

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

AN ELECTROCHEMICAL INVESTIGATION OF SOLID
CADMIUM-GOLD ALLOYSBY ARNE ÖLANDER¹

RECEIVED APRIL 29, 1932

PUBLISHED OCTOBER 5, 1932

For an electrode potential to be of theoretical interest one must know what it means; it is the surface layer that determines the potential, and without a knowledge of the condition of this the potentials are of little value. There seems, then, to be an especially serious risk in measuring the potential of an alloy whose one component is as volatile as cadmium at the temperatures which are to be considered here, but the reproducibility of the present results and their dependence on the gross composition of the electrodes leave no doubt that the latter has also been very near the composition of the surface. Thus the conclusion must be drawn that the diffusion in these alloys is quite considerable—with exceptions that will be dealt with later.

Figure 1 shows the phase diagram of the cadmium-gold alloys as given by the investigations of Vogel,² Saldau³ and Durrant,⁴ with the adjustments and additions caused by the present measurements. A comparison with Durrant's very careful work shows no differences in the existence limits of the various phases, and also transition temperatures work out very much the same; this must be considered as a proof that the surface composition of the electrodes has been the same as that found by analysis of the whole piece of metal.

The phase diagram closely resembles those of the homologous alloys CuZn, CuCd, AgZn, AgCd and AuZn. Saldau has found that the ϵ -, β - and α' -alloys possess a high electrical conductivity, which indicates that the atoms have an ordered distribution, whereas the α -alloys have a much smaller conductivity. Below 135° there is an α'' -modification, which also has a high conductivity.

The alloys were made from 0.9999 gold from Shreve and Co., San Francisco, and c. p. cadmium from Powers, Weightman and Rosengarten, Philadelphia. The metals were melted together in evacuated silica glass tubes, which were sealed to prevent losses. The buttons weighed about 3-4 g. They were remelted in hydrogen and with the aid of this gas forced into 1-mm. capillary silica tubes. When this was done with silver-gold alloys,⁵ the capillary tubes had to be made in spiral form, because on

¹ Rockefeller Foundation Fellow.

² Vogel, *Z. anorg. Chem.*, **48**, 337 (1906).

³ Saldau, *Intern. Z. Met.*, **7**, 3 (1914); *J. Russ. Phys.-Chem. Soc.*, **46**, 994 (1914); **55**, 275 (1924).

⁴ Durrant, *J. Inst. Met.*, **41**, 139 (1929).

⁵ Ölander, *THIS JOURNAL*, **53**, 3577 (1931).

cooling the thermal contraction tore off the wires if they were cast in a straight tube. This precaution was unnecessary here—it would, moreover, not have been possible afterward to straighten the wire—but great care had to be taken when cracking the silica off the brittle α' -, γ - and ϵ -alloys so that they did not break into small pieces. Before the silica was cracked the alloys were annealed for one to three days in hydrogen, the α -alloys at 550° , the β -alloys at 450° and the γ - and ϵ -alloys at 400° .

The alloys with less than 15 atomic per cent. of cadmium were malleable, the other α -alloys soft and brittle, like rotten wood. The β -alloys with less than 50% cadmium were elastic, this property having a sharply marked maximum at 47.5%. A 1-mm. wire of this alloy was so elastic that it almost reminded of rubber. The alloys with more than 50% cadmium were hard and brittle, over 60% very brittle.

The color of the alloys was; α , all yellow; β , reddish-white up to 50%, the rest bluish-white.

For the measurement of the electrode potentials the cells were set up in the same iron furnace that was used for the investigation of the silver-gold alloys.⁶ A 40-cm. Pyrex tube with a diameter of 25 mm. was placed in the furnace, about 25 cm. projecting outside. It contained at the bottom 6–7 ml. of electrolyte and in Runs 1–9 and 14–18 below this about 3.5 ml. of molten cadmium, which was the standard electrode. The upper end of the tube was closed with a cork, which carried six Pyrex tubes and was made air tight with sealing wax. One of these tubes terminated just inside the cork and admitted a very slow current of hydrogen. This gas was taken from a tank, led over hot copper, and dried with phosphorus pentoxide. Another tube, which reached down into the molten cadmium, was closed at its lower end with a short tungsten wire sealed through it, thus making a connection with the cadmium electrode. The tungsten was soldered with German silver to a silver wire, which outside the apparatus was continued by copper wires. The other four tubes—or in the case of no liquid electrode, the other five tubes ended 2 cm. above the surface of the electrolyte. They held the other electrodes, which dipped about 7 mm. down into the liquid. These were 5–10 cm. long and also welded to silver wires.

In order to prevent any air from entering through these tubes capillary "swan necks" were attached to their upper ends with short rubber tubings. The silver leads were run through the rubber.

The electrolyte used was in Runs 1–10 the eutectic mixture of lithium and potassium chlorides (melting at 359°), in Runs 11–18 that of lithium and rubidium chlorides (melting at 312°), and in Runs 19–20 the lowest melting mixture of sodium and potassium acetate (melting at 233°). To each of these a small amount of cadmium chloride or acetate was added.

Runs 19 and 20 could not be made in a hydrogen atmosphere because

this reduced the cadmium acetate; but they were made in nitrogen. This gas was taken from a tank and allowed to pass over hot copper to absorb the oxygen.

An addition of alkali, as used by N. W. Taylor,⁶ was not found to be of any advantage and was omitted. The cell, however, was allowed to remain overnight in order to be thoroughly dried, before the alloy electrodes were put in position.

The electrolyte had no tendency to creep on the metallic surface as in the previous investigation.⁵ Hence it was possible to keep the junction alloy-silver wire inside the furnace. The correction due to thermopotentials was therefore very small. It was determined after the main run. The cork with the electrodes was taken out, the electrolyte, cadmium and tungsten sealing removed, and the cork replaced in its former position after the electrodes had been soldered together at their lower ends. It was only in a few cases, when very long electrodes had been used, that this correction exceeded 0.2 millivolt. All potentials given in this paper are corrected values.

The temperature was measured with a chromel-alumel thermocouple, which was placed outside the Pyrex tube beneath the end of the electrodes. It was checked between runs at the melting point of zinc (419.5°). The potentials were measured with a Leeds and Northrup type K potentiometer. In the main runs the null-point instrument was a Dolezalek electrometer; the readings were made to 0.1 millivolt. The thermopotential correction runs and the thermocouple readings were made with the aid of a galvanometer, the readings being made to 0.01 millivolt. The accuracy of the temperature readings might be estimated at $\pm 1^\circ$.

No such drifting of the potentials occurred as when silver chloride was used as an electrolyte.

The composition of the alloys was determined by analysis. About 0.25 g. of the immersed end of the electrode was broken off and dissolved in aqua regia. The solution was evaporated to dryness, hydrochloric acid added and evaporated, and the chlorides dissolved in water. Then sodium hydroxide was added and the gold reduced with hydrogen peroxide, the excess being destroyed by boiling. Now the solution was acidified and the gold taken on a filter. However, the gold is not completely precipitated by the peroxide, so the filtrate always had to be reduced once more. The second filtrate, however, was free from gold. The gold was ignited and weighed; the cadmium was taken as 100% minus the gold.

The alloys are characterized by their mole fraction of cadmium.

The alloys with a large cadmium content showed a slow drift in their composition (and potential) during the run, and of these another sample was analyzed to ascertain the composition at the beginning of the experi-

⁶ Taylor, *THIS JOURNAL*, 45, 2865 (1923).

ment. In cases where two compositions are given, the potentials at the beginning and the end of the run have been attributed to the composition at the beginning and end, respectively.

This relatively rapid drifting of the composition shows that the diffusion within the metal must be quite considerable.

The α -alloys, which have higher melting points, show a much smaller diffusion. In fact, it was not possible to measure electrodes of this composition against an electrode of liquid cadmium; the surface was at once whitened by the volatile metal and gave potentials which showed the outer part to be of $\alpha + \beta$ or even β -composition. The α -alloys were then measured against standard electrodes of $\alpha + \beta$ -alloys, whose cadmium gas pressure is only one one hundred fiftieth that of pure cadmium. This exchange made it possible to measure alloys down to 20% of cadmium. The alloy with the gross composition 0.158, however, has evidently had a surface composition of about 0.20. The same held good about an electrode of composition 0.11, which, moreover, behaved rather irregularly (not given in the tables). In the table the potential of $\alpha + \beta$ against pure cadmium has been added to the potential measured.

In Runs 19 and 20, where the standard electrode was solid cadmium, the temperature was so low that no drifting of the composition occurred.

In the following table are given: the time in hours from the setting up of the cell, the absolute temperature and the potential of the cell measured, corrected for thermopotential. In the heading of the table are given the compositions of the electrodes, in one case both before and after the run. The standard electrode has been liquid cadmium. Below the table are given interpolation formulas for the potentials and the mean deviation of the readings, together with the temperature of transition points.

RUN 17

<i>t</i>	<i>T</i>	0.640-0.637	0.664	0.676	0.698
2.3	740	39.7	(37.0)	35.3	35.5
2.6	743	39.7	37.2	35.0	35.2
2.9	733	40.2	37.9	36.7	36.7
3.6	731	40.1	37.9	36.8	37.1
4.0	718	41.0	38.8	38.4	38.7
4.4	717	40.8	38.9	38.6	39.0
4.9	704	41.5	40.5	40.1	40.4
5.3	702	41.7	40.9	40.6	40.6
5.9	683	42.9	43.0	42.8	42.9
6.3	681	43.3	43.2	43.0	43.1
6.9	665	45.1	45.0	44.9	44.8
7.3	661	45.3	45.4	45.2	45.4
7.8	650	46.6	46.3	46.5	46.4
8.3	641	47.0	46.8	46.8	46.7
8.6	635	47.3	47.2	47.2	47.1
9.5	630	47.6	47.3	47.5	47.5

<i>t</i>	<i>T</i>	RUN 17 (Concluded)			
		0.640-0.637	0.664	0.676	0.698
9.9	619	48.2	48.1	48.2	48.2
10.3	612	48.7	48.5	48.9	48.8
10.6	611	48.8	48.5	48.9	48.7
10.9	625	47.8	47.6	47.8	47.7
11.3	635	47.0	46.9	47.0	46.9
11.5	644	46.6	46.5	46.6	46.5
11.8	647	46.3	46.3	46.4	46.2
12.5	680	43.3	43.1	43.1	43.3
13.0	702	41.9	41.0	40.8	40.7
13.4	714	(41.7)	39.6	39.1	39.1
0.640:	41.8-0.050(<i>T</i> -700) ± 0.1	<i>T</i> > 688			
(0.639):	41.1-0.110(<i>T</i> -700) ± 0.1	659 < <i>T</i> < 688			
0.637:	42.9-0.066(<i>T</i> -700) ± 0.1	<i>T</i> < 659			
0.664:	40.1-0.07 (<i>T</i> -700) ± 0.1	<i>T</i> > 725			
	41.1-0.113(<i>T</i> -700) ± 0.1	657 < <i>T</i> < 725			
	43.2-0.060(<i>T</i> -700) ± 0.1	<i>T</i> < 657			
0.676:	42.1-0.168(<i>T</i> -700) ± 0.1	<i>T</i> > 728			
	40.7-0.118(<i>T</i> -700) ± 0.1	660 < <i>T</i> < 728			
	42.6-0.070(<i>T</i> -700) ± 0.1	<i>T</i> < 660			
0.698:	42.1-0.163(<i>T</i> -700) ± 0.1	<i>T</i> > 728			
	40.8-0.116(<i>T</i> -700) ± 0.1	662 < <i>T</i> < 728			
	42.5-0.071(<i>T</i> -700) ± 0.1	<i>T</i> < 662			

Similar tables for the other runs are summarized in Tables I-III. Table I shows the temperature interval covered in each run, the number of

TABLE I

Run	Temp., °K.	Number of readings	Electrodes
1	665-748	28	0.401, 0.475
2	670-761	29	.441
3	657-753	20	.467, .478, .493
4	656-740	28	.540, .544, .555
5	655-748	23	.510, .516
6	643-743	28	.606-(.624)-(.628)-.624, .633-(.635)-.627
7	682-869	10	.418, .440
8	661-749	14	.505
9	666-753	14	.409
10	647-780	10	.203, .275
11	632-740	11	.284, .299, .326
12	627-756	15	.158, .253
13	642-750	15	.227, .241, .266, .271
14	614-747	26	.599, .619, .643
15	612-696	16	.714-.712, .733-.728, .741-.739, .758-
16	635-750	19	.471, .473, .482
17	611-743	26	.640-.637, .664, .676, .698
18	615-675	15	.696, .763, .755
19	520-579	19	.563, .577, .668, .669
20	519-566	14	.846, .893, .977, .987

accepted readings for each electrode and the composition of the alloy electrodes, in some cases both before and after the run. Values in parentheses have only been estimated from the value of E_{700° , and have been valid during part of the run.

Mostly the first readings were irregular and have been discarded. Especially the electrodes with large gold content usually did not come to equilibrium until the second day of the experiment. Thus some runs lasted sixty hours. Sometimes hysteresis occurred when passing over a transition point. It has been judged from a graphical plot when a reading should not be used. It is seen that the potentials of these alloys are much better defined than those of silver-gold. The α -alloys often showed hysteresis with respect to changes in temperature and were rather irregular when passing over the α - α' transition. On the whole many α -electrodes had to be discarded because of their irregular behavior. Also with other compositions many electrodes have been discarded, but when care was taken that electrodes with very different compositions were not used in the same run, they were not so liable to drift.

The results are given in Tables II and III. The first column refers to Table I, the second and third describe the alloy electrode, and the fourth gives the potential in millivolts at 700°K . or (for Runs 19 and 20) 500°K .

TABLE II
POTENTIAL OF THE CELL $\text{Cd}_{\text{liquid}}/\text{K}(\text{Rb})\text{Cl}, \text{LiCl}, \text{CdCl}_2/(\text{Cd}, \text{Au})_{\text{solid}}$

Run	Cd	Phase	E_{700°	$dE : dT$	$\pm\delta$	T	$-\Delta\bar{F}_{700^\circ}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
18	0.763	ϵ	6.0	+0.017	0		277	-270	+0.78
15	.758	ϵ	8.1	+ .009	1		374	+ 80	+ .42
18	.755	ϵ	9.0	+ .005	2		415	250	+ .23
15	.741	ϵ	26.4	- .136	2		1218	5610	-6.27
15	.739	ϵ	27.9	- .126	2		1287	5350	-5.81
15	.733	ϵ	31.5	- .125	1		1453	5490	-5.77
15	.728	ϵ	32.3	- .120	1		1490	5370	-5.54
15	.714	ϵ	37.2	- .113	2		1716	5360	-5.21
15	.712	ϵ	38.5	- .110	1		1776	5320	-5.07
17	.698	$\gamma + \epsilon$	42.5	- .071	1	<662			
18	.696	$\gamma + \epsilon$	42.4	- .064	1	<659			
17	.676	$\gamma + \epsilon$	42.6	- .070	1	<660			
17	.664	$\gamma + \epsilon$	43.2	- .060	1	<657			
14	.643	$\gamma + \epsilon$	43.4	- .060	1	<655			
17	.637	$\gamma + \epsilon$	42.9	- .066	1	<659			
			42.8	- .065		<659	1974	4070	-3.00
17	.698	$\delta' + \epsilon$	40.8	- .116	1				
17	.676	$\delta' + \epsilon$	40.7	- .118	1				
17	.664	$\delta' + \epsilon$	41.1	- .113	1				
14	.643	$\delta' + \epsilon$	41.0	- .113	1				
17	(.639)	$\delta' + \epsilon$	41.1	- .110	1				
			40.9	- .114		659-728	1887	5570	-5.26

TABLE II (Continued)

Run	Cd	Phase	E_{700°	$dE:dT$	$\approx \delta$	T	$-\Delta\bar{F}_{700^\circ}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
17	0.698	$\delta + \epsilon$	42.1	-0.163	1	>728			
17	.676	$\delta + \epsilon$	42.1	-.168	1	>728			
			42.1	-.166		>728	1942	7300	-7.66
17	.664	$\delta ?$	40.1	-.07	1	>725	1850	4090	-3.2
17	.640	δ'	41.8	-.050	1	>688	1928	3550	-2.31
6	(.635)	δ'	43.6	-.035	2		2011	3140	-1.61
6	.633	δ'	44.2	-.035	4		2039	3170	-1.61
6	(.628)	δ'	46.8	-.032	1		2159	3200	-1.48
6	.627	δ'	47.7	-.030	1		2200	3170	-1.38
6	(.624)	δ'	48.5	-.030	1		2237	3200	-1.38
6	.624	δ'	48.6	-.030	2		2242	3210	-1.38
14	.619	$\beta + \gamma$	44.8	-.096	1	<654			
14	.599	$\beta + \gamma$	44.8	-.095	1	<653			
			44.8	-.096		<654	2066	5170	-4.43
14	.619	$\beta + \delta'$	49.0	-.005	3	>654			
6	.606	$\beta + \delta'$	49.3	-.004	4				
14	.599	$\beta + \delta'$	49.1	-.004	2	>653			
			49.1	-.004		>654	2265	2390	-0.18
4	.555	β	51.8	-.003	1		2389	2490	-.14
4	.544	β	55.6	-.001	2		2565	2600	-.05
4	.540	β	54.9	-.002	2		2532	2600	-.09
5	.516	β	71.2	+.021	2		3284	3960	+.97
5	.510	β	82.8	+.021	3		3819	4500	+.97
8	.505	β	88.0	.000	3		4059	4060	.00
3	.493	β	128.3	-.110	4		5918	9470	-5.07
16	.482	β	131.0	-.127	3		6043	10150	-5.86
3	.478	β	133.1	-.113	4		6047	9690	-5.21
1	.475	β	133.1	-.115	3		6047	9760	-5.30
16	.473	β	137.3	-.127	2		6333	10440	-5.86
16	.471	β	137.0	-.121	3		6319	10230	-5.58
3	.467	β	143.1	-.118	3		6601	10410	-5.44
2	.441	β	151.0	-.106	3		6965	10390	-4.89
7	.440	β	150.1	-.099	1		6924	10120	-4.57
7	.418	$\alpha + \beta$	153.1	-.063	2				
9	.409	$\alpha + \beta$	153.0	-.064	2				
1	.401	$\alpha + \beta$	153.3	-.067	2				
			153.1	-.065			7062	9160	-3.00
11	.326	α	162.7	-.013	2		7505	7930	-0.60
11	.299	α	177.5	-.009	2		8187	8480	-.42
11	.284	α	185.9	-.002	3		8575	8640	-.09
10	.275	α	191.0	-.004	1	>660	8810	8940	-.18
13	.271	α	193.7	-.004	4	>695	8935	9060	-.18
13	.266	α	194.5	+.010	2	>696	8972	9060	+.46
12	.253	α	201.7	+.018	3	>687	9304	8720	+.83
13	.241	α	209.7	+.007	1		9673	9450	+.32

TABLE II (Concluded)

Run	Cd	Phase	E_{700°	$dE : dT$	$\neq \delta$	T	$-\Delta\bar{F}_{700^\circ}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
13	0.227	α	211.2	+0.031	1		9742	8740	+ 1.43
10	.203	α	225.3	+ .028	3	>685	10392	9490	+ 1.29
12	(.158	α	229.4	+ .040	1	>676	10581	9290	+ 1.85)
13	.266	α'	194.8	+ .112	4	<696	8985	5370	+ 5.17
12	.253	α'	207.6	+ .468	3	<687	9576	-5540	+21.59
10	.203	α'	220	- .29	13	<685	10150	19520	-13.38
12	(.158	α'	222.2	- .258	3	<676	10249	18580	-11.90)

TABLE III

POTENTIAL OF THE CELL $\text{Cd}_{\text{solid}}/(\text{K}, \text{Na}, \text{Cd})\text{OCO.CH}_3/(\text{Cd}, \text{Au})_{\text{solid}}$

Run	Cd	Phase	E_{500°	$dE : dT$	$\neq \delta$	T	$-\Delta\bar{F}_{500^\circ}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
20	0.987	η	0.3	0.000	0		14	14	0.00
20	.977		.5	.000	0		23	23	.00
20	.893	$\epsilon + \eta$.5	+ .006	0				
20	.846		.5	+ .006	0		23	-120	+ .28
19	.669	$\gamma' + \epsilon'$	47.9	+ .007	1	<537			
19	.668		47.9	+ .007	1	<547			
			47.9	+ .007		<542	2209	2050	+ .32
19	.669	$\gamma' + \epsilon$	47.5	+ .018	1	>537			
19	.668		47.1	+ .024	1	>547			
			47.3	+ .021		>542	2182	1700	+ .97
19	.577	$\beta' + \gamma'$	63.5	- .066	1	<538			
19	.563		63.4	- .068	1	<542			
			64.4	- .067		<540	2924	4470	-3.09
19	.577	$\beta + \gamma'$	64.4	- .090	1	>538			
19	.563		64.4	- .092	1	>542			
			64.4	- .091		>540	2971	5070	-4.20

For the sake of uniformity this has been done also when the existence range of a certain modification does not include this temperature. The fifth column gives the temperature coefficient, the sixth the mean deviation $\neq \delta$, in 0.1 mv., of the readings from the linear function given by the table and the seventh transition temperatures. The three last columns give the partial molal free energy, heat content and entropy of cadmium in the alloy minus the same quantities of pure cadmium (respectively, liquid and solid). $-\Delta\bar{F}$ and $\Delta\bar{S}$ are found from E and $dE : dT$ by multiplication with 46,126 cal./int. volt.

In order to compare the measurements made with liquid with those carried out with a solid standard electrode, we must know the heat of fusion of cadmium. The values published vary considerably, but the most recent⁷

Umino, *Science Repts. Tokyo Imp. Univ.*, **15**, 597 (1926).

is 12.90 cal./g. or 1450 cal./atom. The molar entropy of fusion is then 2.44 E. U., and thus the temperature coefficient of a cell would be 2.44: 46126 volt/degree = 0.053 mv./degree greater in the case of a solid cadmium electrode than a liquid one. The heat capacities of solid and liquid cadmium are given rather different values by different authors; if their difference were taken into consideration the value given above would be some microvolts/degree smaller. This has, however, been neglected, as the influence does not exceed the uncertainty of the heat of melting.

The potential of $\beta + \gamma'$ against solid cadmium can be written $55.9 - 0.091(T-594)$ mv. and the potential of $\beta + \gamma$ against liquid metal $55.0 - 0.096(T-594)$ mv. If the latter were measured against solid cadmium, it would thus show the potential $55.0 - 0.043(T-594)$ mv., 594°K . being the melting point of cadmium. This shows that there is a transition point in this alloy and (assuming there is only one) it lies at 613°K .

For $\gamma' + \epsilon$ and $\gamma + \epsilon$ the potentials of the table can be written $49.3 + 0.021(T - 594)$ and $49.7 - 0.065(T - 594)$, and the potential of the latter against solid cadmium will then be $49.7 - 0.012(T-594)$. Here the transition is found to be at 606°K .

This transition of the γ -phase has not been previously observed.

The transition of the $\beta + \gamma'$ -phase at 540°K . and $\gamma' + \epsilon$ at 542°K ., however, cannot be another transition of the γ' -phase, but must be due to transitions in both β - and ϵ -phases, which happen to be at nearly the same temperature. For in $\gamma' + \epsilon$ the partial molal entropy of cadmium is greater above the transition and in $\beta + \gamma'$ smaller, contrary to the case at 606 - 613°K . If the transition were in the γ' -phase, this would mean that the total entropy of this phase is greater below the transition than above, which is easily seen by integration (see Lewis and Randall, "Thermodynamics," p. 38, about the connection between total and partial quantities). But this cannot be true, and we must draw the conclusion that there is one transition⁸ in the β and another in the ϵ -phase. Then the latter should also be seen in the $\epsilon + \eta$ range, but it can be shown that the change in partial molal entropy in this range is so small that it cannot be detected. By integrating the difference in partial molal entropy above and below the transition point = 0.65 E. U. over the $\gamma' + \epsilon$ -range, *i. e.*, from 37 to 27% gold, we find the transition entropy at the latter composition $0.65 \times 10/37 = 0.18$ E. U. This is probably not far from the transition entropy at the other side of the ϵ -range, *i. e.*, 24% gold. The $\epsilon + \eta$ -range extends to 3% gold, and hence the difference in partial molal entropy below and above the transition of these alloys is $0.18 \times 3/21 = 0.025$ E. U., corresponding to a difference in temperature coefficient of only 0.5 microvolt/degree. The present measurements are not accurate enough to show this effect.

⁸ This has been verified by an x-ray investigation. See Ölander, *Zeitschrift für Kristallographie*, (A) **83**, 145 (1932).

If the ϵ' - ϵ transition entropy 0.18 E. U. be multiplied with the transition temperature 542°K., we get the transition heat, 100 cal.

The thermal effects for the other transitions observed are

For $\beta' - \beta$ at 47% gold	$\Delta S = 1.11 \times 8/39.5 = 0.23$ E. U. and	$\Delta H = 120$ cal.
For $\gamma' - \gamma$ at 38%	$2.21 \times 7/45 = 0.34$ E. U. and	210 cal.
at 36%	$1.52 \times 7/29 = 0.37$ E. U. and	220 cal.

Thus the two integrations give the same result 220 cal.

For $\gamma - \delta'$ at 37%	$4.25 \times 5/42 = 0.51$ E. U. and	330 cal.
at 36.5%	$2.26 \times 6.5/30 = 0.49$ E. U. and	320 cal.

also a good agreement, 330 cal.

For $\delta' - \delta$ at 33.5%	$2.40 \times 3.5/30 = 0.28$ E. U. and	200 cal.
---------------------------------	---------------------------------------	----------

All these data refer to one gram atom of alloy.

The $\epsilon' + \eta$ -alloys have such a large temperature coefficient that the potential would be zero at 420°K. = 150°. This indicates that between this temperature and 246°, where the present measurements are ending, there should be another transition yielding a smaller temperature coefficient at lower temperatures. Since the partial molal entropy is smaller at lower temperatures, the transition must lie on the cadmium side of the two-phase range, *i. e.*, in the cadmium phase. No transition of cadmium seems, however, to be reported in this temperature range.

During the thermopotential correction runs it was found that this quantity yields a good means for determining the transition points.

It is possible that there is another transition in the ϵ -phase at 485°. The sharp curves in the boundaries by Durrant suggest this and on his published cooling curves there seems to be a very small arrest at this temperature.

The activity coefficient of cadmium in the 0.987 and 0.977 alloys is 0.999 and 1.000, in both cases equal to unity within the experimental errors.

Figure 2 gives the potentials of the alloy electrodes against liquid cadmium at 700°K. The intersections of the curved one-phase lines and the straight two-phase lines give the existence limits of the various phases at this temperature. The slope of the β -curve at higher cadmium contents is rather small and the composition of the intersection point is not so certain. In accordance with Durrant it has been taken as 57.8% cadmium, although a smaller value would not be impossible. However, it is only with the limit 58.0% at 654° that the entropy of the transition γ - δ' would obtain the same value when the difference of partial molal entropy is integrated over the $\beta + \gamma, \delta'$ range as when integrated over $\gamma, \delta' + \epsilon$.

At this temperature (700°K.) the α -phase exists up to 34.4% cadmium, β between 43.3 and 57.8%, δ' between 62.3 and 64.0% and ϵ from 69.9 to about 76%. Owing to the possibility that the composition might not be exactly the same at the surface as in the interior of the electrode, the deci-

mals are, of course, uncertain. Still, the agreement with Durrant's work (thermal analysis) is good.

Similar curves may be plotted at other temperatures, and it is in this way that the boundaries in the phase diagram, Fig. 1, have been obtained.

The eutectic point $\alpha + \beta$, which Saldau³ gives at 43% and 612° seems to lie at a slightly smaller cadmium content, in order to come to the left of the boundary of the β -phase.

Figure 3 gives the temperature coefficient. The ordinates to the left are valid if the standard electrode is liquid metal, whereas those to the right are to be used for solid cadmium, the difference between the two scales being 0.053 millivolt/degree. On the different branches of the curve is shown to which phase they belong.

A striking feature of this diagram is the pronounced leaps of the values for α' , β and ϵ when the composition passes over 25, 50 and 75%. This phenomenon deserves to be dealt with at some length.

If two kinds of atoms are mixed and form a perfect solution, the entropy of formation of the mixture is $\Delta S = -R(x \log x + (1 - x)\log(1 - x))$, when the quantities mixed are x and $1 - x$ gram atoms. If this value is plotted, the tangent at any point of the curve cuts the axes $x = 0$ and $x = 1$ at the values $\Delta \bar{S}_2 = -R \log(1 - x)$ and $\Delta \bar{S}_1 = -R \log x$ (see Lewis and Randall, *loc. cit.*). This is, however, only the case if the two kinds of atoms are randomly distributed over all points in the crystal lattice.

Let us assume that there were an absolutely ordered distribution at 50%, but at no other composition. That means half of the places are reserved for one kind of atoms, and the others for the other kind. Between 0 and 50% the mixing will then only refer to half the places, and the entropy will be $-R(x \log 2x + (1/2 - x)\log(1 - 2x))$. The same holds good between 50 and 100%, except that the formula will be $-R((1 - x)\log(1 - x) + (x - 1/2)\log(2x - 1))$. In a plot the entropy forms two small arcs similar to the big arc in the first case. The intercepts of the tangent in this case will also give the values of the partial molal entropies, but these quantities have now a discontinuity at 50%, where they change their values from $+\infty$ to $-\infty$. The value of $\Delta \bar{S}_1$ is from 0-50% $-R(\log 2x - 1/2 \log(1 - 2x))$ and from 50-100% $-1/2 R \log(2x - 1)$.

But this cannot occur above the absolute zero; the partial molal entropies will remain finite. For when it is possible to substitute one atom in the lattice for one of the other kind, when the composition is not 50%, one must expect that when the mixture is exactly that, there must still be a small number of atoms substituting one another, or be misplaced—of course the same number of each kind. These misplaced atoms act as impurities and increase the entropy, so there is no sharp cusp at 50% in the plotted curve of entropy, but the cusp is rounded off, as in Fig. 4. Then the partial molal entropies will not pass to infinity at 50%, but the two

branches will bend together and join, and the curve looks like the branch at 50% in Fig. 3.

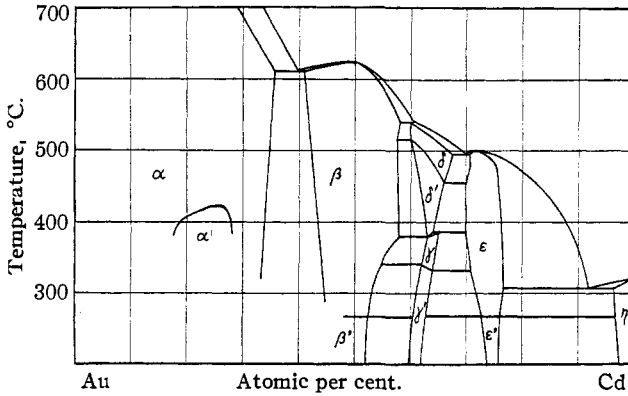


Fig. 1.—Phase diagram of the gold-cadmium system.

In those cases we meet with in practice the lattice will exist only in a limited composition range around 50%, as in the system cadmium-gold. But this does not alter the conditions fundamentally; we must expect that around 50% the mixing term of entropy behaves in the way now described.

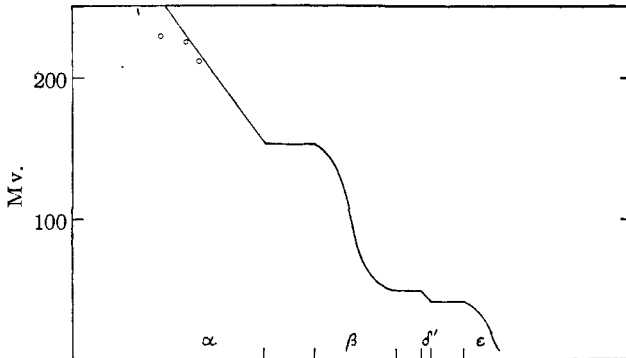


Fig. 2.—Potential of the cell Cd/KCl, LiCl, CdCl₂/(Cd, Au) at 700°K.

To this term is added another, because it is not a perfect solution, being the excess of the formation entropy at the temperature of the experiment over the formation entropy of the same alloy at absolute zero, or $\int_0^T \frac{\Delta c_p}{T} dT$. If this value in the first approximation is a linear function of the composition in some limited range, the corresponding term in the partial molal entropy will in this range be a constant.

If the mixing term of the partial molal entropy in the neighborhood of 50% be plotted after the formulas given and the two branches moved to

join the curve in Fig. 3 experimentally found around 50% in the best way possible, they will fall as shown by the dotted curves. Below 48 and above 52% cadmium each branch deviates from the experimental curve only by 0.004 mv./deg. or 0.18 E. U., a quantity of the same magnitude as the experimental errors. The null-point of the mixing term curve will fall at -0.057 mv./deg. if the standard state of cadmium is liquid, and on -0.004 mv./deg. if it is solid, or in entropy units -2.63 and -0.18 , which thus is the approximately constant second term in the partial molal entropy of alloy formation.

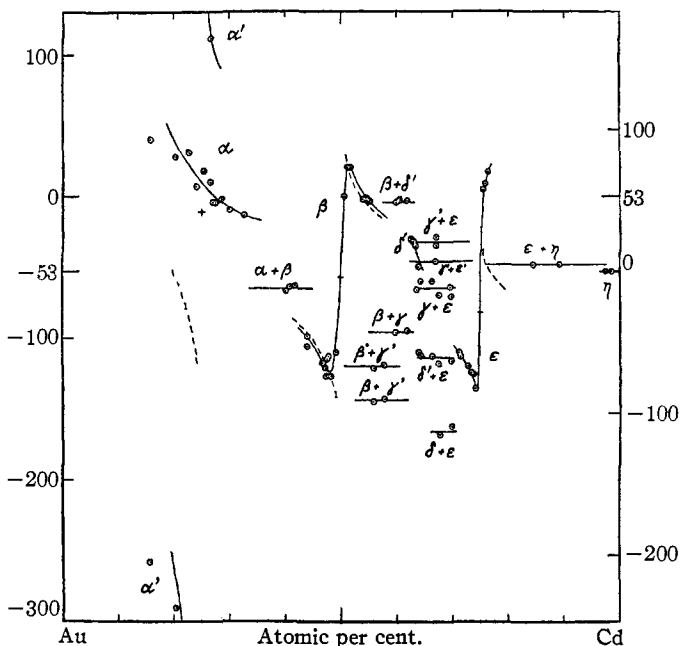


Fig. 3.—Temperature coefficient of the cell Cd/electrolyte/(Cd, Au) in microvolts/degree. Ordinates to the left for liquid cadmium, to the right for solid cadmium. Cf. the phase diagram.

From the fact that the deviation of the experimental curve from the theoretical does not begin until 48 and 52% we shall draw the conclusion that the misplaced atoms must be few as compared with the excess of either kind at the compositions quoted, *i. e.*, much less than 4%.

The mixing term of the total entropy may be calculated for $x = 0.48$ from the formula given, *viz.* $-R(x \log 2x + (1/2 - x) \log(1 - 2x))$; it is 0.167 E. U. The value for 0.52 is of course the same. From the experimental values of the mixing term of the partial molal entropy (*i. e.*, the observed quantities $+2.63$ E. U.) between 48 and 52% we can find the total quantity by a process of integration, starting from 0.167 E. U. at 48

and 52%. Figure 4 shows this mixing term of the total entropy, compared with the hypothetical curve that would exist if the atoms were in perfect order at 50%. The excess entropy which the experimental curve shows at 50%, and which is due to the misplaced atoms, is about 0.06 E. U.

From this value we are able to estimate the deviation from perfect order in the crystal lattice. An x-ray investigation, which is published elsewhere,⁷ shows that at the temperatures in question the β -phase forms

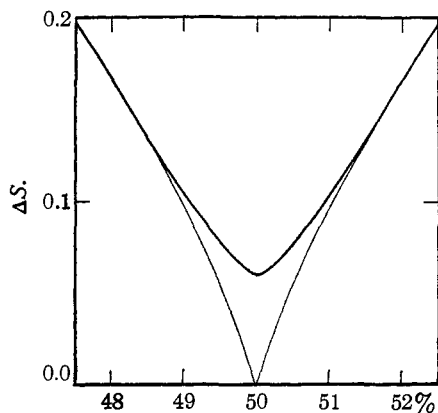


Fig. 4.—The mixing term of entropy around 50 atomic per cent.

a cesium chloride lattice, *i. e.*, the gold and the cadmium atoms form two simple cubic lattices body-centering each other. The elementary cube, containing one gold and one cadmium atom, has an edge of about 3.34 Å.

A few of these elementary cubes AuCd contain misplaced atoms, so their formula will be AuAu or CdCd. At 50% there will be the same number of these two kinds. A much smaller number of cells will contain two misplaced atoms, CdAu. We may neglect these in the first approximation. If the

fraction of cells AuAu or CdCd be x , the excess entropy of one mole AuCd will be

$$-R(x \log x + x \log x + (1 - 2x) \log(1 - 2x)) = 2 \times 0.06$$

(because 0.06 E. U. is the excess entropy for $\frac{1}{2}$ AuCd). This equation has the solution $x = 0.0048$. This means that 0.5% of the atoms are misplaced in the crystal lattice at the temperatures in question, 400–450°.

At 25 and 75% cadmium, however, this simple theory does not work quantitatively. Around the composition AuCd₃ the partial molal entropy is expected to be $-R(\log \frac{4}{3}x - \frac{1}{4} \log(1 - \frac{4}{3}x))$ to the left and $-\frac{1}{4}R \log(4x - 3)$ to the right. The slope of the first branch is the same as that of the experimental curve between 71 and 74%, but if these are made to coincide, yielding the constant term -0.029 mv./deg. or -1.34 E. U. (solid cadmium) the right branch will fall as the dotted line, far below the experimental points.

Around Au₃Cd the two expressions will be $-R(\log 4x - \frac{3}{4} \log(1 - 4x))$ and $-\frac{3}{4}R \log(\frac{4}{3}x - \frac{1}{3})$. The experimental material is somewhat scarce, but if the latter branch is laid through 5.17 E. U. at Cd = 0.266, giving the constant term 0.042 mv./deg. or 1.94 E. U. (solid cadmium), the left branch will fall far above the corresponding points measured. In both these cases the leap experimentally found is much bigger than that ex-

pected. Below 75% cadmium the mixing term seems to describe the conditions, but above this composition the total entropy rises faster, yielding a bigger partial entropy of cadmium. This could be caused if the change in composition were brought about not only by substitution of gold atoms by cadmium, but also by leaving vacant places in the lattice. But this can probably not explain the whole discrepancy. Another possibility is that the quantity $\int_0^T \frac{\Delta c_p}{T} dT$ previously referred to is not a linear function of the composition across 75%, but that $\frac{\partial}{\partial [\text{Cd}]} \int_0^T \frac{\Delta c_p}{T} dT$ changes rapidly in the neighborhood of this composition. At present nothing can be said with certainty about this matter.

Attention may be drawn to the fact that in the α -phase, that has no maximum of its conductivity at 25%, and hence is expected to have a random atom distribution, the temperature coefficient is a monotonous function of the composition, as is to be expected.

Summary

The potential of the cell $\text{Cd}_{\text{liquid}}/\text{K(Rb)Cl, LiCl, CdCl}_2/(\text{Cd, Au})_{\text{solid}}$ and its temperature coefficient have been measured for fifty-four compositions of the alloy electrode for temperatures above 340°.

The potential of the cell $\text{Cd}_{\text{solid}}/(\text{K, Na, Cd}).\text{OCO.CH}_3/(\text{Cd, Au})_{\text{solid}}$ and its temperature coefficient have been measured for eight compositions of the alloy electrode between 250 and 300°.

The phase diagram of the cadmium-gold system has been completed, three new transitions having been found.

The heat effect at some transitions has been calculated.

In those cases where other indications existed that the atoms were distributed in an orderly manner in the crystal, the temperature coefficient showed a dependence on the composition that could be anticipated from statistical considerations of the entropy. At the composition AuCd it has been possible to calculate the degree of randomness in the crystal lattice. Around 450° there are 0.5% of misplaced atoms.

BERKELEY, CALIFORNIA
STOCKHOLM, SWEDEN