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AN ELECTROCHEMICAL INVESTIGATION OF SOLID SILVER-GOLD ALLOYS

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Although a large number of investigations concerning the potentials of alloy electrodes have been published, only a few of them are of interest from a thermodynamic point of view. They have often been carried out at room temperature, where there is little or no diffusion within the metal, leading to serious polarization of the electrodes. This objection of course does not concern molten alloys and also not alloys sufficiently near their melting point, *e. g.*, amalgams. Nevertheless, many such doubtful potentials and in some cases their temperature coefficients have been measured and used as indicators of "intermetallic compounds," the thermodynamic treatment of the matter not always having been correct.

This paper reports on potential measurements on silver-gold alloys at such high temperature that sufficient diffusion in the crystal lattice to maintain thermodynamic equilibrium on the surface could be expected.²

Tammann³ reports measurements on these alloys both in aqueous solution and in molten silver nitrate. At 320° potentials were found from (Ag,Au)/AgNO₃/glass/(K,Na)NO₃,AuCl₃/Au that were constant and were a function of the gross composition of the electrode.

I tried first to measure Ag/AgNO₃/(Ag,Au) at the same temperature but had no success, even at 370°. At higher temperatures the electrolyte is liable to decompose. I therefore employed the cell Ag/AgCl,KCl/(Ag,Au), and this was used with success throughout the whole investigation.

Materials.—0.9999 gold and 0.99975 silver, obtained from Shreve and Co., San Francisco, were carefully weighed and melted together in evacuated silica glass tubes, with borax as a flux, and kept at 1100° for at least thirty minutes. The alloys with the least gold were remelted after

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² On diffusion in silver-gold alloys, see Fraenkel and Houben, *Z. anorg. Chem.*, **116**, 1 (1921); Braune and Hellweg, *Z. physik. Chem.*, **110**, 147 (1924); Jost, *ibid.*, **B9**, 73 (1930); Tanaka and Matano, *Proc. Phys. Math. Soc. Japan*, **12**, 279 (1930).

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

the button had been turned upside down in order to secure a thorough mixing. The buttons weighed 4–5 g. They were then once more melted *in vacuo* and with hydrogen pressed into spiral-wound 1-mm. silica glass capillary tubes. These were kept at 920–930° for one hour for the purpose of homogenization of the metal and after cooling the silica was cracked off. Eventually the wires were annealed for another hour at 930° in hydrogen.

The composition of the electrolyte was near the eutectic of $\text{AgCl} + \text{KCl}$, with some excess of the latter.

Experimental

Runs 1–8 were made in an electrically heated furnace, which consisted of a 20-kg. cast-iron cylinder, heated by a chromel winding and insulated with Sil-o-cel. In its center was a hole, inside which the temperature was very uniform. Herein was placed a Pyrex test-tube containing about 4 cc. of electrolyte. The electrodes—one silver and three alloys—dipped about 1 cm. into the liquid and were insulated from each other with Pyrex tubes.

The electrolyte was liable to creep along the electrodes, which therefore must reach the cooler part of the furnace. They were welded to silver wires which were continued outside the furnace by copper wires. It was hence necessary to subtract the thermopotentials.⁴ After a run was completed the electrolyte was removed and the four electrodes welded together at their lower ends and replaced in their former position. The new potential, π , had the reverse sign and its numerical value had to be added to the values, E' , from the main run, yielding the corrected cell potential E .

The location of the electrode system was exactly defined by a brass rod, on which it hung during the measurements. The junction alloy–silver wire was thus kept at exactly the same place throughout both main run and correction run. All thermal conditions thus being the same in both runs, the possible error introduced by this process amounts only to 0.02–0.03 mv., which occasionally was checked by removing, rewelding and replacing the electrodes once more.

The potentials were measured by a Leeds and Northrup type K potentiometer. The null point instrument used was a Dolezalek electrometer. It was operated with 135 volts' vane potential and had then a sensitivity of 2 div./mv., the scale distance being 2 m. The potentials were read to 0.1 mv. The thermopotentials were of course measured with a galvanometer as a null point instrument. This was also used for the chromel–alumel thermocouple which determined the temperature. The latter was placed outside the Pyrex tube beneath the end of the electrodes. It was checked at the melting point of zinc (419.5°) between every run and kept the potential claimed by the manufacturer (Hoskins Co.) within 1°.

It was first found that the potentials did not keep constant but drifted downward. This had two causes, one being a slight excess of silver in the solution, probably Ag_2^+ ions, which deposited on the alloy surface. This trouble was completely removed by treating the electrolyte with halogen (a drop of ICl) and then stirring with a silver wire to remove the excess of halogen. If silver was allowed to stay in the liquid overnight, the disturbance returned and therefore the electrodes must be kept just over its surface and dipped down only during the measurements. As the surface of metal was wetted by a thin film, the attainment of the electrochemical equilibrium was not hindered.

⁴ Although the thermopotential Ag-Au is small, the potentials against their alloys are considerable. See Sedström, Thesis, Stockholm, 1924; also "Tables Annuelles," Vol. VI, p. 720.

The alloys with less than 40 atom per cent. of gold then gave quite stable potentials. This was not true with the alloys richer in gold, which were affected by another contamination. Pure gold heated with silver chloride to 550° for thirty-six hours reduced a considerable amount of silver. Hence also the gold-richest alloys caused a reduction and their potentials dropped. The value recorded is that extrapolated to the moment of immersion. Fortunately the lifting of the electrodes prevented a continued change. The thin film wetting the metal soon became saturated with gold and the minute excess of silver on the surface diffused into the electrode so that when it was again immersed after some hours the original potential returned. This drifting first made measurements difficult at 0.75 mole fraction of gold. At this point the recorded values are only accurate to 0.5 mv. In the case of still more gold no accurate measurements could be made at all.

The alloys 0.05-0.50 were relatively hard after the runs.

A cell was always set up in the night (day 0 in the tables), the electrolyte "cleaned up" as described and the electrodes put in position. During the following day the three pairs were measured three or four times. In the night the furnace was brought to a new temperature and so on. The behavior of a good electrode and of a less good one may be given in full. T is the absolute temperature; the alloys are described by their mole fraction of gold.

TABLE I

		Run 8, alloy 0.250			Run 7, alloy 0.300		
Day 1	$T =$	856	851	850	837	829	832
	$E' =$	33.6	34.3	34.6	42	43.1	43.6
2		746	750	751	767	760	756
		33.2	33.6	33.5	44.4	44.6	44.7
3		881	879	883	850	842	843
		35.4	35.3	35.3	45.4	45.4	45.5
4		773	771	771	744	739	743
		34.5	34.6	34.5	45.5	45.8	46.1
5	..		732	733	885	..	897
	..		34.1	34.1	46.1	..	45.7
6		820	822	834	790	783	780
		34.8	34.6	35.0	44.7	44.5	44.4
7		875	894	900	707	707	706
		35.6	35.4	35.7	42.7	43.5	42.7
8		756	753	754	866	869	868
		34.5	34.6	34.5	46.2	46.1	45.9
9		856	877	885	761	760	756
		35.5	35.6	35.4	44.4	44.7	45.0
10					818	830	835
					45.9	46.1	46.3

Occasionally the voltage changed considerably owing to the use of apparatus in the neighborhood. Unfortunately this was not watched upon a few days, which hence show a bad temperature constancy.

TABLE II

		Run 1						
Day		1	2	3	4	5	6	
$T =$		814	759	847	775	720	825	
Au = 0.0909	$E' =$	10.8	11.6	11.5	11.9	13.0	11.7	
	$-\pi =$	1.45	1.24	1.59	1.30	1.12	1.50	
	$E =$	12.3	12.8	13.1	13.2	14.1	13.2	$18.2 - 0.0065T \approx 0.5$
Au = 0.250	$E' =$	36.8	35.6	35.9	34.3	33.5	35.5	
	$-\pi =$	1.66	1.40	1.81	1.48	1.25	1.71	
	$E =$	(38.5)	(37.0)	37.7	35.8	34.8	37.2	$17.2 + 0.0243T \approx 0.2$
Au = 0.400	$E' =$	67.5	65.9	67.7	66.9	66.7	69.2	
	$-\pi =$	2.21	1.87	2.43	1.97	1.65	2.29	
	$E =$	69.7	67.8	70.1	68.9	68.3	71.5	$47.9 + 0.0271T \approx 0.8$
		Run 2						
Day		1	2	3	4	5	6	
$T =$		810	759	856	784	873	818	
Au = 0.500	$E' =$	104.6	102.2	106.0	102.1	105.5	103.0	
	$-\pi =$	2.12	1.82	2.44	1.95	2.56	2.18	
	$E =$	(106.7)	104.0	108.4	104.1	108.1	(105.2)	$69.2 + 0.0452T \approx 0.8$
Au = 0.750	$E' =$	168.3	165.5	169.7	166.3	169.8	166.8	
	$-\pi =$	1.66	1.41	1.93	1.52	2.02	1.71	
	$E =$	(170.0)	166.9	171.6	167.8	171.8	(168.5)	$131.2 + 0.0467T \approx 0.6$
		Run 3						
Day		4	5	6	7	8	9	
$T =$		721	815	734	870	789	722	
Au = 0.0625	$E' =$	13.8	10.8	13.6	10.8	12.6	14.4	
	$-\pi =$	1.04	1.35	1.08	1.54	1.27	1.04	
	$E =$	14.8	12.2	14.7	12.3	13.9	15.4	$30.8 - 0.0218T \approx 0.5$
Au = 0.150	$E' =$	26.7	25.2	26.9	24.7	26.2	27.8	
	$-\pi =$	1.46	1.93	1.52	2.21	1.80	1.46	
	$E =$	28.2	27.1	28.4	26.9	28.0	29.3	$38.2 - 0.0131T \approx 0.4$

TABLE II (Continued)

		Run 3						
Au = 0.600	E'	115.4	119.4	117.7	121.0	116.5	114.8	
	$-\pi$	1.57	2.12	1.64	2.46	1.97	1.58	
	E	117.0	121.5	119.3	123.5	118.5	116.4	$87.1 + 0.0416T \approx 0.8$
		Run 4						
	Day	4	5	6	7	8	9	10
	T	775	871	808	729	844	766	886
Au = 0.030	E'		2.2	2.4	3.3	2.7	3.5	2.9
	$-\pi$		0.92	0.78	0.62	0.86	0.70	0.95
	E		3.1	3.2	3.9	3.6	4.2	3.9
								$5.6 - 0.0023T \approx 0.4$
Au = 0.200	E'	25.5	26.3	26.5	26.3	26.9	26.8	27.5
	$-\pi$	1.90	2.51	2.10	1.63	2.32	1.85	2.62
	E	27.4	28.8	28.6	27.9	29.2	28.7	30.1
								$18.5 + 0.0125T \approx 0.6$
		Run 5						
	Day	1	2	3	4	5	6	7
	T	835	735	837	720	800	859	761
Au = 0.530	E'		103.0	106.5	102.4	105.5	107.5	103.4
	$-\pi$		1.34	1.89	1.27	1.67	2.02	1.47
	E		104.3	108.4	103.7	107.2	109.5	109.9
								$72.2 + 0.0435T \approx 0.2$
Au = 0.650	E'	142.8	140.0	142.9	139.5	140.4	142.9	
	$-\pi$	1.91	1.37	1.93	1.32	1.70	2.05	
	E	144.7	141.4	144.8	140.8	142.1	145.0	
								$113.6 + 0.0369T \approx 0.6$
		Run 6						
	Day	4	5	6	7	8	9	
	T	774	848	724	821	882	741	
Au = 0.0909	E'	14.8	13.9	15.3	14.7	14.1	15.2	
	$-\pi$	1.10	1.34	0.93	1.24	1.47	0.99	
	E	15.9	15.2	16.2	15.9	15.6	16.2	
								$19.9 - 0.0051T \approx 0.2$

(This was the same sample as in Run 1, but recast.)

TABLE II (Concluded)

		Run 6								
Au = 0.470	E' =	88.8	91.2	87.5	89.8	91.5	87.8			
	$-\pi$ =	1.69	2.13	1.41	1.97	2.33	1.50			
	E =	90.5	93.3	88.9	91.8	93.8	89.3		$65.2 + 0.0327T \approx 0.2$	
		Run 7								
	Day	3	4	5	6	7	8	9	10	
	T =	845	742	890	784	707	868	759	828	
Au = 0.050	E' =	6.1	8.8	6.0	8.0	10.8	7.0	8.9	8.3	
	$-\pi$ =	1.18	0.90	1.32	1.01	0.81	1.25	0.94	1.13	
	E =	7.3	9.7	7.3	9.0	11.6	8.3	9.8	9.4	$23.3 - 0.0178T \approx 0.6$
Au = 0.120	E' =	14.9	15.8	14.9	15.6	18.0	15.7	17.7	17.2	
	$-\pi$ =	1.70	1.35	1.91	1.41	1.19	1.81	1.40	1.61	
	E =	16.6	17.1	16.8	17.0	19.2	17.5	19.1	18.8	$22.7 - 0.0062T \approx 0.9$
Au = 0.300	E' =			45.9	44.5	43.0	46.1	44.7	46.1	
	$-\pi$ =			2.79	2.07	1.62	2.64	1.91	2.37	
	E =			48.7	46.6	44.6	48.7	46.6	48.5	$27.7 + 0.0243T \approx 0.5$
		Run 8								
	Day	2	3	4	5	6	7	8	9	
	T =	749	881	772	732	825	890	755	873	
Au = 0.015	E' =	2.0	1.7	2.1	2.2	2.2	1.9			
	$-\pi$ =	0.41	0.56	0.44	0.39	0.50	0.56			
	E =	2.4	2.3	2.5	2.6	2.7	2.5			$2.5 \approx 0.14$
Au = 0.250	E' =	33.4	35.3	34.5	34.1	34.8	35.6	34.5	35.5	
	$-\pi$ =	1.73	2.63	1.87	1.64	2.20	2.65	1.77	2.53	
	E =	35.1	37.9	36.4	35.7	37.0	38.3	36.3	38.0	$23.4 + 0.0167T \approx 0.4$

(This was another sample than in Run 1.)

Thus the readings during a day differ by some 0.1 mv.—only in a few cases more than 1 mv.—but the potential usually did not become reproducible with respect to the temperature changes for several days. This was not recognized at once and thus the two first runs are more or less in error. In four cases the electrodes did not behave reproducibly at all; the values were then rejected and the electrode after recasting used for a new run.

The tables (II) give the mean temperature for each day and the mean value of the observed potential E' for each alloy, the corresponding thermo-potential π from the correction run and the corrected cell potential E . For each alloy is given an interpolation formula for E with the standard deviation of the day means: $E = E_0 + \alpha T \pm \sqrt{\Sigma \delta^2 / (n - 1)}$. T is the absolute temperature. The potentials are given in millivolts.

The alloys 0.901 and 0.980 could not be measured exactly. At 880°K. their potentials were about 0.22 and 0.26 volt. These values cannot be regarded as representative of the equilibrium $\text{Ag} \rightleftharpoons \text{Ag}^+ + e^-$, as an electrode of pure gold gave no higher potential than 0.30 volt.

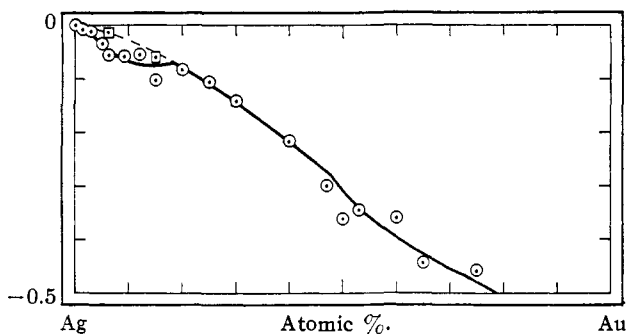


Fig. 1.—Logarithm of activity coefficient of silver at 800° abs.

In Fig. 1 is plotted the logarithm of the activity coefficient of silver at 800°K. At higher temperatures the curve will lie somewhat higher.

Multiplying the potential, written $E = E_0 + \alpha T$, by 23063 cal./int. volt yields the free energy of the cell reaction: $-\Delta F = -\Delta H + T\Delta S$. The values $-\Delta H$ and ΔS , thus immediately gotten, and the probable error of the latter are given below, together with the values of $-\Delta F$ for 800°K. They are the differences of the partial molal quantities for silver in the alloys and those of pure silver, and will, from this point of view, be called $-\Delta\bar{H}$, $\Delta\bar{S}$ and $-\Delta\bar{F}$.

These partial molal heats and entropies of mixing are plotted in Figs. 2 and 3 as circles. They show a remarkable departure from a smooth curve, on which one would expect them to lie, since no intermediate phase is known, although many investigators have looked for one. If the departure

TABLE III
RELATIVE PARTIAL MOLAL QUANTITIES OF SILVER BETWEEN 700 AND 900°K.

Run	Mole fraction of gold	$-\Delta\bar{H}$	$\Delta\bar{S}$	$-\frac{\Delta\bar{F}_{900^\circ}}{\Delta\bar{H} + 800 \cdot \Delta\bar{S}} = -\log \gamma_{900^\circ}$
8	0.015	60	0.00 ± 0.02	60 0.01
4	.030	130	-.05 ± .07	90 .01
7	.050	540	-.41 ± .09	210 .04
3	.0625	710	-.50 ± .08	310 .06
1	.0909	420	-.15 ± .11
6	.0909	460	-.12 ± .03	360 .06
7	.120	520	-.14 ± .13	410 .06
3	.150	880	-.30 ± .07	640 .10
4	.200	430	+.29 ± .09	660 .08
1	.250	400	+.56 ± .21
8	.250	540	.38 ± .04	840 .11
7	.300	640	.56 ± .07	1090 .14
1	.400	1100	.62 ± .18	1600 .22
6	.470	1500	.75 ± .04	2100 .30
2	.500	1590	1.04 ± .16	2420 .36
5	.530	1660	1.00 ± .05	2460 .35
3	.600	2000	0.96 ± .11	2770 .36
5	.650	2610	0.85 ± .12	3290 .44
2	.750	3020	1.08 ± .06	3880 .46

is due to some intermediate phase one might expect this to disappear at higher temperatures as do the phases in the systems Cu-Au and Pd-Au.⁵

Hence the electrodes 0.0625 and 0.150 were measured immediately below the melting point of silver. This could not be carried out in the iron furnace described above, but had to be done in a small platinum-alundum furnace in which the temperature could not be kept so uniform and constant. Each temperature was kept for about twelve hours. Silica glass was used instead of Pyrex. The run was soon discontinued because both silica and electrodes broke off. The results are given in Table IV.

These values are plotted in the figures as squares. It is seen that these values form smooth curves together with the former values for 0.20-0.47 Au.

It was attempted to measure the 0.53 and 0.65 alloys in the same way. The potentials were however much lower than expected and drifted just as the 0.901 and 0.980 alloys did at the lower temperatures. The electrodes were removed after a day and the immersed ends were found to be whitened by silver deposits.

If the interpolation formulas from Runs 3 and 9 be plotted the two lines belonging to each alloy will intersect each other at a point, which yields the transition temperature between the two modifications. For 0.0625 it comes out 1040°K., which is probably somewhat too low; for 0.150, 1110°K.,

⁵ Johansson and Linde, (a) *Ann. Physik*, **78**, 439 (1925); (b) *ibid.*, **82**, 449 (1927); Borelius, Johansson and Linde, *ibid.*, **86**, 291 (1928).

TABLE IV

Run 9

	Day	1	1	2	2	
	$T =$	1109	1215	1115	1207	
Au = 0.0625	$E' =$	5.6	6.0	6.8	6.8	
	$-\pi =$	2.51	2.97	2.54	2.94	
	$E =$	8.1	9.0	9.3	9.7	$1.4 + 0.0066T \approx 0.6$
Au = 0.150	$E' =$	19.5	19.9	20.3	20.2	
	$-\pi =$	3.99	4.83	4.04	4.77	
	$E =$	23.5	24.7	24.3	25.0	$13.2 + 0.0096T \approx 0.3$

(These were the same samples as in Run 3.)

RELATIVE PARTIAL MOLAL QUANTITIES OF SILVER BETWEEN 1100 AND 1200 °K.

Mole fraction of gold	$-\Delta\bar{H}$	$\Delta\bar{S}$	$-\Delta\bar{F}_{800^\circ}$	$-\log \gamma_{800^\circ}$
0.0625	30	$+0.15 \pm 0.12$	150	0.01
.150	300	$+ .22 \pm .06$	480	.06

For the sake of comparison $-\Delta\bar{F}$ and $-\log \gamma$ are given for the same temperature as in the former table.

probably too high. Within the experimental error both values equal 800°C. It is possible that the curve would be smooth above 0.50 Au too if it only could be measured at this higher temperature.

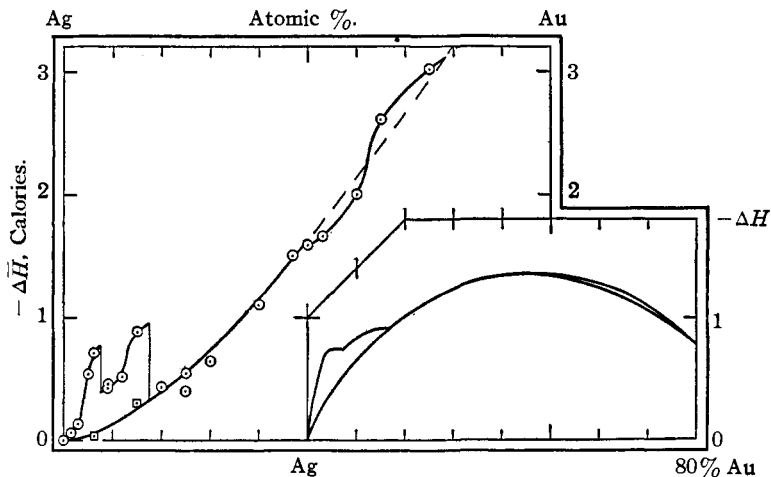


Fig. 2.—Right: heat of alloy formation. Left: relative partial molal heat content of silver (upper curves belong to lower temperatures).

In order to get the total entropy and heat of alloy formation by integration we must know the extension of the partial curves to the gold end of the composition range. Such an extrapolation can perhaps be made for $-\Delta\bar{H}$ although with a large uncertainty; it may end at about 5 Cal. The $\Delta\bar{S}$ curve is impossible to extrapolate; even a plot of $\Delta\bar{S}/R \log n$ does not give much guidance.

If Fig. 2 is integrated using the extrapolation indicated, the curves to the right result, the lower curve referring to higher temperatures. The maximum lies about 0.45 Au. For it to be at 0.50 the $-\Delta\bar{H}$ curve would have to be much steeper than it actually is.

The best way to get the total entropy of mixing may be to assume arbitrarily some probable composition for the maximum of ΔS . This maximum value will then be equal to the $\Delta\bar{S}$ of either component at this composition.⁶ In Fig. 3 this maximum is assumed to lie at 0.50. If it were taken to be 0.45 or 0.55 this would only lower or raise the curve by 0.05 entropy unit in the middle but its general trend would not be altered.

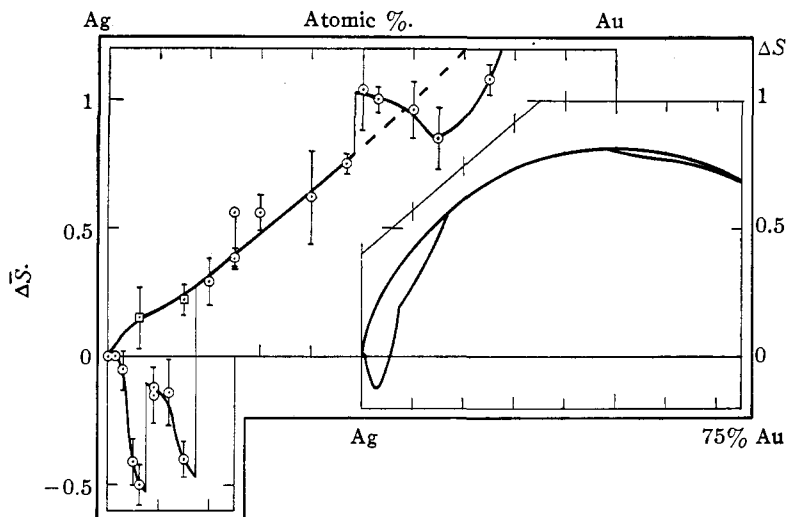


Fig. 3.—Right: entropy of alloy formation. Left: relative partial molal entropy of silver (upper curves belong to higher temperatures).

The difference between the low and supposed high temperature curves between 0.50 and 0.75 Au amounts only to about 0.04 E. U. or 40 calories. Between 0 and 0.18 Au the effect is much more marked, the transition entropy at 0.035 Au being about 0.35 E. U., corresponding to a transition heat of 400 calories. (The pure mixing term of entropy $R\sum n_i \log n_i$ is for $n_1 = 1/32$ equal to 0.28 E. U.)

There seems to be a different state above 0.08 Au than below.

It is of course possible to assume these low entropies to be due to a more or less ordered distribution of the two kinds of atoms. The fact that this effect is not found around the simplest compositions 0.25, 0.50 and 0.75, where one certainly would expect it, causes no very serious objection. In

⁶ Because the tangent at any point of the ΔS curve intercepts the Ag and Au axes at ordinates equal to $\Delta\bar{S}_{Ag}$ and $\Delta\bar{S}_{Au}$ of the point of contact (see Lewis and Randall, "Thermodynamics," p. 38). In the maximum point the tangent is horizontal.

the case of Pd-Au the existence of ordered atom distribution is very unsymmetrical around the compositions Au_3Pd and AuPd (and not found at all around AuPd_3)^{5b} and at certain temperatures this seems to be the case also at Au_3Zn .⁷ Here the effect seems to have its maximum around Ag_{31}Au .

Many people have investigated the silver-gold alloys in this direction^{5a} without finding other than a continuous series of mixed crystals of random atom distribution throughout the whole range. If the effect between 0.50 and 0.75 Au is due to partially ordered distribution, the randomness is nevertheless so predominant that nothing can be detected by x-ray photographs or by electrical resistance measurements, as in the case of the Cu-Au system.

However, at small gold contents there would be some hope of using these methods with success.

Filings of the 0.0625 alloy and of pure silver were annealed for three days at 600° and then photographed in a Davey camera with Mo K_α radiation. However, no "extra lines" due to an ordered distribution could be claimed on the photometer curve but their Laue structure factor is so small anyway that their failing to appear does not exclude a partially ordered distribution.

The exposure gave the result that the lattice constant was diminished by the presence of 6.25% Au, in agreement with Sachs and Weerts.⁸

Some evidence for an ordered distribution may be drawn from the measurements of the electrical resistance by Sedström.⁹ A small amount of a metal added to another usually increases the resistance more than does a further addition, but the increase of resistance by 5 atom per cent. of Au is less than the additional increase at 9.7%. This might perhaps indicate that the alloys of about $1/32$ gold content have an ordered atom distribution, but it must be pointed out that the effect but narrowly exceeds Sedström's experimental errors, and other

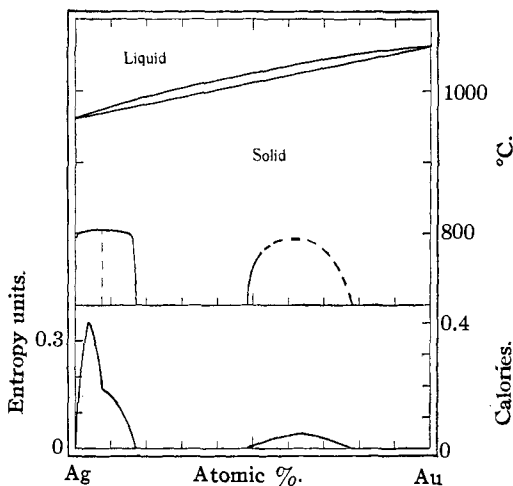


Fig. 4.—Upper: a tentative phase diagram of the silver-gold system. Below: entropy or heat of transition.

⁷ Saldau, *Z. anorg. Chem.*, **141**, 324 (1925).

⁸ Sachs and Weerts, *Z. Physik*, **60**, 481 (1930).

⁹ Sedström, Thesis, Stockholm, 1924; see also "Tables Annuelles," Vol. VI, p. 697.

investigators do not find the effect. This can, however, be due to inadequate annealing.

An investigation of the resistance of these alloys at higher temperatures might then be expected to show the same characteristics as the investigation by Borelius, Johansson and Linde⁵ on Cu-Au and Cu-Pd, *viz.*, increase in resistance above the transition point but with a considerable hysteresis.

Figure 4 gives a tentative phase diagram of the system. Below is plotted the entropy and heat of transition (= difference between curves in Figs. 2 and 3 to the right). The left low entropy phase reaches very near the silver axis, but one might believe that the very lowest percentages are randomly distributed.

My thanks are due to Professor E. D. Eastman for suggesting to me the investigation of electrode potentials of alloys.

Summary

The potential of the cell Ag/AgCl, KCl/(Ag, Au) and its temperature coefficient have been measured between 400 and 625° for seventeen compositions of the alloy electrode and between 840 and 940° for two compositions.

At gold contents smaller than 18 atom per cent. there is a discontinuity and change of sign of the temperature coefficient at 800°.

The activity coefficient of silver has been plotted.

The temperature coefficient gives the difference in partial molal entropy of silver in the alloy from that of pure silver. By integration the total mixing entropy is found.

There exists a phase of low entropy below 800° from 0 to 18 atom per cent. of gold. Another less marked seems to exist above 50%.

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THE DENSITY AND SURFACE TENSION OF THE ISOMERS OF 2-PENTENE AND 2-METHYL-2-BUTENE

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Much interest has been aroused by the discovery of the two isomers of 2-pentene.¹ The exact nature of these isomers is still a matter of some dispute. With the object of obtaining further data that might be used in the solution of the problem Messrs. Clark and Hallonquist of these Laboratories prepared the two isomers and investigated some of their chemical and physical properties, the results of which are recorded in the *Proceedings of the Royal Society of Canada*.²

¹ Lucas and Moyses, *THIS JOURNAL*, **47**, 1459 (1925); Sherrill, Otto and Pickett, *ibid.*, **51**, 3023 (1929); Kharasch and Darkis, *Chemical Reviews*, **5**, 371 (1928).

² Clark and Hallonquist, *Proc. Roy. Soc. Canada*, **XXIV**, 115 (1930).