

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

EXPERIMENTAL ATTEMPTS TO DECOMPOSE TUNGSTEN AT HIGH TEMPERATURES

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With atomic disintegration recognized for 20 years and atomic decomposition¹ now established by the work of Rutherford,² on the impact of α -particles on light atoms, the astronomical evidence that heavy atoms are not stable at high temperatures³ demands laboratory confirmation. This has become possible through the work of Anderson⁴ whose method of exploding wires at temperatures above 20,000°, well above that attributed to the hottest stars, has become valuable in spectroscopy. In our application of this method the wires were exploded within strong glass bulbs so that the gaseous products of the explosions could be collected for analysis. The method thus includes factors, both of cause and of error, analogous to those operative in the voluminous and inconclusive controversy on the evolution of helium in various types of low pressure electrical discharge tubes, extending from 1905 to 1915.

The Apparatus.—The electrical connections are represented in Fig. 1.

The primary circuit of the transformer, T, operates on a 220-volt alternating current power line through an inductive resistance, E. In order to prevent a destructive back pulse into the power line should the charged condenser accidentally be discharged through the secondary circuit of the transformer, 2 condensers of 1 microfarad capacity each are bridged across the primary circuit with a ground connection, as shown at A. The primary circuit was heavy enough to carry 40 amperes during the brief period necessary to charge the large condenser; the secondary circuit furnished 100,000 volts though ordinarily only some 30,000 were used. The secondary circuit was connected to the two sides of the large condenser, C, one side leading through the hot cathode "kenotron" rectifier, R, which was especially designed for heavy service and a large factor of safety. Its cathode filament was heated by the battery of dry cells, B. The discharge circuit led from the two sides of the condenser and contained only the spark gap, S, and the wire to be exploded, H. This discharge circuit was made as short and compact as possible, of heavy copper strip, in order to reduce resistance and inductance

¹ For the sake of clarity it is suggested that the term *disintegration* be reserved for the spontaneous processes of radio-activity, that *decomposition* be applied to the splitting of complex atoms into simpler parts, and that *transmutation* be understood to imply some degree of synthesis of atomic nuclei.

² Rutherford, (a) *Phil. Mag.*, **37**, 537 (1919); (b) *Proc. Roy. Soc. (London)*, **97A**, 374 (1920). Rutherford and Chadwick, (c) *Nature*, **107**, 41 (1921); (d) *Phil. Mag.*, **42**, 809 (1921).

³ See Russell, *Popular Astronomy*, **22**, Nos. 5 and 6 (1914). Vogel, *Potsdam Astrophysik. Observ. Pub.*, **12**, 6 (1899). Rosenberg, *Astronom. Nachr.*, **193**, 358–70 (1913). Wilsing and Scheiner, *Potsdam Astrophysik. Observ. Pub.*, **19**, 102–21 (1909). Scheiner, "Populaere Astrophysik," Teubner, 1912, p. 709.

⁴ Anderson, *Astrophys. J.*, **51**, 37–48 (1920).

to a minimum and thus allow a rapid and non-oscillating discharge through the wire in the minimum time, thus concentrating the energy input and giving the maximum temperature in the material of the wire. To give maximum capacity and hold maximum voltage the condenser was built of 100 glass plates 60 by 75 cm. covered with heavy tin foil and cast into solid paraffin with a gap of 5 mm. between plates. The condenser showed brushing at the edges of the plates at 30,000 volts but held 45,000 volts without puncturing. The capacity was about 0.1 microfarad. The spark gap consisted of two 2cm. brass spheres, their separation adjustable to the maximum voltage of the condenser. Its use is important since it is the only means provided for regulating the voltage at which explosion of the wire occurred, for protecting the condenser from excessive charge by the transformer, and for insuring a complete and sharp discharge at the proper moment.

Tungsten was chosen for the material of the wire to be exploded chiefly because its high atomic weight made its decomposition probable on the hypothesis adopted, and also because it is hard enough to allow convenient manipulation and support even in excessively thin wires. The wires used were 0.035 mm. in diameter, about 4 cm. long and weighed 0.5 to 0.7 mg. They had sufficient strength to be sprung into place between the larger electrodes shown in Fig. 2 without welding or clamping.

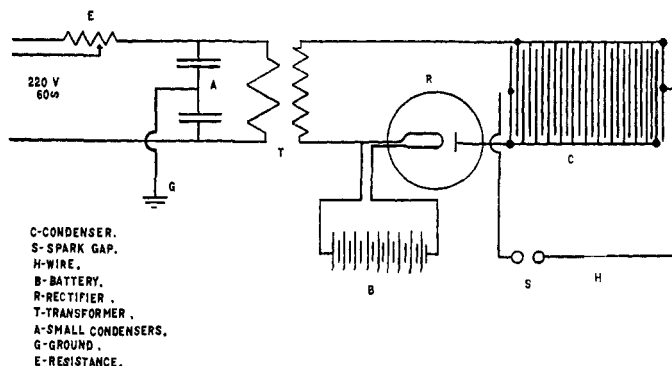


Fig. 1.

The construction of the explosion bulb is shown in Fig. 2. It has a volume of about 300 cc., and was constructed of heavy Pyrex glass without strain and in good spherical form, for it was required to withstand momentarily a tremendous outward pressure. Thick bulbs invariably broke during the explosion because of insufficient elasticity. Thin bulbs may be used if the bulb is immersed in a vessel of water, which gives sufficient support together with elasticity. The large side-tube is the neck at which the bulb was sealed from the pump system after evacuation, and through which the wire was sprung into place between the electrodes by means of pincers. The smaller side tube contained a third sealed-in electrode, and served for the spectroscopic examination of the gas within, one of the other electrodes being used for the other terminal of the exciting induction coil.

The three electrodes were constructed as is shown in detail in Fig. 2. B was the electrode itself, made of B. and S. No. 20 tungsten wire.⁵ This was firmly sealed directly through the Pyrex walls in the manner shown, for mechanical strength. The entire surface of the electrodes was first covered with a thick layer of Pyrex glass, A. The tip was then carefully ground off until the tungsten was exposed. Then a hole, C, was drilled

⁵ For this we are indebted to the Fansteel Products Co., of North Chicago, Ill.

in the end with a No. 80 drill, 0.343 mm. in diameter, the hole being less than 0.76 mm. deep, to receive the fine wire for explosion. The electrodes were then sealed into the bulb. This method of sealing in the electrodes had the two purposes of excluding the chance of leakage of air inward through the seal after evacuation and of preventing the liberation of gas from these electrodes by the heating effect of the explosion itself. With such electrodes only the surfaces of the three small holes were exposed to the effects of the explosion, and one of these, in the spectroscopic capillary, was far removed from the scene of the explosion. In some of the early explosions brass electrodes were used welded to a tungsten wire sealed through the glass.

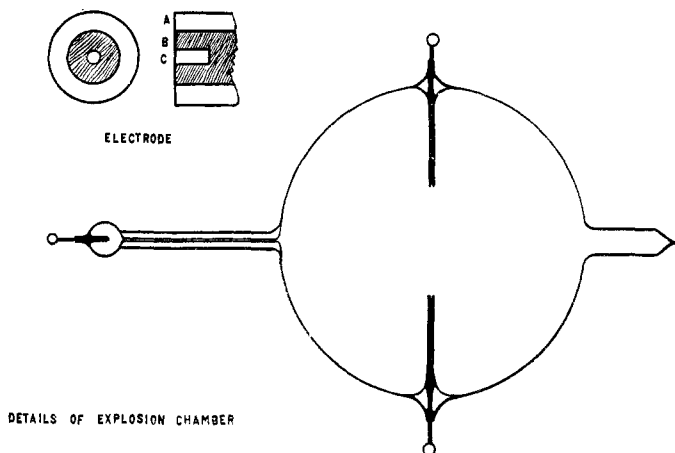


Fig. 2.

Explosions in a Vacuum.—Two general methods of explosion were employed. In one the bulb was evacuated and the resulting gases were tested spectroscopically without opening the bulb. In the other the explosion took place in an atmosphere of carbon dioxide and the gases were then passed through a nitrometer for the absorption of the carbon dioxide, and the residual gas was analyzed.

The vacuum method is the more rigorous in excluding impurities. Both in order to remove all contaminating gases and to render a good explosion possible the evacuation needed to be as complete as could be attained. In an imperfect vacuum the current tends to arc through the gas in the bulb, thus escaping the resistance of the wire and producing only an incomplete and low temperature explosion. The pump system consisted of a good "Hivac" oil-immersed mechanical pump which gave a preliminary evacuation to less than 0.01 mm. of mercury. This was attached to a battery of 2 mercury-vapor diffusion pumps in series. These pumps were operated for 15 hours continuously with the explosion bulb sealed directly to the Pyrex glass of the pumps with a liquid-air trap between the bulb and the pump to catch mercury vapor and a side tube containing about 100 cc. of thoroughly out-gassed coconut charcoal which was im-

mersed in liquid air just prior to sealing off the explosion bulb. During the entire 15 hours of evacuation the explosion bulb was supported within a furnace and kept slightly above 350° in order to drive off the gases adsorbed on the interior glass walls. For the same time a current of about 0.2 ampere from a battery was passed through the two supporting electrodes and the wire to be exploded, so that the wire was well above 2000° for 15 hours, though the heavier electrodes were not heated to redness. In this manner it was hoped to drive from the wire any dissolved or adsorbed gases, particularly hydrogen, with which the wire is treated in the process of its manufacture, and helium, which may arise from an impurity of thorium in the metal. At the end of 15 hours the side tube was immersed in liquid air to complete the evacuation, and after 10 more minutes the bulb was carefully sealed from the pump system. Bulbs so evacuated then showed no spectrum or fluorescence and no conductance when attached to a 50,000-volt induction coil. Several bulbs so tested maintained this condition on standing for 12 hours before explosion.

The bulb was then connected to the leads from the condenser through the spark gap and the wire was exploded by closing the primary circuit of the transformer. There was a delay of a fraction of a second before the condenser was fully charged to the voltage used, about 30,000, but thereafter the wire disappeared in a brilliant flash. The discharge automatically opened the discharge circuit, and the primary circuit was opened before further discharge passed. No dust or smoke or solid residue was ever found after such complete explosions.

Abundant gas was present in the bulbs after explosion. Visual spectroscopic examination of it uniformly disclosed the faint presence of the strongest green line of mercury, probably from back diffusion from the pumps. The only other line uniformly present and positively identified was the strong yellow line of helium. This was always brilliant when sufficient exciting current was used, though it gradually weakened after the current was passed for some time. This is characteristic of helium which, under such circumstances, is easily absorbed by the electrodes. For identification as helium the spectrum was compared with that from a tube of pure helium operated on the same electrical circuit. Other fainter lines which have not yet been identified are two in the red, one bright blue, and one pale violet. Occasionally, two other faint yellow lines were visible, and a second violet line. This is a report of preliminary work, and time was not available for the spectrographic measurement of these lines. It seems, however, that both hydrogen and neon were absent.

The appearance of helium and the absence of hydrogen is interesting for two reasons. In the first place, it seems to dispose of the objection that the helium arose from gas remaining in the wire, for in that case hydrogen should also have been visible, for it was probably originally present

in the wire in much larger quantity than was helium.⁶ In the second place, if the helium does arise from a decomposition of the tungsten atoms, the absence of hydrogen is also interesting because the atomic weight of tungsten is exactly 46 times the atomic weight of helium, and Rutherford⁷ was also unable to detect hydrogen from the bombardment with α -rays of carbon, oxygen, magnesium, silicon, and sulfur, whose weights are multiples of 4, though he did detect it with boron, nitrogen, fluorine, sodium, phosphorus and aluminum, whose weights are not such multiples.

Explosions in Carbon Dioxide.—While the vacuum method is the more rigorous in excluding contamination, it does not permit the measurement of the volume of gas produced nor the collection of successive samples to form a volume sufficient for chemical analysis. For this purpose explosions were conducted with the bulb filled with carbon dioxide at atmospheric pressure. The bulbs were the same except that they were provided with inlet and outlet tubes at top and bottom instead of the capillary side-tube. With the wire in place between the electrodes, the bulb was swept out with the purest carbon dioxide gas. This was prepared by heating sodium hydrogen carbonate in a Pyrex glass tube. The salt had previously been used as a source of carbon dioxide in combustions for nitrogen, and was thus free from ammonium salts, the sodium carbonate formed in this previous use having been regenerated to bicarbonate by precipitation with pure carbon dioxide. The gas was purified and dried by towers of sulfuric acid and of phosphorus pentoxide. It was passed through the bulb until such time as the entire 300cc. volume of the bulb could be transferred to a nitrometer filled with conc. potassium hydroxide solution with the appearance of no more than a mere trace of residual gas unabsorbed by the alkali. No rubber connections were used, all joints being sealed and the entire apparatus constructed of Pyrex glass. The bulb was then closed off from the rest of the system by stopcocks, and the wire was exploded as before. Conc. potassium hydroxide solution was then admitted through the bottom of the bulb. The carbon dioxide was absorbed and the residual gas was driven through a short tube into a graduated nitrometer or gas buret, which was also filled with potassium hydroxide solution. In this manner complete absorption of the carbon dioxide was obtained, and the residual gas collected in the buret.

Table I gives the volumes of gas collected in 21 such explosions. The wires were all 0.035 mm. in diameter, this and the length both being determined by a measuring microscope. The weight is calculated from the

⁶ An adequate method of excluding this error would be to explode the wire, using a greater inductance, thus obtaining a slower explosion and a lower temperature. Temperature could thus be adjusted to give complete vaporization without attaining the temperature of decomposition. We regret that time was not available for this test.

⁷ Rutherford and Chadwick, Ref. 2 d.

volume and density, only 2 or 3 wires being actually weighed as a check on the computation. Wires No. 2, 4, and 9 were strongly heated in a current of carbon dioxide before explosion; the others were not.

TABLE I
VOLUMES OF GAS FORMED IN EXPLOSIONS

Wire	Length Mm.	Weight Mg.	Voltage Kv.	Vol. of gas
				produced Cc.
1	28.65	0.515	22.5	3.62
2	45.20	0.823	37.5	0.86
3	39.90	0.717	25.5	1.95
4	42.51	0.764	31.5	0.18
5	39.90	0.717	31.5	1.50
6	37.24	0.670	31.5	1.04
7	39.88	0.717	31.5	0.56
8	40.91	0.736	31.5	0.20
9	37.05	0.666	34.5	0.80
10	35.24	0.634	25.5	0.40
11	38.76	0.697	25.5	1.76
12	38.42	0.691	25.5	1.64
13	42.50	0.763	31.5	0.50
14	40.61	0.730	31.5	0.50
15	39.81	0.713	31.5	0.70
16	38.50	0.692	31.5	1.50
17	42.00	0.756	31.5	2.30
18	41.85	0.753	25.0	0.20
19	40.13	0.722	25.0	0.20
20	41.24	0.742	31.5	0.50
21	<u>41.72</u>	<u>0.750</u>	<u>37.5</u>	<u>0.30</u>
Mean:	39.62	0.713	29.6	1.01

The gas evolution is very irregular, but this is probably due to irregular conditions of explosion; it is impossible with the present technique to produce explosions of uniform brilliancy and temperature. The volume of gas produced is so large as to exclude its arising from gas dissolved or adsorbed by the wire, for the average volume of the wires was 0.0381 cubic millimeter, and the average volume of gas produced is 26,500 times greater. Residual impurity from the carbon dioxide is much more probable, though excluded by the care in preparation and the blank tests by absorption in alkali. This method of explosion excludes three conceivable sources of contamination which are present in the vacuum method, namely, from leakage of air inward, release of gas from the glass walls, and from the heavy supporting electrodes, for the explosion, while violent, is far too rapid to liberate gas from the walls or electrodes by the heat from the hot vapor.

One possible large error is however introduced, namely, the decomposition of carbon dioxide into carbon monoxide and oxygen by the high temperature of the exploding vapors. Three facts may be mentioned

as excluding this error also. In the first place, when the wire is wrapped in fine tissue paper or in fine cotton insulation, these are torn to shreds by the explosion in air, but there is no evidence whatever of scorching. The duration of the high temperature is too brief to permit it. In the second place, the passage of a powerful spark from the same electrical system, but without the wire in place, for several minutes produced only a minute quantity of unabsorbable gas. Finally, to remove carbon monoxide and oxygen if they had been formed, the nitrometer was provided with 2 sealed-in platinum electrodes, and when 10 cc. of the gas had been collected in successive explosions the pressure was reduced and a powerful spark from an induction coil was passed through the gas for 10 minutes. The two gases should then have recombined as carbon dioxide and been absorbed in the confining potassium hydroxide solution. A reduction in volume of 0.2 cc. was in fact observed within the first few minutes, but prolonged sparking had no further effect. This seems to exclude the presence of carbon monoxide and oxygen, except for 2%, and the large volume of gas remains to be accounted for.

A complete analysis of a 20cc. sample of this gas was then planned, but the sample on hand was lost through an accident, and before another sample could be collected it was necessary to discontinue further work; and this report is, therefore, issued in this preliminary form.⁸

If the entire mean weight of 0.713 mg. of tungsten had been decomposed into helium this should have occupied almost exactly 4 cc. Hence, if we are actually dealing with atomic decomposition, other heavier gases were also produced. A complete analysis of this gas, both chemical and spectrographic, is much to be desired, and is essential before this work can be conclusive.

Summary

Recent successes in atomic decomposition by the application of high concentrations of energy, together with astronomical evidence showing that the heavy metals do not exist on the hot stars, suggested the study of the effect of high temperature on the stability of heavy metals.

The apparatus and method for attaining temperatures above 20,000° are described.

When fine tungsten wires are exploded in a vacuum at such temperatures, the spectrum of helium appears in the gases produced.

⁸ We wish to emphasize that this report is preliminary, and that nothing is proved beyond the importance of the problem and the promise of this method. The work was stopped by the failure of the health of the senior author, necessitating a complete rest for a year or more. The junior author is continuing the research at Iowa State College. We regret the exaggerated earlier published account of this work, which was given wide publicity through the Associated Press upon its oral presentation at an intersectional meeting of ten middle-western Sections of the American Chemical Society at Northwestern University, Evanston, Illinois, on March 11, 1922.

When the explosion is conducted in carbon dioxide, 0.713 milligram of tungsten gives rise to 1.01 cc. of gas which is unabsorbed in potassium hydroxide solution.

The research was made possible only through a research grant from the American Association for the Advancement of Science, with which the costly transformer and condenser were built, and we gratefully acknowledge our indebtedness for this assistance.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE AGRICULTURAL COLLEGE]

THE ADSORPTION AND ORIENTATION OF THE MOLECULES OF DIBASIC ORGANIC ACIDS AND THEIR ETHEREAL SALTS IN LIQUID-VAPOR INTERFACES

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Introduction

It has been only within the last few years that capillarity effects have been regarded as of a chemical nature. Langmuir¹ and Harkins,² working independently, have developed the same theory. According to the chemical theory, surface tension is due to an attraction or residual affinity inherent to the molecule, as a result of which the molecules of the surface of a liquid are oriented in a definite manner. The structure of the surface layer is the principal factor in determining the magnitude of the surface energy. The molecules are composed of a polar group or active end and a slightly polar group, the active group being turned towards the interior of the liquid and the slightly polar group projecting up to form the surface layer. If we consider the electronic theory of matter as valid, then chemical change is due to the presence of the electromagnetic fields surrounding the atoms. Thus the surface tension is actually a measure of the potential energy due to the slightly polar groups, and accordingly the molecules will be arranged in the surface so that the stray magnetic field will be a minimum. It is readily seen that the entire molecule does not function in determining the magnitude of the surface tension, as only the slightly polar groups form the surface layer. The surface tension would also depend upon the character of the slightly polar groups and their arrangement in the surface layer.

If we should inspect the liquid hydrocarbons of the aliphatic series, we should find that they are arranged with the methyl groups forming the surface layer. This being the case we would expect the surface energy

¹ THIS JOURNAL, 39, 1848 (1917).

² *Ibid.*, 39, 354, 541 (1917).