in the case of the singlet P states of the atom. That this sub-hydrogenic character appears in the molecule for a D instead of for a P term as in the atom, may prove instructive in determining the cause of this hitherto unexplained type of deviation from the Balmer formula.

The various electron levels and transitions *now known* for the He_2 molecule are shown in the form of an energy-level diagram in figure 1.

A comparison of molecular and atomic terms, as given in the table, shows distinctly, in spite of certain irregularities, that the "main" series and related terms parallel the "doublet" terms of the atom—which presumably are really triplet terms[11]—while the "second" series terms parallel the singlet terms of the atom. These relations form the basis of the suggestion in the second paragraph as to the formation of helium molecules of two types from the two types of excited atoms. But in *both* cases, as already noted, the *molecular* terms, in the bands hitherto studied, appear to be of a singlet type. The possibility that any of these terms belong to systems of higher multiplicity can almost certainly be excluded by various considerations; this is true even though the triplet or other separations were unresolved—but appreciable separations would seem probable, at least for the $2P$ level. The future discovery of helium bands involving triplet and quintet electronic terms is, however, likely.

[1] R. S. Mulliken, *Physic. Rev.*, **25**, 290–1 and **26**, 561 (1925).
[2] R. T. Birge, *Nature*, 1926 (in press).
[3] A. Fowler, *Proc. Roy. Soc., A*, **91**, 208 (1915).
[4] W. E. Curtis and R. G. Long, *Proc. Roy. Soc., A*, **108**, 513 (1925).
[5] W. E. Curtis, *Proc. Roy. Soc., A*, **101**, 38 (1922).
[6] A. Kratzer, *Zeit. Physik.*, **16**, 353 (1923).
[7] R. Mecke, *Physik. Zeit.*, **26**, 227 (1925); cf. also *Zeit. Physik.*, **31**, 709 (1925).
[8] R. Mecke, *Zeit. Physik.*, **32**, 823 (1925).
[9] R. S. Mulliken, *Physic. Rev.*, **25**, 279 (1925).
[10] W. Heisenberg, *Zeit. Physik.*, **33**, 879 (1925).
[11] J. C. Slater, these PROCEEDINGS, Dec., 1925.

VARIATIONS IN THE PHOTO-ELECTRIC SENSITIVITY OF PLATINUM

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The photo-electric properties of a platinum surface which has undergone an extended process of outgassing by heat treatment have been studied by many recent observers and conflicting results have been reported.

As early as 1914 Wiedmann and Hallwachs,[1] Kustner[2] and others had found that, after prolonged heat treatment, the photo-current from a platinum surface excited by the radiation from a quartz mercury arc had decreased to values which were only a small fraction of those initially observed. This fact led these and later observers[3] to conclude that perfectly gas-free platinum would show no photo-electric sensitivity to the light ordinarily used. More recent observations, particularly those of Tucker[4] and Woodruff,[5] have shown that the decrease in the photo-electric sensitivity, which was observed, was due merely to a shift in the long wave-length limit of the specimen toward the ultra-violet to a value which might be below 1849 Å.U., the shortest line furnished by the quartz mercury arc. On the other hand the experiments of Welo[6] and, more recently, those of Herrmann[7] seem to indicate that even after prolonged outgassing a platinum surface still retains a portion of its activity to wave-lengths longer than 1849.

In view of these results it seemed worthwhile to investigate further the photo-electric properties of platinum and to see whether a condition characteristic of the gas-free metal itself could be reached. Kazda[8] has recently realized this condition with clean flowing mercury and has found a definite, long wave limit which is apparently characteristic of the metal itself.

The procedure was, in general, to heat a platinum strip in the highest attainable vacuum at various temperatures for various intervals of time with the object of determining, first, whether a definite, limiting value of the photo-current and the long wave-limit was reached and, second, how the final value was affected by various conditions of pressure and heat-treatment.

The experimental arrangement consisted merely in a narrow strip of thin platinum foil hung in the form of a loop inside a nickel receiving cylinder, the whole being enclosed in a pyrex tube which was connected through a liquid air trap to a mercury vapor diffusion pump A charcoal tube was placed near the main part of the tube to aid in attaining the lowest possible pressures. The pressure could be read on a McLeod gauge or an ionization manometer. After a thorough baking out of the entire tube at 550°C., and a long period of heating of the platinum specimen and other metal parts within the tube, the pressure reached values which were in no case greater than 5×10^{-8} mm. Hg. The platinum strip could be heated by an electric current and its temperature measured by means of an optical pyrometer. After each heating interval light from a quartz mercury arc or other source could be focussed on to the strip and the photo-current read by means of a Compton electrometer.

The results may be summarized as follows:

1. *For short heating intervals* the photo-current decreases as the tem-

perature of heating is increased, but approaches a definite limiting value *which is not zero.* The following table shows the behavior of a typical filament so treated:

TEMPERATURE °C.	HEATING TIME MINUTES	PHOTO-CURRENT CM. DEFLECTION 1 CM. = 0.3×10^{-11} AMP.
1200	0	32.3
	10	28.0
	200	26.5
1300	20	13.0
1350	15	6.2
	90	4.3
1410	20	3.5
1450	3	3.0
	150	3.0
1550	30	3.0

Several specimens were carried through their fusing point in this manner. All showed the same type of behavior, and all reached practically the same final value of the photo-electric current, though the total times of heating varied widely.

2. If the specimen is heated for *long periods of time* at a constant temperature between 1200° and 1300°C. the photo-current falls off with time of heating, but again approaches a *definite limiting value.* This limiting value is not changed by subsequently raising the heating temperature up to the fusing point, and, for a given set of incident light conditions, the value of the photo-current thus approached is practically the same as that approached in the preceding set of experiments. The following table is typical of the results obtained. The platinum specimen used in this run was cut from the same strip of foil as that used in the preceding run, and was tested in the same tube under the same pressure conditions.

HEATING TEMPERATURE 1200°C.

TIME OF HEATING HOURS	PHOTO-CURRENT CM. DEFLECTION 1 CM. = 0.3×10^{-11} AMP.
0	30.0
1	12.0
2	9.0
3	7.8
6	4.2
17	2.9
30	3.0

These values are plotted in the curve of figure 1.

In order to test whether still longer times of heating would cause a further decrease in the photo-sensitivity of the specimen a number of runs were taken in which the filament was heated for as long as 200 hours at

temperatures from 1100° to 1500°C. The general behavior was in every case the same, i.e., a final low value was reached which was not changed by further prolonged heating, or by further baking and outgassing of the tube. A typical filament is represented in the following table. Since this specimen was tested in a different tube under different incident light conditions the numerical values of the sensitivity cannot be compared with those of the previous tables. The general behavior, however, is significant.

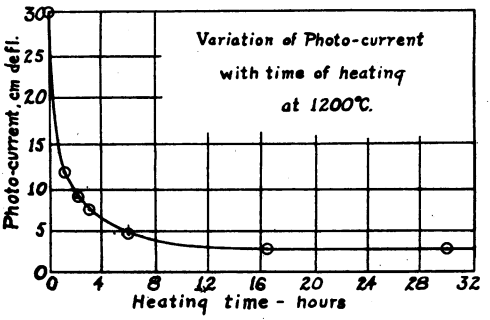

FIGURE 1

HEATING TEMPERATURE 1240°C.

TIME OF HEATING	PHOTO-CURRENT 1 CM. = 8.5×10^{-11} AMP.
0	40.0
10 min.	24.0
1 hr.	3.1
5 hr.	1.5
20	1.3
43	1.2
69	1.2
89	1.4
122	1.3

It is seen at once that during the first 20 hours of heating a low value of the sensitivity is reached which is not appreciably changed after 100 additional hours of heat treatment. This low value could not be reduced by any type of further heat treatment, no matter how high the temperature or how low the pressures. It was not reduced by surrounding the entire tube with a jacket and cooling to liquid air temperatures, nor by cooling with liquid air a mass of thoroughly baked-out charcoal which was placed in the bottom of the tube within 4 cm. of the platinum specimen itself. Cooling the tube and charcoal in this manner *did* cause the photo-sensitivity of the specimen to come *more quickly* to its equilibrium value, but the actual value reached was not changed.

These results point to the conclusion that even after prolonged heat treatment in the highest attainable vacuum a clean platinum surface is still slightly sensitive to the radiation from a quartz mercury arc, and still gives a measurable photo-electric emission.

Variation in the Long Wave Limit.—3. The outgassing of the platinum is accompanied by a shift in the long wave-length limit to a final value which is slightly above 1943 Å.U. Two methods were used to test this

conclusion. A qualitative test of the shift was made by taking simultaneous readings of the photo-electric sensitivity to the mercury arc and to a hydrogen discharge. A hydrogen tube was arranged so that the capillary through which the discharge passed was only about three cm. from the platinum strip and separated from it only by a thin fused quartz window. This furnished to the strip light of wave-lengths as short as 1800 Å.U. The intensity of the discharge was so adjusted that with the platinum in its initial state the photo-current produced by it was about the same as that produced by the arc. The following is a typical set of readings taken as outgassing progressed. In this table the initial high value of the photo-current—80 cm. deflection—is of no significance since the initial photo-currents varied widely depending upon the time of the initial baking, etc. The final values reached, however, were always nearly the same.

TIME OF HEATING	PHOTO-CURRENT		RATIO
	HG ARC	H DISCHARGE	H/HG
0	80.0	86.0	1.07
6	6.0	27.8	4.63
17	5.0	28.0	5.60
37	2.6	24.8	9.54
58	1.6	21.0	13.10
84	1.4	19.0	13.50

The large increase in the ratio H/Hg is clearly definite evidence of a shift in the photo-electric threshold to the region near where the mercury spectrum ends, but where the hydrogen spectrum is still strong, i.e., to the region just above 1849 Å.U.

A more direct test of the final limit reached was made by a method similar to that used by Williamson[9] in determining the threshold for potassium vapor. An absorption cell with fluorite windows was placed in the path of the incident light, and into this were introduced weak solutions of acetic acid in distilled water. By properly increasing the concentration of these solutions the shorter wave-length lines of the mercury spectrum could be cut out one at a time. The approximate location of the threshold was determined by introducing a solution of just sufficient concentration to cause the photo-current to disappear. A photograph was then taken of the spectrum transmitted by this solution.

When a fresh strip of platinum was tested immediately after the initial baking of the tube the threshold was found to be very close to the mercury line 2482. After prolonged outgassing, however, the photo-current was reduced to zero (i.e., to less than 0.05%) by an absorbing solution which cut out the 1943 line and all below it, leaving the 1973 still very strong. The long wave limit thus lies between these two values. This value was checked using an aluminum spark as a source.

This is higher than the threshold for outgassed platinum reported by

Tucker[4] and Woodruff[5] who find that heat treatment caused their specimens to be temporarily insensitive to wave-lengths longer than 1849. They both found, however, that this condition persisted only for a very short time—two minutes—immediately after heating and after ten minutes large photo-currents were again obtained.[10] Experiments made by the author indicate that this unstable condition is due to insufficient outgassing of the specimen. A behavior similar to that reported by Woodruff (see Fig. 4 of his paper) was observed during the *initial stages* of outgassing. After 50 hours or more of intense heat treatment, however, no such instability in the photo-sensitivity was observed and the photo-currents remained constant for hours after the heating current had been shut off. It was while the specimen was in this stable state in a pressure of the order of 10^{-8} mm. Hg that the above reported value of the threshold was observed.

Temperature Variation of Total Photo-Current.—In the results presented above, the photo-current readings were, in every case, taken after the heating current through the platinum filament had been shut off and the specimen had returned practically to room temperature. A number of tests were also made in which the photo-currents were measured while the filament was being heated by an electric current and the temperature variation of the photo-current was studied. The following results were noted:

1. During the initial stages of outgassing, the photo-currents varied widely and irregularly with the temperature of the platinum strip, as would be expected with a surface still filled with gas.

2. After prolonged heat treatment, e.g., 100 hours, the behavior became gradually more regular and ultimately settled down to a consistent variation with temperature such as is shown in the following table. These values are plotted in figure 2.

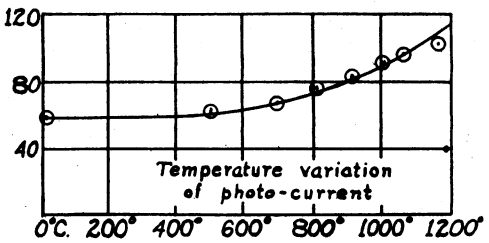

FIGURE 2

HEATING CURRENT AMPS.	FILAMENT TEMP. °C.	PHOTO-CURRENT MM. DEFLECTION
0.0	20	60
0.55	500	65
1.0	700	68
1.5	810	77
2.0	910	85
2.5	1006	92
3.0	1063	98
3.5	1150	102

Readings at higher temperatures became impossible due to the large thermionic emission. At 1150°C. the thermionic current was 50 mm. deflection; at 1063°, 3 mm.; below this, 0.

It should be pointed out that the condition of the filament at each temperature was a stable one and that the values of the photo-currents given above were each characteristic of the temperature at which they were taken, and were independent of how the temperature was reached.

There seem to be three possible explanations of such a temperature variation.

1. It is possible that at every temperature there is a characteristic equilibrium value of the gas content of the surface which gives rise to a photo-current also characteristic of that temperature. For even a "thoroughly outgassed" platinum surface is certainly far from being "gas-*free*," even though the gas-content has been reduced to the point where it no longer affects the photo-emission *at room temperature.*

2. The variation in the photo-currents observed may be due to the *heating current through* the specimen and not primarily to the temperature. Such a variation of the photoelectric emission from a Bismuth crystal whose temperature was held constant has been reported by Shenstone.[11]

3. The observed variation may be a true temperature variation caused by the increase, with rise in temperature, of the energy of the electrons within the metal, thus causing them to be more easily ejected by the incident light. That this thermal energy of the electrons within the metal becomes appreciable only at temperatures higher than about 700°C. is in line with the conclusions recently arrived at by Millikan.[12]

Further tests are now under way to determine which of the above explanations is the true one, and a more complete report will be published in the near future.

The author is greatly indebted to Prof. C. E. Mendenhall for his helpful interest in this problem.

[1] Wiedmann and Hallwachs, *Ber. Dts. Physik. Gesell.*, **16,** 107 (1914).

[2] Kustner, *Ann. Physik.*, **46,** 893 (1915).

[3] See, also, Kober and Hallvachs, *Physik. Zeit.*, **16,** 95 (1915); Sende and Simon, *Physik. Zeit.*, **21,** 562 (1920); Suhrmann, *Ann. Physik.*, **67,** 43 (1922).

[4] Tucker, *Physic. Rev.*, **22,** 574 (1923).

[5] Woodruff, *Ibid.*, **26,** 655 (1925).

[6] Welo, *Physic. Rev.*, **12,** 251 (1918); *Phil. Mag.*, **45,** 593 (1923).

[7] Herrmann, *Ann. Physik.*, **77,** 503 (1925).

[8] Kazda, *Physic. Rev.*, **26,** 643 (1925).

[9] Williamson, *Ibid.*, **21,** 107 (1923).

[10] Woodruff reports a single specimen which had a rather unaccountable abnormal behavior, becoming insensitive after heating and remaining so for two months.

[11] Shenstone, *Phil. Mag.*, **41,** 916 (1921); **45,** 918 (1923).

[12] Millikan and Eyring, *Physic. Rev.*, **27,** 51 (1926).