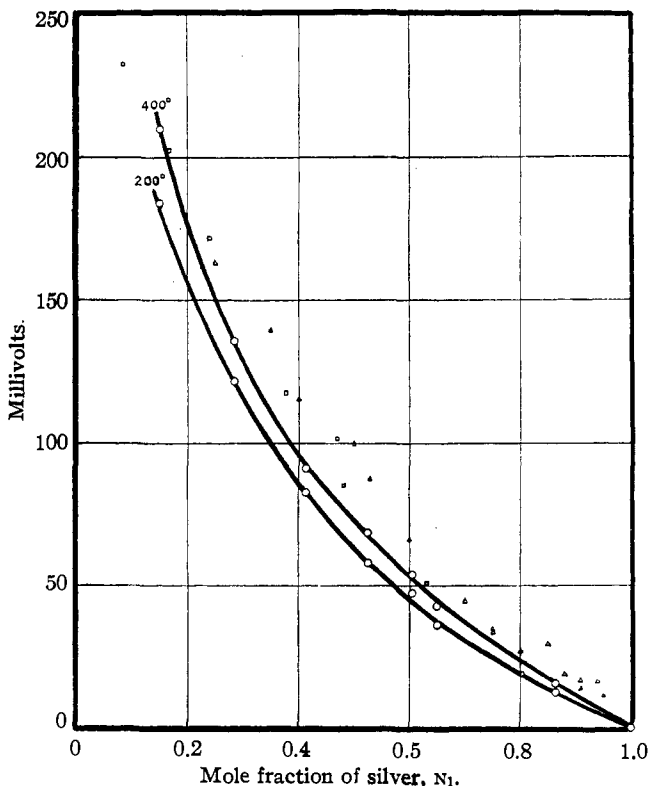

Fig. 2.—Change in e. m. f. of cells with composition at 200 and 400°. The circles are by Wachter, the triangles by Ölander, and the squares by Wagner and Englehardt.

This would explain the higher potentials which Ölander as well as Wagner and Englehardt have obtained. Then, the uncertainty which was introduced by the drop in potential with time of their gold-rich alloys when immersed in the electrolyte leaves us with still less confidence in the reliability of their thermodynamic results. Wagner and Englehardt claim no greater accuracy than ±2 mv. and find no evidence for the existence of abrupt changes in thermodynamic properties for these alloys.

Of especial interest to us are the activity curves given in Fig. 3. Both

the gold and silver show large negative deviations from Raoult's law. The addition of one to the other therefore results in an abnormally large decrease in escaping tendency of each. The formation of an intermetallic compound or a regular arrangement of both kinds of atoms in the lattice of the solid solution would give rise to this pronounced inhibition.
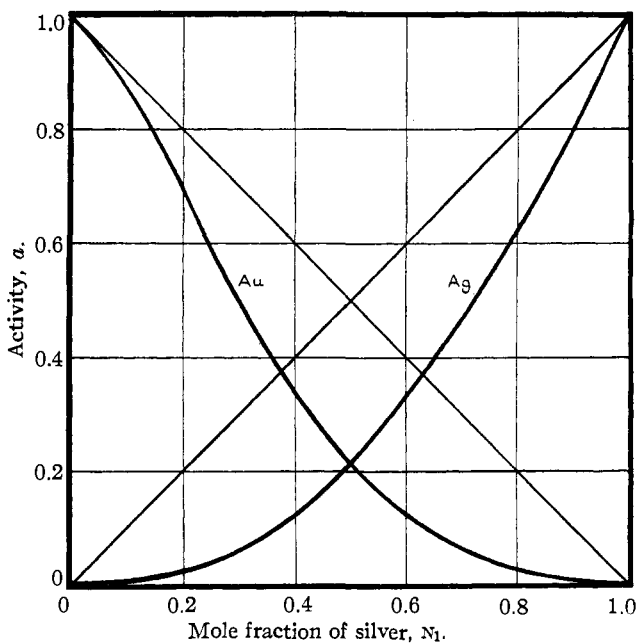

Fig. 3.—Activity curves for silver–gold solid solutions at 200°.

Tammann[3] has long supported the view which originated with him that the atomic or ionic arrangement in solid solutions is regular and that its composition can be represented by multiples of one-eighth mole of the two constituents for cubic crystals. For the gold–silver alloys, which are face-centered cubic, he has postulated, from numerous experiments on their chemical resistance limits, that the regular arrangement has the composition four-eighths mole of silver and four-eighths mole of gold. Although numerous x-ray studies of these alloys have been made,[9] no supporting evidence has been obtained from this quarter.

From a thermodynamic point of view, for any arrangement to be more probable than any of the others it must be the most stable. An examination of the data tabulated in Table II immediately shows that not only the total free energy change of solution but also the corresponding heat content and entropy changes attain a maximum value at about mole fraction 0.5.

[9] (a) Bain, *Chem. Met. Eng.*, **28**, 65 (1923); (b) McKeehan, *Phys. Rev.*, **21**, 380 (1923); (c) Sachs and Weerts, *Z. Physik*, **60**, 481 (1930).

The heat of solution is small and negative with a maximum value of −947 calories for the equi-molal solution.

The interaction between the gold and silver atoms in their solid solutions which can result in negative deviations from Raoult's law and in appreciable heats of solution can only consist of a force of attraction. If Vegard's rule[10] of the additivity of lattice constants in solid solutions is rigidly obeyed it is difficult to understand how any regular arrangement could exist. However, it has been demonstrated many times that the rule is an approximate one only. For the gold–silver alloys we have the very accurate lattice constant determinations of Sachs and Weerts,[9c] which show that the inter-atomic distances are smaller than those predicted by the linear relation. This is in agreement with the experimental fact that the hardness of this alloy series increases from both pure metals to a maximum at the equi-molal mixture.[11]

It is interesting to compare this system with the structurally and chemically similar gold–copper alloys. It has been shown by Johansson and Linde[12] that in the solid solution series of gold and copper at 0.25 and 0.50 mole fraction of gold the atoms in the crystal lattice are regularly arranged when the alloys are annealed for a sufficiently long time at 370°. The regular arrangements were recognized by the existence of extra lines in the x-ray analysis. Rapidly cooled specimens did not show this phenomenon. This latter serves to emphasize the importance of a careful annealing process if measurements are to be made of any other than accidental properties of alloys. Careless heat treatment of these systems in which the more stable regular arrangement differs so little in energy content from the statistically random one may easily result in an unstable frozen-in state which may persist indefinitely.

Summary

1. The energy changes of solid silver upon dilution with gold have been determined at mole fractions of silver varying from 1.000 to 0.150, between the temperatures of 200 and 400°.

2. The solid solution containing 0.500 mole of silver is shown to be the most stable.

3. The thermodynamic properties of these solid solutions are considered compatible with the existence of a regular arrangement of gold atoms in the silver crystal lattice.

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[10] Vegard, *Z. Physik*, **5**, 17 (1921).

[11] Kurnakoff and Schemtschuschny, *Z. anorg. allgem. Chem.*, **60**, 1 (1908).

[12] Johansson and Linde, *Ann. Physik*, **78**, 439 (1925).