

VOLUMETRIC ASSAY OF BULLION, ALLOYS, ETC.

Probably no quantitative analytical process is susceptible of a higher degree of accuracy than that by which the quantity of silver in bullion, coin, plate, etc., is now usually determined, and in point of simplicity as well as accuracy is a good illustration of the volumetric method as applied to the analysis of many other substances.

When a neutral or acid solution containing silver is brought into contact with a solution containing a sufficient quantity of sodium chloride (common table salt) the whole of the silver is precipitated as silver chloride.

A given quantity of pure salt always thus precipitates a certain definite quantity of silver (1 grain of salt corresponding to $1\frac{1}{10}$ grains, nearly, of silver.)

If one grain of salt, silver, or any other substance is dissolved in a quart of liquid, and the quart is then divided into ten, one hundred, or one thousand equal parts or volumes, each of these will contain just one-tenth, one-hundredth, or one-thousandth, as the case may be, of a grain of the dissolved substance. So that, in the case of silver, if it is known just how much salt is dissolved in a given quantity of water it is easy to calculate how much there is in any volume of the solution, and just how much dissolved silver any volume of it will precipitate.

The several pieces of apparatus necessary in preparing, standardizing, and applying this liquid measurer are shown annexed. The glass burette, A, is secured in position by the wooden clamp, B, adjustable on the iron rod of the stand, C. The ground glass stop-cock, *a*, controls the flow of the liquid from the tube. The burette is accurately graduated to one-fifth or one-tenth cubic centimeter by an etched scale.

In the burette, D, the expensive glass stop-cock is dispensed with, a piece of pure gum rubber tubing and a brass wire clamp, *b*, being substituted. The small delivery neck of the burette is joined by the tubing to a small piece of glass tube drawn out at one end to a fine delivery. The wire clamp (quetchon or pinch-cock) retains the liquid by pinching the rubber tube. E and F are pipettes. In using them the lower end is dipped in the liquid, the mouth applied to the upper end, and the liquid drawn up until the tube is nearly full. The mouth is then removed, the finger quickly placed over the end, as shown at G, and a small portion of the liquid allowed to escape until the liquid fills the tube just to the containing mark, *c*. When the finger is removed the liquid runs out. The flask is used where larger quantities of the liquid are to be measured. The containing mark is at *e* on the neck.

The titration bottle, H, is of fine thin glass, the glass stopper being ground to accurately fit the neck, and terminates in a point. These bottles usually have a capacity of about 250 c.c.

In analytical work of this kind the decimal or French system of weights and measures is nearly always used, as they are much more convenient than other systems. The gramme equals $15\frac{1}{2}$ grains, nearly; the milligramme (mg.) $\frac{1}{1000}$ of a gramme; the liter about $1\frac{1}{4}$ pints; the cubic centimeter (c.c.) $\frac{1}{1000}$ of a liter.

In preparing the salt solution $5\frac{1}{2}$ grammes of chemically pure, dry salt is dissolved in a small quantity of distilled water, the solution diluted to one liter with cold distilled water, and put into a clean glass bottle labeled "Salt No. 1." Fifty c.c. of this solution is drawn off with a pipette, diluted with cold distilled water to 500 c.c. (half liter), and put into another clean glass bottle marked "Salt No. 2."

These solutions are then *standardized*—that is, tested to determine just how much silver a given measure of the liquid will precipitate.

One-half gramme of pure silver is dissolved, by aid of gentle heat, in about 3 c.c. of pure nitric acid, and the solution is then diluted to one-half liter with cold distilled water; so that 1 c.c. of the liquid contains just 1 mg. of silver. Fifty c.c. of this solution, drawn off with a pipette, is placed in the titration bottle, and the burette (A or D) is filled to zero with the salt solution No. 2. This solution is then allowed to drop from the burette into the silver solution in the bottle, the flow being discontinued from time to time and the bottle closed and agitated to facilitate the subsidence of the flocculent precipitate. A little experience enables the operator to tell when the silver solution is nearly saturated, and then the contents of the bottle is shaken and allowed to subside between the addition of every two or three drops, so that when at last the drops of salt solution fail to produce any more precipitate in the silver solution, then the total quantity or volume of salt solution used may be accurately read off on the scale of the burette. To avoid any error the test is duplicated, and the results of the two tests, when

compared, should agree very closely. If it is found, for instance, that 50 c.c. of the salt solution corresponds to 50 c.c. of the silver solution, then the solution in bottle No. 2 is marked "1 c.c. = 1 mg. silver;" and bottle No. 1, "1 c.c. = 10 mg. silver," as its contents contain ten times as much salt.

Thus standardized the salt solutions become, when properly used, accurate measures of the amount of silver in a liquid.

In the actual assay of a silver alloy from half to one



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gramme of the metal is weighed out, put into the titration bottle with 4 or 5 c.c. of nitric acid (of sp. gr. 1.2), and the contents heated by placing the bottle obliquely in a hot water bath. From time to time the nitrous fumes are blown out and the bottle frequently shaken to promote their expulsion. When solution is complete the bottle is removed and its contents allowed to cool. If the alloy contains gold, a small quantity of pure sulphuric acid is added, and the liquid boiled until all the gold has separated. The liquid adhering to the stopper and neck of the bottle having been rinsed down with a small jet of distilled water, salt solution No. 1 is gradually let in from a burette until the silver solution is, as before described, nearly saturated; then salt solution No.

distilled water to about ten times its volume, and well shaken. About 50 c.c. of standardized salt solution is mixed with just enough of a strong aqueous solution of pure potassium chromate solution to distinctly color it. Then the dilute silver solution is gradually let in from the burette, the mixture being agitated after every few drops. As long as there is an excess of salt the orange-red silver chromate formed when the drops of silver solution strike the salt liquid is quickly decomposed and decolorized. When the point of complete saturation is reached this decomposition no longer takes place, and the solution assumes a distinct orange-red color.

The quantity of silver solution required to saturate 50 c.c. of the standardized salt solution is then read off on the burette. As the quantity of silver this volume of salt solution corresponds to is known, the rest of the calculation is easy.

DYNAMIC ELECTRICITY.

BY GEO. M. HOPKINS.

GENERATION OF THE ELECTRIC CURRENT.

When two dissimilar metals, such as pure copper and pure zinc, are placed in contact in acidulated water, evidences of activity immediately appear in the form of a cloud of microscopic bubbles constantly rising to the surface of the water. If the metals are individually capable of resisting the action of the acid solution, it will be noticed that on separating the metals the action ceases, but it will commence again as soon as the metals are brought into contact. The same action is noticed if the two metals are connected by a wire, which may be either wholly within or partly out of the acidulated water.

The bubbles which are noticed in this experiment are hydrogen resulting from the decomposition of the water and escape from the copper, and the oxygen resulting from the analysis unites with the zinc, forming zinc oxide.

The copper is scarcely attacked while the zinc slowly wastes away. If the wire connecting the zinc and copper be cut and the two ends placed on the tongue, a slight but peculiar biting sensation is experienced, which will not be felt when the wires are disconnected from the metals.

A piece of paper moistened with a solution of iodide of potassium and starch placed between the ends of the wires exhibits a brown spot, showing that between the ends of the wires there is a species of energy capable of effecting chemical decomposition. If a wire joining the copper and zinc is placed parallel with and near a delicately suspended magnetic needle, it will be found that it is endowed with properties capable of affecting the needle in the same manner as a magnet. This form of energy is dynamic or current electricity, generated in this case by chemical action and confined to, and following a continuous conductor, of which the two metallic elements and the acid solution form a part, the whole comprising a complete electric circuit.

For the purpose of studying the generation and behavior of dynamic electricity the elements referred to may be formed into an electric generator or battery, and the magnetic needle and conducting wire may be combined to form an electrical indicator or galvanometer.

The engraving shows convenient apparatus for making the primary experiments in dynamic electricity. The glass tank or cell is built with special reference to projecting the visible manifestations of the phenomena exhibited in the cell, upon a screen, by means of the lantern, to enable a number of persons to observe simultaneously.

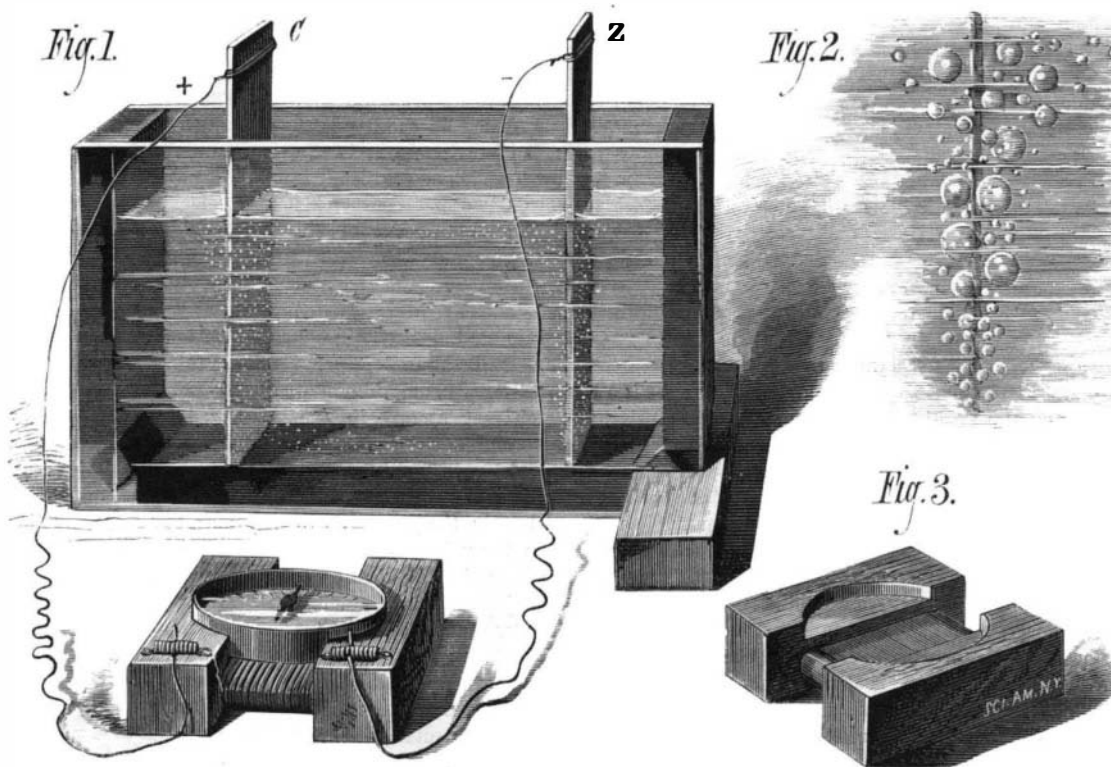
The cell consists of two plates of transparent glass 4 by 6 inches, separated by a half inch square strip of soft rubber, which is cemented to both glasses by means of a cement composed of equal parts of pitch and gutta percha. The cell is nearly filled with the exciting liquid, consisting of dilute sulphuric acid (acid 1 part, water 15 parts), in which are placed two plates, the positive plate consisting of a strip of zinc about one-sixteenth of an inch thick, the negative plate being a strip of copper.

As commercial zinc is so impure as to be violently attacked by the exciting liquid, it is well to dip the zinc strip into the solution, and then apply to it a drop or so of

mercury, which amalgamates the surface of the zinc and prevents local action.

When these two plates are brought into contact with each other in the exciting liquid, hydrogen gas is given off copiously at the copper or negative plate, while the action at the zinc or positive plate is almost unnoticeable. If the plates are connected together by a conductor outside of the solution, the same phenomenon is observed.

The plane flat surfaces of the cell offer facilities for the



EXPERIMENTAL BATTERY AND GALVANOMETER

2, from another burette, is added until the exact point of saturation is noted. The readings from the two burettes properly reduced will then indicate how much pure silver the alloy contains.

Tests of this kind should always be made in duplicate to avoid error.

In testing photographic silver baths the total quantity of bath is measured, and a clean burette is filled to the zero mark with a definite portion of it, previously diluted with

examination of the plates by means of the microscope, and if so examined it will be found that so long as there is no metallic connection between the electrodes they will remain unaltered, and no action is discoverable; but when the circuit is completed, the first visible indication of action is the sudden whitening of the copper plate as if it were frost-covered; the next indication of action is the formation over the entire surface of the plate of myriads of minute silvery bubbles, which grow until they become detached, when they rise to the surface and escape into the air. These bubbles may be discharged into the mouth of a small test tube, and when a sufficient quantity of gas has accumulated it may be ignited, showing that it is hydrogen.

The appearance of the negative plate when the cell is in action is shown in Fig. 2 greatly magnified. The gas bubbles formed on the surface of the copper are at first very minute, but they rapidly increase in size and begin to merge one into another, taking an upward course. When a large bubble has absorbed a large number of the smaller bubbles and becomes sufficiently buoyant to overcome its adhesion to the plate it rises to the surface and is dissipated.

The bubbles of hydrogen are very bright, appearing and acting much like globules of mercury. Often an equatorial belt of very small bubbles will be seen surrounding a larger one.

The accumulation of hydrogen on the negative plate seriously affects the strength of the current. To ascertain to what extent and at what time this happens, a

SIMPLE GALVANOMETER

like that shown in Fig. 1 will be required. This instrument consists of a common pocket compass, a wooden frame or spool, and about 20 feet of No. 32 silk covered copper wire. The wood spool (Fig. 3) has a recess cut in the top at either end to receive the compass, which is placed a short distance from the flat body of the spool, and the wire is wound evenly around the body back and forth until the spool is full. Then the terminals of the wire are connected with two spiral springs fastened to the ends of the spool and forming "binding posts" for receiving the wires from the battery.

In regard to the adjustment of the compass, it should be arranged with the line marked N S parallel with the wires of the coil, and the instrument should be turned until the N S line is exactly under the needle, then a weak current should be sent through the coil and the deflection noted. The current should then be sent in the opposite direction, when the needle will be deflected in the opposite direction. If the amount of deflection is the same in both cases the galvanometer is in condition for use; but if the deflections differ in degree, the compass must be turned in its socket until the proper adjustment is secured. The only precaution necessary in the construction of this instrument is to select a compass whose needle is delicately poised and vibrates freely.

By connecting the galvanometer with the cell as indicated in the engraving it will be noticed that after a limited time the galvanometer needle begins to fall back toward 0°, a point which it ultimately reaches if the circuit is kept closed; and the shorter the circuit the sooner the cessation of the current. This

ENFEBLEMENT OF THE CURRENT

is principally due to three causes, one of which has already been noticed, that is, the accumulation of hydrogen on the negative plate. The film of hydrogen not only prevents contact between the exciting solution and the plate, but it actually renders the surface to a certain degree positive, and consequently in nature, although not in degree, like the positive plate. Another cause of enfeeblement of the current is the reduction on the copper, by the hydrogen, of a portion of the sulphate of zinc accumulating in the liquid. This increases the similarity of the two plates, and consequently assists in diminishing the current. The reduction of the strength of the exciting liquid of the cell and the oxidation of the zinc contribute still further toward the diminution of the current. All this results in making the two plates similar in their action, and in a consequent weakening of the current; but this chemical action cannot be avoided, as to secure any action in a galvanic cell the exciting fluid must be capable of decomposition. The oxidation of the zinc, the accumulation of hydrogen on the positive plate, and the weakening of the exciting solution are the three great causes of inconstancy in batteries. The first may be remedied in a great measure by amalgamation; the remedy for the last is obviously the strengthening of the solution; and the second, the accumulation of hydrogen on the positive plate, or the polarization of the plate, can only be remedied by removing the plate from the exciting solution for an instant, or by brushing it while in the solution, or by violently agitating the exciting solution. The galvanometer needle faithfully indicates the result of either treatment. The polarization of the electrode may be strikingly exhibited by allowing the copper plate to become polarized and then replacing the zinc with a clean copper strip like the one already polarized. The galvanometer needle will be deflected in the opposite direction, showing that the polarized copper plate acts in the same manner as the zinc; that is, it is positive to the clean copper plate. Now by removing the polarized copper plate and wiping and replacing it, the deflection of the needle will be much less, and it will not fall back to 0°, until the very slight coating of zinc which has been deposited on the copper is removed from the polarized plate by means of emery paper or otherwise. Precisely the same effect is noticed when a newly amalgamated zinc plate is opposed to an oxidized zinc plate. The oxidized plate in this case will act as the negative.

This method of showing the effect of the polarization of the plate is much more conclusive and convincing than to employ a secondary battery, or to treat the element under examination as such by connecting it with another battery, as the phenomenon attributed to the polarized plate manifests itself in an unmistakable manner while the plate remains in position and under the conditions of actual use.

Although the zinc is called the positive plate of the battery, and the copper the negative plate, the positive electricity proceeds from the copper through the external portions of the circuit toward the positive or zinc plate, and the negative electricity proceeds from the positive or zinc plate toward the negative or copper plate.

This is extremely confusing to the student of electricity, but still there is a reason for putting it in this way. The zinc plate in all batteries is the active element, and the platinum, copper, or carbon plate is the passive element. In the exciting fluid of the battery the current passes from the zinc or positive plate to the platinum, copper, or carbon, negative or receiving plate, thence outward by the conductor attached to the negative plate. This conductor, as it conveys away the positive electricity, has been called the positive electrode or conductor; and as negative electricity appears on the conductor connected with the positive or zinc plate, this conductor has been called the negative electrode or conductor. All that need be remembered is that on a conductor outside of the exciting solution, the positive electricity proceeds from the passive plate of the battery, and the negative electricity proceeds from the active plate of the battery, and the flow of the electric current outside of the exciting fluid is from the passive to the active plate.

Terms such as "electric current," "electric fluid," "flow of the current," are based on the assumption that the action of dynamic electricity is analogous to that of fluids; but as nothing is known of the form of electricity, these expressions are to be considered as purely conventional.

Artificial Indigo.

At the Royal Institution lately, Professor Roscoe gave an account of the latest advance in the utilization of coal tar products by Baeyer, of Munich, in the fabrication of artificial indigo, which the lecturer considered would eventually become of great commercial importance. At present, it cannot be said that the competition of artificial and natural indigo is at all comparable with that between alizarine and madder, by which the last named dyestuff has been driven out of the market; on the contrary, artificial indigo from coal tar is as yet dearer than the vegetable product from the East. It appears that native indigo was decomposed by Fritzsche so long ago as 1840, and aniline was then obtained from it. Subsequently a crystalline substance called isatin was procured from indigo; and, later, indigo was made from isatin. The next step was the production of isatin from an independent source, and this has been done in three different ways, two of which are too costly for commercial use. Baeyer has alone carried it out in a practicable manner. He commenced with cinnamic acid obtained from oil of bitter almonds, but this was much too costly. It has been found by Dr. Caro and Mr. Perkins that cinnamic acid can be obtained from toluene, which is a product of coal tar. From cinnamic acid, however obtained, a complex acid can be produced which is now for brevity called propiolic acid. This acid gives the colorless isatin, from which, by the use of suitable reagents, the indigo blue dyestuff is obtained. The commercial aspect of the production of indigo in this way is affected by the cost of preparing the dry propiolic acid. At the present time the material is placed in the hands of Manchester calico printers at the rate of 6s. per pound for a paste containing 25 per cent of dry acid. The acid itself is worth 50s. per kilo, of which only 68.58 per cent yields actual dye, so that the price of artificial indigo, being not less than 73s. per kilo, is more than twice the value of the pure natural color. Hence competition with the Oriental product is not possible until the makers can reduce the price of dry propiolic acid to 20s. per kilo, and also obtain the theoretical yield of dye therefrom. Still the fact remains that the artificial process is a chemical reality, only hindered by economical considerations, which may at any time be removed, from taking a good commercial position. At the present exhibition of woollen fabrics, etc., in London, there are several pieces of stuffs dyed with indigo obtained from coal tar. It is impossible to say whether the process will eventually exert much influence on the value of the raw material, or if it will supplant the natural dye. Professor Roscoe thinks there is such a difference between the characteristics and methods of treatment of the two products that there will probably be room enough for both. The new process is at least to be regarded as one of the greatest triumphs of modern synthetical chemistry, which has had no field so fruitful in successes as that which is connected with the development of the hidden riches of coal tar.

Artificial Refrigeration.

The production of cold and even ice by artificial means is now a necessity in many industrial processes. According to the continental systems of brewing, great cold is required not only during the actual brewing process, but also for months afterward while the beers are maturing in the cellars. In this country the natural production of ice is very uncertain, and some winters may pass without sufficient being formed to be worth collection, and even when ice is plentiful here we have no suitable arrangements at hand for storing and preserving it for use in warmer weather. For

these reasons many ingenious contrivances have been devised for the artificial production of ice, and it may not be uninteresting to give some explanation of the theories on which these machines are founded. When a volatile liquid evaporates, a large amount of heat is necessarily absorbed by the resulting vapor, and is rendered latent or imperceptible to the senses and the thermometer. This heat is taken either from some of the remaining liquid or else from the medium in which the liquid is in contact. The cold produced by evaporation is very evident with a volatile fluid like ether; when a little of this liquid is placed in the palm of the hand an intense feeling of cold is observed; the ether, in evaporating, must absorb heat, and therefore takes it from the nearest body, which is the hand, and thus produces a corresponding reduction of temperature. The evaporation of volatile liquids is greatly assisted by a reduction of pressure; and, thus, if a little ether be placed in a shallow dish, floating on a thin layer of water, and the whole be placed under the receiver of an air-pump, there is not much difficulty in freezing the water by a rapid exhaustion of the air; in this case the vapor of ether is renewed almost as fast as it is formed, and fresh quantities of liquid ether are thus volatilized. The various ice-making and refrigerating machines are constructed so as to utilize this property possessed by all volatile fluids. If the ether be placed in a metallic vessel exposing a large surface to water or any other fluid which requires to be cooled, all the heat necessary for the volatilization of the ether must be taken from the water; the volatilization of the ether is assisted by means of an air-pump, and the ether vapor is then conveyed through pipes to another vessel also surrounded by cold water, where it gives up the same amount of heat again, and is thus converted back into a liquid. In this way a comparatively small quantity of ether will cool or even freeze an indefinite quantity of water, and the whole of the ether can be condensed again into the liquid state. Instead of ether, liquid ammonia, sulphurous acid, or other very volatile substances may be used, and a variety of complicated mechanical arrangements are introduced to assist in the volatilization, condensation, and preservation of the volatile agent used. These mechanical arrangements have been so far perfected that even water itself has been used as the evaporating agent, and ice has been successfully produced by such means. Great cold and even ice has also been produced by the expansion and contraction of atmospheric air by machines constructed on a similar principle to those we have just referred to. For brewery purposes ice is not actually required, but rather a reduction of temperature equal to about 25° F. A machine (says the *Brewers' Guardian*, from which we derive the above) that will effect this successfully and economically will probably be required in every brewery of importance before many years have elapsed.

Speed of Locomotives Then and Now.

From the comments of the Philadelphia *Ledger* on the Stephenson centenary, it appears that a greater speed than ten miles an hour for the then projected Liverpool and Manchester Railway was not to be thought of for fear of alarming the people and so defeat the charter. Such breakneck speed was "grossly in the teeth of all experience," fifty years ago. The *Ledger* says:

"The reminiscences are both interesting and curious now, when heavy trains are carried over long distances at steady rates of forty to fifty miles an hour, and when the locomotive has attained to a speed for experimental purposes of seventy miles on good tracks. It is to the steady gait of the railway engine at the forty-mile speed that we desire to invite attention. This is a regular rate on several railways radiating from Philadelphia, but for our present purpose we shall select express trains on the West Jersey Railroad. Suppose a passenger, starting at Cape May at seven o'clock in the morning for Philadelphia. He may have that delicate and accurate piece of mechanism, a chronometer watch, in his hand, and the ponderous locomotive of his train is in front of him. The watch may weigh five ounces, the locomotive thirty tons; yet the leviathan of iron is as precise in its movements and as true to time as the smaller instrument of steel, brass, platinum, and gold. As the passenger, with watch in hand, looks first at its dial, then at the watchful conductor, with his eye on his own timepiece, regulated by standard, he sees the signal to start the moment the hand on the dial shows seven o'clock. Then the engineer, with his hand on the lever, lets loose the pent-up steam, and away goes the engine. It is due at the end of the track in Camden, 81½ miles away, precisely on the moment when the same hand marks the arrival of nine o'clock. Not a minute earlier or a minute later. The engine is to go over the eighty-one and a half miles while the chronometer watch marks precisely one hundred and twenty minutes. When that time has exactly elapsed the engine is at the Camden end of the track; for the instances when this is not accurately accomplished are rare exceptions, and seem to weigh on the minds of conductor and engineer. The wheel that turns the minute hand of the watch has turned 120 times, and traversed about 180 inches, while the five-foot driver of the engine has turned 27,394 times, and has traversed 430,320 feet, or 5,183,840 inches! This, as already said, is done daily with the utmost regularity, and, considering the steadiness with which it is done, and the varying load drawn by the machine, it may be considered as well a marvel of mechanical skill as an eloquent comment on the doings and sayings before that parliamentary committee when the project for the Liverpool and Manchester Railway was under consideration."