

ed, and this enables us to give an exact expression for a balanced action of any type.

Suppose that we have two acids A and A', with their salts S and S', and that A and S' are dissolved in such a quantity of water that their active masses are each represented by 1. Then at the beginning of the action, we have the two interacting to form the other pair A' and S, the chemical equation being $A + S' = A' + S$.

After equilibrium has been reached, i. e., when the two opposed reactions are balanced so that in a given time just as much of the pair A, S' disappears as is produced in the same time by the interaction of the pair A', S, a certain amount χ of the original salt and acid will have been transformed, so that their active masses are now no longer 1, but $1 - \chi$. The rate at which these pass into the other acid and base is proportional to the active mass of each, so that we have—

$$\text{rate } A, S' \rightarrow A', S = k(1 - \chi)(1 - \chi),$$

where k is a constant, expressing the amount of the reaction in unit time when the concentration of each of the reacting substances is unity. Now the active masses of the second acid and base are χ and χ respectively, for just as much of each of them has been formed as there has disappeared of the others. We have therefore—

$$\text{rate } A', S \rightarrow A, S' = k' \chi \chi,$$

where k' is the velocity constant of the second reaction. But the amounts transformed in unit time are equal at the point of equilibrium, so that we have—

$$k(1 - \chi)^2 = k' \chi^2$$

$$\text{or } K = \frac{k}{k'} = \frac{\chi^2}{(1 - \chi)^2}$$

It is therefore easy from a determination of the amounts of the various substances present at the point of equilibrium to ascertain K the ratio of the velocity constants of the opposed reactions. Julius Thomsen employed a thermochemical method for determining the extent to which the action of one acid on the salt of another had taken place.

It could be calculated from known data how much heat would be given out or absorbed when the equivalent of the first acid replaced the equivalent of the second from its salt. On actually performing the experiment the thermal effect was always found to be less than that calculated for total replacement. The ratio then of the observed to the calculated heat gave the extent to which the action had progressed. Methods similar in principle were afterward employed for ascertaining such ratios of distribution, e. g., the change of volume, and the change of the refractive index on reaction, were measured by Ostwald instead of the heat change. When the ratios obtained by balancing a series of acids against the salt of one other acid were tabulated, a set of numbers resulted which were called by Thomsen the "avidities" of the acids. These avidities were proportional to the square root of the velocity constant K . Now the constant K has an important theoretical significance, inasmuch as the maximum work to be obtained from a reversible chemical change isothermally conducted is equal to $RT \log K$, where R is a numerical constant and T the temperature on the absolute scale at which the equilibrium occurs. This maximum external work is the difference of the "free energy" of the two systems, if we employ the term in the sense proposed by Helmholtz, and is not proportional to the change of total energy of the two systems, i. e., to the thermal effect of the reaction. As every spontaneous natural process takes place in the direction in which external work is performed, the total amount of external work which a system can perform must have a close connection with the internal forces (in our case "chemical affinities") causing the change. Thus it has been proposed to take the change of "free energy" as a measure of the affinity instead of the change of total energy adopted by the earlier thermochemists. Little has been done as yet toward calculating affinity constants on this basis, and chemists are at present content with more empirical magnitudes. The relative affinities of the acids in particular have been well investigated from very many different points of view, and the results obtained by the various methods show excellent agreement with each other.

A method which has been found well suited for the comparison of the stronger acids with one another is found in estimating the rate at which they accelerate chemical processes. For example, cane sugar solution will remain at the ordinary temperature for an indefinite period without showing any tendency to pass into a mixture of dextrose and laevulose, but if an acid be present, the inversion of the sugar begins immediately, and goes on until the cane sugar is completely transformed. It was found that the rate of inversion with a given acid is very nearly proportional to the concentration of the acid used; but that for equivalent quantities of different acids, the rate varies greatly. If the acids are arranged in the order in which they accelerate the inversion of cane sugar, it is found that this order is identical with that obtained when the acids are arranged according to their "avidities" as determined by an equilibrium method. Other acceleration processes have now been studied, and all agree in giving the acids in the same order as they appear in the inversion of cane sugar, which order is identical with that obtained when the acids are arranged according to the electrical conductivity of their equivalent aqueous solutions.

There is no obvious connection between these two properties of acids, viz., their chemical reactivity and their power to conduct electricity, but an explanation is found in the electrolytic dissociation theory of Arrhenius. His theory refers both properties to the same cause—to the amount of dissociation of the acids into the positive ion hydrogen, and the negative ion of the acid. Acids are chemically active in the measure that they produce hydrogen ions, which alone determine the specific acid character. These hydrogen ions are also the chief carriers of electricity in an acid solution, so that the more of them an acid can produce when dissolved in a certain quantity of water, the more active will it be chemically and the better will it conduct electricity. The degree of dissociation then of an acid is an excellent measure of its strength. By applying the law of gaseous dissociation to this case of dissociation in solution, Ostwald has been able

to calculate a constant from the conductivities of the weaker acids at different dilutions, which he regards as a good expression of the affinity of the acid. The dissociation constant, or affinity constant, determined in this way, is independent of the amount of water in which the acid is dissolved.

For bases we have methods corresponding to those employed for acids. First of all, we have one acceleration process—the conversion of hyoscyamine into the isomeric alkaloid atropine. Under the influence of strong bases this transformation occurs at a rate depending on the strength of the base, other things being equal. Then we have a class of reactions in which the base participates directly, namely, the saponification of ethereal salts. The rate at which ethyl acetate, for example, is converted by a base into the acetate of that base and ethyl alcohol is a measure of the strength of the base. Again, it is found that the electrical conductivity of aqueous solutions of the various bases is proportioned to their strength as determined by any of the above methods. The explanation given by the theory of electrolytic dissociation is that the specific activity of bases is due to the hydroxyl ions which they produce when dissolved in water, and that the strengths of the bases, together with their electric conductivities, are closely proportional to the number of these ions produced when the bases are in equivalent solution. A dissociation or affinity constant for bases can also be calculated in a manner precisely similar to that adopted for the dissociation constants of acids.

The proximate problem of chemical affinity, then, is to determine as many of these characteristic dissociation constants for acids and bases as possible, for they can be used in solving very many problems of the speed of reactions and the equilibrium of opposed reactions in aqueous solutions, with which the chemist is mostly concerned.

The methods detailed above are well suited for the investigation of all but the weakest acids and bases, but there they fail entirely, and we have to resort to equilibrium methods for ascertaining the affinities of those substances. There is one substance which is very convenient as a standard of comparison against which to compare the strengths of both weak acids and weak bases, namely, water. Weak bases give off comparatively few hydroxyl ions OH, and weak acids few hydrogen ions H.

Now water in the pure state dissociates electrolytically to a minute extent into these ions, $H_2O = H + OH$, so that it can act both as a very weak acid and a very weak base, according as it competes against another acid or another base. The amount of the dissociation of water is extremely slight, a calculation by Kohlrausch showing that a cubic meter, i. e., about a ton, of water at 18° C. contains only 1.64 milligrammes dissociated into hydrogen and hydroxyl ions.

A base like diphenylamine is so weak that, although it can form a hydrochloride, the salt, when treated with water, has the hydrochloric acid washed entirely away, leaving the free base behind. Here the water plays the part of a base against the diphenylamine, and competes with it for the hydrochloric acid. Aniline is a much stronger base than diphenylamine, but still its hydrochloride, when dissolved in water, is split up partially into aniline and hydrochloric acid. By comparing the amounts of free hydrochloric acid obtained from equivalent solutions of the hydrochlorides, we can ascertain the relative strengths of the bases, for the stronger the base is, the less will its salt be decomposed by a given quantity of water. The amount of free hydrochloric acid in the solutions cannot be estimated by any ordinary analytical process, but can be determined indirectly by ascertaining, for example, how rapidly the solution inverts cane sugar, the rate depending on the amount of free acid present.

Similarly salts of weak acids may be decomposed by water. The cleansing properties of washing soda and of soap depend on the fact that these are sodium salts, whose acids are so weak that there is partial, though slight, decomposition into the acid and free caustic soda when the salts are dissolved in water. The amount of soda present may be calculated from the rate at which the solution saponifies ethyl acetate.

These equilibrium methods have now put us in a position to give the order of affinity of both acids and bases from the strongest to the weakest, and even for the weakest an approximation to the dissociation constant can be calculated.

With regard to other affinities, the study of electromotive force seems to promise excellent results in certain directions, but the solution of the general problem is still the task of the future.

JAMES WALKER.

ELECTRIFICATION AND DISELECTRIFICATION OF AIR AND OTHER GASES.*

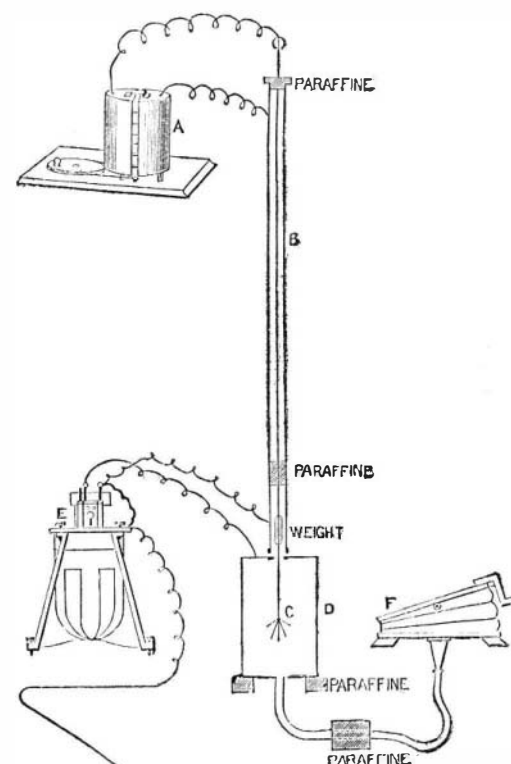
By LORD KELVIN, MAGNUS MACLEAN and ALEXANDER GALT.

§ 1. EXPERIMENTS were made for the purpose of finding an approximation to the amount of electrification communicated to air by one or more electrified needle points. The apparatus consisted of a metallic can 48 cms. high and 21 cms. in diameter, supported by paraffine blocks, and connected to one pair of quadrants of a quadrant electrometer. It had a hole at the top to admit the electrifying wire, which was 5.31 meters long, hanging vertically within a metallic guard tube. This guard tube was always metallically connected to the other pair of quadrants of the electrometer and to its case and to a metallic screen surrounding it. This prevented any external influences from sensibly affecting the electrometer, such as the working of the electric machine which stood on a shelf 5 meters above it.

§ 2. The experiment is conducted as follows: One terminal of an electric machine is connected with the guard tube and the other with the electrifying wire, which is let down so that the needle is in the center of the can. The can is temporarily connected to the case of the electrometer. The electric machine is then worked for some minutes, so as to electrify the air in the can. As soon as the machine is stopped the electrifying wire is lifted clear out of the can. The can and the quadrants in metallic connection with it are disconnected from the case of the electrometer, and

the electrified air is very rapidly drawn away from the can by a blowpipe bellows arranged to suck. This releases the opposite kind of electricity from the inside of the can, and allows it to place itself in equilibrium on the outside of the can and on the insulated quadrants of the electrometer in metallic connection with it.

§ 3. We tried different lengths of time of electrification and different numbers of needles and tinsel, but we found that one needle and four minutes of electrification gave nearly maximum effect. The greatest deflection observed was 936 scale divisions. To find, from this reading, the electric density of the air in the can we took a metallic disk of 2 cms. radius, attached to a long varnished glass rod, and placed it at a distance of 1.45 cm. from another and larger metallic disk. This small air condenser was charged from the



Connected with guard screen (not shown in diagram).

FIG. 1.

electric light conductors in the laboratory to a difference of potential amounting to 100 volts. The insulated disk thus charged was removed and laid upon the roof of the large insulated can. This addition to the metal in connection with it does not sensibly influence its electrostatic capacity. The deflection observed was 122 scale divisions. The capacity of the

condenser is approximately $\frac{\pi \times 2^2}{4\pi \times 1.45} = \frac{1}{1.45}$. The

quantity of electricity with which it was charged was $\frac{1}{1.45} \times \frac{100}{300} = \frac{1}{4.35}$ electrostatic unit. Hence the quantity to give 936 scale divisions was

$$\frac{1}{4.35} \times \frac{936}{122} = 1.7637.$$

The bellows was worked vigorously for two and a half minutes, and in that time all the electrified air would be exhausted. The capacity of the can was 16,632 cubic centimeters, which gives, for the quantity

of electricity per cubic centimeter, $\frac{1.7637}{16,632} = 1.06 \times 10^{-4}$.

The electrification of the air in this case was positive; it was about as great as the greatest we got, whether positive or negative, in common air when we electrified it by discharge from needle points. This is about four times the electric density which we roughly estimated as about the greatest given to the air in the

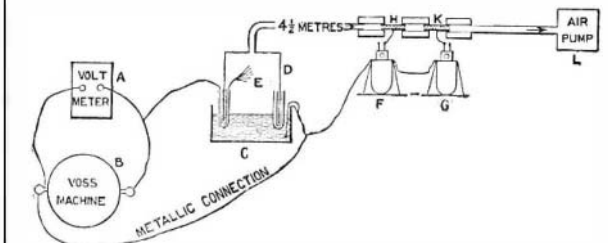


FIG. 2.

inside of a large metal vat, electrified by a needle point and then left to itself, and tested by the potential of a water dropper with its nozzle in the center of the vat, in experiments made two years ago and described in a communication to the Royal Society of date May, 1894.*

§ 4. In subsequent experiments, electrifying common air in a large gas holder over water by an insulated gas flame burning within it with a wire in the interior of the flame kept electrified by an electric machine to about 6,000 volts, whether positively or negatively, we found as much as 1.5×10^{-4} for the electric density of the air. Electrifying carbonic acid in the same gas holder, whether positively or negatively, by needle points, we obtained an electric density of 2.2×10^{-4} .

§ 5. We found about the same electric density (2.2×10^{-4})

* Abstract.—Communicated to Section A, Brit. Ass., September 17, 1895.

* "On the Electrification of Air," by Lord Kelvin and Magnus Maclean.

10-4) of negative electricity in carbonic acid gas drawn from an iron cylinder lying horizontally, and allowed to pass by a U-tube into the gas holder without bubbling through the water. This electrification was due probably not to carbonic acid gas rushing through the stopcock of the cylinder, but to bubbling from the liquid carbonic acid in its interior, or to the formation of carbonic acid snow in the passages and its subsequent evaporation. When carbonic acid gas was drawn slowly from the liquid carbonic acid in their iron cylinder placed upright, and allowed to pass, without bubbling, through the U-tube into the gas holder over water, no electrification was found in the gas unless electricity was communicated to it from needle points.

§ 6. The electrifications of air and carbonic acid described in sections 4 and 5 were tested, and their electric densities measured by drawing by an air pump a measured quantity of the gas* from the gas holder through an India rubber tube to a receiver of known efficiency and of known capacity in connection with the electrometer. We have not yet measured how much electricity was lost in the passage through the India rubber tube. It was not probably nothing; and the electric density of the gas before leaving the gas holder was no doubt greater, though perhaps not much greater, than what it had when it reached the electric receiver.

§ 7. The efficiency of the electric receivers used was approximately determined by putting two of them in series, with a paraffin tunnel between them, and measuring by means of two quadrant electrometers the quantity of electricity which each took from a measured quantity of air drawn through them. By performing this experiment several times, with the order of the two receivers alternately reversed, we had data for calculating the proportion of the electricity taken by each receiver from the air entering it, on the assumption that the proportion taken by each receiver was the same in each case. This assumption was approximately justified by the results.

§ 8. Thus we found for the efficiencies of two different receivers respectively 0.77 and 0.31 with air electrified positively or negatively by needle points; and 0.82 and 0.42 with carbonic acid gas electrified negatively by being drawn from an iron cylinder placed on its side. Each of these receivers consisted of block tin pipe, 4 cms. long, and 1 cm. diameter, with 5 plugs of cotton wool kept in position by six disks of fine wire gauze. The great difference in their efficiency was, no doubt, due to the quantities of cotton wool being different, or differently compressed in the two.

§ 9. We have commenced and we hope to continue an investigation of the efficiency of electric receivers of various kinds, such as block tin, brass, and platinum tubes from 2 to 4 cms. long, and from 1 mm. to 1 cm. internal diameter, all of smooth bore and without any cotton wool or wire gauze filters in them; also a polished metal solid, insulated within a paraffin tunnel. This investigation, made with various quantities of air drawn through per second have already given us some interesting and surprising results, which we hope to describe after we have learned more by farther experimenting.

§ 10. In addition to our experiments on electric filters we have made many other experiments to find other means for the dielectrification of air. It might be supposed that drawing air in bubbles through water should be very effective for this purpose, but we find that this is far from being the case. We had previously found that nonelectrified air drawn in bubbles through pure water becomes negatively electrified, and through salt water positively. We now find that positively electrified air drawn through pure water, and negatively electrified air through salt water, has its electrification diminished, but not annulled, if the primitive electrification is sufficiently strong. Negatively electrified air drawn in bubbles through pure water, and positively electrified air drawn through salt water, has its electrification augmented.

§ 11. To test the effects of heat, we drew air through combustion tubes of German glass about 180 cms. long and $2\frac{1}{2}$ or $1\frac{1}{2}$ cms. bore, the heat being applied externally to about 120 cms. of the length. We found that when the temperature was raised to nearly a dull red heat, air, whether positively or negatively electrified, lost little or nothing of its electrification by being drawn through the tube. When the temperature was raised to a dull red heat and to a bright red high enough to soften the glass, losses up to as much as four-fifths of the whole electrification were sometimes observed, but never complete dielectrification. The results, however, were very irregular. Non-electrified air never became sensibly electrified by being drawn through the hot glass tubes in our experiments, but it gained strong positive electrification when pieces of copper foil, and negative electrification when pieces of carbon, were placed in the tube, and when the temperature was sufficient to powerfully oxidize the copper or to burn away the charcoal.

§ 12. Through the kindness of Mr. E. Matthey, we have been able to experiment with a platinum tube 1 meter long and 1 millimeter bore. It was heated either by a gas flame or an electric current. When the tube was cold and non-electrified air drawn through it, we found no signs of electrification by our receiver and electrometer. But when the tube was made red or white hot, either by gas burners applied externally or by an electric current through the metal of the tube, the previously non-electrified air drawn through it was found to be electrified strongly positive. To get complete command of the temperature, we passed a measured electric current through 20 centimeters of the platinum tube. On increasing the current till the tube began to be at a scarcely visible dull red heat we found but little electrification of the air. When the tube was a little warmer, so as to be quite visibly red hot, large electrification became manifest. Thus 60 strokes of the air pump gave 45 scale divisions on the electrometer when the tube was dull red and 395 scale divisions (7 volts) when it was a bright red (produced by a current of 36 amperes). With stronger currents, raising the tube to white hot temperature, the electrification seemed to be considerably less.

* The gas holder was 38 cms. high and 81 cms. in circumference. Ten strokes of the pump raised the water inside to a height of 8.1 cms., so that the volume of air drawn through the receivers in the experiments was 428 cubic centimeters per stroke of the pump. This agrees with the measured effective volume of the two cylinders of the pump.

ELECTRIC ELEVATORS.

PASSENGER elevators are now of the greatest necessity in the high buildings that are being constructed. For a long time, lifts for different kinds of merchandise sufficed. It was only in 1867, at the Universal Exposition, that Mr. Edoux exhibited the first model of a hydraulic passenger elevator. Water under pressure was at that epoch the best agent capable of raising a given weight to a certain height. All the necessary arrangements were made for assuring a proper operation of this apparatus, such as regulating devices, safety devices, balancing of a part of the weight, etc. It is certain that hydraulic elevators established under such conditions rendered the greatest

lutation. As long ago as 1890, however, numerous experiments had been made in France, Germany and America with a view to substituting electric elevators for the hydraulic ones supplied by city water, or by water forced into a reservoir by a pump actuated by a gas motor. The electric elevator was set in motion by an ordinary rope windlass. We may mention, without being able to describe them, the electric elevators of Edoux, of the Société d'Eclairage Electrique, of Neu, of Otis, of the Keystone Electric Company, of Messrs. Morse, Williams & Company, etc. At the beginning of 1895 there existed at New York, upon the distributing line of one electric company, 250 elevators of a total 3,000 horse power.

Up to this epoch electric elevators were considered

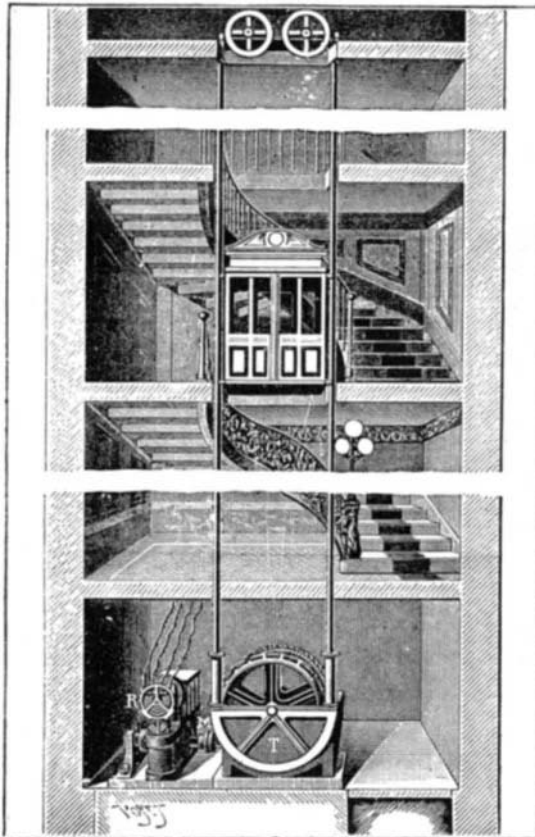


FIG. 1.—GENERAL VIEW OF AN ELECTRIC ELEVATOR.

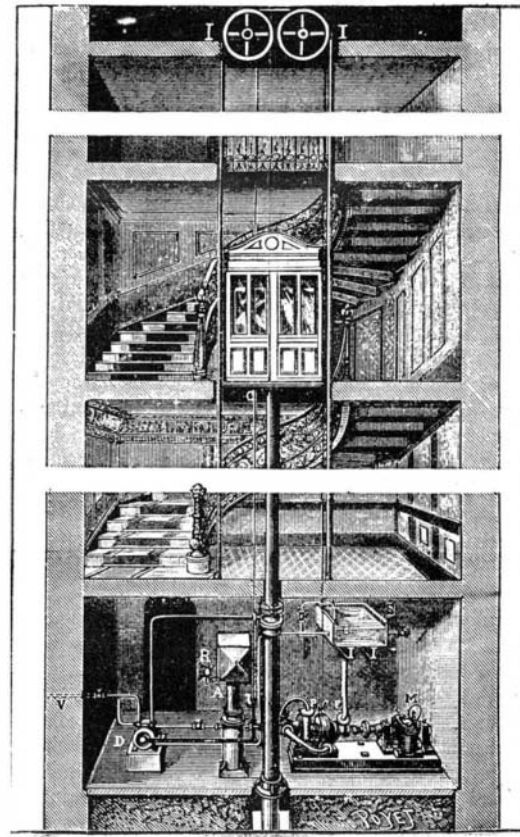


FIG. 2.—GENERAL VIEW OF A HYDRO-ELECTRIC ELEVATOR.

services at that epoch, and have always been, since then, greatly appreciated.

Only one grave objection could be urged against them, and that concerned their establishment. They necessitated the use of a cast iron cylinder placed in a well of a depth somewhat greater than the height of the car's travel, and in which a piston was capable of moving and of wholly entering when the elevator was at the bottom of its travel. There were also constructed elevators without wells, among which may be mentioned that of Samain, with telescopic piston, that of Roux & Combaluzier, with jointed piston, etc. The various difficulties were put up with because of the advantages that elevators presented.

The maneuvers of starting and stopping were effected by acting, through a cable running through the car, upon a distributor designed to put the cistern of the piston in communication with the water conduit or the discharge pipe. Improvements were afterward made, and, in 1887, Mr. Edoux substituted a hydro-

as interesting applications at Paris, but few owners of buildings thought of adopting them, by reason, on the one hand, of the good service that the hydraulic elevators already installed were rendering them, and, on another hand, by reason of the cost of transformation that would be necessary. A municipal regulation concerning the concession of the water of the city of Paris, published in the Official Municipal Gazette of December 22, 1894, changed all such arrangements. According to this regulation, the water used for actuating the engines by means of the pressure that it possesses in the public pipe line had to be paid for apart and at the rate of 0.6 franc per cubic meter of water consumed, conformably to the readings of a meter through which it was to pass isolatedly. The cost of the water consumed was thus doubled, and the expenses increased in large proportions, and the more so in that the consumption of hydraulic elevators is constant, whatever be the number of passengers, and even when empty. It has been calculated that a three-

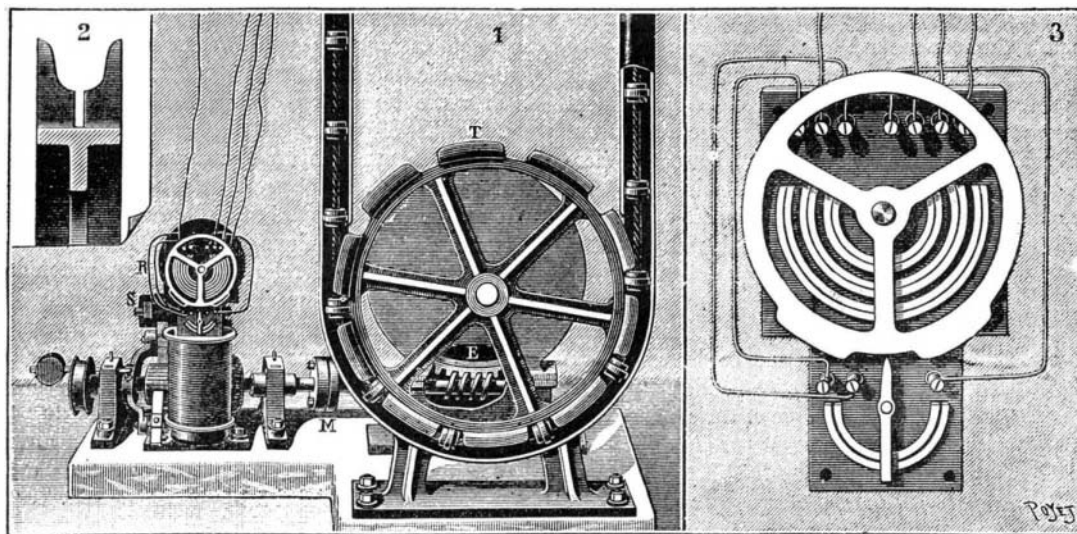


FIG. 3.—DETAILS OF AN ELECTRIC WINDLASS FOR AN ELEVATOR.

1. Electric control. 2. Section of a notch. 3. Rheostat.

electric maneuver for that by means of a cable. It sufficed to establish a contact that closed a battery circuit upon electro-magnets in order to effect the displacing of the distributor and consequently the opening or closing of the water cock. We must add that these latter arrangements, although they sometimes operated well, also often presented numerous difficulties. Since then, however, electric elevators have often been mentioned, and we must recall here the first apparatus of Mr. Werner Siemens that figured at the exposition of Mannheim, and the electric elevators of Mr. Chretien at the exposition of 1889. But the question had not as yet received a really practical so-

passenger elevator making, upon an average, twenty-five trips a day at the rate of 275 liters of water a trip, would cost 1,500 instead of 800 francs a year at the old tariff of 0.32 franc per cubic meter of water. All the manufacturers of elevators became stirred up and endeavored to modify their systems in order to remedy this state of things. Afterward an examination was made of electric, compressed air and what are called hydro-electric elevators. Under several circumstances, the project was likewise examined of preserving the present hydraulic elevators and of supplying them with water under pressure pumped by gas or electric motors. These latter arrangements are evidently