Physics. — *Measurements on Thermo-Electric Forces down to Temperatures Obtainable with Liquid or Solid Hydrogen.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. (Communication N⁰. 217*d* from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 30, 1932.)

§ 1. *Introduction.* While preparing and performing our measurements on thermo-electric forces down to liquid helium temperatures we had an opportunity to collect a number of data on thermoelectric forces at temperatures obtainable with liquid or solid hydrogen. We give these data in this paper for those metals or alloys for which we did not get numbers at liquid helium temperatures.

The apparatus used and the method followed were the same as described in our preceding paper on measurements at liquid helium temperatures [1]).

§ 2. *Results for Ag and for an alloy of Ag with Au.* The silver was supplied for spectroscopic purposes by HILGER in London. The spectroscopical analysis had given small traces of *Ca* as the only considerable impurity. As a matter of fact we tried to investigate this silver also at the liquid helium temperatures. We got however no good measurements on it at those temperatures. The results for the thermo-electric force per degree, obtained when the coldest junction was at the boiling point of helium, was not in harmony with those, obtained with the coldest junction at the temperature of solid hydrogen. The reason may be, that, on account of the great heat conductivity, which is to be expected for such a pure silver at the temperature of liquid helium, a considerable part of the temperature difference takes place at the junctions. It may be necessary to use long and thin wires in such measurements. Though we thus cannot give any numerical values for the thermo-electric forces below 10° K., it is to be noted that they were found to be positive against our normal, which was an alloy of *Ag* with 0.37 at. % *Au*. The results for temperatures above 10° K are given in table I.

We have also measured another alloy of *Ag* with 0.91 at. % *Au*. As might be expected it falls on the other (negative) side of the normal than the pure *Ag* does. In this figure for comparison the curve for a wire of silver got from KAHLBAUM and measured in 1929 [2]) (here marked Ag_{29}) is also again traced. This silver seems to contain some thermo-electrically rather active impurity.

[1]) These Proceedings **34**, 1365, 1931. Comm. Leiden N⁰. 217*c*.

[2]) These Proceedings, **33**, 17, 1930. Comm. Leiden N⁰. 206*a*.

TABLE I.

Thermo-electric force in microvolt per degree for pure and alloyed Ag against silveralloy-normal.					
Ag_{31} (HILGER)				Ag + 0.91 at. % Au	
°K.	e	°K.	e	°K.	e
10.1	+0.19	42.5	+0.73	17.3	−0.15
12.0	0.22	42.7	0.66	17.3	0.16
13.7	0.24	47.2	0.68	23.9	0.20
15.8	0.22	48.0	0.66	30.4	0.25
17.3	0.34	58.9	0.51	36.8	0.27
19.4	0.35	67.9	0.45	42.8	0.33
24.0	0.57	78.9	0.37	48.0	0.33
26.7	0.55	86.3	0.32	59.3	0.32
30.3	0.70	94.2	0.30	68.3	0.33
36.5	0.71	102.7	0.28	77.3	0.33
36.7	0.74	275.4	0.21	85.9	0.33
				94.0	0.35
				102.2	0.35
				275.3	0.38

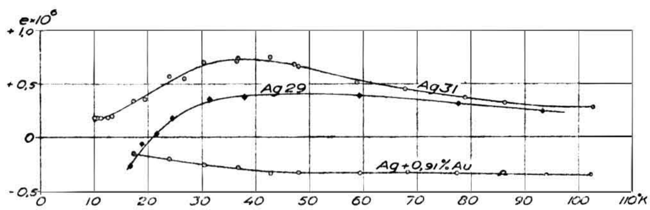

Fig. 1. Thermo-electric force in volt per degree. Against silveralloy-normal.

In Fig. 2 we have also given the thermo-electric force per degree for pure and alloyed silver on the absolute scale[1]). The influence of the added gold appears here more clearly. It seems rather probable that the pure silver approaches zero from the positive side of the axis in the absolute thermo-electric scale. However the measurements have not yet

[1]) Cf. These Proceedings, **35**, p. 10, 1932. Comm. Leiden Suppl. N⁰. 69*b*.

given any clear knowledge of the thermo-electric properties of pure not supra-conductive metals at the lowest temperatures.

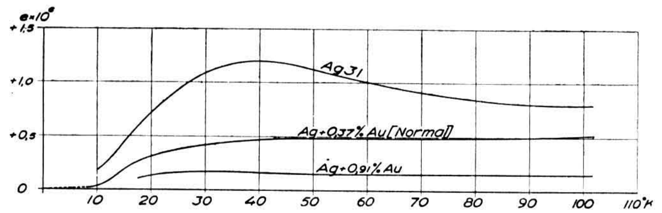

Fig. 2. Thermo-electric force in volt per degree in the absolute thermo-electric scale for *Ag*, *Ag* with 0.37 at. % *Au* (Normal) and *Ag* with 0.91 at. % *Au*.

§ 3. *Au with small quantities of Fe.* As we were interested to see if perhaps the high thermo-electric forces observed in the system *Cu Fe* at the liquid helium temperatures (c.f. our next paper) are due to the high degree of supersaturation of these alloys, we also investigated the analogous system *Au Fe*, where the solubility is much higher, the saturation limit being at room temperature about 20 at. % *Fe*. The

TABLE II.

Thermo-electric force in microvolt per degree for dilute alloys of Au with Fe against silveralloy-normal.

Au + 0.065 at. % Fe		Au + 0.19 at. % Fe		Au + 1.09 at. % Fe		Au + 1.89 at. % Fe	
°K.	e	°K.	e	°K.	e	°K.	e
17.5	−13.77	17.4	−13.64	17.3	−8.37	17.5	−6.33
17.5	13.80	17.4	13.92	17.3	8.42	17.5	6.30
24.1	12.47	24.7	13.75	24.0	10.07	24.1	8.10
30.7	11.29	31.3	13.40	30.3	11.30	30.7	9.55
36.9	10.26	38.3	13.01	36.7	11.88	36.9	10.40
42.9	9.63	45.8	12.43	42.7	12.33	42.9	11.20
48.3	8.98	50.6	11.86	47.2	12.63	48.3	11.36
92.4	5.25	62.1	10.73	58.8	12.20	94.2	11.78
102.3	5.29	68.0	10.65	67.8	11.97	102.3	11.78
102.3	5.42	102.0	8.90	79.0	12.10	102.3	11.78
293.1	0.9	293.1	3.76	86.2	11.97	293.1	7.5
				94.2	12.30		
				102.6	11.81		
				275.4	7.28		

measurements were carried out down to the hydrogen temperatures for four alloys with 0.065 to 1.89 at. % *Fe*. The results are given in table II and are shown in the temperature diagram Fig. 3 and the concentration diagram Fig. 4.

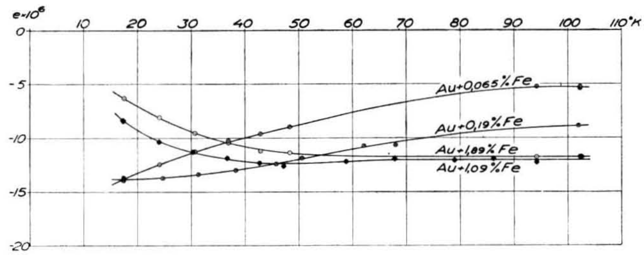

Fig. 3. Thermo-electric force in volt per degree.
Against silveralloy-normal.

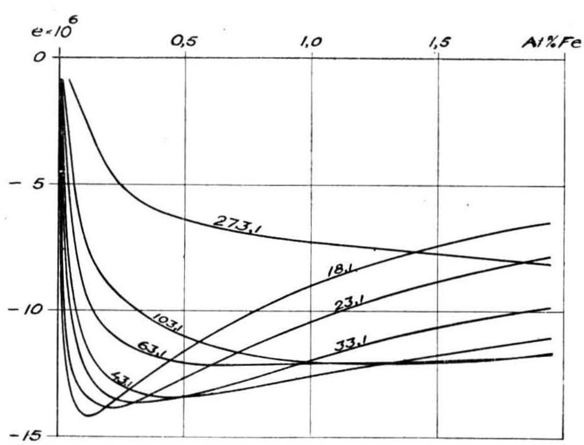

Fig. 4. Thermo-electric force in volt per degree for dilute alloys of *Au* with *Fe* as a function of the concentration of *Fe*. The numbers give the temperature of the isotherms on the Kelvinscale.
Against silveralloy-normal.

In fact the curves are quite analogous to those for the system *Cu Fe* (next paper § 3) and the negative maximum value of e is of the same order of magnitude. There is, however, a quantitative difference between the two systems in so far as the negative maximum in the system *Au Fe* as compared with the system *Cu Fe* is displaced for a given temperature towards higher concentrations (observe the different scales in the Figures 4 of this and 3 of the next paper) and for a given concentration towards lower temperatures. This may perhaps depend upon the fact that the characteristic temperature of *Au* is smaller than that of *Cu*. Any signs of a specific difference as to the degree of supersaturation have not been found.

§ 4. *Au with small quantities of Co.* Measurements on an alloy of

Cu with 0.09 at. % *Co* carried out in 1929[1]) down to the liquid oxygen temperatures made it probable that *Co* as well as *Fe* was a suitable metal to add for getting high thermo-electric forces at low temperatures. This time we measured five alloys of *Au* with 0.061 to 6.71 at. % *Co*. The results are given in Table III and the Figs. 5 and 6. They show, that

TABLE III.

Thermo-electric force in microvolt per degree for dilute alloys of Au with Co against silveralloy-normal.

Au + 0.061 at. % Co		Au + 0.21 at. % Co		Au + 0.95 at. % Co		Au + 2.11 at. % Co		Au + 6.71 at. % Co	
°K.	e	°K.	e	°K.	e	°K.	e	°K.	e
17.5	−11.52	17.4	−13.09	17.4	−13.93	17.5	−15.00	17.4	−11.74
17.5	11.54	26.7	17.34	23.9	17.64	17.5	15.03	26.7	15.64
24.1	12.85	36.5	20.40	30.3	21.28	24.1	18.87	36.5	19.10
30.4	13.56	42.5	21.90	36.5	24.00	30.7	22.27	42.5	20.80
36.9	13.70	48.0	22.34	42.5	26.18	36.9	24.60	48.0	22.12
42.9	13.97	57.5	23.2	48.0	27.7	42.9	27.1	58.8	23.6
48.3	13.90	60.8	23.3	56.8	28.7	48.3	28.3	60.7	23.8
94.2	13.11	66.8	23.8	62.1	29.8	94.2	37.8	67.5	25.3
102.3	12.97	93.9	25.6	68.3	30.9	102.3	38.1	87.7	28.5
102.3	12.96	275.3	19.4	102.3	35.8	102.3	37.8	275.3	39.4
293.1	7.2			275.3	37.1	293.1	47.5		

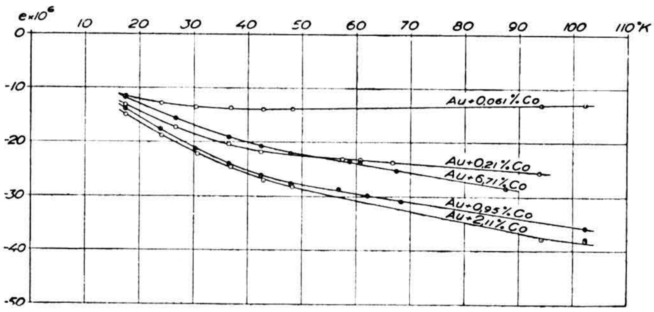

Fig. 5. Thermo-electric force in volt per degree. Against silveralloy-normal.

above about 15° K. the addition of *Co* to *Au* can give higher thermo-electric forces than the addition of *Fe*, whereas below this temperature the case is most probably the reverse. A detailed comparison between the systems

[1]) These Proceedings **33**, 32, 1932. Comm. Leiden N⁰. 206*b*.

Cu Co and *Au Co* is not yet possible, as only the one alloy of copper with 0.09 at. % *Co* has been measured. For the present we can only state

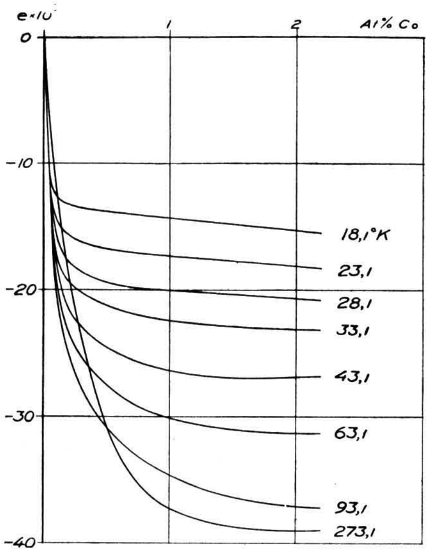

Fig. 6. Thermo-electric force in volt per degree for dilute alloys of *Au* with *Co* as a function of the concentration of *Co*. The numbers give the temperature of the isotherms on the Kelvinscale. Against silveralloy-normal.

that 0.1 at. % *Co* has a larger thermo-electric influence on *Au* than on *Cu* at about 100° K. A qualitative analogy of the two systems is, however, quite possible.

§ 5. *Au with small quantities of Ni.* We have measured three alloys of *Au* with 0.04, 0.18 and 1.16 at. % *Ni*. The results are given in Table IV and Fig. 7. The concentration diagram constructed in Fig. 8 is of course somewhat uncertain in the details as only three concentrations have been examined.

It seems probable, that the most dilute alloys of *Au* with *Ni* (just as those of *Au* or *Cu* with *Fe*) have a negative maximum of the thermo-electric force below the liquid hydrogen temperatures. However, it is not yet quite sure to what extent the shape of the curves at the lowest temperatures are influenced by small impurities of iron.

A comparison of the present curves for the system *Au Ni* with those for the system *Cu Ni*, given in our earlier paper[1]), show, that the same concentration of *Ni* has a larger influence on *Au* than on *Cu* (with *Co* the case was the same as with *Ni*, with *Fe* it was the opposite). A qualitative analogy of the two systems *Cu Ni* and *Au Ni* seems quite possible.

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[1]) Comm. Leiden N°. 206*b* Fig. 2.

TABLE IV.

Thermo-electric force in microvolt per degree for dilute alloys of Au with Ni against silveralloy-normal.					
Au + 0.04 at. % Ni		Au + 0.18 at. % Ni		Au + 1.16 at. % Ni	
°K.	e	°K.	e	°K.	e
17.3	—3.02	17.3	—3.59	17.3	—4.13
17.3	3.04	17.3	3.60	17.3	4.16
23.9	2.25	23.9	3.53	24.0	4.88
30.4	1.61	30.4	3.31	30.3	5.54
36.8	1.22	36.8	3.08	42.7	6.38
42.8	0.987	42.8	2.95	47.2	6.64
48.0	0.855	48.0	2.84	58.9	6.94
59.3	0.722	59.3	2.66	67.8	7.41
68.3	0.685	68.3	2.64	79.0	8.17
77.3	0.643	77.3	2.66	86.2	8.37
85.9	0.633	85.9	2.67	94.1	9.21
94.0	0.633	94.0	2.80	102.6	9.28
102.2	0.610	102.2	2.80	275.4	14.48
273.3	0.417	273.3	3.24		

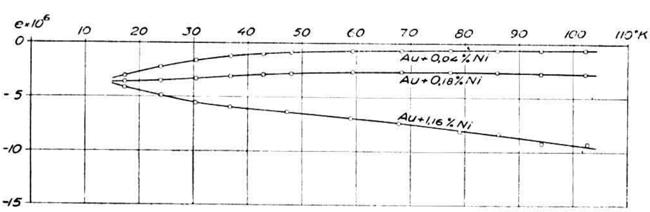

Fig. 7. Thermo-electric force in volt per degree. Against silveralloy-normal.

As far as can be made probable by extrapolations, it seems not possible to get the same high thermo-electric forces against the pure metals *Au* or *Cu* at low temperatures by adding *Ni* as by adding *Fe* or *Co*.

§ 6. *Au with small quantities of Mn, Cr and Ti.* We have also measured some dilute alloys of *Au* with *Mn, Cr* and *Ti*, the neighbours of *Fe, Co* and *Ni* in the transition group of the fourth period of the periodic system. The results are given in Table V and Fig. 9. These alloys

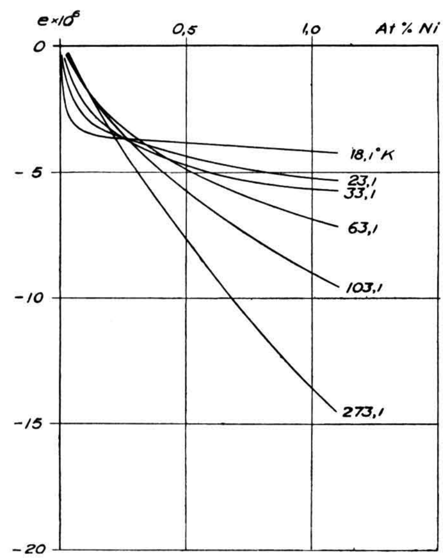

Fig. 8. Thermo-electric force in volt per degree for dilute alloys of *Au* with *Ni* as a function of the concentration of *Ni*. The numbers give the temperature of the isotherms on the Kelvinscale. Against silveralloy-normal.

TABLE V.

Thermo-electric force in microvolt per degree against silveralloy-normal.					
Au + 0.2 at. % Ti		Au + 3.65 at. % Cr		Au + 2.08 at. % Mn	
°K.	e	°K.	e	°K.	e
17.4	—0.855	17.4	—0.508	17.3	—1.23$_5$
24.7	0.883	17.4	0.503	17.3	1.25
31.3	0.807	24.7	0.917	23.9	1.59
38.3	0.756	31.3	1.243	30.4	1.76$_5$
45.8	0.633	38.3	1.594	36.8	1.86$_5$
50.6	0.562	45.8	1.916	42.8	1.88
62.1	0.361	50.6	2.10	48.0	1.85$_5$
68.0	0.251	62 1	2.48	59.3	1.71
102.0	+0.236	68.0	2.75	68.3	1.65
295.0	1.97	102.0	3.77	77.3	1.54
		295.0	8.42	85.9	1.48
				94.0	1.45
				102.2	1.24
				275.3	0.09

TABLE VI.

Thermo-electric force in microvolt per degree against silveralloy-normal.

°K.	°C.	Au — Fe				Au — Co					Au — Ni			Au — Ti	Au — Cr	Au — Mn
		0.065 at. % Fe	0.19 at. % Fe	1.09 at. % Fe	1.89 at. % Fe	0.061 at. % Co	0.21 at. % Co	0.95 at. % Co	2.11 at. % Co	6.71 at. % Co	0.04 at. % Ni	0.18 at. % Ni	1.16 at. % Ni	0.2 at. % Ti	3.65 at. % Cr	2.08 at. % Mn
18.1	—255	—13.66	—13.85	—8.65	—6.54	— 11.65	—13.4	—14.3	—15.35	—12.1	—2.95	—3.60	— 4.24	—0.86	—0.60	—1.30
23.1	250	12.64	13.74	10.08	7.94	12.65	15.8	17.3	18.25	14.2	2.44	3.52	4.82	0.86	0.83	1.55
28.1	245	11.71	13.48	11.06	9.05	13.3	17.9	20.05	20.8	16.2	1.82	3.39	5.33	0.85	1.10	1.73
33.1	240	10.88	13.32	11.66	9.94	13.7	19.6	22.5	23.2	18.0	1.43	3.23	5.73	0.82	1.33	1.83
38.1	235	10.18	13.00	12.07	10.62	13.9	20.9	24.6	25.25	19.55	1.16	3.06	6.00	0.76	1.56	1.87
43.1	230	9.57	12.61	12.37	11.10	13.95	21.85	26.3	26.95	20.85	0.99	2.93	6.23	0.68	1.78	1.87
53.1	220	8.4	11.70	12.30	11.58	13.85	22.8	28.45	29.4	22.8	0.77	2.75	6.69	0.52	2.18	1.80
63.1	210	7.3	10.77	12.10	11.70	13.7	23.5	30.0	31.3	24.5	0.70	2.70	7.15	0.34	2.55	1.70
73.1	200	6.4	10.05	12.05	11.75	13.5	24.2	31.5	33.3	26.1	0.66	2.66	7.70	0.17	2.89	1.60
83.1	190	5.7	9.45	12.05	11.76	13.3	24.9	32.9	35.3	27.7	0.64	2.57	8.29	± 0	3.20	1.50
93.1	180	5.4	9.10	12.05	11.78	13.15	25.55	34.4	37.2	—	0.61	2.74	8.90	+0.13	3.51	1.40
103.1	170	5.3	8.87	12.05	11.76	12.95	—	35.9	38.6	—	0.60	2.83	9.50	0.25	3.80	1.29
273.1	± 0	—	—	7.4	—	—	19.5	37.1	—	39.4	0.42	3.24	14.4	—	—	0.09
293.1	+ 20	0.9	3.8	—	7.5	7.2	—	—	47.5	—				1.96	8.4	—

give no such high thermo-electric forces against *Au* as the alloys of *Au* with *Fe* and *Co*. It should be noticed that the alloy of *Au* with *Ti* at high

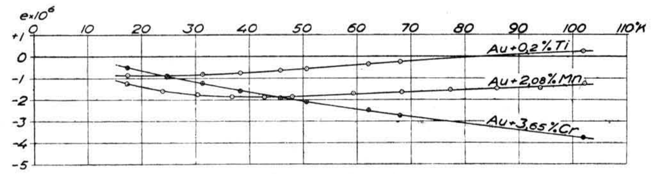

Fig. 9. Thermo-electric force in volt per degree. Against silveralloy-normal.

temperatures is positive and at low temperatures negative against the pure metal (analogous to the dilute alloys of *Pt* with *Rh*, investigated in 1929) [1]).

§ 7. *Thermo-electric forces per degree at corresponding temperatures.* Table VI gives graphically interpolated values of the thermo-electric forces against the normal of the gold alloys dealt with in this paper. The temperatures are the same as given in the corresponding tables of our earlier papers. The thermo-electric force per degree on the absolute thermo-electric scale introduced in Suppl. N⁰. 69*b* is to be obtained by adding the values of Table III of that paper.

Summary.

Thermo-electric forces against a silver-alloy normal were measured down to the temperatures obtainable with liquid or solid hydrogen for *Ag* and an alloy of *Ag* with *Au* and for *Au* with small quantities of *Fe*, *Co*, *Ni*, *Mn*, *Cr* or *Ti* respectively.

[1]) Comm. Leiden N⁰. 206*b* Fig. 2.