GETTERS AND CLEAN-UP OF GASES. GASES IN METALS

57. Deleterious Action of Gases.

In order to function reliably it is of the utmost importance that vacuum tubes be exhausted to, and maintained at, a high degree of vacuum. The presence of even very small amounts of gases is harmful, owing either to their direct effect on the cathode or to their effect on the character of the electron discharge through space. The gases may "poison" the electron emission from the cathode by oxidizing it, or, in the case of inert gases, positive ions formed by collision with electrons may sputter the active material off the cathode surface and so deactivate it. The effect of positive ions on the electron discharge itself is to neutralize the space charge and fundamentally alter the characteristics of the tube. This will be discussed in Chap. VIII.

In order to obtain a high vacuum it is necessary, first, to free all parts of the tube from occluded gases; second, to pump out as far as possible all gas from the tube; third, after sealing off the tube from the vacuum system, to reduce the residual gas pressure still further by chemical or electrical means.

58. Gases from Glass.

The walls of glass bulbs give off large quantities of gas upon heating. This is very largely water vapor with a small admixture of carbon dioxide and nitrogen. On heating at any temperature, there is a large evolution of

gas which gradually ceases. On heating to a higher temperature, more gas is given off. The amount and nature of the gas evolved vary with the nature of the glass, and different methods of treatment are practiced in order to remove it. In general, it is necessary to heat the glass walls of any vacuum tube at temperatures varying from 360°C. for soft glass to 500°C. for hard glass for a considerable time in order to insure that no more gas will be evolved during the life of the tube. If this bake-out is not properly carried out, there will be a gradual evolution of gas from the walls of the bulb during the operating life.

59. Gases from Metals.

The metal parts used for electrodes contain large amounts of gas in solution as well as gases adsorbed on the surface. These gases are removed in part by treatment before the tube is exhausted and in part by a special procedure during the exhaust. The total quantity of gas that can be extracted from commercial metals by heating *in vacuo* is usually, according to Smithels, between 20 and 200 cu. mm. per gram. Much of this is carbon monoxide.

In the case of molybdenum, which has been studied more in detail than any of the other metals, Norton and Marshall found it necessary to heat the metal to 1760°C. in a vacuum of the order of 0.001 micron for a time which varied linearly with the thickness, in order to reach a condition where no more gas is evolved by the sample. When the metal is first heated, hydrogen is given off very readily at the lower temperatures. Carbon monoxide is given off at temperatures in the neighborhood of 1000°C. At higher temperatures the gas given off is very largely nitrogen. Grease and dirt on the surface of the metal usually increase the percentage of carbon monoxide in the gas which is evolved.

The gas evolution from molybdenum is greatly affected by the method used in cleaning it. The most effective method is electrolysis in concentrated sulphuric acid. Dipping in caustic, or filing the surface clean and washing in benzol, is less effective. Contamination of the surface of the metal is a source of a great deal of the gas, and, if the metal has once been degassed, it will stay degassed if precautions are taken to keep the surface clean. A carefully cleaned sample of molybdenum weighing 5.1 g. gave off 21.4 cu. mm. of gas (measured under normal conditions of temperature and pressure) when heated to 1760°C. for 20 min. The composition of the gas was 95 per cent nitrogen and 5 per cent carbon monoxide.

The amount of gas contained in tungsten ranges from 15 to 25 per cent of that obtained from a similar sample of molybdenum. In order to degas tungsten at a rate comparable to molybdenum at 1800°C., it is necessary to heat the tungsten to 2300°C.

Nickel cannot be heated to much above 1030°C., owing to its high rate of evaporation. At this temperature the gas evolved is largely carbon monoxide.

Graphite can be degassed at 2150°C., so that on subsequent heating at a higher temperature no further gas is evolved. At the higher temperatures the gas evolved from graphite is predominantly nitrogen.

Hydrogen firing before exhausting is very effective in reducing the gas content of most metals. This consists in heating the metal to a temperature of about 950°C. in an atmosphere of hydrogen for about 10 min.

In exhausting vacuum tubes the metal parts are cleaned as carefully as possible by one of the methods outlined above before sealing in. After the tube has been baked out to remove the gases from the glass walls, the metal parts are heated to incandescence by high-frequency induction or by electron bombardment. The filaments likewise are degassed by operating them

at as high a temperature as possible for a considerable period.

60. Clean-up by "Getters."

No matter how well a vacuum tube has been exhausted, there always remains a small residual pressure of gas. This may perhaps be of the order of 0.0001 mm. of mercury in commercial tubes. Even at this low pressure the number of molecules per cubic centimeter reaches the astounding figure of more than 10^{12}. Two methods are in use for reducing the pressure still further, chemical clean-up and electrical clean-up. The chemical clean-up takes place through the agency of a "getter." This is a substance which is usually volatilized onto the surface of the bulb wall just before the tube is sealed off from the vacuum system.

The getters most commonly used at present are phosphorus, calcium, magnesium, barium, strontium, aluminum and various mixtures or alloys of these. Phosphorus is used in the red form. This is quite inert, but, when it is vaporized from the surface of the filament or one of the electrodes, the vapor condenses as the active yellow form.

Barium and strontium are very active getters but have the disadvantage of oxidizing rapidly when exposed to air so that it is difficult to introduce them in a tube without having them completely oxidized. For this reason they are often used in the form of alloys with aluminum, which are quite stable in air and from which the active metal can be vaporized by heating, after exhausting the tube.

The alkali metals are extremely active getters, but the fact that their vapor pressure is high limits their usefulness to tubes where a small pressure of alkali-metal vapor is not harmful.

The getter is effective both in the chemical and in the electrical clean-up. In part the gas reacts chemically with the getter. This is particularly true in the case of water vapor, oxygen and carbon dioxide. In part the gases are simply adsorbed and held as a monatomic layer on the surface of the getter. The getter not only functions at the time that it is vaporized, but it continues to take up gases which may be evolved during the life of the tube.

The getter may function in several different ways. At the instant of vaporizing it, there is a high vapor pressure of getter in the bulb and there will be collisions between the molecules of the residual gas and those of the getter. Chemical combination may take place at these collisions, and the resultant products will be deposited on the bulb wall. In this way some of the gas is removed.

After the getter has been condensed on the bulb wall, since its pressure is negligible, any further clean-up is due to the adsorption of the molecules which strike the walls. The formation of a monatomic layer of gas molecules on the surface of the getter may account for a great reduction in pressure. For example, a monatomic layer of oxygen formed over a surface of 10 sq. cm. will consist of 10^{16} molecules. This same number of molecules, if they occupied the volume of a 100-cc. bulb, would give a pressure of 3×10^{-3} mm., a relatively high pressure.

The action of the getter, however, does not necessarily stop when a monatomic film has been formed on the surface, since diffusion may take place into the getter. For this reason getter action is accelerated by a rise in temperature, since this increases the rate of diffusion. Thus the gas which has been condensed on the surface is enabled to diffuse into the interior of the getter. Most getters are effective in clean-up, roughly in the order of their chemical activity.

The activity of getters is greatly increased by previously degassing them. In the case of receiving tubes the getter is usually fastened to the anode, from which it evaporates when the latter is heated by high-frequency induction before the tube is sealed off. In the case of large power tubes this method is not suitable, because the anodes are given a prolonged heat treatment and the getter would become saturated with gas long before the tube is ready to be sealed off. In such cases the getter is placed on an auxiliary electrode which can be heated separately at the end of the exhaust process.

Activated charcoal when cooled in liquid air is capable of absorbing large quantities of gas and producing very low pressures. It is not convenient, however, for use in sealed-off tubes.

61. Electrical Clean-up.

In the case of electrical clean-up, an electron current is drawn to the anode under the influence of a potential of 100 or 200 volts. This is sufficient to form ions by collisions between electrons and gas molecules. The ions acquire fairly high velocities in the electric field and are actually driven into the walls of the bulb or the metal electrodes. While this can take place in well-exhausted tubes where no getter is present, it is greatly facilitated by the presence of a getter on the exposed surfaces. The ions formed also react chemically with the getter.

62. Quantitative Aspects.

The effects of low pressures of gas in vacuum tubes are often underestimated, possibly because of the small units in which the pressure is ordinarily stated. If a bulb having a volume of 250 cc. contains a gas at a pressure of 0.01×10^{-3} mm. of mercury, the total number of molecules of gas present is 10^{14}. Assuming that the gas is oxygen having a molecular diameter of 3×10^{-8}

21.11. Degassing of Glass and Metals. Materials used in vacuum tubes must be heated to drive off gases during the evacuation process. Some of the gas is merely condensed on the surface, in which it is said to be *adsorbed*. Other gases are in chemical combination with the material, in which case they are said to be *absorbed*. With metals there will generally be considerable quantities of gas trapped in crevices, seams, and flaws. Such gases are said to be *occluded*.

In general, tubes should be degassed by heating at temperatures appreciably greater than the temperatures the tube will encounter in practice. The time required for outgassing may range from 15 min for receiving tubes to hours or days for high-power transmitting tubes.

The gases encountered with glass are mostly adsorbed. A 40-watt lamp bulb will evolve about 500 cm^3 of gas (measured at room temperature and pressure) when heated at 500°C. About 90 per cent of this gas is in the form of water vapor. Glasses should be heated at about 90 per cent of their annealing temperature to drive off adsorbed gases. At higher temperatures the glass may soften, and some gases will be given off by decomposition of the glass. The time required for outgassing of glass is about 15 min at top temperature. Heating may be done with either soft gas flames or with a baking oven that surrounds the entire tube. Heating with a baking oven allows a better control of temperatures, though receiving tubes are frequently degassed with gas flames. Degassing of a tube should not be begun until the tube has been evacuated to a pressure of 10^{-3} mm of mercury or less.

The gases encountered with metals are mostly in the form of occluded gases. Metal electrodes and parts may be degassed by heating to about 50 per cent of the melting temperatures of the metals. The amount of gas evolved from a metal will depend upon the area multiplied by a depth of a few thousandths of an inch, except for tungsten and molybdenum, which have a laminar structure. The principal component of the gases involved is generally carbon monoxide, which is present to the extent of about 30 to 90 per cent of the total gases. The remainder of the gas is mostly nitrogen, which comes off at a higher temperature than carbon monoxide. Interestingly enough, when a metal has been degassed by heating in a vacuum it will pick up very little gas upon subsequent exposure to air at atmospheric pressure, if carefully handled.[1] Degassing of metals is commonly achieved by r-f induction heating. Radiation-cooled transmitting tubes may be degassed by direct electronic bombardment of the elements.

21.12. Getters. Getters are materials used in vacuum tubes to clean up residual gases by chemical combination. The alkali metals are most extensively used. Barium seems to be most effective in cleanup action though magnesium, calcium, sodium, and phosphorus have also been used.[2,3] The getter material is usually enclosed in the pure metal form in a small cup or wire cage of base metal and then reduced and vaporized, after the tube is sealed off, by heating to a temperature of about 700°C by r-f induction currents. Sometimes the getter material is contained in a tube formed of a rolled nickel sheet, in which case the vaporized metal escapes through the crack in the tube. The vaporized metal deposits on the wall of the tube, care always being taken that it does not deposit on any of the insulators. When gas molecules come in contact with this layer, they will combine (except for the noble gases), with the result that the vacuum gets progressively better with time. A

[1] NORTON, E. J., and A. L. MARSHALL, The Degassing of Metals, *Gen. Elec. Co. Research Lab. Rept.* 613, March, 1932.

[2] LEDERER, E. A., and D. H. WAMSLEY, Batalum, a Barium Getter for Metal Tubes, *RCA Rev.*, vol. 11, pp. 117–123, July, 1937.

[3] LEDERER, E. A., Recent Advances in Barium Getter Techniques, *RCA Rev.*, vol. 14, pp. 310–318, January, 1940.

getter in a receiving tube will usually be sufficient to improve the vacuum obtained from a mechanical pump to 10^{-6} mm of mercury in about 10 min. Previous treatment of the getter to remove gases seems to be more important then the material of the getter itself.[1,2]

The absorption properties of other metals may also be used in the form of an auxiliary filament. Tungsten, molybdenum, and tantalum can be used for this purpose if heated to 1000°C or higher. Most interesting of all the metals in its cleanup action is zirconium.[3,4] Zirconium will absorb 5 times its own volume of hydrogen at 400°C, while at 1400°C it will absorb carbon monoxide and carbon dioxide as well as 40 times its own volume of oxygen and 20 times its own volume of nitrogen. At temperatures below 200°C, protective oxides and nitrides form. For complete getter action, two filaments, one to work at 400°C and one to work at 1400°C, are necessary. Zirconium-filament getters are seldom used in commercial tubes but are useful in experimental tubes. Zirconium is often used in the form of a sprayed powdered coating applied to metal anodes. This gives increased thermal emissivity and also a continuous getter action during operation.

[1] ANDREWS, M. R., and J. S. BACON, The Comparison of Certain Commercial Getters, *Gen. Elec. Research Paper* 574, June, 1931, also published in *Jour. Amer. Chem. Soc.*, pp. 1674–1681, May, 1931.

[2] DUSHMAN, "The Production and Measurement of High Vacuum," *op. cit.* The last half of this book is devoted to the subject gas sorption and degassing of materials.

[3] FAST, J. D., Zirkon und seine hochschmelzenden Verbindungen, *Philips Tech. Rev.*, vol. 3, pp. 353–360, December, 1938.

[4] FAST, J. D., Metals as Getters, *Philips Tech. Rev.*, vol. 5, pp. 217–221, August, 1940.

APPENDIX I

PROPERTIES OF THE ELEMENTS

A. Atomic Weights and Numbers

	Symbol	Atomic number	Atomic weight		Symbol	Atomic number	Atomic weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protoactinium	Pa	91	231.
Caesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222.
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulphur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

Figure 15.4 shows twelve ignitrons assembled into a complete rectifier rated at 3000 kw., 600 volts. (Circuits for this service are presented in Chap. VII.)

Comparison of Ignitron with Mercury-arc and Mercury-vapor Tubes. The principal fault of mercury-arc tubes was shown to be the need for a keep-alive circuit to maintain the arc, thus increasing the danger of arc back due to the continuous existence of positive ions in the tube chamber. The principal fault of

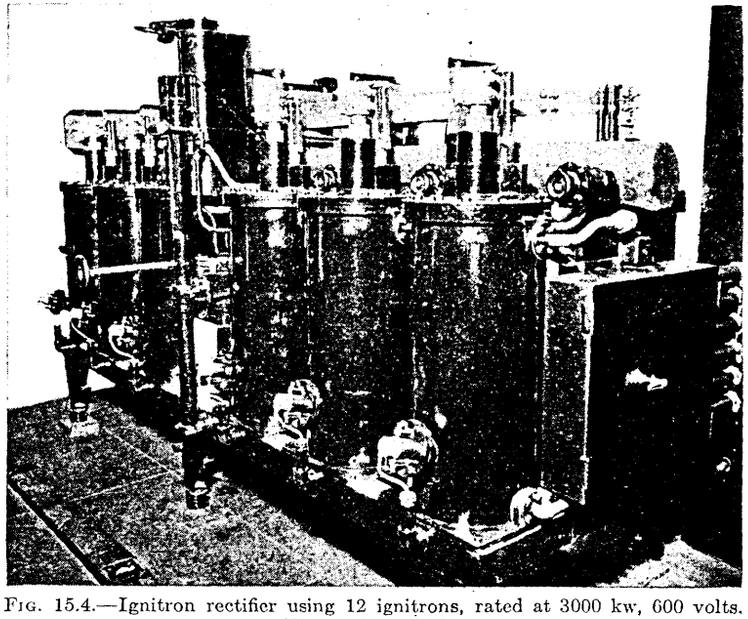

FIG. 15.4.—Ignitron rectifier using 12 ignitrons, rated at 3000 kw, 600 volts. (*General Electric Co.*)

mercury-vapor tubes was seen to be the limitation in permissible overload current imposed by the maximum emission of the cathode. The ignitron very successfully eliminates both these faults. The overload capacity is the same as that of the mercury-arc, and it is not necessary to sustain the arc, the tube being ready for service at all times.

Unfortunately these advantages of the ignitron are not obtained without cost, since it is necessary to use auxiliary tubes and circuits to energize the ignitor (see page 201). As a result the ignitron is rapidly replacing the mercury arc in heavy-duty service where the cost of this auxiliary equipment is not too large

a percentage of the total investment, but the mercury-vapor tube continues to be superior for lighter services.

Tungar Tubes.[1] The tungar tube (Fig. 16.4) was developed to supply a demand for a high-current, low-voltage tube to charge storage batteries or for other similar services. It consists of a rather heavy, coiled, thoriated-tungsten filament mounted horizontally between two vertical supports and a small graphite button or target mounted above the filament that serves as a plate. The bulb is well evacuated, and then argon gas is admitted to a pressure of about 5 cm. of mercury. A ring of magnesium is secured around the plate, and after evacuation it is volatilized by heating of the anode. This magnesium *getter* serves the same purpose in this tube as in the high-vacuum tubes; it deposits on the glass walls of the bulb and absorbs any air that may be present after evacuation or that may appear during operation.

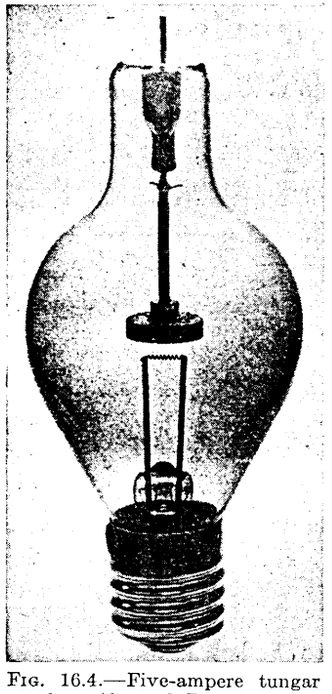

FIG. 16.4.—Five-ampere tungar tube. (*General Electric Co.*)

The filament of the tungar tube is operated at a much higher temperature than can be used in a thoroughly evacuated bulb so that its emission efficiency (milliamperes of emission per watt of filament heating power) is many times that of the filaments used in high-vacuum tubes. This high operating temperature would cause rapid evaporation, were it not for the presence of the gas. It has been found that cathode evaporation is practically negligible in the presence of an inert gas at the pressure used in this tube. Consequently a very large increase

[1] Tungar is the General Electric trade name for the type of tube discussed in this section. Although the use of trade names in a textbook is considered undesirable, there are several types of tubes to which no simple, common name has been applied and to which most engineers refer by the trade name, *e.g.*, tungar, thyratron, ignitron.