FURTHER EXPERIMENTS ON THE VOLATILIZATION OF PLATINUM

G. K. Burgess, Physicist, and R. G. Waltenberg, Assistant Physicist

The experiments here described are an extension of those of Burgess and Sale,[1] undertaken at the suggestion of Dr. W. F. Hillebrand, chairman of the committee on quality of platinum utensils of the American Chemical Society. In the earlier papers are described a convenient thermoelectric method of testing platinum purity and observations on loss of weight of crucibles subjected to heating at 1200° C and subsequent acid treatment, together with certain magnetic and photomicrographic observations.

The present investigation consists of a series of observations on change in weight of several platinum crucibles of various degrees of purity when subjected to heating at 700°, 1000°, and 1200° C. Determination of the loss of iron content after successive heatings and of other materials soluble in hydrochloric acid have also been made, as well as a few observations by treatment with hydrofluoric acid to detect the presence of silica, which may come largely if not entirely from the marquardt porcelain portions of the furnace described in previous papers, to which papers reference should also be made for the details of apparatus and methods.

The choice of heating temperatures of 700°, 1000°, and 1200° C proved a fortunate one, in that it not only covers the temperature range to which platinum crucibles are ordinarily subjected in practice, but besides it so happens that there also occurs within this temperature interval a reversal from a loss to a gain in weight of all grades of platinum ware observed in this investigation.

[1] J. of Ind. and Eng. Chemistry, 6, p. 452, 1914; 7, p. 561, 1915; Scientific Paper No. 254, this Bureau, 1915.

The observations and the numerical inferences from them are recorded in Tables 1 and 2 for the seven crucibles of this investigation, ranging from the purest thermoelement and "tiegel platin" ware of Heraeus to crucibles containing up to 2.7 per cent iridium and 8 per cent rhodium and with divers amounts of iron and other unknown soluble materials (including probably Pt itself, which in presence of Fe is slightly soluble in HCl) also as impurity. Five of these crucibles—all except I and II, which are practically new—had been used in the previous investigation at 1200° C.

The crucibles which had been previously heated at 1200° C were heated at 1000° C and then at 700° C; the others were heated in the reverse order: 700°, 1000°, and 1200° C. When crucibles have been prepared for use by strong ignition and treatment with acid there is apparently no difference in the loss in weight due to reversing the order of heating. This would be expected from the previous work at this Bureau. The experimental operations were, in brief, as follows:

Before heating, each crucible was cleaned and weighed. The furnace was brought to the temperature desired, then the crucible was placed in it and allowed to remain for four hours. (In the work of Burgess and Sale at 1200° C the crucibles were heated for two-hour periods.) The crucibles were then taken out of the furnace, cooled in a desiccator, and weighed. A treatment for five minutes with boiling hydrochloric acid (1 acid to 4 water) followed. They were again weighed after washing followed by a slight ignition over a Bunsen burner. The iron in the hydrochloric acid solution was weighed as ferric oxide after precipitating with ammonium hydroxide; slight discrepancies appear in some of the results due to the ash uncertainty on ignition of the filter paper. The crucibles were usually heated three times at each temperature with similar treatment after each heating.

Table 1 shows the results of each treatment in milligrams per 100 cm^2 of platinum surface. Crucibles *b* and *n* are alloys containing about 0.19 and 7.95 per cent rhodium, respectively; the others contain iridium; *n* was made up specially and *b* is presumed from its behavior to contain rhodium.

For several crucibles the first treatment results in a loss appreciably greater than the succeeding ones. This illustrates the necessity of proper preparation of the crucibles before using for accurate determinations.

TABLE 1

Observations on Platinum Crucibles

Source or maker	Crucible reference	Weight (grams)	Volume (cm^3)	Area of surface (cm^2)	Emf (mv)	Iridium (per cent)	Rhodium (per cent)	Four hours at 700° C (loss in mg/100 cm^2)			Four hours at 1000° C (loss in mg/100 cm^2)			Four hours at 1200° C (loss in mg/100 cm^2)		
								Heat	Acid	Fe_2O_3	Heat	Acid	Fe_2O_3	Heat	Acid	Fe_2O_3
Heraeus, normal thermoelement Pt	a	17.2	27	77	0.1	0.05	.....	+0.03	0.03	0.05	0.38	0.05	0.08	4.36	0.10	0.29
								+ .01	.06	.09	.23	.01	.00	1.68	.60	.43
								+ .01	.08	.05	.31	.04	.06	3.70	.12	.21
Heraeus, Tiegel platin....	I	18.0	26	82	2.6	.8	.....	+ .00	.10	.11	1.06	.27	.18	.....	.....	.....
								+ .07	.13	.07	.88	.24	.21	.....	.....	.....
								.05	.16	.02	.51	.09	.00	.....	.....	.....
Johnson Matthey Co., best crucible ware	b	26.2	33	106	.5	.....	0.2	+ .02	.23	.08	.29	.20	.04	3.96	.48	.25
								+ .02	.16	.05	.35	.03	.02	1.92	.70	.40
								+ .08	.17	.06	.33	.10	.07	4.08	.30	.20
Baker & Co., commercial ware	k	23.9	34	79	6.5	2.4	.....	+ .10	.65	.46	3.64	.25	.18	12.48	2.28	.....
								+ .09	.48	.28	1.46	.15	.10	10.90	.78	.....
								+ .03	.23	.18	1.50	.29	.09	5.88	2.02	.....
Do.....	l	39.6	56	108	6.9	2.7	.....	+ .08	.20	.14	.59	.52	.09	4.32	10.66	.....
								+ .06	.17	.08	1.02	.21	.13	4.64	4.94	.....
								+ .05	.15	.10	.80	.22	.19	10.16	5.58	.....
Baker & Co., special Rh ware	n	19.9	24	79	9.7	.....	8.0	+ .11	.10	.09	.56	.04	.05	1.22	.04	.18
								+ .13	.10	.....	.10	.08	.01	2.88	.26	.34
								+ .10	.09	.08	.16	.07	.14	2.42	.08	.00
Quenessen, De Belmont, Legendre et Cie	II	15.4	22	78	2.7	.9	.....	.07	.14	.13	2.47	.55	.45	4.02	.45	.38
								.27	.15	.10	1.01	.60	.46	3.98	.14	.43
								.00	.33	.15	1.00	.49	.21	.....	.....	.....

Table 2 gives a summary of the results. The change in weight on heating at 700° C was very small, and in most cases was an increase (0.005 to 0.028 mg/100 cm^2/hour), but the loss with acid treatment was greater than the gain on heating in all but one case. The 8 per cent rhodium alloy, crucible *n*, gained a little more weight on heating than it lost with acid. This is due possibly to a small amount of silica deposited on the crucible from the furnace tube. On treating these crucibles with strong hydrofluoric acid, after the hydrochloric acid treatment, there was a loss, which for crucible *n* amounted to 0.24 mg/100 cm^2. There was no additional loss on repeating the treatment with hydrofluoric acid.

TABLE 2

Summary of Heating and Acid Tests

	Crucible, a; emf against Pt, 0.1 mv; equivalent alloy, 0.05 per cent Ir. Temperature of heating, ° C			Crucible, b; emf against Pt, 0.5 mv; equivalent alloy, 0.2 per cent Rh. Temperature of heating, ° C			Crucible, I; emf against Pt, 2.6 mv; equivalent alloy, 0.8 per cent Ir. Temperature of heating, ° C			Crucible, II; emf against Pt, 2.7 mv; equivalent alloy, 0.9 per cent Ir. Temperature of heating, ° C			Crucible, k; emf against Pt, 6.5 mv; equivalent alloy, 2.4 per cent Ir. Temperature of heating, ° C			Crucible, l; emf against Pt, 6.9 mv; equivalent alloy, 2.7 per cent Ir. Temperature of heating, ° C			Crucible, n; emf against Pt, 9.7 mv; equivalent alloy, 8.0 per cent Rh. Temperature of heating, ° C		
	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200
Heat treatment loss, mg/100 cm^2/hr..	+0.004	0.077	0.812	+0.010	0.081	0.830	+0.002	0.204	.....	0.028	0.374	1.001	+0.018	0.550	2.438	+0.016	0.201	1.593	+0.028	0.069	0.543
Acid treatment loss, mg/100 cm^2/hr...	.014	.008	.068	.047	.023	.123	.033	.050	.....	.052	.137	.074	.113	.058	.423	.043	.079	1.765	.024	.016	032
Iron recovered as Fe_2O_3, mg/100 cm^2/hr.....	.016	.012	.078	.016	.011	.072	.017	.033	.....	.032	.093	.100	.077	.031	.....	.027	.034	.....	.020	.017	.044
Total loss, heat+acid, mg/100 cm^2/hr..	.010	.085	.880	.037	.104	.953	.031	.254	.....	.080	.511	1.075	.095	.608	2.861	.027	.280	3.358	+ .004	.085	.575
Iron compared to total loss, per cent..	160	14	9	43	11	8	55	13	.....	40	18	9	81	5	.....	100	12	.....	.....	20	8
Iron compared to acid loss, per cent..	114	150	115	34	48	59	52	66	.....	62	68	135	68	53	.....	63	43	.....	83	106	137
Acid compared to total loss, per cent..	140	9	7	127	22	13	106	20	.....	65	26	6	119	10	15	159	28	52	.....	19	6

The curves showing the relation between loss at 1200° C and the emf against pure platinum at 1100° C, including observations of Burgess and Sale, are reproduced in Fig. 1 and similar diagrams could be constructed for 700° and 1000° C. The loss on heating plus the loss with acid treatment is termed "total loss," and it is also shown in the plot for several crucibles. It is evident that crucibles containing iron lose less on heating than those which

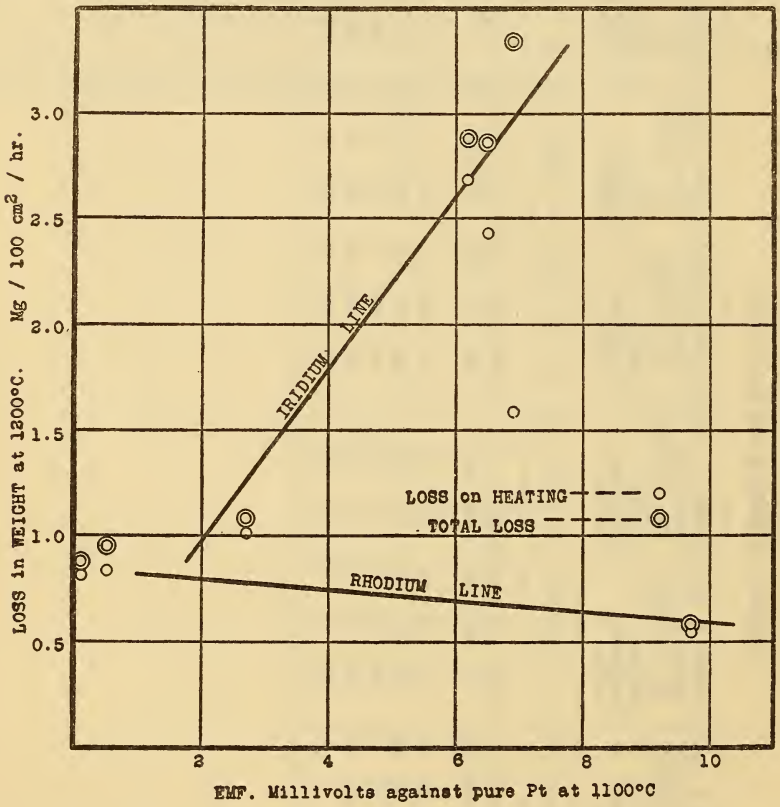

FIG. 1.—*Heating losses for crucibles containing Ir or Rh in terms of emf against pure Pt*

contain no iron, but their loss after the acid treatment is correspondingly greater. On some crucibles a surface film of iron oxide may be detected after heating, and the decreased loss on heating and increased loss with acid treatment is probably due to this iron oxide, as previously explained.

The relation between temperature and loss on heating for several crucibles is shown in Fig. 2. These curves are typical of certain classes of laboratory ware, i. e., pure platinum, platinum containing rhodium, and platinum containing iridium.

The loss in weight of platinum laboratory ware is here shown to be negligible below 900° C, but for all crucibles tested the loss at 1000° C is appreciable and rapidly increases with temperature.

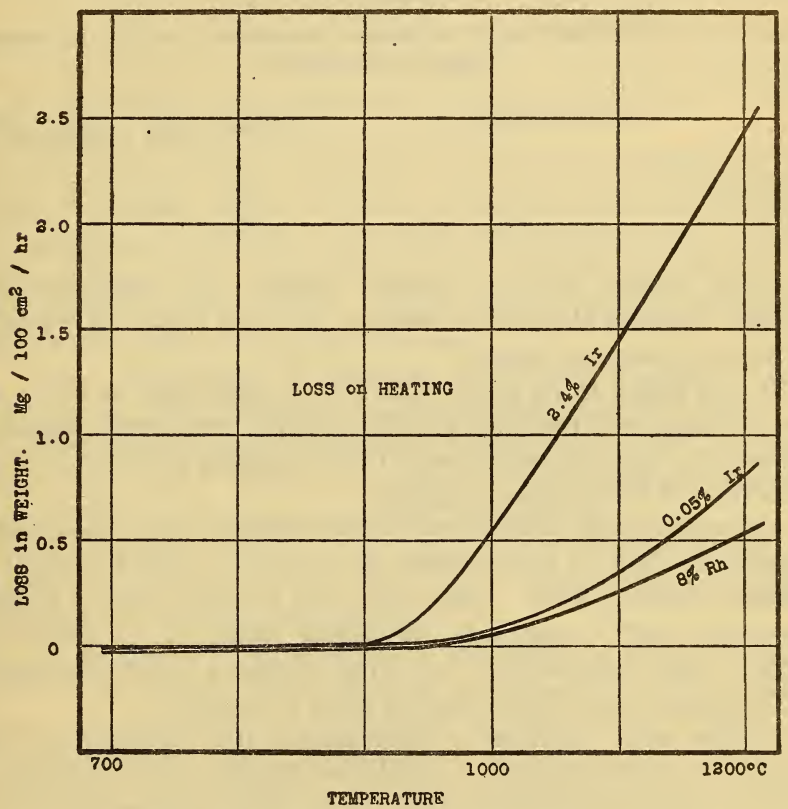

FIG. 2.—*Loss of weight, on heating crucibles containing rhodium or iridium, in terms of temperature*

The presence of rhodium, iridium, and iron in platinum produces similar results on heating at 1000 and at 1200° C. Rhodium decreases and iridium increases the loss of weight. Iron is objectionable because of the surface film of oxide which forms on heating the platinum containing it.

It is possible to predict the loss in weight of an iridium or rhodium alloy crucible on heating below 1200° C, provided the ware contains little iron.

In Table 3 are given the approximate changes in weight to be expected in mg/100 cm² of surface and per hour of heating of platinum nearly free from iron. The presence of iron in appreciable quantities renders the prediction uncertain, but it always acts in the direction of lowering the volatilization loss; silica, if taken up from the furnace, will also tend to lower the results slightly.

TABLE 3

Approximate Loss in Weight, mg/100 cm²/hour, at Temperatures Indicated for Platinum Nearly Free from Iron

Platinum containing—	Pure Pt	1 per cent Ir	2.5 per cent Ir	8 per cent Rh
900° C or less	0	0	0	0
1000° C	0.08	0.30	0.57	0.07
1200° C	.81	1.2	2.5	.54

Other metals, such as osmium, alloyed with platinum, may further decrease the loss on heating, and it is hoped to try some of them in the near future.

It was hoped to be possible, in this investigation, to carry out experiments with platinum crucibles alloyed with small quantities of osmium, but this was found to be impossible on account of the condition of the platinum market.

Experiments by other observers have recently been made which contribute data to this problem of the loss or gain in weight of heated platinum ware. Thus Vinal and Bovard [2] find on heating to about 600° C platinum voltameter dishes of 38 and 80 g. weight, freed from silver "very little change if any in the weight of the empty cups due to heating them to redness."

Sosman and Hostetter [3], investigating the reduction of iron oxides by platinum show, as would be expected from a consideration of the phase relations, that "if the existing pressure of oxygen is less than this equilibrium pressure, the oxide will dissociate and metallic iron will be absorbed by the platinum. If the pressure of oxygen be greater, on the other hand, iron from the platinum solution will be oxidized, the oxide will separate on the surface of the metal, and the concentration of the iron in the platinum will be reduced." In the experiments listed in the above tables we are of course working at a pressure high enough and at temperatures low enough for the second operation—oxidation of the iron.

[2] Scientific Paper No. 271, this Bureau; 1916.
[3] J. Wash. Acad., 5, p. 293; 1915.

SUMMARY AND CONCLUSIONS

In addition to the conclusions from the previous work of Burgess and Sale (loc. cit.), there may be noted the following:

1. Platinum ware in the form of crucibles of whatever degree of purity behaves, with respect to gain or loss of weight, on heating in air at ordinary atmospheric pressure in a manner characteristic only of the temperature of heating.

2. Each impurity as iridium, rhodium, or iron appears to exert its effect on the volatilization of platinum independently.

3. For platinum crucibles of all degrees of purity containing Ir, Rh, Fe, Si (up to a content of at least 3.0 per cent Ir) the loss on heating is negligible below about 900° C.

4. Below this temperature there may even be a slight gain in weight on heating platinum, owing to the iron content diffusing to the surface and oxidizing. At higher temperatures the presence of iron will lower the volatilization loss by amounts depending on the quantity of iron present. There appears to be no platinum made which does not contain some iron.

5. The volatilization of platinum containing rhodium is less than that of pure platinum at all temperatures above 900° C.

6. The volatilization of platinum containing iridium is, above 900° C, very much greater than that of pure platinum, and increases with the Ir content and with temperature.

7. It appears to make no material difference in the volatilization results, in the range 700° to 1200° C, what is the order of heating, ascending or descending temperatures.

8. In an oxidizing atmosphere at temperatures of the order of 1000° C. platinum, in the presence of, but not in contact with silica, will apparently take up small quantities of this substance.

9. The loss in crucible weight due to the solution of soluble matter in HCl, after heating, is variable, depending on the crucible, and may be large. This loss is relatively greater at low than at high temperatures.

10. All of the above losses, caused by heating, acid treatment, and iron diffusion, apparently continue with undiminished magnitude after the first treatment, which is usually erratic; although, eventually of course, the concentration of iron, etc., must become appreciably diminished.

WASHINGTON, April 13, 1916.