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THE THEORY OF EMULSIFICATION. VIII

BY WILDER D. BANCROFT

Since the adsorption of gases by liquids and solids plays a part in ore flotation, it is desirable to consider the general question, and I shall begin with the adsorption of gases by solids in so far as it affects our problem. The fact has long been known that solids, such as charcoal, silica, metals, wool, glass, etc., adsorb gases selectively; but people have not been so much interested in the effect that the adsorbed gas may have on the properties of the solid. If the film of condensed air on a small particle remains of approximately the same thickness, irrespective of the diameter of the particle, the ratio of air film to mass of particle will increase as the particle is made smaller, and may increase even if the thickness of the air film decreases with decreasing size of particle. If the ratio of air film to mass of particle increases continuously, there will come some point where the ensuing change in properties will become distinctly noticeable. Cushman and Coggeshall[1] found that a powder which would pass through a 200-mesh sieve surged like a liquid. When poured into a vessel it only filled 46 percent of the space, while a coarser powder filled more. It is not surprising that the air cushion round each particle should make the particles move over one another like a liquid. Stoney[2] points out that this freedom of motion becomes more marked when there is a temperature gradient. He cites "the mobility imparted to a very fine powder (as, for example, magnesium carbonate or precipitated silica) by heating it in a metal dish. When the dish is disturbed, the powder glides about as if floating; and it is in fact floating on the compressed Crookes' layer, which will spring into existence whenever the powder is able by radiation to maintain a lower temperature than the dish."

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[1] Jour. Franklin Inst., 174, 672 (1912).

[2] Phil. Mag., (5) 4, 443 (1877).

The existence of an air film can be shown in other ways. In a paper on the disruptive discharge of electricity through gases, Schuster[1] says: "The most remarkable fact connected with disruptive discharge seems to me to be the apparent diminution of dielectric strength with a diminution of pressure. Imagine the state of a molecule in the gas just before the spark passes at an atmospheric pressure; next imagine half the number to be suddenly removed. Why should the discharge now pass? What difference can the removal of some molecules make in the state of those which are still left? None, so far as I can see, unless a great change in the inductive capacity has taken place. But no sufficient diminution of inductive capacity is observed within the bulk of the gas; and, unless our present ideas are altogether wrong, I can see no way out of the difficulty except by using a surface layer of gas in contact with the solid having a large inductive capacity. If the layer is thin, the electric displacements will not be materially changed by its presence; and if the discharge begins within the layer we have to substitute in B/λ [B = electric induction], for λ the inductive capacity not of the gas itself, but that of the condensed layer. If *k* [specific inductive capacity] is large...., λ will be nearly proportional to the density of the layer, and will therefore diminish with the pressure. There seems to me no difficulty in imagining the value of *k* in a gas to be large close to the surface of the solid; and if we once admit the possibility of such a contact-layer which diminishes in density by a reduction of pressure, some of the most puzzling facts of the disruptive discharge admit of explanation. One objection, which occurs to me, must be answered. It may be said that if λ is large near the surface of the solid, the spark will start wherever B/λ is largest, and therefore not within the condensed layer, but between it and the remainder of the gas. This objection would be justified if we take the discharge to be a passage of electricity between the molecules; but, according to the

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[1] Phil. Mag., (5) 29, 197 (1890).

theory I advocate, the dissociation of the molecules may, as already explained, take place more easily in the condensed layer, and probably soonest in direct contact with the metal."

Breuer[1] points out that the adsorbed air film plays an enormous part in every-day life by preventing the coalescence of solids. "Just as the attraction of the smallest particles of a solid for each other cause the solid to offer a greater or lesser resistance to being pulled apart, so the two substances adhere more or less firmly when the two surfaces are in intimate contact at as many points as possible. This direct contact is not so easily brought about, however. If we take a thick porcelain plate, for instance, and break it in two, the two parts should of course go together with mathematical exactness. The one is the absolute complement of the other. It would therefore seem that if the two pieces were brought together carefully, intimate contact would be set up over the whole surface and the two pieces would stick together without trouble. Anybody, who has with sorrowful countenance instinctively pressed together the fragments of a broken work of art, knows that this is not the case and that the pieces fall apart as soon as one lets go of them.

"The reason for this is as follows: All solids condense on their surfaces certain amounts of gases from the air and hold them with great force. The new surfaces which are formed when a porcelain plate is broken, are covered instantaneously with particles from the surrounding atmosphere, and these are held in place powerfully as a thin, adherent, elastic cushion. The portion of this layer which is next to the porcelain is believed nowadays to be as solid and dense as the porcelain itself, while the outer surface has the density of the air. A simple mechanical pressure, no matter how strong, is therefore not sufficient to bring the porcelain surfaces into intimate contact."

If one were to break a plate in an absolute vacuum and were to bring the pieces together in the same vacuum, the

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[1] Kitte and Klebstoffe, 23 (1907).

plate should theoretically be as good as new. This is not likely to happen practically, because we cannot get an absolute vacuum. If we heat the fragments of any broken object, we accomplish several results. At the higher temperature less gas is adsorbed and it is held less firmly. The solids become more malleable and it is therefore easier to get contact at a number of points. As everybody knows, it is possible to fasten two glass rods together at temperatures at which the glass is still very viscous. It may be urged that glass at these temperatures is obviously a liquid and not a solid; but this criticism does not apply to platinum. To weld platinum it is only necessary to put two clean pieces of platinum in contact, to heat them to a moderate temperature far below the melting point of platinum, and to give them a light tap with a hammer. Since the object in these cases is to bring two like surfaces into contact, it is easy to see why clean surfaces are essential when soldering or brazing metals, and why it is important to use a flux.

While it is not possible as a usual thing to mend a broken object by pressing the two pieces together at ordinary temperatures, Spring[1] has shown that powders may be welded into massive blocks by the use of sufficiently high pressures. That means that the pressure has been sufficient to squeeze out the air films coating the powders.

Since glass may be considered either as a solid or as a super-cooled liquid, and since glass adsorbs gases, it seems reasonable to suppose that gases might also be adsorbed by mobile liquids and this proves to be the case. Campbell[2] has made a study of the so-called bubbling method of determining vapor pressures of liquids, and he draws some distinctly interesting conclusions. "It has generally been assumed that failure to get satisfactory results of vapor pressure measure-

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[1] Bull. Acad. roy. belg., (2) 49, 323 (1880); Ann. Chim. Phys., (5) 22, 170 (1881); Ber. deutsch. chem. Ges., 15, 395 (1882); Bull. Soc. chim. Paris, (2) 40, 520 (1883); Friedel: Ibid., (2) 39, 626; 40, 526 (1883); Jannetz, Neel and Clermont: Ibid., (2) 40, 51 (1883); Tammann: Zeit. Elektrochemie, 15, 447 (1909).

[2] Trans. Faraday Soc., 10, 197 (1915).

ments in presence of a gas, almost always air, has been due to experimental error, and, in cases in which a stream of gas was used, to incomplete saturation. Regnault convinced himself that the differences he found were due to actual differences of pressure. He suggested that the molecular attraction between the substance of the walls and the vapor particles causes condensation and that equilibrium is never reached, because the rate of evaporation of liquids in presence of gases is slow and because a film of liquid of the thickness requisite to saturate the walls cannot form on account of the force of gravitation.

"It is suggested that an explanation more in consonance with the facts recorded in this paper is that gases form films on the surface of the liquids, as on those of solids; in other words, that liquids, like solids, adsorb gases. It is known that, of the three gases, carbon dioxide, oxygen and hydrogen, that nearest to its critical temperature under ordinary conditions—carbon dioxide—is the most freely soluble and is adsorbed to the greatest extent by solids, notably by charcoal, and that hydrogen, the farthest removed from its critical temperature, is least soluble and least adsorbed by charcoal. The order is the same when we arrange the gases according to the magnitude of the vapor pressure lowering which they cause. This parallelism lends weight to the hypothesis of the existence of a highly concentrated film of gas at the surface of a liquid, and further, certain of Regnault's observations receive satisfactory explanation upon this assumption.

"In his first series of statical experiments Regnault found that the greatest pressure at any particular temperature was developed immediately after the mixture of gas and vapor had been raised to that temperature, and that the maximum pressure was greater when the alteration in temperature took place quickly; in all cases, however, a gradual fall followed. In the second series the highest vapor pressure at any particular partial pressure of gas was developed immediately after a reduction in volume; as before, a gradual fall followed. It is evident that, in either case, a fresh film of liquid must be formed, which exerts a pressure equal to or approaching that developed *in vacuo*, and that, on standing, gas is adsorbed and the pressure falls in consequence.

"In reference to the results obtained by Krauskopf and others, it is noteworthy that they resorted to violent agitation of the liquid, while Regnault and Tammann passed the gas over the surface of the unstirred liquid. It would seem that the success of the former was due to the prevention of the formation of a gas film on the liquid surface, not, as they seem to imply, solely to having saturated the gas.

"The hypothesis does not account equally well for the fact that Regnault found that ether in air and hydrogen gave the lowest partial pressures at the lowest total pressures and that it increased with the latter until, when the gas pressure was approximately 1–5 atmospheres, that of ether was very nearly the same as *in vacuo*. It is almost certain that at the low pressures the amount of liquid ether was so small that there was no true free surface. Were this the case the difficulty largely disappears, for it has been proved that, even *in vacuo*, thin liquid films exert a lower pressure than the normal."

If Campbell is right in believing that a condensed air film on the surface of a liquid introduces a possible error into determinations of molecular weights by the bubbling method, this may throw some light on some curious results obtained by Orndorff and Carrell[1] a good many years ago. They found that "the rate at which the air current passes through the apparatus influences the results markedly. In some cases, however, results agreeing with the theoretical are obtained whatever be the rate as is seen in the case of urethane, while with phenol the results do not agree very well with the theoretical whatever the rate. It is quite likely that some other factor comes in here, possibly that the surface tension of the solution plays some part." It is now possible, though not proved, that the varying amount of adsorbed air is an important factor.

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[1] Jour. Phys. Chem., 1, 753 (1897).

Campbell deduced the existence of an adsorbed gas film from his quantitative measurements on evaporation. The existence of such a film is shown directly by Rayleigh's experiments on liquid jets[1]. "It has been known for many years that electricity has an extraordinary influence upon the behavior of fine jets ascending in a nearly vertical direction. In its normal state a jet resolves itself into drops, which even before passing the summit, and still more after passing it, are scattered through a considerable width. When a feebly electrified body is brought into its neighborhood, the jet undergoes a remarkable transformation, and appears to become coherent; but under more powerful electrical action, the scattering becomes even greater than at first. The second effect is readily attributed to the mutual repulsion of the electrified drops, but the action of electricity in producing apparent coherence has been a mystery hitherto.

"It has been shown by Beetz that the coherence is apparent only, and that the place where the jet breaks into drops is not perceptibly shifted by the electricity. By screening various parts with metallic plates, Beetz further proved that, contrary to the opinion of earlier observers, the seat of sensitiveness is not at the root of the jet where it leaves the orifice, but at the place of resolution into drops. As in Sir W. Thomson's water-dropping apparatus for atmospheric electricity, the drops carry away with them an electrical charge, which may be collected by receiving the water in an insulated vessel.

"I have lately succeeded in proving that the normal scattering of a nearly vertical jet is due to the rebound of the drops when they come into collision with one another. Such collisions are inevitable in consequence of the different velocities acquired by the drops under the action of the capillary force, as they break away irregularly from the continuous portion of the jet. Even when the resolution is regularized by the action of external vibrations of suitable

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[1] Rayleigh: Proc. Roy. Soc., **28**, 406; **29**, 71 (1879); **34**, 130 (1882).

frequency, as in the beautiful experiments of Savart and Plateau, the drops must still come into contact before they reach the summit of their parabolic path. In the case of a continuous jet the 'equation of continuity' shows that as the jet loses velocity in ascending, it must increase in section. When the stream consists of drops following the same path in single file, no such increase of section is possible, and then the constancy of the whole stream requires a gradual approximation of the drops, which in the case of a nearly vertical direction of motion cannot stop short of actual contact. Regular vibration has, however, the effect of postponing the collisions and consequent scattering of the drops, and in the case of a direction of motion less nearly vertical may prevent them altogether.

"Under moderate electrical influence there is no material change in the resolution into drops, nor in the subsequent motion of the drops up to the moment of collision. The difference begins here. Instead of rebounding after collision, as the unelectrified drops of clean water generally or always do, the electrical drops *coalesce*, and thus the jet is no longer scattered about. When the electrical influence is more powerful, the repulsion between the drops is sufficient to prevent actual contact, and then of course there is no opportunity for amalgamation.

"These experiments may be repeated with extreme ease and with hardly any apparatus. The diameter of the jet may be about 1/20 inch, and may be obtained either from a hole in a thin plate or from a drawn-out glass tube. I have generally employed a piece of glass tube fitted at the end with a perforated tin plate, and connected with a tap by India-rubber tubing. The pressure may be such as to cause the jet to rise 18 or 24 inches, or even more. A single passage of a rod of gutta-percha, or of sealing-wax, along the sleeve of the coat is sufficient to produce the effect. The seat of sensitiveness may be investigated by exciting the extreme tip only of a glass rod, which is then held in succession to the root of the jet and to the place of resolution into drops. An effect is observed in the latter, but not in the former position. Care must be taken to use an electrification so feeble as to require close proximity for its operation, otherwise the discrimination of the positions will not be distinct.

"The behavior of the colliding drops becomes apparent under instantaneous illumination. I have employed sparks from an inductorium, whose secondary terminals were connected with the coatings of a Leyden jar. The jet should be situated between the sparks and the eye, and the observation is facilitated by a piece of ground glass held a little beyond the jet, so as to diffuse the light; or the *shadow* of the jet may be received on the ground glass, which is then held as close as possible on the side towards the observer.

"If the jet be supplied from an insulated vessel, the coalescence of colliding drops continues for a time after the removal of the influencing body. This is a consequence of the electrification of the vessel. If the electrified body be held for a time pretty close to the jet, and be then gradually withdrawn, a point may be found where the rebound of colliding drops is re-established. A small motion *to* or *from* the jet, or a discharge of the vessel by contact of the finger, again induces coalescence.

"Although in these experiments the charges on the colliding drops are undoubtedly of the same name, it appeared to me very improbable that the result of contact of two equal drops, situated in the open, could be affected by any strictly equal electrifications. At the same time an opposite opinion makes the phenomena turn upon the very small *differences* of electrification due either to irregularities in the drops or to differences of situation, and is at first difficult of acceptance in view of the efficiency of such very feeble electric forces. Fortunately, I am able to bring forward additional evidence bearing upon this point.

"When two horizontal jets issue from neighboring holes in a thin plate, they come into collision for a reason that I need not now stop to explain, and after contact they frequently rebound from one another without amalgamation.

This observation, which I suppose must have been made before, allowed me to investigate the effect of a passage of electricity across two contiguous water surfaces. The jets that I employed were about $^1/_{16}$ inch in diameter, and issued under a moderate pressure (5 or 6 inches) from a large stoneware vessel. Below the place of rebound, but above that of resolution into drops was placed a piece of insulated tin plate in connection with a length of gutta-percha-covered wire. The source of electricity was a very feebly excited electrophorus, whose cover was brought into contact with the free end of the insulated wire. When both jets played upon the tin plate, the contact of the electrified cover had no effect in determining the union, but when only one jet washed the plate, union instantly followed the communication of electricity, and this notwithstanding that the jets were already in communication through the vessel. The quantity of electricity required is so small that the cover would act three or even four times without being recharged, although no precautions were taken to insulate the reservoir.

"In subsequent experiments the colliding jets were about $^8/_{100}$ inch in diameter, issued horizontally from similar glass nozzles, formed by drawing out a piece of glass tubing and dividing it with a file at the narrowest part. One jet was supplied from the tap, and the other from the stoneware bottle placed upon an insulating stool. The sensitiveness to electricity was extraordinary. A piece of rubbed gutta-percha brought near the insulated bottle at once determined the coalescence of the jets. The influencing body being held still, it was possible to cause the jets again to rebound from one another, and then a small motion of the influencing body *to* or *from* the bottle again induced coalescence, but a lateral motion was without effect. If an insulated wire be in connexion with the contents of the bottle, similar effects are produced when the electrified body is moved in the neighborhood of the free end of the wire. With care it is possible to bring the electrified body into the neighbourhood of the free end of the wire so *slowly* that no effect is produced; a sudden movement of withdrawal will then usually determine the coalescence.

"Hitherto statical electricity has been spoken of; but the electromotive force of even a single Grove cell is sufficient to produce these phenomena, though not with the same certainty. For this purpose one pole is connected through a contact key with the interior of the stoneware bottle, the other pole being to earth. If the fingers be slightly moistened, the body may be thrown into the circuit, apparently without diminution of effect. This perhaps ought not to surprise us, as in any case the electricity has to traverse several inches of a fine column of water. On the other hand, it appeared that most of the electromotive force of the Grove cell was necessary.

"Further experiment showed that even the discharge of a condenser charged by a single Grove cell was sufficient to determine coalescence. Two condensers were used successively; one belonging to an inductorium by Ladd, the other made by Elliott Brothers, and marked 'Capacity $^1/_2$ Farad.' Sometimes even the 'residual charge' sufficed.

"It must be understood that coalescence of the jets would sometimes occur in a capricious manner, without the action of electricity or other apparent cause. I have reason to believe that some, at any rate, of these irregularities depended upon a want of cleanness in the water. The addition to the water of a very small quantity of soap makes the rebound of the jets impossible. The last observation led me to examine the behavior of a fine vertical jet of slightly soapy water; and I found, as I had expected, that *no scattering took place*. Under these circumstances the approach of a moderately electrified body is without effect, but a more powerful influence scatters the drop as usual. The apparent coherence of a jet of water when the orifice is oiled was observed by Fuchs, and appears to have been always attributed to a diminution of adhesion between the jet and the walls of the orifice.

"Some further details on this subject, and other investigations respecting the phenomena of jets, are reserved for another communication, which I hope soon to be able to present to the Royal Society but I cannot close without indicating the probable application to meteorology of the facts already mentioned. It is obvious that the formation of rain must depend very materially upon the consequences of encounters between cloud particles. If encounters do not lead to contacts, or if contacts result in rebounds, the particles remain of the same size as before; but if the issue be coalescence, the bigger drops must rapidly increase in size and be precipitated as rain. Now, from what has appeared above, we have every reason to suppose that the results of an encounter will be different according to the electrical condition of the particles, and we may thus anticipate an explanation of the remarkable but hitherto mysterious connexion between rain and electrical manifestations."

In the third paper Rayleigh[1] points out that soap at Cambridge did *not prevent the scattering of the drops.*[2] This turned out to be due to the fact that the soap at Cambridge was a clarified specimen prepared for toilet use whereas the soap previously used was common, yellow soap containing unchanged grease. On the assumption that grease was the active agent, a small amount of milk was added to the water and worked admirably. Caustic potash, sulphuric acid, alcohol, glycerine, sugar and gum arabic had no appreciable effect.

"When the diameter of the nozzle from which a water jet issues is reduced to below $^1/_{100}$ inch, the scattering cannot be completely prevented by the presentation of an electrified body.[3] One possible reason for this is evident. The mutual repulsion of the similarly electrified drops increases rapidly relatively to the masses as the size is reduced, and thus it may happen that before the differential electrification sufficient to rupture the separating envelope at contact is arrived at, the repulsion may be powerful enough to prevent most of the

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[1] Proc. Roy. Soc., 34, 130 (1882).

[2] [This is confirmed independently by the fact that soap-bubbles do not coalesce.]

[3] [Cf. also Aganin: Drude's Ann., 45, 1026 (1914).]

drops from coming into contact at all. In connexion with this it may be remarked that two perfectly equal and equally electrified spheres would repel one another at all distances; but that if there be the slightest difference in the size or electrification, the repulsion will be exchanged for attraction before actual contact is attained. This attraction will be local, and thus the opposed parts of the surfaces may come into contact with considerable violence, even when the relative motion of the centres of the masses is small. It is easily shown experimentally that violence of contact tends to promote coalescence, so that we have here a possible explanation of the action of electricity.

"With respect to the persistent scattering of very fine jets, however, it would appear that the principal cause is simply that many of the fine drops fail to come into contact in any case. The capillary forces act with exaggerated power, and doubtless impress upon the minute drops irregular lateral velocities, which may easily reach a magnitude sufficient to cause them to clear one another as they pass. At any rate little difference is observable in this respect between a fine jet of clean water under feeble electrical influence, and one to which a little milk has been added, but without electrification.....

"The jets hitherto under discussion are such as resolve themselves naturally into drops soon after leaving the nozzle, or at any rate before reaching the summit of their path. If the diameter be increased, we may arrive at a condition of things in which the undisturbed jet passes the summit unbroken. In such a case the addition of milk, or the presentation of an electrified body, produces no special effect."

Experiments were also made with two jets impinging at a small angle. "The colliding jets coalesced in a manner entirely capricious, the only principle observable being that they coalesced even more readily with high pressures (12 inches) than with low, and with lower pressures would stand collisions at greater angles." Removing traces of grease, bubbling air through the water, heating the water, etc., did not eliminate the capriciousness of the results. It was finally suggested that the anomalies were due to dust. "We tried dropping dust on the colliding jets and found that union was always produced. The following powders were tried....powdered cork, sand, lycopodium, plaster of Paris, flowers of sulphur, sugar, dust that had accumulated upon a shelf, and later emery and putty powder. The lycopodium was a little more uncertain in its action than the others, but apparently only because, owing to its lightness, it was difficult to ensure its falling upon the jets. Whenever we were quite sure it did so, union followed. When mixed with the water, powders acted differently. Emery and putty powder were not effective, but sulphur caused immediate union. Much probably depends upon the extent to which the extraneous matter is wetted. A precipitate of chloride of silver, formed in the liquid itself, seemed to be without influence.....

"Although there is no reason to suppose that any other cause than dust was operative in the above experiments, it remains true that very little impurity of a greasy character will cause immediate union of colliding jets. For this purpose the addition of milk at the rate of one drop of milk to a pint of water is sufficient. It may be noticed too that the effect of milk is not readily neutralized by caustic potash.

"With respect to the action of electricity, further experiments have been made to determine the minimum electromotive force competent to cause union. The current from a Daniell cell was led through a straight length of fine wire. One end of the wire was connected by platinum foil with the liquid in an insulated glass bottle, from which one of the jets was fed. The glass bottle supplying the second nozzle was similarly connected with a movable point on the stretched wire. The electromotive force necessary to cause union, as measured by the distance between the two fine wire contacts, though definite at any one moment, was found to vary on different occasions, possibly in consequence of forces having their seat at the surfaces of the platinum foil. From one-half to three-quarters of the whole force of the Daniell was usually required.

"With a view to further speculation upon this subject, an important question suggests itself as to whether or not there is electrical contact between colliding and rebounding jets. To solve this question it was only necessary to introduce a fine wire reflecting galvanometer into the arrangement just described, taking care that the electromotive forces employed fell short of what would be required to cause the union of the jets. Suitable keys were introduced for more convenient manipulation, and sulphuric acid was added to the water, in order to make sure that absence of strong galvanometer deflection could not be due merely to the high resistance of the thin columns of water composing the jets. Repeated trials under these conditions proved that so long as the jets rebounded, their electrical insulation from one another was practically perfect.

"As to the explanation of the action of electricity in promoting union, it would be possible to ascribe it to the additional pressure called into play by electrical attraction of the opposed water-surfaces, acting as plates of a condenser. But it appears much more natural to regard it as due rather to actual disruptive discharge, by which the separating skin is perforated, and the equilibrium of the capillary forces is upset. A small electromotive force, incapable of overcoming the insulation of the thin separating layer, is without effect."

Newall[1] has also made some experiments on liquid jets. "Two horizontal jets of water, issuing from similar glass nozzles, and fed from two glass bottles, are made to collide at a small angle. When certain precautions are taken, such as using clean and tolerably dust-free water, the jets rebound from one another; but they are made to unite if each bottle is connected with the pole of a cell (such as Grove's or Leclanché's). It is convenient to introduce a key.

"I have lately in repeating this experiment, observed that the colours of thin plates (Newton's rings) are formed with remarkable brilliancy between the colliding jets. The jets

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[1] Phil. Mag., (5) 20, 31 (1885).

are of circular section but on impact they become flattened against one another, so that the surfaces of separation are more or less plane and vertical. Between these surfaces, which Lord Rayleigh has shown to be electrically insulated from one another, there is a very thin film (of air, I presume) in which the colours are visible. These afford a mode of observation by which one may possibly gain information as to the nature of the action of electricity in determining the coalescence of the jets.....

"Lord Rayleigh regards the union as most probably due to perforation of the separating skin, brought about by disruptive discharge. Let us consider the case when the colour of lowest order produced in the film between the jets is green of the third order at normal incidence: the thickness of the film is, roughly speaking, $2.5/2 \times 6000 \times 10^{-8}$ centimeters, that is, 0.000075 centimeter. It appears that the highest minimum electromotive force to produce union is about 0.75 volt. This gives a difference of potential in volts per centimeter of 10.000. Now Sir W. Thomson's experiments show that, to produce a spark between brass plates nearly 100 times further apart that the jets in the case we are considering, an electromotive force of about 80.000 volts per centimeter is required. De la Rue and Müller have lately shown that the substitution of saturated aqueous vapour for dry air between the plates does not make any difference. It is however conceivable that there is diminished pressure between the jets."

Burton and Wiegand[1] surrounded the glass nozzle by a short vertical cylinder of brass which could be charged to any voltage whereby "a charge is induced on the drops as they break from the main earth-connected stream of water issuing from the nozzle. Other things being equal, the charge induced on the drops depends merely on the potential of the inductor, so that, even with a piece of ebonite or glass rubbed very slightly, the potential of these inductors, and consequently the charge induced on the drops, may be very large."

They found the following facts:

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[1] Phil. Mag., (6) 23, 148 (1912).

"1. The presence or absence of a charge on the inductor does not seem to affect perceptibly the size of the drops breaking away from the stream.

"2. There is by no means uniformity in the size of the drops, large and small ones occurring at random, whether the drops are charged or not.

"3. The uncharged stream almost immediately begins to scatter in all directions.

"4. No matter how large the charge on the inductor ring, *i. e.*, no matter how large the charges on the drops, there is in every case of the charged drops an absolute alignment of the drops for at least part of their journey. For lower voltages (dependent probably on the size and velocity of the stream) there is complete alignment to the top of their course.

"5. For lower voltages on the inductor tube there is coalescence of the drops in the region of slow velocities.

"6. For higher voltages the stream begins to scatter after a region of absolute alignment, and the indications are given of the splitting up of larger drops into smaller in this region of scattering."

Burton and Wiegand consider that no difficulty should be found in the explanation of coalescence if one keeps in mind the electrostatic forces. "When two drops bearing unequal charges, or two unequal drops bearing equal charges, are brought closely enough together there are immensely strong, increasing forces of attraction between them, and coalescence will surely take place if the resulting drop is not too large to be unstable. One would expect that at the moment of collision there would be an electric discharge between the two adjacent spheres. Many influences conspire to bring the drops in the stream closer and closer together. If in a stream the velocity of the drops is sufficient to carry them a vertical distance of 10 cm, two drops breaking away 1/1000 of a second part will be distant from one another approximately 0.14 cm at the beginning of their journey. When the first one has reached the top of its course, taking into consideration only gravity, the distance between the drops will be approximately 5 ×

10^{-4} cm. Again, the friction of the air for a given velocity will cause a greater retardation in the case of small drops than in the case of large ones, which will tend to bring a large drop nearer to the smaller one ahead of it."

This explanation, which was suggested by Rayleigh himself, seems good enough as far as it goes; but it includes no definite statement in regard to the film of adsorbed air which evidently surrounds each drop, and it is no help in accounting for the effect of milk, dust, etc. Consequently there must be another factor which has not yet been taken into account. If Schuster[1] is right in his hypothesis that a thin film of adsorbed air interferes with the passage of a current, it follows from the theorem of Le Chatelier that a difference of potential will tend to remove the film of adsorbed air. Under slight electrification the drops will coalesce more readily because they come more nearly in contact, the thinner the film of adsorbed air. With higher electrification, a marked charging of the drops takes place and the repulsion of the like charges causes the drops to scatter. The amount of electrification necessary to make the drops scatter depends on the size of the drop. Nipher[2] states that drops of 1 mm radius do not attract each other when charged to 0.0031 volt. Milk and dust may act in two different ways. They cut down the film of adsorbed air or they may act more or less as projecting points which rupture the air films on the colliding drops. The first explanation seems improbable for milk because Worthington's work on splashing drops[3] shows that the substitution of milk for water introduces no special change. The hypothesis of projecting points seems a plausible one for dust; but it is not one which is strikingly satisfactory when there is one drop of milk in a pint of water. Special experiments will have to be made by somebody before the matter can be considered as settled; but there seems to be no question but that the coalescence under moderate electrification is due chiefly to the cutting down of the film of adsorbed air.

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[1] Phil. Mag., (5) 29, 197 (1890).

[2] Science, 34, 442 (1911).

[3] Worthington: Proc. Roy. Soc., 34, 217 (1882).

Further evidence of the presence of adsorbed air on liquid surfaces is furnished by Worthington's experiments on splashes.[1] When a drop of water, 5 mm in diameter, falls on a sheet of water from a height of less than 1 meter, it makes a hollow into which "the drop descends, passing below the surface and becoming completely submerged, to emerge again at the head of a column of adherent liquid, but with its upper portion apparently unwetted by the liquid with which it has been covered." With a solid sphere dropping into a liquid from any height less than 150 cm, the character of the splash depends entirely on the state of the surface of the sphere. With a polished sphere of marble, 1.28 cm or 1.55 cm in diameter, "rubbed very dry with a cloth just beforehand, the water spreads over the sphere so rapidly that it is sheathed with the liquid even before it is below the general level of the surface. The splash is insignificantly small and of very short duration. If the sphere be roughened with sand-paper or *left wet*, it is followed by a cone of apparently adherent air, while the water seems to find great difficulty in wetting the surface completely. Part of this column of air was carried down to a depth of at least 40 cm, and then detached only when the sphere struck the bottom of the vessel."

It is interesting to note that water will apparently remove a film of adsorbed air much more rapidly from a polished surface of ivory or marble than it will from a water surface. We do not know whether this is true for all solids or not. Sakulka[2] obtained somewhat different results with lead shot; but this may have been because they were not polished. "If a lead shot is allowed to drop into water from a height of a few centimeters or more, the sphere falls so rapidly that the water which is forced aside by it, cannot close in at once behind the falling shot because a definite time is necessary. Consequently an air bubble continues to cling to the sphere and tears loose only when the shot strikes the bottom of the vessel. If the sphere is dropped from a slight distance above

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[1] Worthington: Proc. Roy. Soc., 34, 217 (1882).

[2] Drude's Ann., 25, 892 (1908).

the water level, the rate of fall is so small that no air is carried down. If it is dropped from a height of several decimeters, there is formed at first a very long air bubble. Since the sphere falls more slowly after it strikes the water, the long air bubble becomes instable and several smaller bubbles break loose during the fall, though one bubble is carried down with the sphere to the bottom of the vessel. If the sphere is dropped from a height of several centimeters and close to the wall of the vessel, the air bubble does not have the symmetrical form that it had when the sphere was dropped in the center of the tube, because it is more difficult for the liquid near the wall to flow round the sphere. It often happens, therefore, that the air bubble comes in contact with the wall of the vessel. The unsymmetrical form of the air bubble when the sphere is dropped close to the wall of the vessel, is probably the reason why the sphere sometimes moves to the wall and strikes it. At any rate no striking of the sphere against the wall of the vessel was noticed when the sphere was dropped from so small a height that no air bubble was carried down."

The phenomenon of rolling drops depends on the presence of an adsorbed air film.[1] "It is possible to have drops of many liquids rolling on a surface of the same liquid. This phenomenon may occur with all liquids and is very often to be observed out of doors. These drops, which we will call rolling drops, are to be seen on water alongside a moving row-boat where the oar is raised out of water and where the water drips from the oar on the recover. We get them also if we strike a water surface with a stick or a branch. At every water-fall drops of water are thrown off into the air and these may rest quite a while on the surface of the stream if the current is not too swift. A similar result is sometimes to be obtained when filtering a liquid provided the drops do not fall from too great a height. Wüllner cites an experiment which comes under the same head.[2] If a bell is filled half full of water and is then rubbed with a violin bow, vibrations are set

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[1] Kaiser: Wied. Ann., 53, 681 (1894).

[2] Wüllner: Lehrbuch der Experimentalphysik, 4 I, 652.

up which show themselves in movements of the water. Often drops are formed at the places of most marked vibration and these drops remain for quite a while on the surface of the liquid, forming regular figures.

"The rolling of these drops on *curved* liquid surfaces has been observed previously by Gossart;[1] but one may observe the same thing on any plane surface if one allows a jet of liquid to flow out of a capillary tube at such a rate that the jet breaks into drops 5–10 mm above the surface. The single drops then roll round rapidly over the surface. If one lets a single drop fall upon the surface from a height of a few millimeters, it will remain there quite a while.

"The rolling drops remind one in some ways of the so-called Leidenfrost phenomenon in spite of the fact that the causes are quite different in the two cases. The rolling drops can be observed under a bell-jar connected with an air-pump when the air in the bell-jar is saturated completely with the vapor of the liquid. Under these conditions there is no evaporation and consequently no Leidenfrost phenomenon. If the pump is now started, the drops can be obtained more satisfactorily the more rapid the evaporation from the liquid surface and from the drops. During the evacuating of the bell-jar the drops remain for an exceptionally long time, sometimes reaching a considerable size when several small drops coalesce to form a single one. In the same way the drops become larger and persist longer at higher temperatures where one has a combination of the rolling drops with the Leidenfrost phenomenon.

"These drops are separated from the liquid surface by an air film because total reflection of light occurs at all points where the drops seem to rest on the liquid surface. The drops can therefore unite with the mass of the liquid when the air between the surface is squeezed out by the pressure due to the weight of the drop.

"The rolling drops are just as sensitive to the approach

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[1] Comptes rendus, 113, 537 (1891).

of electrified substances as are jets of water or soap-bubbles. The difference is that the drops coalesce with the mass of the liquid only when the liquid is a conductor of electricity or a good semi-conductor. A similar phenomenon would probably be observed with jets if one used other liquids than water."

Since soap-bubbles are hollow drops we should expect them to behave in some ways like liquid drops, though not necessarily like the drops of a pure liquid. Boys[1] has brought out this fact very clearly. "Everyone is familiar with the fact that a soap-bubble may be supported or even struck by a piece of baize or wool without coming into real contact with the material; it is also well known that two bubbles supported on the pipes from which they are blown, or on rings, may be pressed or knocked together with such violence as materially to alter their shape, and yet they do not come into real contact; there is a film of air between them which they are unable to squeeze out. This film, though thin to ordinary tests, is so thick that the colours of Newton's rings are only seen when one of the bubbles is very small, so that the air is squeezed out the more readily. If the pressure is increased so as to make a real contact, the bubbles both instantly burst. That this pressure may be made great before the true contact takes place will be shown in a variety of ways hereafter; but the following simple experiment makes it very evident that the air-film will prevent the contact of two soap-films that are pressed together.

"*Exp. 1.*—Blow a bubble about 9 cm in diameter, and place it on a ring with a diameter of about 7 cm. This bubble may be pulled or pushed through the ring by means of a smaller wire ring which serves as a handle. It may be so adjusted that the weight of the ring will not pull it through. Then a ring larger than the bubble, carrying a plane film, can be used to push it up and down through the ring, and yet the two films do not touch.

"Bearing this fact in mind, that two bubbles may press

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[1] Phil. Mag., (5) 25, 409 (1888).

one another without true contact, I hoped to be able to blow and detach one bubble within another, and let it roll about within the larger bubble. This, however, is made difficult by the accumulation of a small quantity of solution at the bottom of each, the weight of which is able immediately to press through the air-film between them and so cause both bubbles to burst. However, the experiment can be performed in the following manner:

"*Exp. 2.*—Blow a bubble on the lower side of the same ring that was used in *Exp. 1*, and if a large drop does not remain hanging to the bubble slowly apply solution to any part until as great a drop as can safely be carried has accumulated. Then pass the end of the pipe through the upper side of the bubble and blow another inside, but take care in this case to have no excess of liquid. When the inner bubble is about twice as large as the outer one was at first, remove the pipe with a rapid movement. The inner one will now fall gently and rest within the outer one, the heavy drop pulling the thick part of the outer bubble out of reach of the inner one. The air of the outer bubble may then be withdrawn until the space between the highest point of the two bubbles is no more than two or three millimeters.

"The great pressure which the air-film will carry is well shown by the next experiment, which, moreover, is more easily carried out than the last.

"*Exp. 3.*—Proceed as in the last experiment, but instead of making a large drop on the first bubble, hang on a moistened ring of wire rather smaller than the fixed ring. This ring should be weighted until it pulls the bubble so much out of shape that a tangent to the curve at the points where the film meets the hanging ring makes an angle of 20° or 30° with the plane of the ring. A bubble may then be blown inside and allowed to drop, when it will be found to rest on the conical seat provided by the outer bubble, while the heavy drops of liquid are kept apart, and thus there is no fear of contact. These drops may now be both removed with the end of the blowpipe; then, if the lower ring is pulled down slowly, it will be found that the inner bubble is being squeezed out of shape until it becomes a beautiful oval, while the outer bubble shows the effect of the pressure by a corresponding enlargement. If the lower ring is pulled down still further, the outer bubble is simply pulled in half, and the inner one, often unbroken, gently floats away. This shows that contact was not made, as in that case both would be immediately broken. If, however, instead of pulling the ring too far, it is held in the original position, it will be found that it is possible to swing the pair of bubbles round and round, and yet in spite of this violent treatment the bubbles refuse to touch one another. Or, if the lower ring is cautiously inclined and pulled away, the outer bubble will peel off it and remain attached to the upper one only. The two bubbles will now be spherical again, but there will be no heavy drop as in the first experiment. The air of the outer bubble may be withdrawn as before, until the two bubbles are barely separate.

"This experiment, and many of those that follow, may be made more beautiful by using for the inner bubble a solution strongly colored by fluoresceine, or still better by uranine (for the knowledge of which I am indebted to Mr. Madan); then, if sunlight, electric or magnesium light is thrown on to the bubbles, the inner one appears a brilliant green, while the outer one remains clear as before.....

"There is one other property of a pair of soap-films resting against one another, but not in contact, to which I have referred. In a lecture at the Royal Institution a few years ago Lord Rayleigh showed that two water-jets if perfectly clean will, if directed so as to meet one another at a small angle, be reflected again and fall as two separate jets, never really coming into contact at all. If the water is not perfectly clean, the experiment will not succeed. He showed that such a pair of mutually reflected jets form a very delicate electroscope, so that if a piece of excited sealing-wax is held even at a considerable distance they instantly coalesce. As the two jets in his experiments and the two bubbles in those which I am about to describe are in each case kept apart by a thin film of air, I expected to find a pair of bubbles attached to two rings in the same way act as a delicate electroscope.

"*Exp. 16.*—If a pair of bubbles are blown in such a way that the two bubbles are pressing one against the other on rings which must be insulated from one another, and if the cover of a small electrophorus is raised even at some yards distance, the two bubbles coalesce instantly, but do not burst as they have hitherto been found to do. Or, if the two rings are connected with a key and a single bichromate cell so that when the key is not pressed the rings are connected together, but when depressed they form the terminals of the cell, then at the moment of making the contact the bubbles unite because the electrostatic attraction between surfaces so very close together is able to squeeze out the air, which mere pressure has hitherto failed to do.

"*Exp. 17.*—Bearing in mind how exceedingly delicate this is as a test of difference of potential, the following experiment seems the more decisive. The cover of the electrophorus may be brought so close to the side of the concentric bubble in *Exp. 3* as to pull them completely out of shape, and yet the outer film so completely screens the inner from the electrical action, even though the inner one is to all appearance in contact with the outer one, that there is no difference of potential between them, and so the film of air is not destroyed. I do not know any experiment which shows so clearly as this that electrical force is confined to the absolute surface of a conductor, and is not felt at any depth within it however small.

"Plateau has mentioned that a hemispherical film blown on a plate will screen a smaller hemisphere blown within it, and also resting on the plate, from electrical disturbance; but in this case the two films are widely separate, and there is not the same delicate test as in the case of two bubbles apparently coincident, which join instantly when the smallest electrical stress exists between them."

Kaiser[1] discusses the reason for electrification causing

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[1] Wied. Ann., 53, 667 (1894).

soap-bubbles or jets of water to coalesce. He considers two possibilities. The two liquid surfaces may act like two condenser plates and may be drawn together, squeezing out the air film just as mechanical pressure would or there may be a disruptive discharge through the air film at a definite difference of potential. The second hypothesis is the one favored by Rayleigh,[1] while the first is the one which Kaiser considers right. He showed that Boys was wrong in saying that two soap-bubbles cannot be made to coalesce by pressure alone. This will happen if sufficient time be allowed. Kaiser makes what seems to me the erroneous assumption that there is no condensed air film on the surface of a soap-bubble. He then says that if "one is to assume that the passage of a spark causes the complete coalescence, it is not evident why this should take place only when the air film separating the surfaces is so extraordinarily thin. The experiments of Smith and Ferguson, quoted by W. Thomson, show that electrostatic forces of 527.7 absolute units are necessary to cause a spark discharge between condenser balls 0.00254 cm apart, while smaller forces are necessary. The force necessary for this spark length is about 160,000 volts per centimeter. In my experiments the electrostatic force of one Daniell cell was used which works out to 11600 volts per centimeter since the distance between the films was 95×10^{-6}. The distance in my experiments was twenty-six times as small as in the other case. In my experiments it is out of the question that a spark should have passed. That could not have happened even if I had used three Daniell cells.

"The assumption of a spark discharge is contradicted by an experiment made by Joly[2] who allowed the spark from a Ruhmkorff coil to pass between two slightly curved glass plates which were brought very close together and were backed with platinum foil. The sparks did not pass at the narrowest point but at points farther apart, which corresponded to colours of the fourth or higher order. This could be

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[1] Proc. Roy. Soc., 34, 145 (1882).

[2] Ibid., 47, 78 (1890).

proved because the sparks left traces of mechanical disturbances at these points. According to these observations the spark should have jumped at a greater distance provided the electromotive force were high enough.

"From these considerations it follows that the coalescence caused by electrostatic differences of potential is due to the drawing together of the films which squeezes out the air that prevents the coalescence, thus causing the films to unite.

"Newall[1] attempted to prove theoretically the accuracy of Lord Rayleigh's assumption that the passage of a spark is what causes two jets of water to unite.[2] He came to the conclusion that there would be no spark under normal conditions and he consequently assumed that the air between the jets might be under diminished pressure, and that this made it possible for the spark to pass. He has apparently overlooked the experiments of Peace[3] which cannot be reconciled with such a hypothesis. Peace found that under diminished air pressure a higher electromotive force is necessary to make a spark pass between two condenser balls when these latter are as close together as in the cases under consideration. The assumption made by Newall will therefore not account for the passage of the spark. Further, the outward current of air between soap-bubble and soap-film shows that there is no diminished pressure there, but rather a pressure which is a little higher than atmospheric pressure. It is quite impossible to make the assumption that the air between two jets of water is under diminished pressure. The jets must carry with them as much air as is driven out of the space between them by the pressure. If not, it would be impossible to explain why Newall[4] always found the colours at a perfectly definite place."

Kaiser's reasoning seems to prove that the union of two jets under an electrical difference of potential is not due to a disruptive discharge. On the other hand, I do not believe

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[1] Phil. Mag., (5) 20, 35 (1885).

[2] Rayleigh: Proc. Roy. Soc., 34, 145 (1882).

[3] J. J. Thomson: "Recent Researches," 89.

[4] Phil. Mag., (5) 34, 32 (1882).

that the mechanical pressure resulting from the electrostatic attraction is the sole factor, as Kaiser believes. Such an assumption ignores Schuster's work explicitly, which is the more unfortunate because Kaiser is laying special stress in his argument against Rayleigh on the fact that the potential gradient for a disruptive discharge is greater the less the distance between the surfaces, which is what Schuster pointed out.[1] While not denying that the mechanical pressure resulting from the electrostatic attraction plays some part, I am inclined to lay much more stress on the decrease of the adsorbed air film as a result of electrification. I intend before long to show the great importance of this factor for the theory of the coherer.

Freundlich[2] cites the difference between the static and the dynamic determinations of the surface tension of mercury as a proof that gases are adsorbed by mercury but it seems to me that the results cannot be accounted for on this assumption alone and it seems a pity that Freundlich should not have stated this clearly. Stöckle[3] measured the surface tension of mercury in a vacuum of 0.004–0.0010 mm and obtained a value of 436 dynes/cm at 15° regardless of whether the measurement was made at once or after standing. The time factor was important when hydrogen was present, a value of 470 dynes/cm being obtained when the measurement was made quickly but dropping to 434 dynes/cm on standing. Similar results were obtained for oxygen, nitrogen, carbon dioxide, and air. These general results were confirmed by G. Meyer[4] who made use of Rayleigh's jet method for the rapid measurements and consequently obtained higher values than Stöckle. The data of Stöckle are given in Table I and those of Meyer in Table II.

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[1] The experiments cited by Kaiser go beyond the conclusions of Schuster, because they show that not only the potential gradient but also the absolute potential difference may increase with decreasing distance between the plates.

[2] "Kapillarchemie," 85 (1909).

[3] Wied. Ann., 66, 49 (1898).

[4] Ibid., 66, 523 (1898).

TABLE I

Surface Tension of Mercury

Medium	(Rapid)	(After 60′)
Vacuum (15°)	436 dynes/cm	434 dynes/cm
Hydrogen (21°)	470 dynes/cm	436 dynes/cm
Oxygen (25°)	478 dynes/cm	432 dynes/cm
Nitrogen (16°)	489 dynes/cm	438 dynes/cm
Carbon dioxide (19°)	480 dynes/cm	436 dynes/cm
Dry air (17°)	476 dynes/cm	429 dynes/cm
Moist air (17°)	481 dynes/cm	429 dynes/cm

TABLE II

Surface Tension of Mercury

Medium	(Vibrating jet)	(Curvature of fresh surface)
Hydrogen	554 dynes/cm	470 dynes/cm
Oxygen	504 dynes/cm	478 dynes/cm
Carbon dioxide	487 dynes/cm	480 dynes/cm
Nitrogen	496 dynes/cm	489 dynes/cm

Freundlich[1] comments on these data as follows: "The following facts point to a condensation of the gases on the surface of the mercury:

"1. An ageing takes place which does not occur in a vacuum.

"2. The change of the surface tension with the time is similar to that when a dissolved substance is adsorbed on a surface and the rate of condensation depends in a characteristic way on the properties of the gases.

"There are no data as to the way in which a fresh water surface behaves toward air. From the analogy with the experiments of Stöckle and of Meyer on mercury, it seems probable that the dynamic determination of the surface tension would give values distinctly larger than those obtained by static measurements. In all cases where fresh

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[1] "Kapillarchemie," 87 (1909).

surfaces come in contact with the air there is always the possibility to be considered that too large surface tensions may be obtained, values larger than the largest which can be obtained statically under ideal conditions. Stöckle, Meyer, and Kalähne[1] are therefore right in insisting that the highest value obtained is not necessarily the right one. For a pure substance the real surface tension is the one measured in a vacuum, preferably by a dynamic method, with all impurities excluded. In all other cases one must distinguish, as has been pointed out, between dynamic and static surface tensions."

This sounds well but will scarcely bear examination. It is easy to see that the adsorption of a gas on a mercury should lower the surface tension; but it is not easy to see why different gases should bring down the surface tension practically to the same value which the mercury maintains where there is supposed to be no gas. The dynamic methods should start at the value for mercury in a vacuum, if no factor has been overlooked, and should give values which drop off from that. It is not clear why the presence of an unadsorbed gas should raise the surface tension of mercury so very much. It seems to me that we have no satisfactory explanation of the phenomenon as yet and that a good deal of careful study is needed.

Lenard[2] has brought up a point which may have a bearing on this. If we have a partially polymerized liquid such as water, the modification having the lower surface tension will concentrate in the surface. If we form a new surface suddenly, we shall then get a higher concentration, temporarily, of the modification having the higher surface tension. If equilibrium is reached relatively slowly, the dynamic methods will give a higher value for the surface tension than the static methods. If equilibrium is reached instantaneously there will be no difference. We can account for the facts observed with mercury if we make the assumptions that mercury is a

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[1] Drude's Ann., 7, 467 (1902).

[2] Cf. Aganin: Drude's Ann., 45, 1020 (1914).

partially polymerized liquid, that equilibrium between the modifications is reached practically instantaneously in a vacuum, and that equilibrium is reached relatively slowly in presence of gases. The difficulty with this is that we have no independent proof of these assumptions.

The general results of this paper are:

1. All solids show selective adsorption of gases and vapours.
2. The film of condensed gas shows itself in the abnormal mobility of very fine powders, in a resistance to the passage of an electric spark between solid terminals, and in the fact that two pieces of a broken object will not reunite when pressed together.
3. All liquids show selective adsorption of gases and vapours.
4. The film of condensed gas shows itself in the behavior of fountains, impinging jets, rolling drops, and soap-bubbles; it causes errors in the determination of molecular weights by the air-bubbling method.
5. The adsorption of gas on the surface of mercury is not sufficient to account for the change of the surface tension of mercury with time.

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THE ADSORPTION OF CAUSTIC SODA BY CELLULOSE

BY ALAN LEIGHTON

In 1844–1850, Mercer[1] showed that cold concentrated caustic soda solution has a remarkable effect on cotton. Though the alkali can all be removed by washing with water, the mercerized cotton has changed markedly in properties. There has been a shortening and swelling of the fiber, and the cotton takes dyes better than before. At that time the natural assumption was that this change was due to the formation of a compound which decomposed when washed with water. Gladstone[2] undertook to determine the composition of this hypothetical compound. Since the product could not be washed with water, it was necessary to find some solvent which would remove the uncombined alkali, and Gladstone believed that he had found this in alcohol. He treated one lot of cotton with dilute caustic soda solution and another with a concentrated solution; washed both repeatedly with absolute alcohol, and dried in a vacuum over sulphuric acid. The sample which had been treated with dilute caustic soda solution weighed the same as before the treatment and contained no soda. The other sample had increased in weight by over twenty percent and contained soda which was determined by leaching with water, neutralization with sulphuric acid, and evaporation in a platinum dish. The soda was weighed as sodium sulphate, the excess of sulphuric acid having been removed during ignition by means of solid ammonium carbonate. It was afterwards shown that hot alcohol of specific gravity 0.825 behaved practically like cold absolute alcohol. Starting with a caustic soda solution of specific gravity, 1.342, or higher, Gladstone found that one hundred grams of cotton retained 11.97, 13.24, 13.29, 11.62, 12.10 grams NaOH after treatment.[3] These figures do not vary much and the average

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[1] Thorpe: Dictionary of Applied Chemistry, 3, 437 (1912).

[2] Jour. Chem. Soc. 5, 17 (1853).

[3] These have been recalculated because Gladstone apparently took 23.3 for the atomic weight of sodium instead of 23.

12.44 differs but slightly from the value 12.34 corresponding to the formula $C_{12}H_{20}O_{10}.NaOH$. Gladstone, therefore, assumed that a definite compound of this composition was formed. While this was a legitimate conclusion at that time, these results do not meet the modern requirements for the existence of a compound. Gladstone worked with one solution only, hot alcohol of specific gravity 0.825, or with its equivalent, cold absolute alcohol. There is nothing to show that he would have got the same results with a different aqueous alcohol at the same temperature or with absolute alcohol at a different temperature. Since the phase rule was not known at that time, there are no experiments to show whether the concentration of the caustic soda solution remains constant while the soda content of the cotton varies from approximately nothing up to 12.34. While these omissions were necessary ones in 1853, there are some curious inconsistencies in Gladstone's results. Before determining the amounts of caustic soda retained by the cotton, Gladstone determined the increase in weight per hundred grams of cotton after washing with alcohol and drying in a vacuum over sulphuric acid. These increases were 13.2, 16.05, 17.1,[1] 14.8, 17.05 grams. These values are far from being constant though theoretically they should be. The discrepancies show up even more if we subtract the values for sodium hydroxide, the differences being 1.23, 2.81, 3.81, 4.95 grams, presumably water. If we are dealing with a definite compound it should come to the same constant weight each time and should contain the same amount of water each time, which is not the case. While Gladstone's experiments make the existence of a compound, $C_{12}H_{20}O_{10}.NaOH$, seem probable, they do not furnish proof which is satisfactory today. Later experiments by Hübner and Teltscher[2] have cast doubt on the accuracy of Gladstone's work.

Margosches[3] says that Crum[4] studied the reaction be-

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[1] Gladstone gives 11.2, but this is evidently a misprint.

[2] Jour. Soc. Chem. Ind., 28, 641 (1909).

[3] "Die Viscose," 14 (1906).

[4] Jour. Chem. Soc., 16, 406 (1863).

tween cellulose and alkali, reaching the conclusion that the composition of the compound was $C_{12}H_{20}O_{10}.NaOH$. This statement is quoted by Schwalbe.[1] There is nothing of the sort in the paper referred to. In an earlier paper, published the same year, Crum[2] accepts Gladstone's formula. It seems probable that Margosches has become confused by the changes in atomic weights and has assumed that NaO as written then is the same as Na_2O as written now, whereas it is really the same as Na.1/2O according to our present nomenclature.

In 1907, Vieweg[3] made some more experiments to determine the composition of the alleged compound. He placed 3 g cotton, which had been dried at 90°, in 200 cc caustic soda solution, shook for an hour in a shaking machine, allowed to stand for two hours, pipetted off 50 cc solution and titrated with sulphuric acid, using phenolphthalein as an indicator. From the change in titer he calculated the absolute amount of caustic soda adsorbed, calculated this to grams caustic soda per hundred grams cellulose, and then tabulated these data in connection with the original concentrations of the caustic soda solutions. The data thus obtained do not correspond to equilibrium conditions[4] because the concentrations of the caustic soda solutions change somewhat when the cotton adsorbs caustic soda. Fortunately sufficient data are at hand to enable a correction to be made if desired. The total change in concentration of the caustic soda solution is less than one percent except for the most dilute solution. This shows, however, that the determination of the amount of caustic soda adsorbed is subject to large error. A mistake of 0.1 percent in the titer means an error of over ten percent in the adsorption. Vieweg's data, as calculated by him, are given in Table I and are plotted in Fig. 1. From the constant compositions at about 13.0 and 22.5 percent Vieweg deduces the existence of the compounds $C_{12}H_{20}O_{10}.NaOH$ and $C_{12}H_{20}O_{10}$.-

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[1] "Die Chemie der Cellulose," 41 (1911).

[2] Jour. Chem. Soc., 16, 3 (1853).

[3] Ber. deutsch. chem. Ges., 40, 3876 (1907).

[4] Cf: Bancroft: Jour. Phys. Chem., 18, 119 (1914).

TABLE I

Vieweg's Data

Solution g NaOH per 100 cc	Cellulose g NaOH per 100 g	Solution g NaOH per 100 cc	Cellulose g NaOH per 100 g
0.4	0.4	20.0	13.0
2.0	0.9	24.0	13.0
4.0	2.7	28.0	15.4
8.0	4.4	33.0	20.4
12.0	8.4	35.0	22.6
16.0	12.6	40.0	22.5

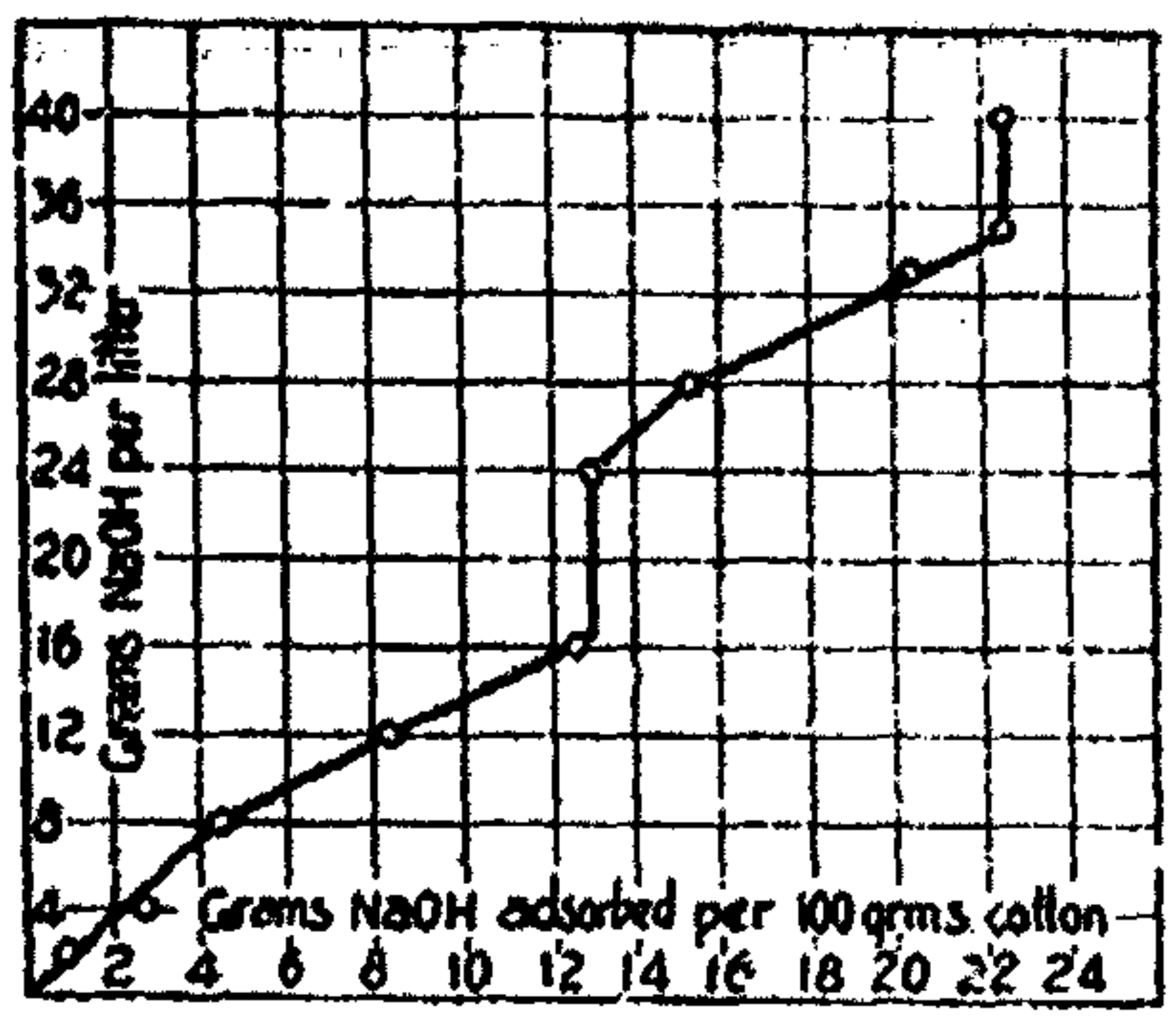

Fig. 1

2NaOH which call for 12.34 and 24.69 grams NaOH, respectively, per hundred grams cotton. One difficulty with this hypothesis is that it does not agree with Vieweg's own data. If we have compounds along the verticals, we must have two phases along the other curves; the concentrations of these solutions should remain constant and these curves should be parallel to the axis of ordinates. While it is possible that the slant of these curves may be due to experimental error, the difficulty is that Vieweg did not know that his diagram was theoretically impossible.

Vieweg's whole method of experimenting is unsound. It is customary to determine the amount of adsorption from the change in concentration, but this method rests on the assumption that no water is taken up by the solid phase; it becomes inaccurate the moment this assumption fails to hold. This is easy to see if we consider an extreme case. Suppose that cotton adsorbs water and caustic soda from a given solution in the same ratio that they occur in the solution. By hypothesis there will be no change of titer and consequently apparently no adsorption of the caustic soda even though all the caustic soda may actually have been adsorbed. While this extreme case may not occur often, we do know that cotton will take up a large amount of water and that this fact was overlooked by Vieweg. Consequently all of Vieweg's data, as calculated, are wrong even though we make the improbable assumption of absolute accuracy in his titrations. The same criticisms apply to the data in a later paper.[1] The columns are labelled wrongly, evidently through a misprint.

Working in the same general way as Vieweg, Miller[2] obtains a smooth curve with no breaks. Miller heated his cotton in a one percent caustic soda solution to 150° for eight hours in the absence of air, treated with hydrochloric acid, and gave a slight chlorination. After this treatment the cotton had an ash content of 0.08%. In the actual experiments the cotton was shaken in the caustic soda solution at 25° for an hour, Miller having satisfied himself that equilibrium was reached in this time. Miller used 500 cc NaOH and 21.35 g cotton on each run. His data are given in Table II.

TABLE II

Miller's Data

Solution g NaOH per 100 cc	Cellulose g NaOH per 100 g
0.98	0.56
2.97	1.92
15.0	9.72
24.2	12.96
31.2	17.27

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[1] Vieweg: Ber. deutsch. chem. Ges., 41, 3272 (1908).

[2] Ber. deutsch. chem. Ges., 40, 4903 (1907).

Miller concludes that there is no evidence of any compound being formed; but Vieweg claims that one experiment between 15 g and 31 g NaOH per 100 cc is not enough on which to base any conclusions. Miller's method, being the same as Vieweg's, is subject to the same criticism on the ground of inaccuracy.

Hübner and Teltscher[1] have checked Gladstone's experiments, getting results entirely different from his and from Vieweg's. They say: "Unfortunately Gladstone gives comparatively few data as to the manner in which the experiments were carried out, and in one experiment only are we informed as to the kind of cotton which he has employed. No description is given as to the treatments which the cotton had undergone previous to immersion in the soda solutions, and no statement is made as to whether the experiments were carried out with one and the same quality of cotton. These are points which may exercise a considerable influence upon the results. In his experiments Vieweg used cotton wool as employed for medical purposes; this, however, usually contains oxycellulose and is thus of doubtful uniformity.[2] In the investigation set forth in this paper special care was therefore taken to obtain a pure and uniform material for all the experiments carried out. For this purpose a large quantity of a loosely twisted cotton yarn, made from a very fine Egyptian cotton, was boiled twice with sodium carbonate solution in a high pressure kier, thoroughly washed, and bleached with sodium hypochlorite solution obtained by electrolyzing a solution of common salt. The bleaching operation was carefully regulated so as to avoid the formation of oxycellulose, and both boiling and bleaching were performed under the customary technical conditions. The yarn was well washed and transferred to a drying stove in which it remained for seven days at a temperature of about 60° C. After this treatment the cotton contained 6.77 percent of moisture and

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[1] Jour. Soc. Chem. Ind., 28, 641 (1909).

[2] [Since Vieweg purified his cotton with caustic soda, this statement seems inaccurate.—A. L.]

0.086 percent of ash. The yarn was now cut into pieces of about two inches in length and 150 samples, each corresponding to 10 grams of absolutely dry cotton, were weighed out in the stove. These were then carefully wrapped up and used as required in the experiments."

A ten gram sample of the purified cotton was immersed for twenty hours in 200 cc caustic soda solution containing about 3.3 g NaOH per 100 cc. "After pressing out lightly the cotton was transferred to a Soxhlet and extracted with absolute alcohol. The extraction was carried on until the alcohol syphoned from the cotton did not react with phenolphthalein. It was now treated as described by Gladstone and was found to yield 0.043 gram of sodium sulphate, corresponding to 0.024 gram of sodium hydroxide. Eight other experiments in which the cotton was immersed in solutions of various strengths gave similarly low results. Practically all the soda is extracted by hot alcohol from the cotton; it is, therefore, evident that the 'soda cellulose' is decomposed by hot alcohol and that no reliable results could be expected by this method.

"Two parallel experiments were now carried out by immersing 20 grams of cotton as in the first experiment but washing it afterwards with absolute alcohol at ordinary temperature. The cotton containing the soda was placed in glass-stoppered bottles and repeatedly shaken with absolute alcohol (about 280 cc of alcohol for each 10 grams of cotton); the alcohol was frequently changed until phenolphthalein produced a very faint pink coloration when added to the alcohol. The washing of the samples occupied about 18 days. One of the washed samples was decomposed with water in the Soxhlet and the water evaporated, the residue treated with sulphuric acid in a platinum basin and the amount of sodium sulphate remaining was found to be 0.7852 gram. The second sample was incinerated in a platinum basin, the residue repeatedly treated with sulphuric acid, and finally heated until the weight remained constant. The sample gave 0.7897 gram of sodium sulphate. This result agreeing so well with the one found by decomposition with water, it was decided to employ this method as the more convenient one in all experiments. In carrying out the tests with phenolphthalein the following interesting observation was made. Cotton which still contains free caustic soda gives a very strong reaction with phenolphthalein, while cotton which had been freed from all the soda removable by washing with absolute alcohol does not react with phenolphthalein while immersed in alcohol. On removing the cotton from the alcohol and exposing it to the air for a short time moisture is attracted in sufficient quantities to produce decomposition of the soda cellulose; the free alkali then reacts readily with the phenolphthalein.

"Gladstone, in his experiment No. V, used rectified spirit for the washing in place of absolute alcohol, and it seemed, therefore, of interest to ascertain whether the results obtained by washing with 90 percent alcohol would differ appreciably from those obtained when absolute alcohol was employed. For this purpose two lots of cotton (20 grams) were treated as in the last two experiments and washed with 90 percent alcohol. After washing for about 18 days, the alcohol from both samples still showed a distinct alkaline reaction with phenolphthalein. One of the samples was then incinerated and found to yield 0.783 gram of sodium sulphate; from this it is seen that the weaker alcohol gives a slightly lower result—no doubt due to slow decomposition of the 'soda cellulose.' After washing the other sample for five months the alcohol still showed a distinct alkaline reaction. On incinerating this sample it was found to contain much less sodium sulphate (0.3435 gram) than the sample which had been washed for 18 days. Washing with 90 percent alcohol can, therefore, not be expected to give satisfactory results. One very important conclusion can, however, be drawn from the two experiments, namely, that there is no danger of any interference with the results by minute quantities of water which the absolute alcohol may attract from the air during the operation of washing and during the changing of the alcohol. . . .

"All the results obtained during the preliminary experiments indicate very much lower absorptions than those recorded by Gladstone and by Vieweg. It became of interest to ascertain Gladstone's method of working. For this purpose it was considered advisable to use litmus as indicator in place of phenolphthalein, on the presumption that this indicator was used by Gladstone. In the first experiment 20 grams of cotton were immersed for 20 hours in caustic soda solution of 45° Tw. (20 g. NaOH per 100 cc) and washed with absolute alcohol for about two days or until no alkaline reaction could be detected with litmus. This sample again gave a much lower result than that obtained by Gladstone, namely, 1.02 grams of sodium sulphate from 20 grams of cotton; but a much higher value than those obtained in the other experiments. In a further experiment the conditions observed in one of Gladstone's experiments were exactly adhered to: 20 grams of cotton were immersed in 600 cc of caustic soda lye of 1.24 sp. gr. (24.5° Tw.) for one hour, slightly pressed out and very quickly washed in about eight changes of absolute alcohol, using for every washing operation about one liter of alcohol; after the last washing the alcohol showed practically no alkaline reaction with litmus. The sample was then allowed to remain over night in a tightly stoppered bottle out of contact with the air. On examination of the alcohol which had run out of the cotton it was found to give a strongly alkaline reaction. The sample of cotton was then incinerated and yielded 2.39 grams of sodium sulphate. The average amount of sodium sulphate obtained in Gladstone's experiments was 2.35 grams. A further experiment was carried out by immersing the cotton for one hour in 600 cc of caustic soda solution of sp. gr. 1.342 (68° Tw.). The washing of the same with absolute alcohol was conducted similarly to the last experiment and, on incinerating, 4.59 grams of sodium sulphate were obtained. Gladstone obtained on the average 4.475 grams of sodium sulphate. It has thus been clearly demonstrated in what manner Gladstone obtained his values and further, that his values cannot be accepted as representing the actual amount of caustic soda which is retained by cotton in such a manner that it cannot be removed by washing with absolute alcohol." Final quantitative experiments on adsorption were then made by Hübner and Teltscher. For solutions up to and including 114.7 g NaOH per liter (26° Tw.) the amount of sodium hydroxide retained by the cotton after numerous washings with alcohol increased with increasing concentration of the caustic soda solution. For concentrations varying from 133.9 to 365.4 g NaOH per liter (30°–80° Tw.) the amount of caustic soda retained is approximately constant at about 3.2 g NaOH per 100 g NaOH. This is only about one-fourth the value found by Gladstone and by Vieweg. "The authors consider themselves justified, therefore, in stating that the results obtained in the experiments brought forward are to be regarded as a correct explanation of the manner in which caustic soda is absorbed by cotton fibers from solutions of different strengths, but that the results of their experiments do not support the suggestion of the existence of distinct chemical compounds or 'soda celluloses,' which has been advanced by Gladstone and by Vieweg."

As a matter of fact these experiments by Hübner and Teltscher are absolutely without value except in bringing out clearly the errors in Gladstone's work. Hübner and Teltscher have shown how much caustic soda is retained by cotton when the cotton is washed with absolute alcohol at ordinary temperatures. They have also shown that practically all the caustic soda is removed when the cotton is washed with hot absolute alcohol. Consequently any intermediate value can be obtained by washing with absolute alcohol at the suitable intermediate temperature, and consequently the data show absolutely nothing in regard to the adsorption of caustic soda from aqueous solution by cotton.

In my own experiments it was necessary to start with a normal cotton, one that could be reproduced by anybody at any time. A modification of Parker's method was found satisfactory. Parker[1] heated absorbent cotton with dilute caustic potash in a bath at 130°–140° for three hours or more. The final product, insoluble in alkali, weighed 7–8 percent less than the original sample, 4–5 percent of the loss being due to products soluble in alkali, and about 3.3 percent of the loss being due to water. The objection to the method is that bumping is so bad that it is very difficult to purify any considerable quantity of cotton in this way. Experiments were, therefore, made to see what would be the effect of prolonged heating at 100°. Samples of the best grade of absorbent cotton were placed in balloon flasks fitted with reflux condensers. A solution of 20 g NaOH per liter was added and heated for varying times on a water bath. The cotton was washed with water, then with dilute hydrochloric acid, and again with water until the wash was neutral to litmus. It was next washed with alcohol and ether and dried in an oven at 115° for five hours. The data are given in Table III.

TABLE III
20 g NaOH per liter
Volume of solution = 50 cc
Temperature, 100°

Cotton grams	Time hours	Cellulose grams	Percentage cellulose
0.9836	3.5	0.9366	95.23
0.8118	3.5	0.7768	95.50
0.8632	5.0	0.8074	93.53
1.0919	5.0	1.0220	93.67
1.2850	18	1.1890	92.53
1.3975	18	1.2890	92.27

From these data it is clear that results agreeing with those of Parker are obtained when approximately one gram of cotton is heated for eighteen hours at 100° with 50 cc $M/2$ NaOH.

The good feature about Gladstone's work on adsorption was that he determined the caustic soda in the cotton directly and not by difference. The weak point was that he washed

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[1] Jour. Phys. Chem., 17, 219 (1913).

with alcohol, thereby introducing a new variable. While Vieweg did not introduce any new substance, he determined the caustic soda by difference. At the suggestion of Professor Bancroft I have tried to combine the good points of the two methods. Cotton was treated with caustic soda solutions and then centrifuged to remove the excess of solution. The caustic soda in the cotton was then determined directly This method is accurate only in case the centrifuged cotton is to be considered "dry." In so far as this is not the case, the amount of caustic soda in the cotton will come out high because one is including the adhering solution. There is no way at present of telling what the error is under these circumstances. All we know is that the error has the opposite sign from the error in Vieweg's method and that the error with the centrifugal method is smaller in the case of cotton than the error with the Vieweg method. As I also analyzed the solution after removing the cotton, I have both sets of data. Also, the results by the centrifugal method can be duplicated at any time, so that it will be an easy matter to apply a correction whenever anybody finds out what correction to apply.

The centrifuge consisted essentially of a brass basket, 4.5 inches in diameter, designed to rotate at about 4000 revolutions per minute. After the cotton had been centrifuged, it was treated with sulphuric acid in a platinum crucible, ignited, and the caustic soda weighed as sodium sulphate. This is Gladstone's method as modified by Hübner and Teltscher. Ammonium carbonate was added to prevent the formation of anything but the normal sulphate. Since the amount of adsorption does not vary enormously with the temperature, it was thought that a sufficient accuracy for the purposes of this investigation would be reached by working at ordinary temperature without using a constant temperature bath. This simplified the centrifuging tremendously.

Since preceding workers had apparently reached equilibrium in much less than an hour, the cotton in the first runs was left for one hour in contact with the caustic soda solutions, One hundred cubic centimeter portions of lyes of different concentrations were prepared and from 1.0 to 1.2 grams of cotton shaken with each concentration for one hour after which the cotton was centrifuged and analyzed. The data for these runs are given in Table IV and are plotted in Fig. 2. The change in concentration of the solution is so small that it makes no real difference whether initial or final concentrations are plotted.

TABLE IV

Volume of solution = 100 cc
Weight of cotton = 1.0–1.2 g
Time of run = 1 hour

Solution g NaOH per liter	Adsorbed g NaOH per gram cotton	Solution g NaOH per liter	Adsorbed g NaOH per gram cotton
500	1.09	200	0.58
375	0.95	125	0.32
275	0.74	375	—
250	0.64	then	—
225	0.63	125	0.48

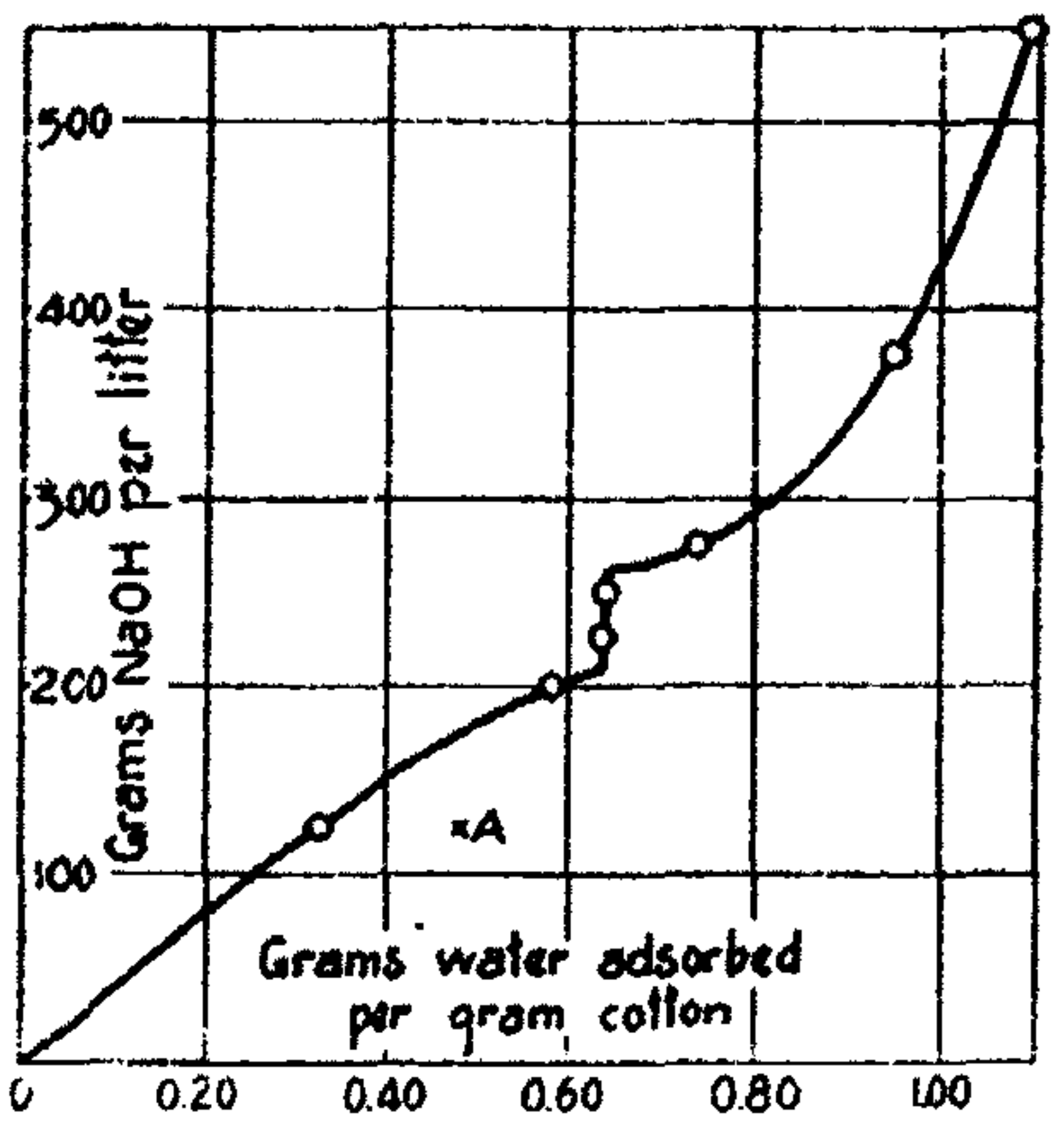

Fig. 2

The curve is similar to Vieweg's. There is one point at which the apparent composition of the solid phase remains practically constant at about 63 g NaOH per 100 g cotton which would coincide approximately with the 61.7 g required for $C_{12}H_{20}O_{10}.5NaOH$, were it not for the fact that the rest of the curve cannot be so interpreted. If a compound really exists there must be two flats in the curve, one above and one below the vertical portion. These might be negligible in length, in which case we should have two series of solid solutions with a definite compound occurring between them. While this might be the case, the assumption of experimental error seemed more plausible especially in view of the errors into which previous experimenters have fallen. To check the results a sample of cotton was shaken for one hour with a lye containing 375 g NaOH per liter and then for three hours with a lye containing 125 g NaOH per liter. This gave point A in the diagram (last experiment in Table IV). From this it was evident that equilibrium was not reached in one hour. Observation also showed that the centrifuge was not running up to speed and was not removing all the solution from the cotton. This accounts for the apparent adsorption being greater for the high concentrations than was found later. The two errors of incomplete centrifuging and of failure to reach equilibrium work against each other and must neutralize each other at some point. This would necessarily give a curve with a point of inflection which is what we get in a distorted form in Fig. 2.

Special experiments showed that equilibrium was reached and that the cotton was apparently freed practically completely from adhering solution if the cotton were shaken for three hours with the caustic soda and centrifuged for one hour. Runs were, therefore, made under these conditions; the data are given in Table V and are plotted as gravimetric curve in Fig. 3.

The results form a smooth curve indicative of adsorption and there is no evidence of the formation of any chemical compound. It seemed desirable to check the Vieweg titration curve because the preliminary treatment which I had given to the cotton might have had some effect. It was found very difficult to get satisfactory duplicates when titrating as Vieweg

TABLE V

Volume of solution = 100 cc
Weight of cotton = 1.0–1.2 g
Time of run = 3 hours

Solution g NaOH per liter	Adsorbed g NaOH per gram cotton	Solution g NaOH per liter	Adsorbed g NaOH per gram cotton
474	0.916	230	0.664
427	0.887	212	0.642
415	0.875	190	0.594
379	0.846	189	0.579
323	0.782	184	0.572
276	0.733	138	0.461
231	0.665	125	0.433

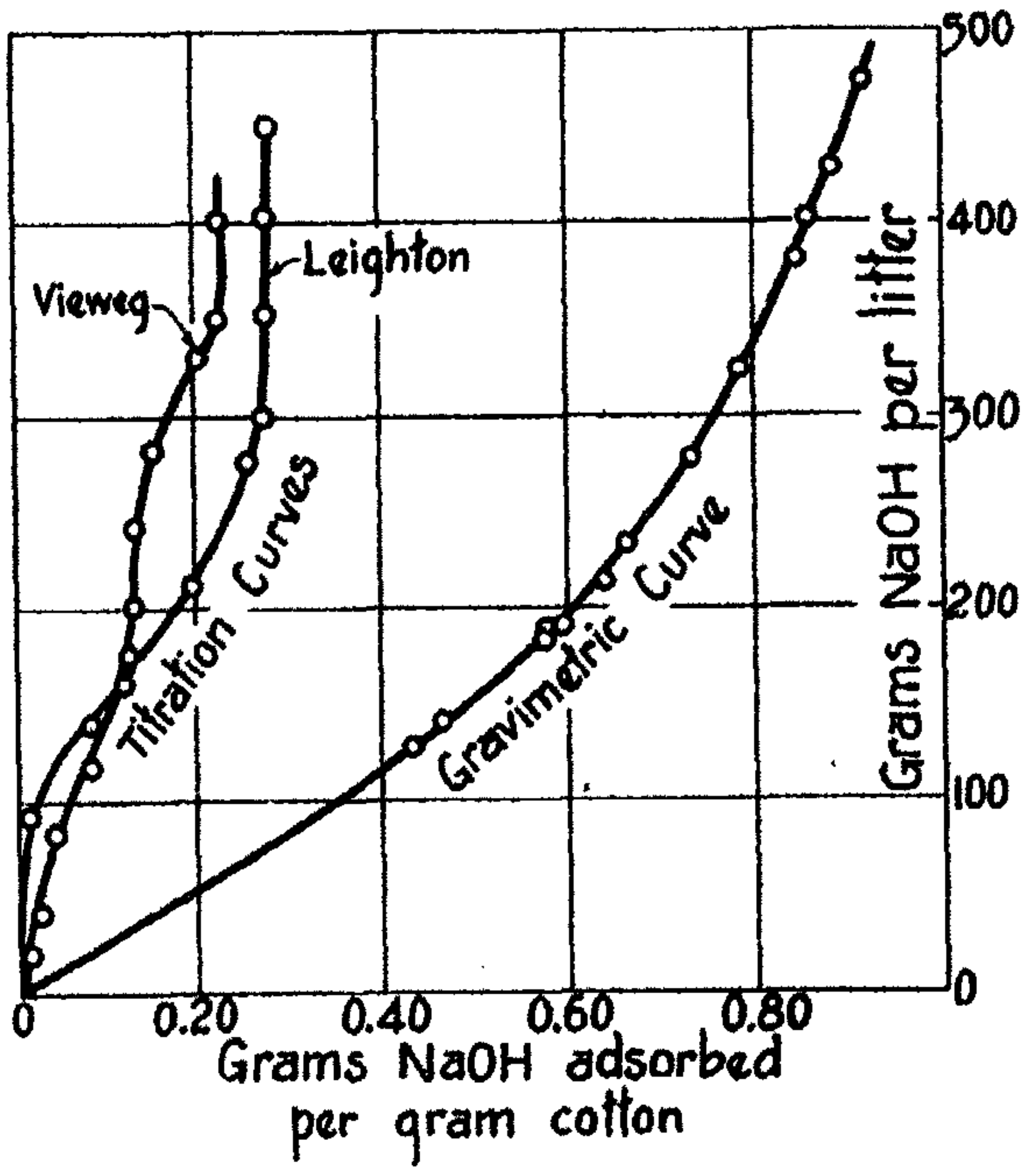

Fig. 3

did. Consequently fifty cubic centimeters of the alkali were run from a burette into a measuring flask and diluted to one liter. Fifty cubic centimeters of this solution were then titrated with dilute and accurately standardized acid. The resulting data are given in Table VI and are plotted, along with Vieweg's data, as titration curves in Fig. 3.

TABLE VI

Volume of solution = 100 cc
Weight of cotton = 1.0-1.2 g
Time of run = 3 hours

Solution g NaOH per liter	Grams NaOH adsorbed per gram cotton		Solution g NaOH per liter	Grams NaOH adsorbed per gram cotton	
	Vieweg	Leighton		Vieweg	Leighton
450	—	0.28	175	—	0.12
400	0.22	0.27	160	0.12	—
350	0.22	0.27	140	—	0.08
330	0.20	—	120	0.08	—
300	—	0.27	90	—	0.01
280	0.15	—	80	0.04	—
275	—	0.25	40	0.03	0.0
244	0.13	—	25	—	0.0
210	—	0.19	20	0.01	—
200	0.13	—	—	—	—

My data in Table VI give a smooth adsorption curve. The only peculiarity is that below 90 g NaOH per liter there is no apparent adsorption. This seems to be due to the fact that up to this concentration the caustic soda and the water are taken up by the cotton in the same relative proportions —within the experimental error—in which they occur in the solution. The difference between the titration curve and the gravimetric curve is very marked. For a concentration of 200 g NaOH per liter we get an adsorption of 0.27 g NaOH per gram of cotton by analyzing the solution and an adsorption of 0.75 g NaOH per gram of cotton by analyzing the centrifuged cotton. While it is not claimed that the second set of data really gives the true adsorption, these data are much more accurate than those of the first set.

From these two sets of data it is possible to calculate the amount of water adsorbed by the cotton in each case. We know the total weight of cotton and the amount of caustic soda adsorbed by it. We know the total weight of the solution, the change of titer, and the amount of caustic soda removed. It is an easy matter to calculate how much water must have been removed in order to give the observed change of titer. This calculation has been made; the data are given in Table VII and are plotted in Fig. 4.

TABLE VII

Solution g NaOH per liter	Adsorbed per gram cotton		Solution g NaOH per liter	Adsorbed per gram cotton	
	g H_2O	g NaOH		g H_2O	g NaOH
475	0.82	0.92	100	3.65	0.37
350	1.16	0.83	75	4.00	0.30
250	1.66	0.70	50	4.00	0.20
250	2.68	0.50	25	4.00	0.10

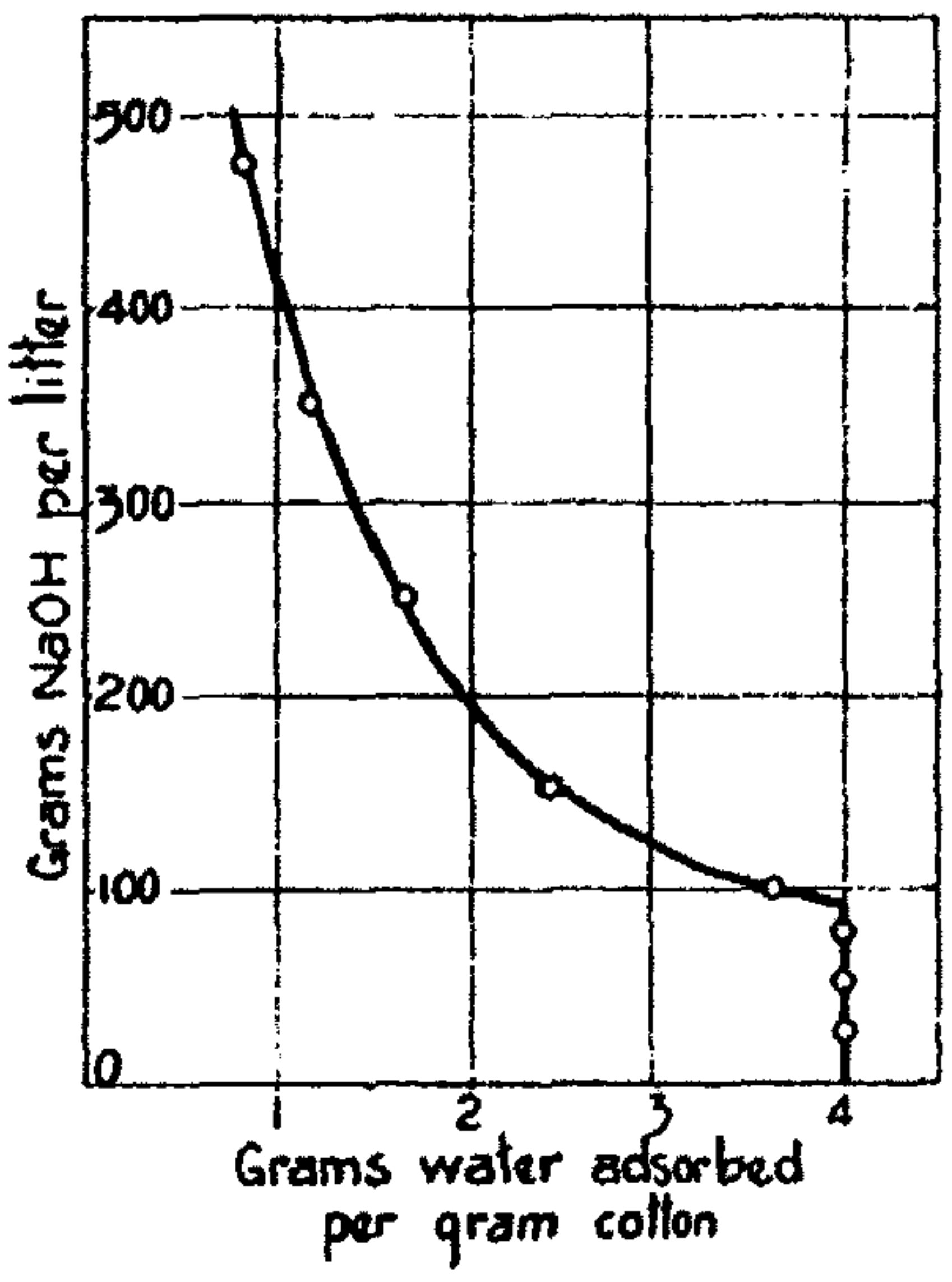

Fig. 4

It will be noticed that the water content of the cotton remains practically constant at first, the caustic soda being taken up without any displacement of water. When the amount of adsorbed caustic soda rises above about 0.34 g per NaOH gram cotton, the caustic soda displaces the water to some extent. Of course, it must be remembered that these figures are only first approximations. The gravimetric curve is accurate only in case all adhering solution is removed by centrifuging. The titration curve is obtained by calculation from small differences in titer and is, therefore, affected seriously by slight errors in titration. The data in Table VII are based on the differences between the titration and gravimetric curves thus introducing a new set of errors.

In Fig. 5 the data are tabulated for the simultaneous change of adsorbed water and adsorbed caustic soda. This is really an adsorption isotherm. It could have been plotted on triangular coördinates; but that seemed hardly worth while.

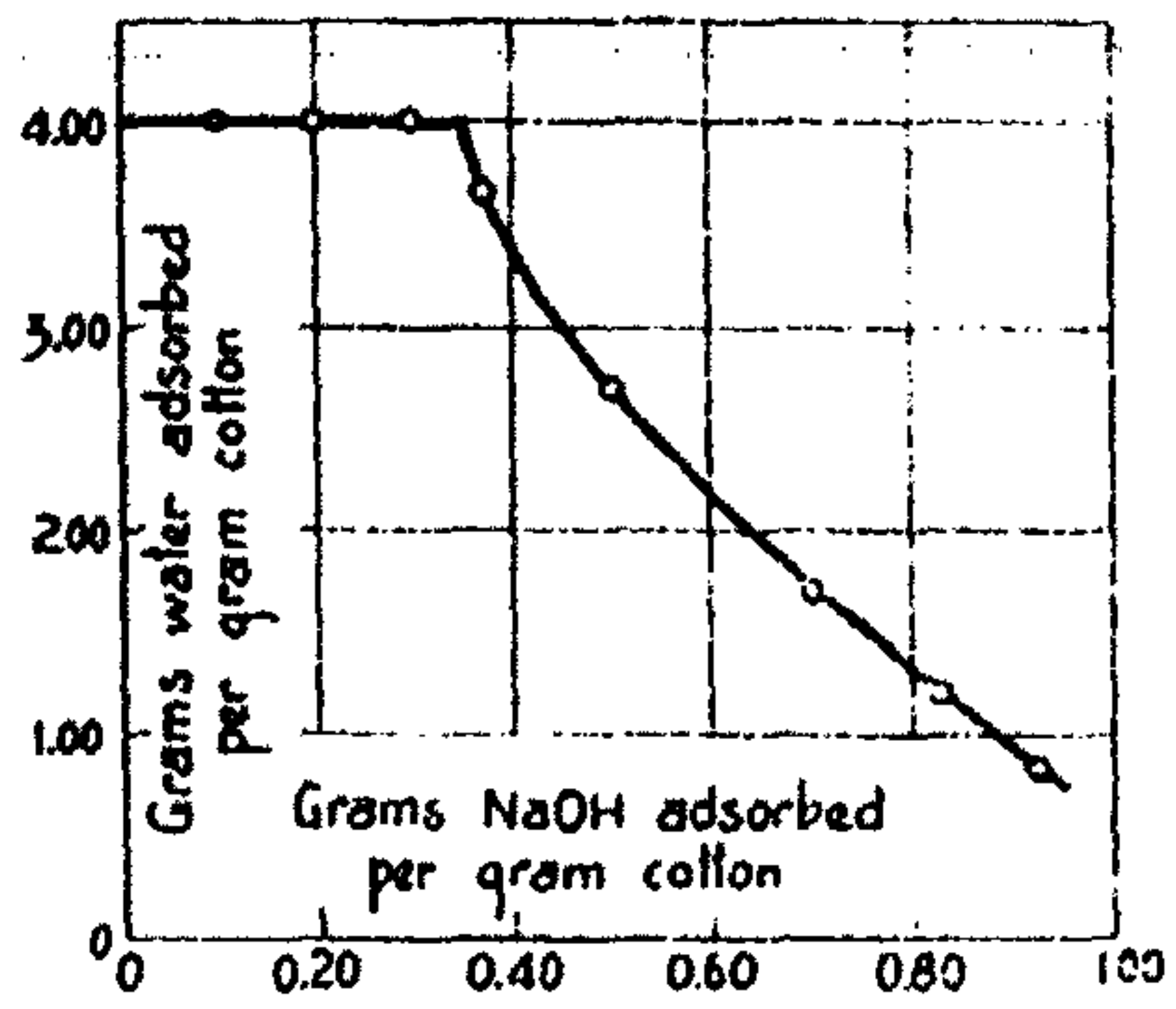

Fig. 5

The general results of this paper are:

1. Gladstone's experiments on the composition of the soda-cellulose compound are inaccurate because, as shown by Hübner and Teltscher, he did not reach equilibrium when washing with alcohol.

2. Hübner and Teltscher's experiments are unsatisfactory because the amount of caustic soda not washed out of cellulose by alcohol is a function of the temperature. Their data show nothing in regard to the way in which cotton adsorbs caustic soda from aqueous solution.

3. It seems probable that equilibrium was not reached

in Vieweg's experiments. The curve that he gets is theoretically impossible.

When his experiments are repeated, an adsorption curve is obtained.

4. Vieweg's titration method, though the one generally employed, is hopelessly inaccurate if the solid phase adsorbs water as well as the solute. The error is a very serious one in the case of cotton

5. By centrifuging the cotton for one hour at about 4000 r. p. m. it is possible to remove most, and perhaps all, of the adhering liquid. An analysis of the cotton gives the amount of caustic soda adsorbed, subject to a correction for any failure to get the cotton dry.

6. The data, obtained by analysis of the cotton after centrifuging, give a smooth adsorption curve.

7. There is no experimental evidence for the formation of any chemical compound when cotton is treated with caustic soda solutions running up to concentrations of 500 g NaOH per liter. The caustic soda is adsorbed by the cotton.

8. Mercerization of cotton is not due to the formation and decomposition of any compound of cellulose and sodium hydroxide.

9. Until the amount of adsorbed caustic soda equals about 0.34 g NaOH per gram cotton, there is apparently no displacement of water from the cotton. With higher amounts of adsorbed caustic soda there is a decrease in the amount of water adsorbed.

10. A standard and reproducible cellulose can be obtained by heating absorbent cotton with one percent caustic soda solution for eighteen hours on the water bath. This is an improvement over Parker's method because it obviates the difficulties due to bumping.

Cornell University
February, 1914

THE ADSORPTION OF POTASSIUM BY THE SOIL

BY A. G. MCCALL, F. M. HILDEBRANDT AND E. S. JOHNSTON

Resume of Previous Work

As early as 1866, Frank[1] studied the retention of potassium chloride by the soil. In his experiments he used metal cylinders three inches in diameter and varying in length from three feet to six feet. His solution contained 1 gram of potassium chloride per liter of water. As a result of his experiments Frank found that the first foot of soil retained 91 percent of the potassium chloride, while the first 18 inches removed 95.5 percent of the salt. The solution appearing at the bottom of his 6-foot columns had lost all but 2 percent of their original salt content. The addition of sodium chloride to the solution diminished the amount of potassium chloride retained.

As the result of his experiments with potassium salts, Treutler[2] concluded that deeper penetration of the potassium into the soil was to be secured by the use of potassium chloride than by the application of potassium sulphate as a fertilizer.

Peat and preparations of the "humic" acids were found by Heiden[3] to have the power of removing a part of the salt when brought into contact with solutions of potassium chloride. The greater part of the salt was readily recovered by the use of a small quantity of water. Liebermann[4] reported that aqueous solutions of potassium chloride showed no change as to acidity or alkalinity after passing through animal charcoal, but that the concentration was decreased.

More recent work has not only confirmed these earlier observations but has brought out the fact that finely divided substances exercise a selective action with respect to the solu-

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[1] Landw. Vers.-Stat., 8, 45 (1866).

[2] Ibid., 12, 184 (1869); 15, 371 (1872).

[3] Hoffman's Jahresb., 1866, p. 29.

[4] Sitzungsber. Akad. Wiss. Wien, 74, 331 (1877).

tions with which they are brought into contact. In some cases the effect of this selective action is to remove one ion of the salt more rapidly than the other, leaving the solution acid or alkaline depending upon which ion is removed to the greater extent. Cameron and Bell[1] found that absorbent cotton has the power of removing the potassium ion from a solution of potassium chloride more rapidly than the chlorine, leaving the solution decidedly acid to ordinary indicators. Previous to this work, van Bemmelen[2] had shown that the treatment of a soil with a solution of potassium chloride resulted in an almost complete exchange of potassium for sodium, calcium and magnesium. In one experiment he determined the chlorine and found that the amount had not changed.

Schreiner and Failyer[3] percolated a solution of potassium chloride through a short column of clay soil at the rate of 50 cubic centimeters in 24 hours. The first few hundred cubic centimeters of the 200 parts per million solution, in passing through the soil, was reduced in concentration to approximately 60 parts per million of potassium. In the succeeding fractional percolates the concentration gradually increased until it reached 173 parts per million when 1100 cubic centimeters had passed. Up to this point the soil had retained approximately 900 parts per million of potassium. The effect obtained with clay loam was less than that observed in the clay, while loam soil gave results intermediate between the clay and the clay loam. For the sandy loam soil used the result was much less marked than in the finer textured soils, but was, nevertheless, quite marked in the first fractional filtrates. At the close of the contact periods the clay and the clay loam soils were washed with distilled water, the percolation of water being at the same rate as that used in passing the potassium solution. After about 450 cubic centimeters of water had passed through the clay soil the successive fractional percolates showed a practically constant composition

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[1] Bull. 30, Bureau of Soils, Dept. Agr. (1905).

[2] Landw. Vers.-Stat., 21, 135–191 (1877).

[3] Bull. 32, Bureau of Soils, Dept. Agr. (1906).

of 20 parts per million of potassium. The washing was continued until over two liters of water had passed, at which time the quantity of potassium retained in the soil had been reduced to 350 parts per million from an initial concentration of 900 parts. With the clay loam the removal of the retained salt was more rapid. The quantity of potassium in this soil was reduced from 570 to 250 parts per million with the passing of approximately 800 cubic centimeters of water.

Patten and Waggaman[1] have recalculated the results of Peters' work on the removal of potassium chloride from aqueous solutions by the soil. They bring out the fact that the effect is nearly twice as great with dilute solutions as with the strong concentrations. With his most dilute solution, (1.011 grams of potassium per kilo of soil), 94 percent of the total potassium present was removed, while from a solution 20 times as strong only about 55 percent was removed. In the same publication, Patten and Waggaman call attention to the fact that the maximum retentive capacity of an adsorbent, while a perfectly definite quantity, is of little practical interest in soil studies, because of the fact that maximum effect can be secured only in the presence of a solution which is saturated with respect to the solute and at the same time is in equilibrium with the material with which it is in contact. From a solution which is less than saturated there can be removed a quantity of the solute which is less than the maximum capacity of the medium but which is, nevertheless, a definite amount for any particular concentration. They use this quantity as a measure of the specific capacity of the medium with respect to that particular solution. A solution of potassium chloride brought into contact with the soil will lose some of its potassium at a rate which gradually decreases until the salt reaches an equilibrium between the soil and the solution. The weight of potassium chloride removed by one gram of soil represents the specific capacity of the soil for that

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[1] Bull. 52, Bureau of Soils, Dept. Agr. (1908); Landw. Vers.-Stat., 2, 129 (1860).

concentration of the salt at that particular temperature. If conditions in the soil are altered more salt may be taken up or a part of the salt already removed may go back into solution. Thus it is seen that the process is a reversible phenomenon. In summarizing his recent work at the Bureau of Soils, Parker[1] states that "the rate of adsorption of the chlorine ions from solution by soils is much less than of potassium ions. The selective adsorption of potassium from a potassium chloride solution by a soil increases in amount with the concentration up to a certain point and then remains practically constant. In general, the smaller the soil particles the greater the selective adsorption of the potassium from a potassium chloride solution by the soil."

Williams[2] has recently called attention to some special cases of selective adsorption to which he has given the name "negative adsorption." He cites the work of Gore[3] as the first cases of negative adsorption. He also calls attention to the work of Lagergren,[4] who observed that upon shaking solutions of electrolytes with charcoal or silica the concentration of the salt solution increased instead of decreasing. Using blood charcoal Williams found negative adsorption with potassium chloride at certain concentrations. Up to a concentration of 0.0563 gram of salt per gram of solution the adsorption was positive, becoming negative with further increase in concentration. In Gore's work, which was cited above, there are instances of negative adsorption at low concentrations becoming positive in less dilute solutions of the same salt. In all of the work cited the investigators have had their interest centered upon the condition of the solution after equilibrium had been reached; consequently, the solutions were left in contact with the adsorbing medium for from 24 hours to several days. In the extensive studies made in

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[1] Journal of Agricultural Research, Dept. Agr., 1, No. 3 (1913).

[2] Trans. Faraday Soc., 10, Part 1, Aug. (1914).

[3] Chem. News, 69, 23, 33–44 (1894).

[4] Bihangtill K. Svenska Vet-Akad. Handlinger, 24, II, 4 (1898).

the Bureau of Soils, United States Department of Agriculture,[1] the contact time was usually a 24-hour period. Throughout the work in which soils have been the adsorbing medium there exists a very great deal of uncertainty concerning the fundamental character of the phenomenon. The evidence from the use of chemically inert substances, such as charcoal and silica would indicate that the process is a physical one, the magnitude of the adsorption depending upon the extent of the surface presented by the adsorbing medium. On the other hand, some of the very earliest work with soils gave strong evidence of the chemical replacement of the bases of the soil by the base contained in the solution. With these facts in mind a series of experiments were planned for the purpose of studying: (1) the effect of a short-time contact between the soil and the salt solution; and (2) the effect of the extent of surface upon the amount and the rate of adsorption.

Present Investigations

In the following experiments a sample of Durham Sandy[2] Loam soil from Cabarrus County, N. C., was used as the adsorbing medium and potassium chloride as the material adsorbed. For the first series of experiments a sample of the soil was dried and passed through a 2 mm sieve. For the second series a sample of the same soil type was reduced to very fine condition by grinding for four days in a porcelain lined ball mill. The mechanical analyses of the two samples as made by the Bureau of Soils, United States Department of Agriculture, are given in the following table. It will be seen from the table that practically all of the sand has been reduced by the grinding to the silt and clay groups, thereby making an enormous increase in the amount of surface exposed by the two samples of what is otherwise identical material.

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[1] Bull. 32 (1906) and Bull. 52 (1908).

[2] Bureau of Soils Classification, Bull. 96, p. 32.

TABLE I—MECHANICAL ANALYSES OF SOIL SAMPLES

Soil	Fine gravel Coarse sand Medium sand 2.0 to 0.25 mm	Fine sand Very fine sand 0.25 to 0.05 mm	Silt 0.05 to 0.005 mm	Clay 0.005 to 0.0 mm
Durham sandy loam natural soil	47.1	31.4	17.9	3.8
Durham sandy loam pulverized four days in ball mill	0.5	9.7	78.1	12.0

The solution used was potassium chloride of approximately five-hundredth normal concentration.

Description of the Apparatus

In order to secure a short-time contact between the soil and the solution a special apparatus was used whereby the solution could be percolated through the soil at any desired rate. The apparatus consisted of a porcelain lined filter chamber into which was fitted a short filter tube, made by cutting off the upper end of a Pasteur-Chamberland filter tube and forcing it down over the projection on the rubber gasket at the bottom of the chamber. Surrounding the filter tube is a brass jacket which serves as a container for the soil. After the introduction of the soil the solution is poured into the outer jacket, the air-tight cap is screwed down over the top of the filter chamber and the system connected to an automobile tire pump. The filter tube serves to hold back the fine soil particles and give a clear filtrate for analysis. The apparatus is charged by putting 20 grams of the air-dry soil in the brass jacket surrounding the filter tube and pouring the salt solution into the porcelain lined chamber which surrounds the system.

Series 1

Preliminary to the use of the soils for the adsorption work, samples of both the natural and the finely pulverized soil were tested for soluble potassium by percolating pure distilled water through them at the approximate rate of 200 cubic centimeters per hour. Each successive 50 cubic centimeter portion of the filtrate was saved and separate determinations made for potassium by the colorimetric method used by the Bureau of Soils.[1]

Table II contains the results of this preliminary work. The numbers in the first column indicate the successive filtrates, while the second column gives the concentrations of the successive portions of the filtrate in parts per million of the solution. The figures given in Table II will be used in the subsequent work in order to correct the results for the soluble potassium originally contained in the soil. Although it has no direct bearing upon the questions under consideration, it is of interest to note that the grinding of the soil in the ball mill has increased the solubility of its potassium in distilled water approximately tenfold.

TABLE II—WATER SOLUBLE POTASSIUM IN SAMPLES OF DURHAM SANDY LOAM SOIL

Fractional filtrates	Parts per million of potassium in filtrates	
	Natural soil	Pulverized 4 days in ball mill
1	3.6	37.5
2	2.2	22.0
3	1.8	20.0
4	1.6	20.0

Series 2

In this series a 20 gram sample of the same natural soil as was used in Series 1 was percolated with 250 cubic centimeters of a solution of potassium chloride, containing 62 parts per million of potassium. The flow was maintained at the approximate rate of 50 cubic centimeters in 10 minutes. The percolate was collected in fractions of 50 cubic centimeters each and the potassium determined colorimetrically. Immediately following the percolation with the solution of potassium chloride, pure distilled water was forced through the

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[1] Bull. 31, Bureau of Soils, p. 31.

sample at the same rate in order to study the removal of the adsorbed potassium. As a check upon the colorimetric determinations the specific conductivity of the fractional filtrates was determined by measuring the conductivity of the solutions in a standardized Arrhenius cell, according to the method described by Jones.[1]

TABLE III—ADSORPTION OF POTASSIUM BY A SANDY LOAM SOIL FROM A SOLUTION OF POTASSIUM CHLORIDE CONTAINING 62 PARTS PER MILLION OF POTASSIUM

Fractional filtrates	Parts per million of potassium in the fractions	Potassium retained in parts per million of dry soil	Specific conductivity at 0°
1	40	58	92
2	36	124	82
3	40	181	79
4	44	226	79
5	59	233	78

TABLE IV—THE REMOVAL OF THE ADSORBED POTASSIUM BY LEACHING WITH DISTILLED WATER

Fractional filtrates	Parts per million of potassium in the fractions	Potassium retained in parts per million of dry soil
1	7	214
2	11	188
3	9	165
4	9	142
5	9	118
6	8	99

It will be seen from Table III that the first ten-minute contact of the solution with the soil reduced its concentration from 62 parts per million to 40 parts per million. At the end of the second ten-minute period the strength of the solution is further reduced to 36 parts per million, but from this point the concentration of the solution rises until the fifth and last fraction is reached when the concentration is within

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[1] "Elements of Physical Chemistry," 4th Ed., pp. 377-383.

three parts per million of the concentration of the original solution. The third column shows that the amount of potassium retained by the soil rises gradually to 233 parts per million of the dry soil when 250 cubic centimeters of solution have passed through.

Figures 1 and 2 represent graphically the results given

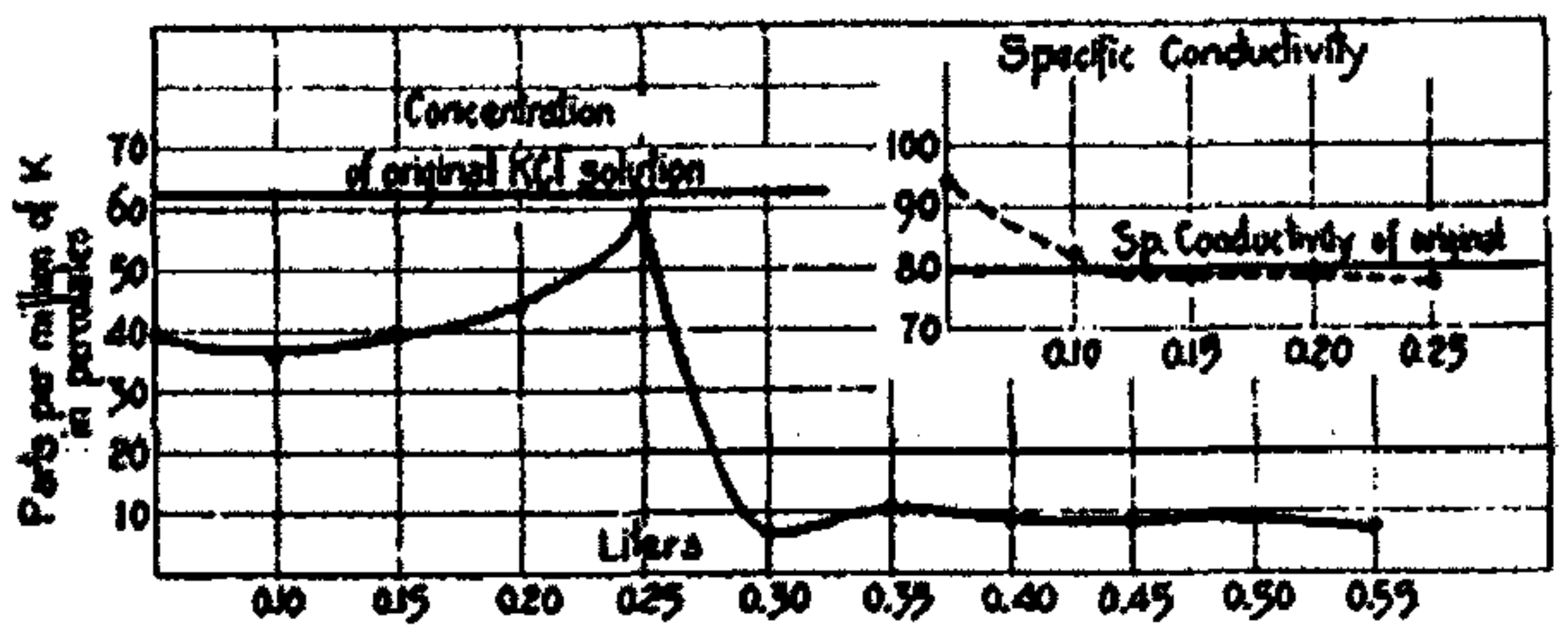

Fig. 1

Series 2—Durham Sandy Loam (natural soil). Adsorption of potassium from a KCl solution containing 62 p. p. m. of potassium. Abscissas, the volume of solution or of water passed through the soil. Ordinates, p. p. m. of potassium in the successive percolates

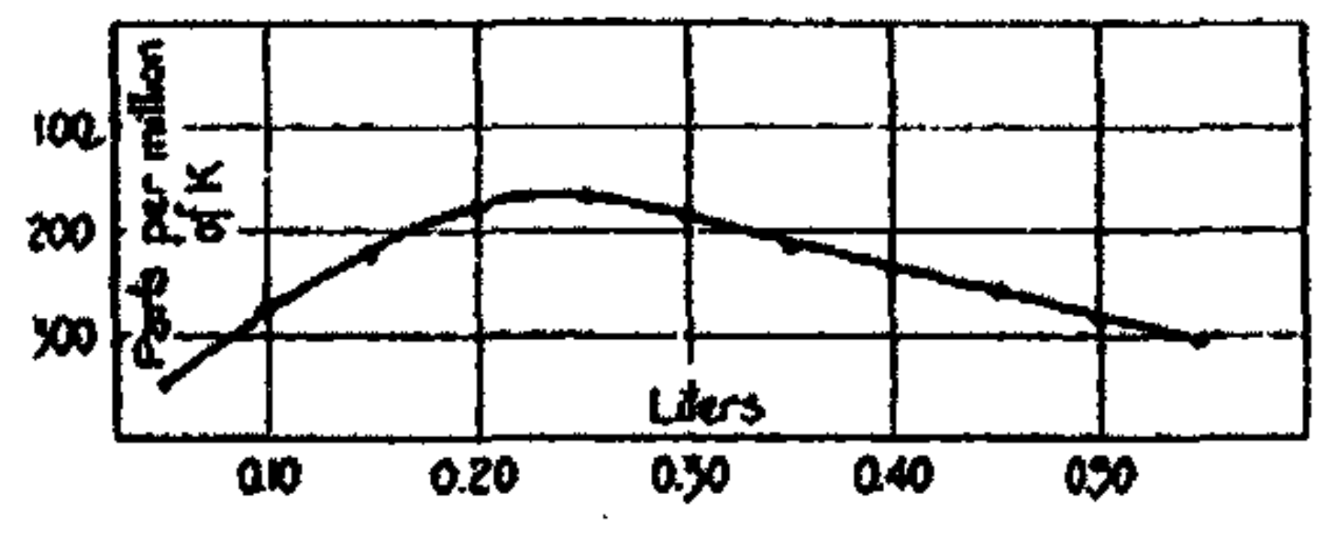

Fig. 2

Series 2—Durham Sandy Loam (natural soil) soil curves. Adsorption of potassium from a KCl solution containing 62 p. p. m. of potassium. Abscissas, the volume of solution or water passed through the soil. Ordinates, the amount of potassium retained, expressed as p. p. m. of dry soil

in Tables III and IV. In Fig. 1 are shown the results based upon the concentration of the successive fractional filtrates; the large curve representing the concentration in parts per million of potassium and the small curve the specific conductivities. The curve for the potassium shows that the first three fractions of the filtrate are reduced approximately to two-thirds of the strength of the original solution. With the increase in the volume of the filtrate the curve rises and almost reaches the upper boundary of the figure which line represents the original strength of the solution. At this point the removal of the adsorbed potassium is begun by leaching with pure distilled water. It should be noted that at this point the curve falls rapidly to practically a straight line.

Figure 2 gives the results expressed in terms of the soil, the abscissas being the volume of the solution of water percolated through the soil and the ordinates the amount of potassium adsorbed expressed in parts per million of the air-dry soil. While it is possible, and indeed quite probable, that complete equilibrium was not reached, it is apparent that the soil is rapidly approaching a saturated condition after having retained 230 parts per million of potassium as a result of the percolation of 250 cubic centimeters of the salt solution. The part of the curve representing the removal of the retained salt by leaching with distilled water is a straight line, showing the uniformity with which the material is removed by the leaching. This removal of the adsorbed potassium was accomplished by filling the filter chamber with distilled water and continuing the percolation at the same rapid rate as was used with the solution of potassium salt.

Series 3

For this series Durham sandy loam, pulverized four days in a ball mill, was used. The manipulation was the same as for Series 2. An inspection of Table V brings out the sur-

TABLE V—ADSORPTION OF POTASSIUM SOLUTION BY A FINELY PULVERIZED SANDY LOAM FROM A SOLUTION OF POTASSIUM CHLORIDE CONTAINING 78 PARTS PER MILLION OF POTASSIUM

Fractional filtrates	Parts per million of potassium in the fractions		Specific conductivity of solutions at 0°
	Original determinations	After correction for water-soluble potassium	
1	144	107	112
2	112	91	82
3	100	82	82
4	112	92	84

prising fact that the amount of potassium in the solution has been increased instead of decreased by its contact with the soil.

TABLE VI—THE REMOVAL OF THE ADSORBED POTASSIUM BY LEACHING WITH DISTILLED WATER

Fractional filtrates	Parts per million of potassium in the fractions
1	39
2	24
3	21
4	18
5	15
6	18

A part of this increase in concentration is undoubtedly due to the fact that the pulverized soil has given up some of its potassium to the percolating solution. However, this is not sufficient to account for all of the increase in potassium content. In Column 3 of the table is given the potassium in the fractional percolates after they have been corrected for the water-soluble potassium of the soil. This correction is based upon the assumption that pure water in contact with the soil will dissolve potassium at the same rate and in the same amounts as the very dilute solution of potassium chloride used in these experiments. Proceeding upon this assumption pure water was percolated through the sample of pulverized soil and the amount removed by the water applied as a correction to the corresponding fractional percolates of the salt solution.

The results given in the table are shown graphically by the curves in Fig. 3. The dotted line forming the upper arm of the curve represents the original concentration of the successive fractions while the solid line represents the strength of the solutions after the correction has been applied. It will be seen that even after the correction has been made the solution still maintains a concentration higher than the original salt solution. This appears to be a case of selective adsorption in which the solvent (water) is adsorbed more rapidly than the dissolved potassium salt with the result that the percolate is more concentrated than the original solution. It should be borne in mind, however, that we are probably not dealing with equilibrium conditions. The mechanism by which this negative adsorption is effected may be explained by assuming that the solvent and the dissolved substance are capable of being adsorbed more or less independently and at different rates. The rapid advance of the liquid through the fine pores of the soil results, for a time, in the more rapid adsorption of the water than of the salt, leaving the liquid in the larger non-capillary spaces more concentrated. This more concentrated solution then moves through the large spaces and appears as the percolate. It is quite probable that after a few hundred cubic centimeters have passed through, equilibrium will have been established and the negative adsorption will become positive. This so-

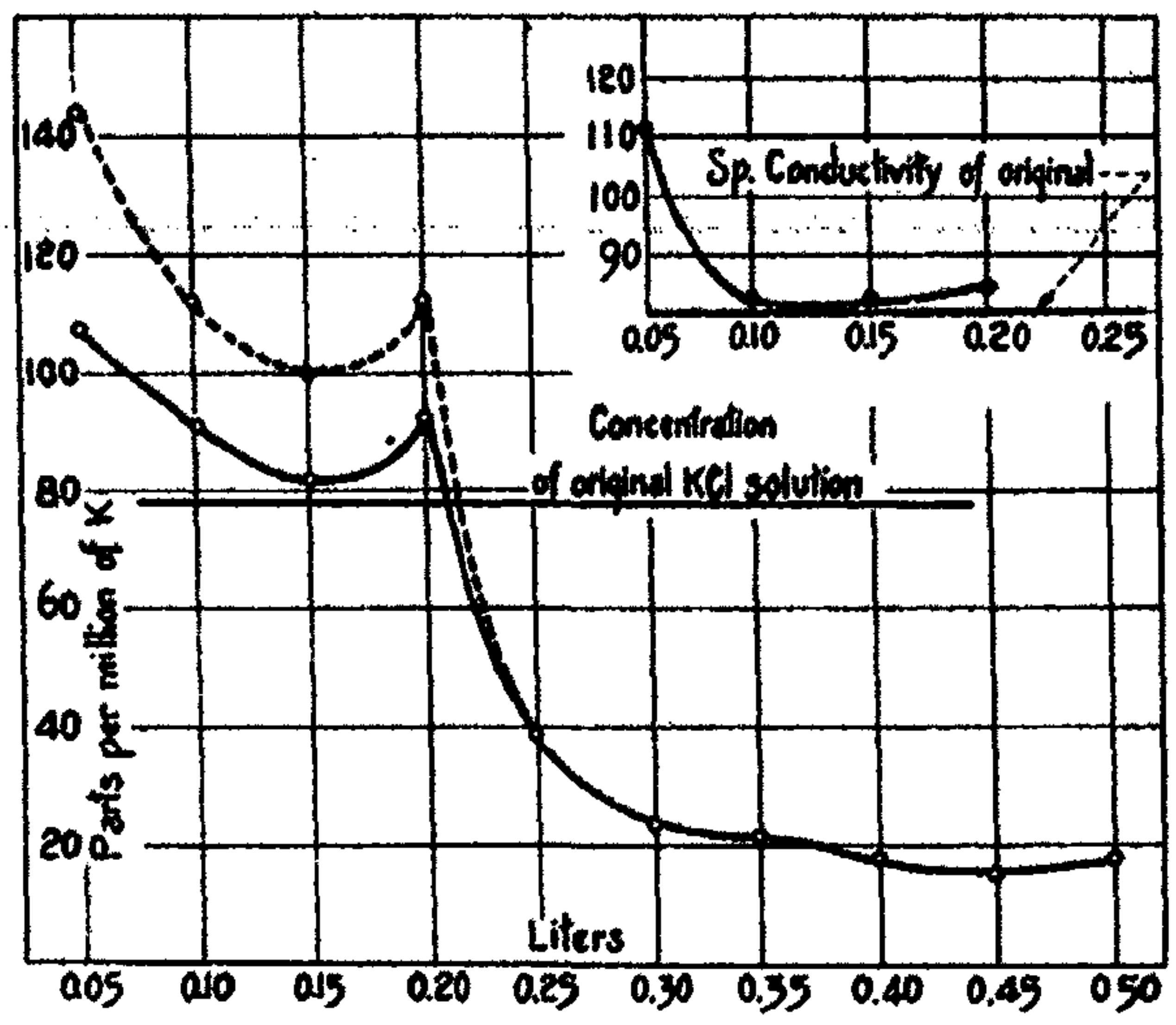

Fig. 3

Series 3—Solution curve showing concentration of successive 50 cc portions of a KCl filtrate from pulverized Durham Sandy Loam Soil. Concentration of original solution 75 p. p. m. of potassium called negative adsorption, therefore, may be considered as a special case of selective adsorption and serves to point out the fact that there is no fundamental difference between the "wetting" of the soil particles and adsorption.

From the work of Williams, to which reference was made earlier in this paper, it appears that the adsorption of the solute and the solvent is dependent upon the relative masses present. With some electrolytes in water it has been found experimentally that the adsorption is at first positive, increases to a maximum, decreases through zero, and finally becomes negative, but there seems to be no case on record in which the initial adsorption effect is negative.

The writer wishes to acknowledge his indebtedness to Dr. H. C. Jones for apparatus and laboratory facilities and to the Bureau of Soils, United States Department of Agriculture, for special apparatus and for the mechanical analyses of the soil samples.

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ELECTROMOTIVE FORCES

BY WILDER D. BANCROFT

The present theory of the electromotive force of the voltaic cell is due primarily to Nernst[1] and consequently the subject is usually presented in text-books in the form adopted by Nernst, with subsequent modifications to meet special cases. It so happens that the historical development is not a logical or a consistent one; and consequently the different types of cells are not co-ordinated as they should be.

If we have a reversible electrode such as zinc in zinc sulphate, we make use of Nernst's deduction and write for the single potential

$$(1) \qquad E = \frac{RT}{nF} \log \frac{P_{Zn}}{p}$$

where P_{Zn} is the hypothetical solution pressure of zinc, p the osmotic pressure of zinc in the solution, n the valence of the zinc ions and F the Faraday constant.

If we make up a cell of two different concentrations of zinc sulphate we write for it the equation

$$(2) \quad E = \frac{RT}{nF}\left\{\log \frac{P_{Zn}}{p_d} - \log \frac{P_{Zn}}{p_c}\right\} + x = \frac{RT}{nF} \log \frac{p_c}{p_d} + x$$

where x is the potential difference between the two solutions, p_c is the more concentrated solution and p_d the more dilute. If we make up a cell of the Daniell type, the equation becomes

$$(3) \qquad \begin{aligned} E &= \frac{RT}{nF}\left\{\log \frac{P_{Zn}}{p_{Zn}} - \log \frac{P_{Cu}}{p_{Cu}}\right\} + x = \\ &\frac{RT}{nF} \log \frac{P_{Zn}}{P_{Cu}} \cdot \frac{p_{Cu}}{p_{Zn}} + x. \end{aligned}$$

If the metallic electrode is a phase of varying composition such as a dilute amalgam, it is usual to consider the cell as a whole and to calculate the work done in transferring the dissolved metal from one electrode to the other as pointed out

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[1] Zeit. phys. Chem., 4, 129 (1889).

by von Turin[1] and by Meyer.[2] The equation for the cell is

$$E = \frac{RT}{mnF} \log \frac{p'_1}{p'_2} \tag{4}$$

where p'_1 and p'_2 are the osmotic pressures of the metal in the two mercury solutions and m is the ratio of the molecular weight of the metal in the mercury solutions to the weight of the ion in solution. LeBlanc[3] writes for the single potential

$$E = \frac{RT}{nF} \log \frac{P'}{p} \tag{5}$$

where P' is the electrolytic solution pressure of the zinc in the amalgam and m is unity because zinc is monatomic in mercury. This solution pressure is not the one introduced by Nernst because that was a constant. As a matter of fact, LeBlanc gets out of the difficulty only by saying that, since the osmotic pressures of zinc in mercury are proportional to the concentrations, the electrolytic solution pressures of the amalgams may be assumed to be proportional to the osmotic pressures of the dissolved zinc. In a cell with two amalgam electrodes the proportionality factor cancels and everything comes out as it should; but it would be a very clever student who could find out from LeBlanc's book the equation for a cell consisting of zinc and dilute zinc amalgam in zinc sulphate solution. If we assume that the apparent solution pressure is proportional to the osmotic pressure of the monatomic metal in the mercury, the equation for the single potential becomes

$$E = \frac{RT}{nF} \log \frac{P_{Zn}}{p_0} \cdot \frac{p'_1}{p} \tag{6}$$

where P_{Zn} is the solution pressure of zinc against an aqueous solution as in Equation 1, p'_1 is the osmotic pressure of zinc in the amalgam, p_0 is the osmotic pressure of a solution of zinc in mercury which is in equilibrium with pure zinc, and p is the osmotic pressure of zinc ions in the solution.

When it comes to gas cells the orthodox thing is to treat

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[1] Zeit. phys. Chem., 5, 340 (1890); 7, 221 (1891).

[2] Wied. Ann., 40, 244 (1890); Zeit. phys. Chem., 7, 477 (1891).

[3] "A Text-Book of Electrochemistry," 184 (1907).

them exactly like amalgam cells only considering the solution pressures as proportional to the gas pressures. The equation for the single potential therefore becomes

$$E = \frac{RT}{mnF} \log \frac{p''_1}{p} \tag{7}$$

where p''_1 is the gas pressure. For hydrogen $m = 2$ and $n = 1$. We are not only ignoring the electrode, but also the unknown concentration in the electrode. While this is justifiable thermodynamically, it is of doubtful wisdom pedagogically. We can get back to the strict Nernst formulation if we postulate Henry's law for the relation between the gas pressure and the unknown osmotic pressure in the electrode and substitute this in an equation analogous to Equation 6. If the ratio of the molecular weight of the gas to the molecular weight in the metal electrode is q, we have

$$E = \frac{RT}{qmnF} \log \frac{P}{Kp_o} \cdot \frac{p''_1}{p} \tag{8}$$

where K is the constant in the equation $p''_1 = K(p'_1)^q$ and p'_1 is the osmotic pressure of hydrogen in the electrode. For hydrogen we know that $qm = 2$. Since there is no concentration at ordinary temperatures for which solid hydrogen is in equilibrium with a platinum electrode, for instance, it is simpler to substitute P_1 for P/Kp_o in which case we may write

$$E = \frac{RT}{2F} \log \frac{P_1 p''_1}{p} \tag{9}$$

remembering however that P_1 is not the solution pressure of solid hydrogen.

When it comes to oxidation and reduction cells, the Nernst formulation is practically ignored. For reversible electrodes such as platinum in a mixture of ferrous and ferric salts we follow the lead of Peters[1] and write one modification of the van't Hoff formulation

$$E = A - \frac{RT}{nF} \log \frac{p_2}{p_1} \tag{10}$$

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[1] Zeit. phys. Chem., 26, 193 (1898).

where p_1 is the osmotic pressure of the ferrous ions in the solution, p_2 the osmotic pressure of the ferric ions, n the difference in valence of the ferric and ferrous ions ($n = 1$), and A the value of the electromotive force when p_1 and p_2 are equal.[1] While this same formula could probably have been deduced from the Nernst theory, I am not aware that it has ever been done. Nernst has suggested treating reduction electrodes as hydrogen electrodes; but it is not very satisfactory to call a ferric-ferrous electrode a hydrogen electrode, and the overvoltage complicates the theory of the hydrogen electrode a good deal.

When avowedly measuring chemical affinity, as involved in the reaction $TlSCN + KCl \rightleftarrows TlCl + KSCN$, for instance, we make use of another modification of the van't Hoff formulation[2] and write for the cell

$$(11) \qquad E = \frac{RT}{nF} \log \frac{Kp_1}{p_2}$$

where p_1 is the osmotic pressure of the sulphocyanate ion, p_2 the osmotic pressure of the chloride ion, K is the equilibrium constant in the equation $Kp_1 = p_2$, and x is the potential difference between the solutions. The Nernst formulation could have been used in this case. Ostwald[3] has shown that the equation for such single potential differences as Tl | *TlSCN* KSCN may be written

$$(12) \qquad E = \frac{RT}{nF} \log \frac{Pp_1}{S_1^2}$$

where P is the solution pressure of thallium, p_1 the osmotic pressure of the sulphocyanate ions, and S_1 the solubility of thallous chloride expressed in osmotic pressure units. For the cell Tl | *TlSCN* KSCN | KCl *TlCl* | Tl we have the equation

$$(13) \qquad E = \frac{RT}{nF}\left(\log \frac{Pp_1}{S_1^2} - \log \frac{Pp_2}{S_2^2}\right) = \frac{RT}{nF} \log \frac{S_2^2}{S_1^2} \cdot \frac{p_1}{p_2}$$

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[1] Peters uses the plus sign in his equation; but this is not in keeping with the Nernst formulation that the current flows from the metal to the solution when E is positive. See Haber: Zeit. Elektrochemie, 7, 1047 (1901).

[2] Knüpffer: Zeit. phys. Chem., 26, 255 (1898).

[3] Lehrbuch allgem. Chemie, 2, I, 877 (1893).

provided we consider the potential difference between the solutions as zero.

I have distinguished five types of cells: cells with reversible metallic electrodes; amalgam cells; gas cells; oxidation and reduction cells; chemical affinity cells. These are usually treated in five more or less different ways, which may be advantageous but which is certainly unsound theoretically. Suppose we take the Daniell cell, Zn | $ZnSO_4$ | $CuSO_4$ | Cu. This is usually considered—and very properly—as a cell with reversible metallic electrodes. It may, however, be considered as an oxidation and reduction cell because the zinc is oxidized and the copper salt is reduced.[1] It can also be considered as a case of chemical affinity because we are really studying the reaction

$$Zn + CuSO_4 = Cu + ZnSO_4.$$

If we start with a zinc amalgam and a copper amalgam instead of with the pure metals, we have the same reaction taking place as before; but it is now an amalgam cell with electrodes of varying composition. If we were to take into account the unknown vapor pressures of zinc and copper, we could consider the cell as a gas cell. Our types are not mutually exclusive and one given combination may be considered from any one of the five differing points of view. Obviously it would be better for the student to have a uniform treatment of the subject and yet I do not know of any text-book on electrochemistry which attempts this. I am not in a position to do much criticizing because I have never attempted it myself in my lectures in the past, though I have pointed out the inter-relation of the different types.

The proper starting point, as Haber[2] has pointed out, is van't Hoff's formula for the reaction isotherm. In the case of a reversible reaction, A, the chemical affinity per unit chemical weight is given by the equation

$$\text{(14)} \qquad A = RT \log K\Sigma p_1 / \Sigma p_2$$

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[1] Haber: Zeit. Elektrochemie, 7, 1046 (1901).

[2] Ibid., 7, 1045 (1901).

where Σp_1 refers to the substances which are consumed during the reaction and Σp_2 to the substances which are formed. If it is possible to arrange the reaction so that electricity is generated, we have the relation

$$A = n\mathrm{FE} \tag{15}$$

By combining Equations 14 and 15, we get the working equation

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \mathrm{K}\Sigma p_1 \,/\, \Sigma p_2. \tag{16}$$

If we apply Equation 16 to the Daniell cell,

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{CuSO_4} \mid \mathrm{Cu},$$

which involves the reaction

$$\mathrm{Zn} + \mathrm{CuSO_4} = \mathrm{Cu} + \mathrm{ZnSO_4},$$

we have

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \mathrm{K} \,.\, \mathrm{Zn} \,.\, p_{\mathrm{Cu}} \,/\, \mathrm{Cu} \,.\, p_{\mathrm{Zn}} + x \tag{17}$$

where x represents the potential difference between the solutions and Zn and Cu are written to denote the unknown constant terms for zinc and copper respectively. By combining these latter with K we get

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \mathrm{K}_1 p_{\mathrm{Cu}} \,/\, p_{\mathrm{Zn}} + x \tag{18}$$

which is identical with Equation 3, provided we put $\mathrm{K}_1 = \mathrm{P}_{\mathrm{Zn}} \mid \mathrm{P}_{\mathrm{Cu}}$. The single potential difference at the zinc electrode can be written

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \mathrm{K} \,.\, \mathrm{Zn} \,/\, p_{\mathrm{Zn}} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \mathrm{K}_2 \,/\, p \tag{19}$$

which is the same as Equation 1 with K_2 written for P_{Zn}. The equation for a concentration cell with zinc electrodes and two zinc sulphate solutions becomes

$$\mathrm{E} = \frac{\mathrm{RT}}{n\mathrm{F}} \log \frac{\mathrm{K}_2 \,.\, p_1}{\mathrm{K}_2 \,.\, p_2} \tag{20}$$

which is the same as Equation 2, p_1 being the more concentrated solution. The direction of the current is to be predicted from the Theorem of Le Chatelier.

If the molecular weight of zinc in a zinc amalgam is m times the atomic weight of zinc the potential difference between it and the solution will be given by the equation

$$(21) \qquad E = \frac{RT}{mnF} \log Kp'_1 / p$$

which is the same as Equation 6 with K written for P_{Zn} / p_0. The equation for an amalgam cell with electrodes of different concentrations becomes

$$(22) \qquad E = \frac{RT}{mnF} \log \frac{Kp'_1}{Kp'_2} \cdot \frac{p}{p} = \frac{RT}{mnF} \log \frac{p'_1}{p'_2}$$

which is the same as Equation 4.

In the case of a gas electrode we can write at once

$$(23) \qquad E = \frac{RT}{qmnF} \log Kp''_1 / p$$

where qmn is the ratio of the molecular weight of the gas to the ionic weight, p''_1 is the gas pressure and p is the osmotic pressure of the ion for which the electrode is reversible. In the case of hydrogen or chlorine $qmn = 2$. Equation 23 is the same as Equation 9 if $K = P_1$.

The equation for a reversible reduction electrode consisting of platinum in a mixture of ferrous and ferric salts becomes

$$(24) \qquad E = \frac{RT}{nF} \log Kp_1 / p_2$$

where p_1 refers to the ferrous salt and p_2 to the ferric salt. This is the same as Equation 10 when one writes $A = (RT/nF) \log K$.

I have already shown that the equation for the Daniell cell simplifies to

$$(25) \qquad E = \frac{RT}{nF} \log K_1 p_{Cu} / p_{Zn} + x$$

whether we consider the cell as a case of chemical affinity or as made up of two reversible electrodes. For the cell Tl | *TlSCN* KSCN | KCl *TlCl* | Tl the reaction is

$$TlSCN + KCl \rightleftarrows TlCl + KSCN.$$

Considering this as a case of chemical affinity and combining the constant terms for thallous chloride and thallous sulphocyanate with the equilibrium constant we get

$$(25) \qquad E = \frac{RT}{nF} \log K_1 p_{SCN} / p_{Cl} + x$$

which is identical with Equation 11.

It is possible to apply the general equation of van't Hoff to the contact electromotive force between two solutions, in case the process is a reversible one.[1] For the same electrolyte in different concentrations, Nernst has derived the expression

$$(26) \qquad E = \frac{u - v}{u + v} \cdot \frac{RT}{nF} \log \frac{p_1}{p_2}$$

where the valence n of the ions is the same, p_1 and p_2 are the osmotic pressures of the ions in the concentrated and dilute solutions, respectively, and u and v refer to the ionic mobilities.

One may imagine the potential difference between two solutions of hydrochloric acid to be produced by two opposing tendencies, one of these being the diffusion of hydrogen ions into the dilute solution and the other being the diffusion of chlorine ions in the same direction. If the rates of ionic diffusion are equal no boundary electromotive force is produced.

Consider separately the part played by the hydrogen ions. Since the ion concentrations in the two solutions are equal when equilibrium is reached, K in the van't Hoff formula becomes unity and disappears. The substance consumed is the ionic hydrogen in the concentrated solution and Σp_1 refers to its osmotic pressure; similarly Σp_2 refers to the dilute solution where hydrogen ions are increasing in number. If the total electromotive force were produced by the migration of hydrogen ions only, the following expression would hold for this hypothetical single potential:

$$(27) \qquad E_1 = k_1 \frac{RT}{nF} \log \frac{p_1}{p_2}$$

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[1] This was pointed out to me by Professor Briggs, who has written this section for me.

where k_1 is a constant proportional to the relative rate of ionic diffusion.

On the other hand, negatively charged chlorine ions are passing from the concentrated into the dilute solution. Considering the chlorine ions separately, the hypothetical single potential would be:

$$(28) \qquad E_2 = -k_2 \frac{RT}{nF} \log \frac{p_3}{p_4}$$

where p_3 is the osmotic pressure of the chlorine ions in the concentrated solution, p_4 refers to the dilute solution and k_2 is a constant proportional to the relative ionic mobility of the chlorine ions.

Actually, therefore, the contact potential is equal to the sum of the effects due to the cation and anion and, since $p_1 = p_3$ and $p_2 = p_4$, we may combine Equations 27 and 28 into the following:

$$(29) \qquad E = E_1 + E_2 = (k_1 - k_2) \frac{RT}{nF} \log \frac{p_1}{p_2}$$

If we substitute $\frac{u}{u + v}$ for k_1 and $\frac{v}{u + v}$ for k_2, Equation 26, the Nernst equation, is obtained.

I have tried to make clear that all the different types of reversible cells which have been discussed can be treated from one point of view if one makes use of the van't Hoff formula given in Equation 16. This is, in my opinion, a much better way of treating the subject than the ordinary, haphazard and illogical method. On the other hand this treatment ignores the historical development and fails absolutely to bring out the important part played by Nernst. It seems to me that the following compromise ought to be fairly satisfactory both to the historical and the logical enthusiasts. First give Nernst's deduction of the potential difference between solutions. This would also include Planck's modification of Nernst's formula,[1] and later work along this line.

Then take up Nernst's formula for the potential difference between a metal and a solution, applying it to con-

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[1] Planck: Wied. Ann., 39, 161; 40, 561 (1890).

centration cells, to the Clark cell, and to the Daniell cell, much as Nernst has done; but introducing at once Ostwald's explanation of electrodes of the second class. Next, deduce the van't Hoff formula, Equation 16, and apply it to the case already studied, after which one should take up in order the so-called chemical affinity cells, the oxidation and reduction cells, the amalgam cells, and the gas cells. It is usual, I know, to discuss gas cells before oxidation and reduction cells, but I think that this is another case of a too slavish following of the historical development. It is certainly more logical to study first the effect of varying concentration in the solution, then the effect of varying concentration in the electrode, and lastly the effect of varying concentration in the vapor phase. Certainly nobody can question the advantage of having studied the relation between chemical affinity and electromotive force before taking up the case of the hydrogen-oxygen gas cell.

The general results of this paper are:

1. Five types of reversible cells have been recognized, which are usually treated in five more or less different ways, even though a particular cell could be classed under any one of the five types.

2. The five so-called types of cells are: cells with reversible metallic electrodes; amalgam cells; gas cells; oxidation and reduction cells; chemical affinity cells.

3. All these cells can be treated from the same point of view provided one starts with the van't Hoff formula

$$E = \frac{RT}{nF} \log K\Sigma p_1/\Sigma p_2,$$

where Σp_1 refers to the substances which are consumed during the reaction and Σp_2 to the substances which are formed.

4. It has been shown how the van't Hoff formula is to be applied in the special cases.

5. Since a consistent logical development of the theory of the electromotive force of voltaic cells does not do justice to the pioneer work of Nernst, a compromise treatment is suggested.

6. It is suggested that Nernst's work be presented as an historical introduction, after which the van't Hoff equation should be deduced and applied to all cases.

7. It is desirable to study, in order, the effect of varying concentration in the solution, in the electrode, and in the vapor. Consequently the amalgam cells should be considered after the oxidation and reduction cells, and before the gas cells.

Cornell University

A STUDY OF DOUBLE SALTS IN STANDARD CELLS

BY G. F. LIPSCOMB AND G. A. HULETT

There are only two combinations which have been found to possess the qualifications necessary for a standard of electromotive force. The Clark cell and the Weston cell.

Zn Amg | $ZnSO_4 7H_2O$ | Hg_2SO_4 | Hg and
Cd Amg | $CdSO_4 8/3H_2O$ | Hg_2SO_4 | Hg.

This situation is due to several factors. A metal in the solid state does not exhibit a constant or reproducible potential against a solution of its salts; but mercury, a liquid, does, and also liquid amalgams. Consequently we are restricted to mercury and amalgams. Further, if the metals form more than one series of salts, difficulties are encountered. It also seems to be necessary that the metals used should have a relatively large solubility in mercury, and be as far removed from mercury in the voltaic series as possible, but should not liberate hydrogen from solution. Now zinc and cadmium are the only two metals which fulfil these conditions, and cadmium more nearly so than zinc, which slowly liberates hydrogen. The electrolyte about the mercury electrode must contain a mercury salt, and this must have the same acid radical as the base metal. The sulphate of mercury has been practically exclusively used, but the chloride is also suitable, as we have shown in a previous paper. If mercury sulphate is used on mercury electrode, the sulphate of the metal of the anode must be used for the solution. So it will be seen that in fact, the possibilities for standard cells are quite limited and especially, as it is also necessary that the base metal salts used be well defined, stable and form good crystals. It is, however, possible to use double salts of the base metal, that is, $ZnSO_4K_2SO_4.6H_2O$ which is a stable salt and crystallizes in large well-formed crystals. Also there are the following possibilities: Cadmium sulphate forms a double salt with potassium sulphate, which has the composition $K_2SO_4CdSO_4.6H_2O$. So it is obvious that this double salt can be used in the place of $CdSO_4.8/3H_2O$. Further the two chlorides of cadmium and zinc form well-defined double salt crystals with potassium chloride of the composition $ZnCl_22KCl$ and $CdCl_2.6H_2O$. These double chloride salts also offer some possibilities for their use in standard cells.

Furthermore, with one double salt we may have three different saturated cells, *viz.:*

$$\text{(1) Zn Amg}\{K_2SO_4ZnSO_4.6H_2O\}Hg_2SO_4 \mid Hg$$

$$\text{(2) Zn Amg}\left\{\begin{matrix}K_2SO_4ZnSO_4.6H_2O\\ ZnSO_4.7H_2O\end{matrix}\right\}Hg_2SO_4 \mid Hg$$

$$\text{(3) Zn Amg}\left\{\begin{matrix}K_2SO_4ZnSO_4.6H_2O\\ K_2SO_4\end{matrix}\right\}Hg_2SO_4 \mid Hg$$

where the double salt or double salt and simple salt, with their saturated solutions, represent reproducible equilibrium points in the phase rule diagram. In view of the reproducibility and constancy of cells of this character, liquid metallic electrodes and well-defined soluble salts, this field offers the possibility of an interesting study of double salts, as well as the thermodynamics of such cells.

It was necessary before employing double salts, in such combinations to investigate the phase relationships of the respective salts in order to determine the limits of concentration over which they were stable at a given temperature, their temperature range of stability, and also their behavior toward aqueous solutions; in other words, whether the double salt existed in stable equilibrium with its own saturated solution.

To this end the three-component system of the salt, the corresponding potassium salt, and water, was studied. In order to elucidate the phase rule study of double salts, a typical diagram is given. The ordinates represent reacting weights of one salt, and the abscissae the reacting weights of the other salt, both in a constant amount of H_2O.

In most cases addition of a salt to a saturated solution of second salt, either the acid or the basic radical being common, produces a decrease in the solubility of the second salt. The three branches in Fig. 1, (AC), (CD), (DB), represent the change in concentration, when one of the salt components is added continuously to a solution, kept at a constant temperature. The points (A) and (B) in the diagram represent the number of grams respectively of the anhydrous salts in 100 grams of their saturated solutions. Along the curve (AC) the salt (A) is present in the solid phase with increasing amounts of (B) in solution; and the salt (B) along (DB). The curve (CD) represents the saturated solution of the double salt with varying amounts, one or the other of (A) or (B) in solution, except at the point (E) where the line (OE), bisecting the angle (AOB), cuts the curve. Here only does the solution contain equimolecular quantities of (A) and (B) which is the saturated solution of the pure double salt. (CD) then represents the composition of all the saturated solutions which are in equilibrium with the double salt at that temperature. If the temperature is continuously changed this part of the curve disappears and finally a temperature is reached where the double salt does not exist in stable equilibrium with any solution, and under such conditions the double salt always decomposes. The curve then takes the form given in Fig. 2. The solution is in equilibrium with the solid phase (A) along (AQ), and the salt (B) along (QB). At (Q) the solution is in equilibrium with the two salts (A) and (B).

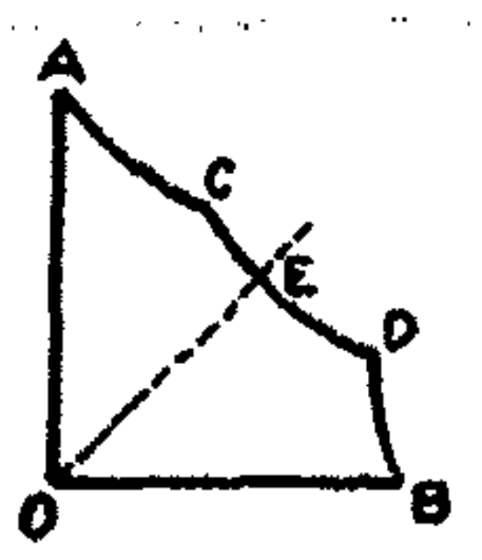

Fig. 1

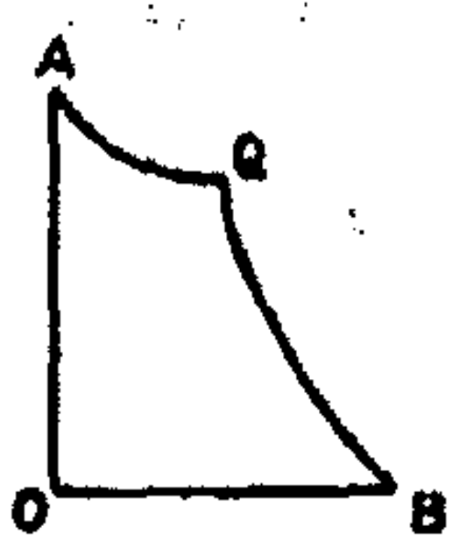

Fig. 2

Proceeding from (A) the double salt appears as solid phase at (C) and further addition of (B) causes no change in the concentration of the solution, until all of (A) in the solid phase has been converted into double salt. When this has happened the system will pass along the line (CD) until at (D), (B) appears as solid phase, and further addition of this component produces no change in the concentration of the solution.

Experimental

For the phase rule study the following general procedure was adopted: Solutions of varying concentration of the potassium salt were taken, and rotated with excess of the corresponding zinc or cadmium salts in sealed tubes 15 × 2 cm. Analyses of the liquid phase were made from time to time to determine when equilibrium had been attained, and in all cases the rotation was continued several days beyond this point. In certain cases the reverse procedure was adopted, the potassium salt was added to a solution of the zinc or cadmium salt and rotated till equilibrium was established. The change from single to double salt was in all cases found to be a fairly rapid one. The solutions thus obtained were analyzed by the following method:

A weighed amount of the solution was electrolyzed in a platinum crucible using mercury as cathode according to the procedure described by Hulett and Perdue.[1] The residual solution was evaporated in a platinum dish and the potassium weighed as sulphate. Careful tests were made in all cases to insure that electrolytic deposition of the cadmium and zinc was complete. In the case of the chloride the above procedure was employed after conversion of the chloride to sulphate or an alternative method was in some cases adopted, and gave concordant results.[2]

As a control the chloride content was estimated volumetrically in a portion of the solution by the Volhard method in the presence of acid, and the zinc was estimated in a further portion by precipitation and weighing as zinc ammonium phosphate.

The details of the cell construction were in all cases similar to the one described previously for the $CdCl_2.2^1/_2H_2O$ cell, and call for no further description here.

The phase relationship ascertained, it only remained to prepare quantities of the respective salts, to construct a series of such cells, and to determine their respective electromotive forces, and their temperature coefficient. The three following combinations were studied particularly:

(1) $ZnHg(K_2SO_4ZnSO_4.6H_2O), Hg_2SO_4 \mid Hg$

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[1] Jour. Phys. Chem., 15, 155 (1911).

[2] Ibid., 17, 755 (1913).

$$(2)\ \mathrm{ZnHg}\left\{\begin{matrix}\mathrm{K_2SO_4ZnSO_4.6H_2O}\\ \mathrm{K_2SO_4}\end{matrix}\right\},\ \mathrm{Hg_2SO_4}\mid\mathrm{Hg}$$

$$(3)\ \mathrm{ZnHg}\left\{\begin{matrix}\mathrm{K_2SO_4ZnSO_4.6H_2O}\\ \mathrm{ZnSO_4.7H_2O}\end{matrix}\right\},\ \mathrm{Hg_2SO_4}\mid\mathrm{Hg}$$

Results of the Work

The three-component system K_2SO_4, $ZnSO_4$, H_2O at 25°. The curve obtained in Fig. 3 has three branches corresponding to the substance K_2SO_4 double salt, and $ZnSO_4$.$7H_2O$ as solid phase in equilibrium. The double salt is capable of stable existence between the range of concentration 38 grams in 100 grams solution, and 128 grams in 100 grams solution. The solubility data from which the curve is plotted are collected in Table I.

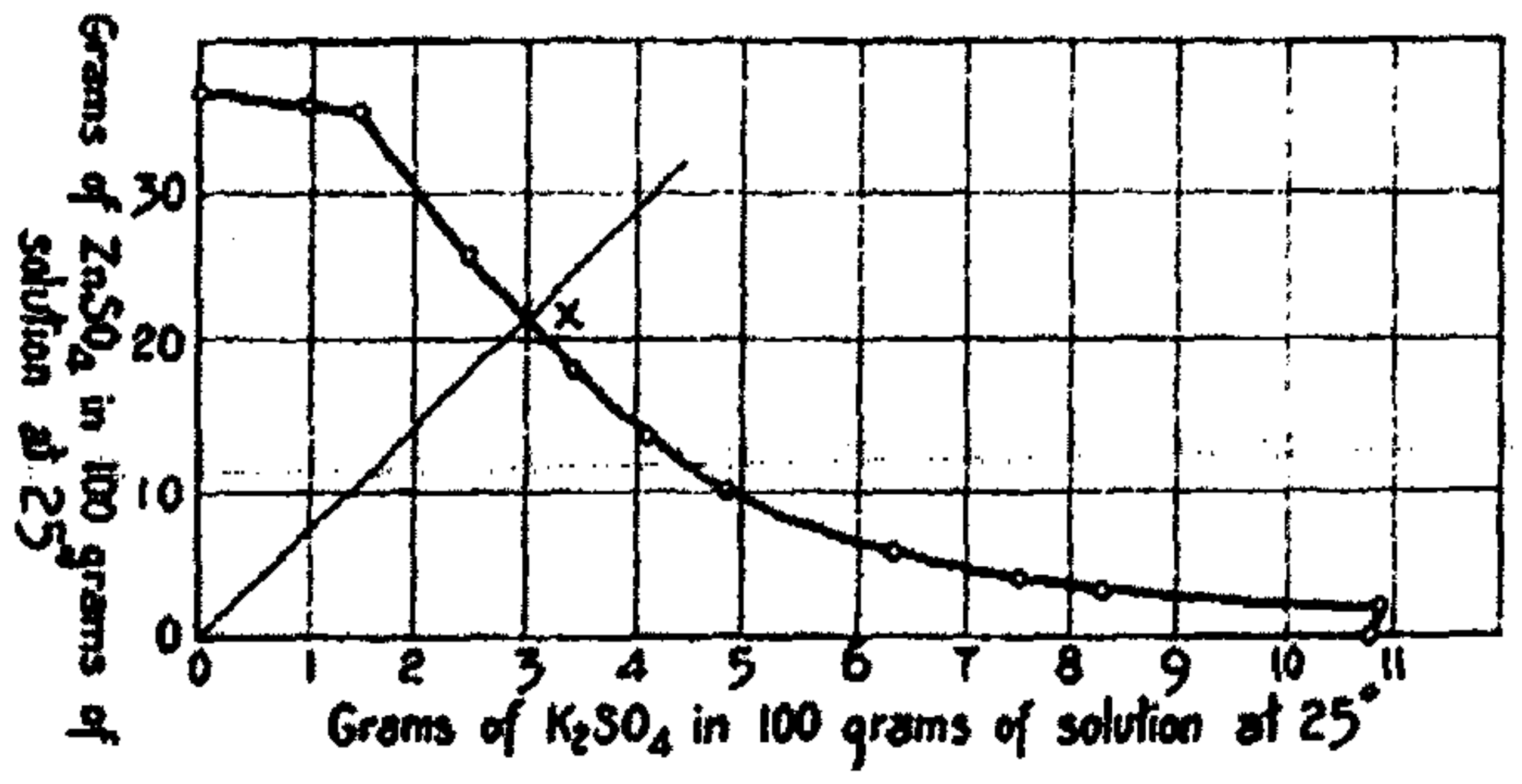

Fig. 3

TABLE I

	Solubility of $ZnSO_4$ in 100 grs. solution at 25°	Amount of K_2SO_4 in 100 gms. solution at 25°	Solid phases
1	37	0	
2	35.6	1	$ZnSO_4.7H_2O$
3	35.30	1.48	$ZnSO_4.7H_2O$, $ZnSC_4$-$K_2SO_4.6H_2O$
4	25.90	2.48	$ZnSO_4K_2SO_4.6H_2O$
5	17.90	3.40	$ZnSO_4K_2SO_4.6H_2O$
6	9.10	4.80	$ZnSO_4K_2SO_4.6H_2O$
7	6.00	6.33	$ZnSO_4K_2SO_4.6H_2O$
8	3.90	7.53	$ZnSO_4K_2SO_4.6H_2O$
9	3.00	8.33	$ZnSO_4K_2SO_4.6H_2O$
10	2.00	10.9	K_2SO_4
11	0	10.8	

It is evident that the double salt can exist in stable equilibrium with its own saturated aqueous solutions as the line drawn from the origin representing the composition of the salt cuts the curve of the double salt at X.

The three-component system $ZnCl_2$, KCl, H_2O was also investigated. The curves obtained with the solubility data from which the curve in Fig. 4 was constructed are given below.

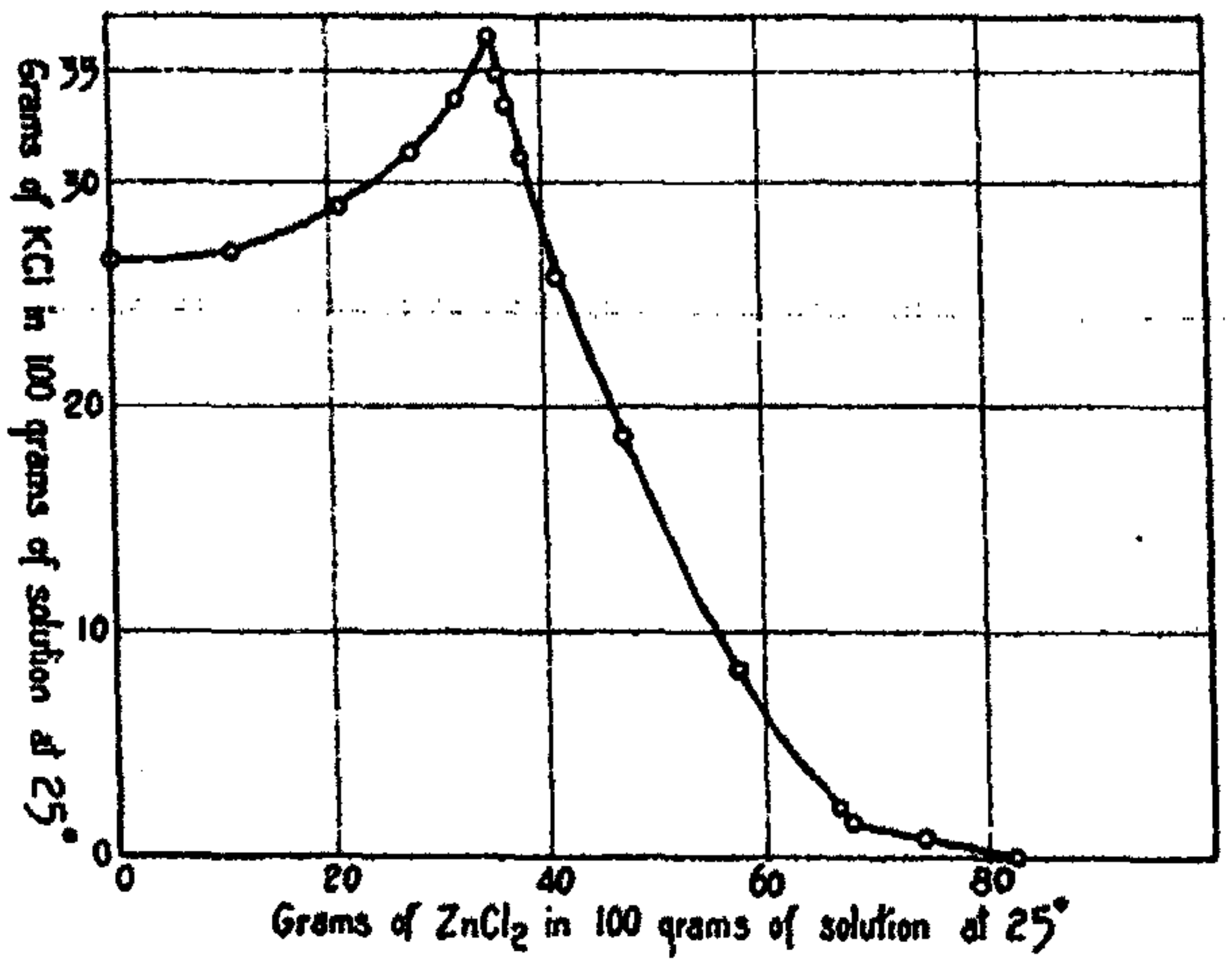

Fig. 4

TABLE II

	Solubility of $ZnCl_2$ in 100 grs. solution at 25°	Amounts of KCl in 100 grs. solution at 25°	Solid phase
1	82	0	
2	74	0.75	$ZnCl_2$
3	67.5	1.50	$ZnCl_2$ and double salt
4	66.5	2.00	Double salt
5	64.0	3.33	Double salt
6	57.5	8.25	Double salt
7	46.8	18.75	Double salt
8	41.0	25.75	Double salt
9	38	31.00	Double salt
10	36.5	33.50	Double salt
11	35.5	35.00	KCl and double salt
12	35	36.50	KCl
13	31.75	33.75	
14	21.5	29.00	
15	0	26.5	

The electromotive force of the cells containing either the double salt alone or potassium sulphate, and the double salt in the solid phase, varied considerably. Their electromotive forces at 25° were 1.46965 and 1.48680 respectively.

$$\text{Zn Amg} \mid (K_2SO_4ZnSO_4.6H_2O),\ Hg_2SO_4 \mid Hg$$

$$\text{Zn Amg} \mid \left\{\begin{matrix} H_2SO_4ZnSO_4.6H_2O \\ K_2SO_4 \end{matrix}\right\},\ Hg_2SO_4 \mid Hg$$

The saturated solutions of the double salt alone or potassium sulphate, and the double salt, seem to hydrolyze the depolarizer, and this fact may account for the inconstancy of these two combinations. On the other hand, if the combination

$$\text{Zn Amg} \mid \left\{\begin{matrix} K_2SO_4ZnSO_4.6H_2O \\ ZnSO_4.7H_2O \end{matrix}\right\},\ Hg_2SO_4 \mid Hg$$

is used, this difficulty of hydrolysis of the Hg_2SO_4 is overcome. The electromotive force of this cell was found to be 1.41976 at 25°, with a negative temperature coefficient of 0.00133.

Since the investigation on the cadmium chloride cell, employing calomel as depolarizer with cadmium chloride as salt, gave results which for constancy and reproducibility left nothing to be desired, it was decided to investigate cells containing the chloride double salt. The constancy and reproducibility of the combination Cd Amg | ($2KClCdCl_2.6H_2O$), Hg_2Cl_2 | Hg is given in Table III:

TABLE III

Date of Construction, March 4, 1915

No. of cell	March 9, 1915 25°	March 12, 1915 25°	May 1, 1915 25°	June 1, 1915 25°	Aug. 8, 1915 25°
1	0.70505	0.70506	0.70506	0.70504	0.70504
2	0.70503	0.70504	0.70505	0.70505	0.70504
	March 13 15°	March 15 15°			
1	0.70355	0.70355	—	—	—
2	0.70350	0.70350	—	—	—
	April 2 30°	April 3 30°	April 26 30°		
1	0.70575	0.70577	0.70577	—	—
2	0.70570	0.70570	0.70572	—	—

The temperature coefficient of this combination was +0.00015 at 18° C.

The electromotive force of the combination Zn Amg | ($2KClZnCl_2.6H_2O$), Hg_2Cl_2 | Hg was 1.01857 at 25°. The double salt although crystallized in a beautiful form when brought into solution, did not seem to be stable and hydrolyzed.

Laboratory of Physical Chemistry
Princeton, N. J., Aug., 1915

NEW BOOKS

Elements of General Science. *By O. W. Caldwell and W. L. Eikenberry. 20 × 14 cm; pp. 14 + 308. Boston: Ginn & Company, 1914. Price: $1.00.* In the preface the authors say, "Science instruction in the first year of the high school has presented one of the most serious problems in secondary school work. First-year pupils do not possess a large fund of information about the common phenomena of nature, or they may not attempt a scientific interpretation of these phenomena. This lack in abundant, concrete, and rationalized experience has made it extremely difficult to secure the desired results from the first science course through presentation of any one of the differential sciences. Experiments have been under way in different parts of the United States for several years with the purpose of securing an organization of science materials and a method of presentation which shall prove more educative. It has been the object of these experiments to develop a more usable fund of knowledge about common things and a more scientific attitude in interpreting common problems, and to discover and utilize interest and ability in such ways that more effective and more profitable work may thereafter be done in the differentiated sciences. These experiments have shown uniformity in their attempt to use the point of view of the relatively uninformed pupil, and while they have followed several lines of effort in the main they have come to use a similar body of knowledge.

"The course presented in this book is the result of six years of experiment with a number of pupils, averaging about one hundred per year. During this time several persons have assisted in teaching the course and have made contributions to it. Teachers of subjects other than science, and particularly the administrative officers who are studying the efficiency of the whole high-school curriculum, have been constant observers and critics of the experiment. The success of the course has been such as to justify its presentation, with the hope that it may prove helpful in increasing the efficiency of science teaching."

The subject is divided into five parts: the air; water and its uses; work and energy; the earth's crust; life upon the earth. Under the general heading of the air the special chapters are: some characteristics of the air; temperature changes and the seasons; the water of the air; the weather; structure of air; composition of air; relation of air to food manufacture; dusts, molds, and bacteria of the air; distribution of bacteria and other disease germs. Under water and its uses the special chapters are: ice, water, and steam; water pressure; climatic influences of bodies of water; commercial relations; water supply and sewage disposal. Under work and energy the chapters are: work by running water; work; mechanical energy. In the fourth section, dealing with the earth's crust, the chapters are entitled: natural forces upon the surface of the earth; physical structure of the soil; soil water, drainage, and irrigation; erosion and sedimentation; life in the soil. Under the general heading of life upon the earth, the special topics are: the plant covering of the earth; absorption from the soil by plants; the world's food supply; utilization of food in the plant; nutrition of animals; hygienic aspects of nutrition; reproduction in plants and animals.

For pupils who are not going to college a course in general science is much more important than a course in a single subject like physics or chemistry. The reviewer is inclined to believe that a course of this sort is also desirable for the minority who expect to go to college. A general survey is an admirable preparation for a more detailed study. It gives the student a point of view and also shows him something about the interdependence of the sciences.

The authors appear to have done their work very well. Some of the chapters seem a trifle scrappy; but the proof of the pudding is in the eating, and it is quite possible that the test of experience will justify the authors in their allotment of space. A few errors have crept in. On p. 20 the authors say that "The rays of the sun pass through the glass with little loss, but the heat which is given off by the objects in the greenhouse, after they have been warmed by the sun, does not easily pass through the glass. The heat is therefore retained in the greenhouse." This view has been overthrown by Wood's experiments. The account of freezing mixtures on p. 116 is not very happy. It is no longer true to say, p. 134, that "neither the submarine nor the dirigible balloon has passed beyond the experimental stage."

The worst thing in the book is an introduction by Charles H. Judd which is in very bad taste and which might profitably be omitted in future editions.

Wilder D. Bancroft

A Laboratory Manual for Work in General Science. *By O. W. Caldwell, W. L. Eikenberry and C. J. Pieper. 20 × 27 cm; pp. xi + 134. New York: Ginn & Company, 1915. Price: 50 cents.* The publishers announce that this volume provides laboratory work to accompany Caldwell and Eikenberry's "Elements of General Science." "The exercises are the result of the co-operative work of several high-school teachers throughout several years and have been tried with more than a thousand pupils. Only those exercises have been included which have proved their value for use in the first year of high school." There are 108 experiments in all. The first two show whether air can occupy space and whether air can be made to exclude water. The last two deal with the relation between the weights of the grains and of the cob in ears of corn and with the questions whether variations in parents are transmitted to offspring. The last experiment involves a study of data obtained by Galton. In fact, a good many of the experiments consist in a study of data obtained from the Weather Bureau or other sources. The experiments seem to be well selected.

Wilder D. Bancroft

Metallurgy of Copper. *By H. O. Hofman. 17 × 24 cm; pp. xiv + 556. New York: McGraw-Hill Book Company, 1914. Price: $5.00.* This very complete treatise is of the same high standard as the author's General Metallurgy. It is packed full of information not only of a general nature but also of details that are as valuable as they are scarce in books of this nature. The book covers: properties of copper and its alloys, impurities and their effects, chemistry of copper compounds, roasting sulphide ores, smelting in blast furnaces, reverberatory furnaces and converters, smelting oxide ores and native copper, fire refining, leaching of copper ores, matte and metallic copper, electrolysis by series and multiple systems. The footnotes are not only very numerous, but up to date as well, many 1914 references being given.

H. W. Gillett

THE THEORY OF PEPTIZATION

BY WILDER D. BANCROFT

Peptization consists in the disintegration of particles so that they form a colloidal solution. We get a permanent colloidal solution[1] whenever the particles are small enough to be kept in suspension by the Brownian movements and in some way are prevented from coalescing. Freundlich[2] has postulated that all adsorption is accompanied by a lowering of the surface tension of the adsorbing phase. The theoretical deduction is unsound because the Gibbs theorem applies explicitly to true solutions and not to suspensions. On the other hand, Freundlich's assumption seems to be true experimentally in all the cases which have been studied from this point of view. If we accept Freundlich's generalization as true empirically, a theory of peptization follows at once. Any substance which is adsorbed by a second will lower the surface tension of the second substance and will therefore tend to disintegrate it, in other words, to peptize it.[3] If every adsorbed substance tends to peptize the adsorbing substance, we may expect to get peptization by a solvent; peptization by a dissolved non-electrolyte; peptization by an ion; peptization by a salt; peptization by a colloid. I shall take up these cases in detail.

Since glass adsorbs water, water should tend to peptize glass. At ordinary temperatures, the adsorbed surface film of water is not able to disintegrate the glass; but we get a very different state of things at higher temperatures where the cohesion of the glass is less.[4] Barus[5] found that when a

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[1] Bancroft: Jour. Phys. Chem., 18, 552 (1914).

[2] Kapillarchemie, 52, 154 (1909); Patrick: Zeit. phys. Chem., 86, 545 (1914).

[3] I have used the word "peptonize" previously, but Graham coined the word "peptize," Jour. Chem. Soc., 17, 325 (1864), and it seems better to use that word since peptonize is used in a different sense by the biological chemists.

[4] At higher temperatures the adsorption is less; but this is often more than counterbalanced by the decreased cohesion of the substance to be peptized.

[5] Am. Jour. Sci., (3) 41, 110 (1891); (4) 6, 270 (1898); 7, 1 (1899); Phil. Mag., (5) 47, 104, 461 (1899).

thread of water in a capillary tube is heated to 185°, the thread of water becomes white and milky though translucent, and changes finally into semi-solid siliceous water. He was able to impregnate glass with water to such an extent that it was fusible below 200°. He concludes that glass as a colloid is miscible in all proportions with water. "On cooling, bubbles appear in the clear water-glass in great number, showing it to contract on solidifying from the center outward (centrifugally) like a Prince Rupert drop. The solid water-glass is in appearance as hard and brittle as ordinary glass, from which it differs in refraction and density * * * Made in quantities in a large digester, water-glass[1] is obtained as a nearly homogeneous compact body, adhering forcibly to the walls of the retort, from which it must be removed with wedge and hammer. A small lump held above a candle flame soon fuses with loss of water to a milk-white pumice. Left without interference in the cold for several weeks or months, it spontaneously cracks and crumbles, eventually becoming a loose mass breakable in the fingers, while the original lump could be broken only with a hammer. Water is set free, probably under great pressure, and hence the gradual crumbling of the mass. When compared with the disintegration of minerals, we have here an example of an enormously rapid chemical reaction in solids."

In another paper Barus[2] applied the same principle to the peptization of vulcanized rubber. "In my work on the solubility of glass in water, I showed that in proportion as the state of dissociation or the molecular instability of glass is increased with rise of temperature, the solvent action of water increases at an enormously rapid rate; that inasmuch as the solution takes place between a solid and a liquid, sufficient pressure must be applied to keep the fluid in the liquid state, whenever the vapor tension at the temperature in question exceeds the atmospheric pressure. Thus, at 100°, the action

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[1] [Barus uses this term to mean glass impregnated with water and not to mean a solution of sodium silicate.]

[2] Am. Jour. Sci., (3) 42, 359 (1891).

of liquid water on glass is nearly negligible; but even at 185° solution occurs at so rapid a rate that capillary tubes may become filled with solid hydrated silicate in place of water, in an hour. Here, however, about 10 atm. must be applied to keep the solvent in the liquid state essential to speedy reaction.

"Having attempted to apply the same principle to the actual solution of vulcanized India rubber, I obtained confirmatory results at once. To my knowledge this material has not heretofore been advantageously dissolved in a volatile reagent, or in any reagent by which it is speedily and copiously taken into solution, and from which it may be conveniently obtained."

Barus worked with five samples of rubber of the following character:

a. Very elastic sheet rubber, usually not pigmented, translucent in thin films, brownish in color, used for rubber bands and sheeting, chemical rubber, tubing, etc.

b. Less elastic and harder rubber, pigmented gray, opaque, largely used for rubber tubing, etc.

c. Non-elastic, pigmented rubber, flexible, opaque gray, used for low class rubber tubing and low class merchandise in general.

d. Ebonite.

e. Same as *a*, rotted by age and exposure.

"From experiments made at 100° and 160°, it appears that elastic sheet rubber (*a*) is not fully soluble in CS_2 in a reasonable time, if at all. It is quite soluble at 185°, and soluble to a remarkable degree and at a remarkable rate at 210°. Hence the pressure under which solution is to take place, should here be greater than 15 atm., but need not exceed 30 or 40 atm. Inasmuch as CS_2 thus unites with rubber in any proportions, clear brown solutions of any viscosity may be obtained. Diluting such (thick) solutions with cold CS_2, the solvent is first greedily absorbed; but the final solution of the unagitated syrupy rubber takes place very slowly. Finally, by exposing any of the solutions to air, the CS_2 evaporates, and the dissolved vulcanized rubber is regained without sacrifice of its original non-viscid quality. Similarly, fissured brittle sheet rubber or tubing (*e*) which has become useless for practical purposes by age, is quite soluble in CS_2 at 200°, so far at least as its undecomposed portion is concerned. Elastic gray rubber (*b*) dissolves completely to a gray liquid, in which the pigment is suspended. The concentrated solution hardens at once on exposure to air, reproducing a rubber of nearly the qualities (*b*). The same is true of the non-elastic sample (*c*). Treatment at 310° resulted in a decomposition of the rubber.

"Commercial ebonite (*d*) is first partially devulcanized at 200° (excess of rubber) and eventually dissolved in excess of solvent. The partially devulcanized product is elastic on drying, but finally hardens to a tough solid having a leathery quality. The solution leaves a black stain, with free sulphur apparent after evaporation. Gases are frequently evolved during solution of highly vulcanized rubber in CS_2. As a whole my experiments show that excess of sulphur is first removed by the solvent, after which the vulcanized rubber itself passed into solution.

"The elastic rubbers (*a* and *e*) dissolve easily in liquid mineral oils at 200°. The pressure necessarily will, of course, vary with the boiling point of the oil used, and may be as high as 50 atm. in the very volatile gasolenes. Commercial gasolene, though a good solvent of the rubbers *a* and *e*, is less powerful in case of *b* and *c*, unless excess of solvent be used. On exposure to air, the gasolene evaporated, leaving a residue which soon hardens. Mineral oils of a higher carbon order than gasolene, petroleum for instance, dissolves the rubbers *a* and *e* even more easily. The solution, however, dries only after much time and probably only in thin films. Solubility seems to increase as the oil lies higher in the carbon series....

"Elastic sheet rubber (*a*) dissolves at once in liquid $CHCl_3$ at 210°. Pressure should exceed 15 atm. and need not be larger than 25 or 30 atm. Solutions of any degree of viscosity seem to be obtainable. They dry at once on exposure to air, leaving a hard residue relatively dark in color. Possibly this was due to the presence of sulphur in the chloroform. Gray rubber (*b*) is attacked with decomposition of the solvent and evolution of gas. The elastic sheet rubber (*a*) dissolves at once in liquid C_6H_6 at 200°. Pressure should exceed 7 atmospheres, but need never be higher than 30 atm. The solution exposed to air hardens rapidly. Solution of gray rubber (*b*) is less easy. Solution of elastic rubber (*a*) in liquid toluol at 200° also takes place with great ease. The liquid dries slowly. Pressures of less than 10 atm. suffice . . . . . At 200° India rubber (*a*) is not dissolved in liquid methyl or in liquid ethyl alcohol, and only slightly so in liquid amyl alcohol . . . . . In no case was there a trace of true solution at 210° [in water or mineral acids]. Water probably enters the physical pores of the elastic rubber (*a*), as this substance becomes superficially rough and warty on drying in steam at 200°, after being treated with liquid water at the same temperature....

"Very interesting is the direct vulcanization of a rubber solution to liquid ebonite, by aid of a solution of sulphur. In case of elastic sheet rubber (*a*), this even begins at 160°; but it is more complete at 185° and 210°. In case of pure (non-vulcanized) rubber dissolved in CS_2 with excess of sulphur, scarcely any change of the flesh color is observed at 160°, and the sulphur crystallizes out of the solvent in needles, on exposure. At 185° and 210°, however, the charge turns black, showing complete vulcanization. If equal masses of vulcanized rubber (*a*) and sulphur be treated, the product, after heating to 210°, is not dissolved nor soluble, until the excess of sulphur is removed. Gas is often evolved. In proportion as less sulphur is used relatively to the rubber, the product becomes more immediately soluble and less gas is evolved. Adding about 20 percent of dissolved sulphur to the elastic rubber (*a*), I obtained serviceable solutions of ebonite, on treating at 200° either in CS_2 alone, or in mixtures of this liquid with gasolene, benzol, etc. In most cases these harden very quickly to a jet-black enamel. With less sulphur the color is brown in thin films....

"If vulcanized India rubber be impregnated or saturated by digesting it with the cold reagent (any solvent of pure rubber) for a suitable time (a few minutes to many hours), the swelled mass not only shows a relatively low melting point, but it remains liquid after cooling, provided the solvent is not allowed to escape. This is an observation of practical importance, since the retorts[1] can thus be charged with solid or dry rubber, a minimum of solvent be used in treating or lost by evaporation, and concentrated solutions be obtained often fit to be used at once. Finally the pressure necessary in this case is the smallest possible,[2] and may be below the data given for the divers solvents above.

"The quantity of solvent retained by solid rubber is very large: Thus elastic sheet rubber will hold 7 or 8 times its weight of CS_2, or 1 to 2 times its weight of naphtha. Gray rubber (elastic) absorbs more than its weight of naphtha; etc. Experiments may be cited as follows: non-impregnated vulcanized rubbers (*a* to *e*) do not melt if exposed in a closed tube at 210°. Only in the case of very slightly vulcanized pure rubber gum is there a trace of fusion perceptible at the edges, and here it may even be due to a stain of dirt (oil) accidentally left there. Gray rubbers (*b*, *c*) with a superficial coating of exuded sulphur, turn black from the formation of a film of ebonite.

"All the India rubbers (*a* to *e*) fuse at 210°, when previously saturated, or nearly so, with cold carbon disulphide, and exposed in a close-fitting glass tube. If the pressure be reduced by a capillary aperture at one end of the otherwise closed glass tube, or if the tube be only partially filled and the empty end kept cool, the impregnating solvent is merely distilled off, and no fusion takes place. Whereas at 160° fusion scarcely occurs, melting seems to be complete in the well-impregnated elastic rubber (*a*) at 175°. There is there-

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[1] The present experiments were made in *closed* glass tubes nearly filled with the impregnated rubber. After fusion the mass frequently appeared to have shrunk.

[2] [This is true only in case a real solution is formed. W. D. B.]

fore an approximate coincidence of the thermal data in the present and in the above paragraphs.

"Similar results were obtained with benzol, with gasolene and higher petroleum oils, etc. Fusion is absent or only incipient at 160°, and more than complete at 210°, provided the gasolene be not too volatile. In general the gray rubbers (*b*, *c*) fuse to a more viscous mass than the gum rubbers (*a*); the consistency of cold solutions in the latter case is about that of treacle.

"The occurrences of this paragraph therefore would resemble the fusion of a salt in its water of crystallization, but for the exceptional behavior that impregnated vulcanized rubber after fusion retains a consistency which is liquid relatively to the original non-impregnated charge. The analogy with the solution of starch, or of gluten, is thus more close and immediate. In all these cases the solid swells up when impregnated with the solvent, and fuses to a relatively less viscous consistency, or to a thin solution, when a certain temperature (below 100° in the case of starch and gluten and above 160° in case of vulcanized rubber) has been reached. Hence it is not unreasonable to suspect that even ordinary dry wood, or woody tissue, which swells to a marked degree when impregnated with water, may pass into actual solution if the temperature at which the water acts is sufficiently high, and the pressure above the vapor tension of water at that temperature.[1]

"I mention finally that the reduction of melting point produced in vulcanized India rubber by the impregnating reagents may perhaps advantageously be discussed in accor-

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[1] I have since tested this surmise at some length, but found in every case that cellulose is decomposed before solution in water takes place. In spite of the presence of water under pressure, the phenomenon seems to be a dry distillation. I may here refer to the remarkably close analogies in the thermal behavior of rubber and gelatine which have recently been discovered by Bjerken: Wied. Ann., 43, 817 (1891). The author has reason to believe that moist gelatines are heterogeneous mixtures of solid and liquid. The behavior of rubber, as discussed above, is characterized at low temperatures by a fixed maximum of absorbed solvent. The term mixture is scarcely applicable at once.

dance with Raoult's law; but owing to the difficulty of defining the melting point of the unimpregnated rubber, and the close proximity of the melting points after impregnation with different reagents ($CS_2.C_6H_6$, gasolene) my views on this subject have not taken shape. It is known that in general the melting point produced by a dissolved colloid is relatively very small, from which an exceedingly large molecular weight of the colloid has been inferred. The above results show that, in the converse experiment, where the melting point of the colloid is lowered by a solvent, the effects will probably be normal and pronounced.[1]

"Nevertheless I doubt whether the thin rubber fluids obtained are true solutions, *i. e.*, represent a case in which the division of the solid has actually reached a definite molecule; for on long standing in sealed vessels a gradual thickening of the liquid with final coagulation seems to be the invariable result. Thus there must be a gradual growing together of the individual particles, until finally the whole solution forms one coherent gelatinous mass.

"To summarize: Suppose the coherence of rubber to be due to (cohesive) affinities, capable of being saturated like ordinary affinities. Then in case of impregnation with a solvent, a part of these combine with the similar affinities of the solvent. The result is the decided decrease of tenacity (observed). To liquefy the impregnated sample, the residual cohesive forces of the rubber must be withdrawn, and this can be done by heat. The liquid so obtained I do not conceive to be a true solution, but rather a suspension of particles, the exceeding fineness of which is determined by conditions discussed elsewhere.[2] Diffusion is thus an excessively slow process, and hence the liquid on cooling need not become solid again. In proportion as the individual particles unite however, coagulation gradually sets in, and its structure is probably that of a fine sponge holding solvent in its inter-

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[1] [The error is in assuming that the rubber has fused; it has only been peptized. W. D. B.]

[2] Barus: Am. Jour. Sci., (3) 37, 126 (1889).

stices. If the coagulated solution be reheated (under pressure), a thin viscid solution is again obtained, which in its turn coagulates."

With glass and water a temperature of at least 185° was necessary to cause peptization; with rubber and many organic liquids peptization becomes marked at 160°. Denaeyer[1] claims to have peptized coagulated albumin by heating it in water under pressure of one atmosphere. When silica is ground very fine, it is peptized by boiling water.[2] Water peptizes gelatine at about 30° and tannin instantaneously at ordinary temperatures. Pyroxylin is peptized by amyl acetate at ordinary temperatures. When a substance is peptized by water at moderate temperatures we call it a water-soluble colloid; but the phenomenon is general. Any substance which adsorbs a liquid will be peptized by that liquid at some temperature, provided decomposition does not take place before that temperature is reached. In the case of water and cellulose, it is not certain to what extent peptization takes place[3] before decomposition takes place. The metallic fogs[4] are apparently cases of peptization of liquid metals by melts at comparatively high temperatures.

Relatively little work has been done on direct peptization by means of a non-electrolyte; but a good deal of stress has been laid on the cases where a non-electrolyte prevents the formation of a visible precipitate.. In all these cases the non-electrolyte would cause peptization under favorable conditions, so I am going to take up a few of the cases here.

Graham[5] studied what he called the sucrate of copper. "The deep blue liquid obtained by adding potash to a mixed solution of chloride of copper and sugar appears to contain a colloidal substance. Placed on a dialyser for four days, the blue liquid became green, and no longer contained either

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[1] Jour. Chem. Soc., 60, 1269 (1891).

[2] Desch: The Chemistry and Testing of Cement, 58 (1911).

[3] Schwalbe: Die Chemie der Cellulose, 23 (1911).

[4] Lorenz: Gedenkboek aan van Bemmelen, 395.

[5] Jour. Chem. Soc., 15, 253 (1862).

potassium or chlorine; it, in fact, consisted of oxide of copper united with twice its weight of sugar. The external liquid remained colorless and gave no indication of copper when tested with sulphuretted hydrogen. The colloidal solution of sucrate of copper was sensitive in the extreme to pectizing agents. Salts and acids generally gave a bluish green precipitate; even acetic acid had that effect. The precipitate, or pectous sucrate after being well washed, consisted of copper oxide with about half its weight of sugar, and is therefore a subsucrate. When the green liquid is heated strongly, it gives a bluish green precipitate, and does not allow the copper to be readily reduced to the state of suboxide. The subsucrate of copper possesses considerable vivacity of color, and might be used as a pigment. A solution of sucrate of copper absorbs carbonic acid from the air with great avidity. The sucrate of copper dries up into transparent films of an emerald-green color. These films are not altered in appearance or dissolved in cold or boiling alcohol. In water they are resolved into sugar and the pectous subsucrate of copper.

"The perchloride of iron with an addition of sugar is not precipitated by potash, provided the temperature is not allowed to rise. The peroxide of iron combined with the sugar is colloidal, and remains on the dialyser without loss. At a certain stage, however, the sugar appears to leave the peroxide of iron, and a gelatinous subsucrate of iron pectizes. The subsucrate of iron thrown down from the soluble sucrate by the addition of sulphate of potash, consisted of about 22 parts of sugar to 78 parts of peroxide of iron.

"A similar solution may be obtained by adding potash to a mixture of the nitrate or chloride of uranium with sugar, avoiding heat. The solution is of a deep orange-yellow color, and on the dialyser soon loses the whole of its acid and alkali. This fluid sucrate has considerable stability, but, like the sucrate of copper, is readily pectized by salts. The subsucrate pectized has considerable solubility in pure water.

"The well-known solution of lime in sugar forms a solid coagulum when heated. It is probably, at a high temperature, entirely colloidal. The solution obtained on cooling passes through the septum, but requires a much longer time than a true crystalloid like the chloride of calcium."

Riffard[1] has based a method of analysis of sugar on the fact that sugar prevents the precipitation of hydrous ferric oxide from ferric chloride solution by ammonia. A weak point in the method is that invert sugar is about seven times as effective as cane sugar in holding up the hydrous ferric oxide. Grimaux[2] showed that glycerine prevents the precipitation of hydrous ferric oxide by caustic potash. Weisberg[3] found that calcium silicate appears to dissolve in a sugar solution. What really happens is that it is peptized by a sugar solution. Lobry de Bruyn[4] has prepared colloidal solutions of silver chromate and silver chloride in presence of sugar.

Peptization by a non-electrolyte is a familiar phenomenon in the pyroxylin industry, though even here the data are not in any way complete. Benzene, toluene, xylene, the petroleum naphthas, and the alcohols do not peptize cellulose nitrates. One may get peptization, however, by adding a liquid which does peptize pyroxylin. More interesting, however, is the case of alcohol and ether, neither of which peptizes collodion, while a mixture of the two does. Worden[5] says that "the literature contains many statements of the solubility of cellulose nitrates in ether, but the author has never been able to dissolve a pyroxylin in ether free from alcohol. The lower nitrated celluloses gelatinize, but attempts to filter such a gelatinized mass does not give a filtrate with a nitrogen-containing residue. As is well known, ether containing as small amount as 2 % of alcohol dissolves pyroxylin appreciably, and as alcohol is the usual impurity in commercial ether, from which it is removed only with difficulty, all statements of the solvent action of ether on the cellulose nitrates, in the

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[1] Comptes rendus, 77, 1103 (1873).

[2] Ibid., 98, 1485, 1540 (1884).

[3] Bull. Soc. chim. Paris, (3) 15, 1097 (1896).

[4] Ber. deutsch. chem. Ges., 35, 3079 (1902).

[5] Nitrocellulose Industry, 1, 167 (1911).

writer's judgment, should at least be accepted with some mental reservation. The phenomenon of two non-solvents, alcohol and ether, combining to a pyroxylin solvent is not an isolated instance, aqueous calcium chloride and alcohol, aniline and ether, phenol and ethyl alcohol, furnishing additional instances of two non-solvents uniting to a fluid of solvent action. The hygroscopicity and low boiling point (35°) would prevent the use of ether as a simple solvent, even if energetic."

Since ether is adsorbed by pyroxylin, it is probable that it would peptize the latter if the two were heated together in a sealed tube. If this is so, the problem then is to account for the fact that addition of alcohol lowers the temperature at which peptization takes place. There seems no reason to suppose that the alcohol exerts any appreciable effect on the cohesive power of the cotton; but, if not, we must then assume that it increases the disintegrating action of the ether. It seems to me quite probable that there is a greater difference of surface tension between ether adsorbed by pyroxylin and alcoholic ether than between ether adsorbed by pyroxylin and ether. If this be conceded, the increased peptization follows at once. While this is a plausible hypothesis, it should be tested quantitatively. Other cases are not unknown and many could probably be found if the matter were taken up systematically. Oudemanns[1] reports that cinchonine is more soluble in alcoholic chloroform than in alcohol or chloroform alone. It is at least a question whether he was not studying peptization[2] rather than one of solution. Galeotti and Giampalmo[3] found that zein is soluble in a mixture of alcohol and water, but not in either liquid alone. This is undoubtedly a case of peptization.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptize the adsorbing material and to give rise to a colloidal solution containing positively or

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[1] Zeit. anal. Chem., 11, 287 (1872).

[2] Bancroft: Jour. Phys. Chem., 18, 553 (1914).

[3] Zeit. Kolloidchemie, 3, 118 (1908).

negatively charged particles according to the nature of the ion adsorbed preferentially. According to Schulze's law[1] the adsorption of an ion depends primarily on its valence and is greater the higher the valence. In a previous paper,[2] I have shown that Schulze's law is merely a first approximation. Univalent ions are not all adsorbed alike; nor are bivalent ions or trivalent ions. The order of adsorption is specific with each colloid. Certain univalent ions are adsorbed by certain colloids more than certain bivalent or trivalent ions. In many cases there is, however, a marked tendency to increased adsorption with increasing valence. It seems to be a general rule that insoluble electrolytes show marked adsorption for their own ions. Consequently a soluble salt having an ion in common with a sparingly soluble electrolyte should tend to peptize the latter.

Lottermoser[3] titrated twentieth-molecular silver nitrate with twentieth-molecular potassium chloride, bromide, and iodide. With a slight excess of the alkali halide the silver halide remained in suspension. This was due to the adsorbed halogen ion as was shown by the fact that the colloidal silver halide moved to the anode under electrical stress. When a slight excess of silver nitrate was added to the alkali halide, the resulting silver halide remained suspended as in the previous case; but it then moved to the cathode under electrical stress, showing that it was the adsorbed silver ion which stabilized the colloidal solution. The potassium and nitrate ions are apparently adsorbed to a much less extent and Lottermoser considers that they may be neglected. This cannot be strictly true because a larger excess of silver nitrate or of alkali halide causes coagulation, which means the neutralization of the ion adsorbed preferentially.

A. Müller[4] peptized thorium hydroxide in thorium nitrate

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[1] Schulze: Jour. prakt. Chem., (2) 25, 431 (1882); 27, 320 (1884).

[2] Bancroft: Jour. Phys. Chem., 19, 363 (1915).

[3] Jour. prakt. Chem., (2) 68, 341 (1903); 72, 39 (1905); 73, 374 (1906); Zeit. phys. Chem., 62, 371 (1908).

[4] Ber. deutsch. chem. Ges., 39, 2857 (1906); Zeit. anorg. Chem., 52, 316 (1907).

solution and zirconium hydroxide in zirconium nitrate solution; and Szilard[1] peptized a number of the rare earth hydroxides by means of the chlorides or nitrates of the same elements. A chromic chloride solution appears to dissolve a certain amount of hydrous chromic oxide; but Nagel[2] has shown that the oxide is peptized and not dissolved. It seems probable therefore that we are dealing with colloidal solutions in many cases of what have hitherto been considered solutions of basic salts. Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash; but the green oxide can be filtered out completely by means of a collodion filter, a colorless solution passing through.[3] The oxide is therefore peptized and no chromite is formed. This is in accord with the earlier experiments of Fischer and Herz.[4] Hantzsch[5] considers that beryllium hydroxide is peptized by caustic potash. Hydrous copper oxide is apparently peptized to some extent by caustic alkali[6] and so is cobalt oxide.[7] In ammoniacal copper oxide solutions part of the copper oxide is apparently colloidal and part dissolved.[8] The case of zinc oxide is more complex. Hantzsch[9] claimed that alkaline solutions of zinc hydroxide were chiefly colloidal. Fischer and Herz[10] decided that they were partly colloidal, while Klein[11] maintained that a definite sodium zincate was formed. Hantzsch[12] was so impressed by Klein's arguments that he changed his views. From experi-

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[1] Jour. chim. phys., 5, 488, 636 (1907).

[2] Jour. Phys. Chem., 19, 569 (1915); cf. Graham: Jour. Chem. Soc., 15, 254 (1862); Fischer: Zeit. anorg. Chem., 40, 39 (1904).

[3] Nagel: Jour. Phys. Chem., 19, 331, 569 (1915).

[4] Zeit. anorg. Chem., 31, 352 (1902).

[5] Ibid., 30, 289 (1902).

[6] Loew: Zeit. anal. Chem., 8, 463 (1870); Fischer: Zeit. anorg. Chem., 40, 39 (1904).

[7] Tubandt: Zeit. anorg. Chem., 45, 368 (1905).

[8] Grimaux: Comptes rendus, 98, 1434 (1889).

[9] Zeit. anorg. Chem., 30, 289 (1902).

[10] Ibid., 31, 352 (1902).

[11] Ibid., 74, 157 (1912).

[12] Ibid., 75, 371 (1912).

ments in the Cornell laboratory, which will be published later, it seems probable that everybody was right. Freshly precipitated zinc hydroxide is peptized by alkali; but the solution is very instable, the zinc hydroxide often coagulating inside of half an hour. The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate. Depending on the moment selected for examination, the zinc oxide is chiefly colloidal, partly colloidal, or not colloidal at all. This was realized distinctly by Hantzsch[1] in his first paper; but he seems to have forgotten it later. The bulk of the evidence seems to be that alumina is not peptized appreciably by alkali and that it goes into solution as sodium aluminate,[2] though the other view has been supported.[3]

I have discussed the peptization of the hydrous oxides of chromium, beryllium, copper, cobalt, and zinc by alkali as a case of peptization by a common ion because we generally look upon these oxides as basic. This is not essential to the argument in any way. We can consider that these oxides are peptized by the preferentially adsorbed hydroxyl ion. We have to do this in the case of the peptization of silica or caseine by sodium hydroxide. Graham[4] points out that gelatinous silicic acid may be liquefied by contact with a very moderate amount of alkali. The change "is gradual, one part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100° C. Gelatinous stannic acid is also easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyser." This

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[1] Zeit. anorg. Chem., 30, 300 (1902).

[2] Herz: Zeit. anorg. Chem., 25, 155 (1900); Hantzsch: Ibid., 30, 289 (1902); Rubenbauer: Ibid., 30, 331 (1902); Fischer and Herz: Ibid., 31, 355 (1902); Slade: Jour. Chem. Soc., 93, 421 (1908); Zeit. anorg. Chem., 77, 457 (1912); Trans. Far. Soc., 10, 150 (1914); Blum: Jour. Am. Chem. Soc., 35, 1499 (1913).

[3] Mahin, Ingraham and Stewart: Jour. Am. Chem. Soc., 35, 30 (1913).

[4] Jour. Chem. Soc., 17, 324 (1864).

last statement is inaccurate because the silicic acid forms a jelly before all the caustic soda is removed since the caustic soda is what stabilizes the hydrosol. What happened was that it was necessary to have more than enough soda if peptization is not to take place very slowly. The excess of caustic soda can then be removed by dialysis.

A. Müller[1] has prepared colloidal solutions of aluminum, iron, cobalt, thorium, and yttrium oxides by peptization with dilute hydrochloric acid ($M/20$). Bentley and Rose[2] obtained a colloidal solution of alumina by treating freshly precipitated alumina with 8 percent acetic acid. Since these colloids are positively charged, they have been peptized by a cation, presumably by hydrogen ion. It is possible of course that a slight formation of an aluminum salt has occurred in the last case and that the aluminum salt is the peptizing agent; but this does not seem very probable.

The peptization of sulphides by hydrogen sulphide[3] is a case where we are dealing with peptization by a common ion, the sulphide or hydrosulphide ion being the one adsorbed. Spring[4] found that if copper sulphide, prepared by passing hydrogen sulphide through a dilute solution of copper sulphate in ammonia, is washed by decantation with water containing hydrogen sulphide, until the precipitate is perfectly free from ammoniacal salts, the copper sulphide dissolves, forming a dark brown solution. The solution may be boiled without decomposition, but the addition of small quantities of metallic salts causes the sulphide to precipitate. On evaporating the solution on a water bath, the copper sulphide remains as a dark resinous mass. If the copper sulphide is dried in a vacuum, it loses its property of dissolving in water. Pure dry copper sulphide has a dark green color. Under a pressure of 6500 atmospheres, it forms a dark blue compact mass, possessing metallic luster.

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[1] Svedberg: Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe, 400 (1909).

[2] Jour. Am. Chem. Soc., 35, 1490 (1913).

[3] Linder and Picton: Jour. Chem. Soc., 61, 114; Picton, 137 (1892).

[4] Ber. deutsch. chem. Ges., 16, 1142 (1883).

Prost[1] says that "colloidal cadmium can be prepared by completely precipitating an ammoniacal solution of cadmium sulphate with hydrogen sulphide, washing the sulphide with water by decantation, suspending the milky precipitate in water, and submitting it to a slow stream of hydrogen sulphide. The precipitate first becomes flocculent, then milky, and finally disappears entirely. The solution is then boiled until lead paper shows the absence of hydrogen sulphide. The solution is a beautiful golden yellow by transmitted light and fluorescent by reflected light. The composition of the dissolved substance is CdS. Dilute solutions remain unchanged for a long time. A solution containing four grams of sulphide to the liter remained clear many days; but another solution containing eleven grams to the liter coagulated in twenty-four hours."

Winssinger[2] states that colloidal zinc sulphide is easily obtained by washing freshly precipitated zinc sulphide with a dilute solution of hydrogen sulphide or by passing hydrogen sulphide through water containing pure zinc hydroxide in suspension. The solution is slightly opalescent, and can be boiled until the whole of the hydrogen sulphide is expelled without undergoing change; when boiled for a longer time the sulphide is precipitated, but, after cooling, it is readily dissolved when a stream of hydrogen sulphide is passed through the solution.

When authors state, as they so often do, that all the hydrogen sulphide can be removed without affecting the stability, they are speaking inaccurately. There must be an excess of hydrogen sulphide to cause peptization.[3] What they mean is that the unadsorbed hydrogen sulphide can be removed. Linder and Picton[4] showed that it was very difficult to remove all of the hydrogen sulphide even from the coagulated sulphides. "The first result of our experiments

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[1] Jour. Chem. Soc., 54, 653 (1888).

[2] Bull. Soc. chim. Paris, (3) 49, 452 (1888).

[3] Cf. Meunier: Comptes rendus, 124, 1151 (1897).

[4] Jour. Chem. Soc., 61, 116 (1892).

was to prove that excess of sulphur was present in these precipitates; it was also found that the amount is not always constant. As in many cases the excess was small, the question naturally arose as to whether this could be free sulphur liberated during precipitation. To lessen the chances of such precipitation, boiled water was used in many cases. The only certain proof, however, was to make a searching examination in one of the cases where sulphur might most readily be expected to be formed; and for this purpose mercury sulphide was chosen; it gives a very small excess of sulphur and the liability to deposit sulphur unless due precautions are taken is well known. The precipitate, after washing with alcohol, was carefully extracted with carbon bisulphide, but still yielded the same excess as before; and in order to obviate the objection that this extraction might be imperfect, another method more easily applied was used. This consisted in heating the precipitated compound in a current of hydrogen; in this way the sulphuretted hydrogen was driven off and absorbed by soda, and there was no longer any possibility of the excess being due to free sulphur. But though washed to all appearance perfectly free from sulphuretted hydrogen, it might yet perhaps be thought that some small quantity of the gas was mechanically retained in the interstices of the precipitate. As a final test, therefore, the precipitate, after complete washing, was extracted carefully with carbon bisulphide, washed free from every trace of carbon bisulphide, and then completely dried in a vacuum. The substance so dried still retained sulphuretted hydrogen, however, which was slowly given off on heating and collected in soda. The same result was obtained in this case as in the others. The sulphur is, therefore, without any doubt *combined* with the freshly precipitated sulphide in the form of sulphuretted hydrogen."

The possibility of peptization by an adsorbed salt seems to have been pretty generally overlooked in the books on colloid chemistry, presumably because an increase in the concentration of a peptizing salt is apt to cause coagulation. Theoretically the matter is quite simple. We start with an ion peptization because one ion is adsorbed more than the other. With increasing salt concentration we reach the point where the adsorption of the first ion varies but slightly with the concentration. The adsorption of the second ion continues to increase relatively to the first ion until we get what has been called neutralization of the adsorbed ion,[1] and consequently coagulation. At the same time the adsorbed salt is tending to peptize the substance; but if its peptizing action is relatively small, there may be quite a large range of concentrations over which the ion peptization has ceased to be effective and the salt peptization has not begun to be effective. With still greater salt concentration, we should expect to get salt peptization; but a number of disturbing factors may come in. The salt may not be sufficiently soluble at the temperature of the experiment or it may react with the substance to be peptized. If we increase the hydrochloric acid concentration with the oxides of aluminum, iron, cobalt, etc., we finally get the chlorides of these metals in true solution. If we increase the caustic soda concentration with silicic acid, we consider that we get sodium silicate in true solution. If we increase the potassium bromide concentration with silver bromide we say that we get a complex salt in true solution. It may be that we are wrong in this and that we are getting peptization in some of these cases. For years we thought that the so-called basic chlorides were definite compounds forming true solutions, whereas now we know that many of them are not.[2] With silver iodide and a concentrated silver nitrate solution[3] we apparently get a definite compound, $2AgNO_3.AgI$; with silver bromide also a definite compound, $AgNO_3.AgCl$; but it is not probable that there is any such compound as $18AgNO_3.AgCl$, so it may be that here we have a case of peptization by an undissociated electrolyte.

It is possible that von Weimarn's peptization of cellulose[4]

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[1] Bancroft: Jour. Phys. Chem., 19, 363 (1915).

[2] For optical turbidity see Picton and Linder: Jour. Chem. Soc., 61, 154 (1892).

[3] Risse: Liebig's Ann., 111, 39 (1859).

[4] Von Weimarn: Zeit. Kolloidchemie, 11, 41 (1912).

by salt solutions may come under this head. Three grams of cellulose were heated with about 100 cc concentrated salt solution and were thereby peptized, the mixture usually cooling to a jelly. With NaI, CaI_2, SrI_2, $CaBr_2$, $Ca(SCN)_2$ and $Ba(SCN)_2$ peptization took place at atmospheric pressure. With NaCl a temperature of 170° and a pressure of 8 atm. were necessary, and incipient decomposition seemed to take place. Deming[1] peptized cellulose with salts dissolved in acid solutions. In all these cases of possible peptization by undissociated salts, there may be an ion peptization and a water peptization superposed which, of course, complicates matters considerably. Oxides of mercury or less noble metals are adsorbed by mercury. I do not know any conditions under which they will peptize mercury unassisted, though it is very possible that this might take place at higher temperatures. If we disintegrate the mercury mechanically, it is possible to obtain a colloidal solution and here we unquestionably have an undissociated salt.

Under the general heading of peptization by a colloid, we can distinguish several types. The most important is peptization by a water-soluble colloid, such as gelatine, agar-agar, dextrine, etc. Gelatine peptizes freshly precipitated silver bromide. The effect seems to be more striking in presence of a slight excess of potassium bromide or silver nitrate, in which case one gets the ion peptization in addition. Eder[2] says: "If we precipitate silver bromide from a cold aqueous solution containing no gelatine or other similar substance, we get a coarse, compact precipitate which can easily be washed on a filter. If we pour this precipitate into a warm solution of gelatine and shake, the silver bromide disintegrates and forms a fine emulsion. Under these circumstances the silver bromide behaves differently, depending on whether it has been precipitated in presence of an excess of bromide or of silver salt. This difference is noticeable no matter how carefully the silver bromide is washed."

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[1] Jour. Am. Chem. Soc., 33, 1515 (1911).

[2] Eder's Handbuch der Photographie, 5th Ed., 31, 28 (1902).

Luppo-Cramer[1] points out that "the peptization of the silver iodide and silver bromide gels by the corresponding halogen ions takes place in quite a striking way in presence of gelatine. Starting from the coarsely flocculent silver bromide, obtained by precipitation in absence of a binder, we can obtain very fine-grained, homogeneous, though by no means colloidal, emulsions. Further experiments have shown that the same results can be obtained more rapidly with ammonia than with bromine ions. The reaction was carried on in precisely the same way as the preceding one, merely substituting 2 cc of ammonia (sp. gr. 0.91) for the bromide. The disintegration of the flocculent silver bromide in the gelatine took place immediately and the resulting completely homogeneous, creamy emulsion showed under the microscope (oil immersion) only very small particles which looked like fine splinters. Ammonia does not disintegrate the silver bromide in collodion, while an emulsion is very easily obtained under the influence of a bromide....

"The state of the silver bromide was of fundamental importance for the emulsification in gelatine by means of bromine ions and the same thing is true for the emulsification by means of ammonia. The silver bromide gel loses completely its peptizable properties just by standing. Samples which had stood for one, three, six, ten, and twelve hours in the dark at ordinary temperature showed a gradual decrease in the tendency to form an emulsion. After twelve hours' standing, no emulsion could be formed at all.

"If the silver bromide is formed from ammoniacal silver oxide instead of from silver nitrate, it differs in shape and color from that precipitated from a neutral solution and it cannot be peptized in presence of gelatine.[2] Even when not precipitated in presence of ammonia, it only requires a few minutes' shaking of the silver bromide with a very dilute solution of ammonia to bring the silver into such a state that

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[1] Phot. Correspondenz, 44, 578 (1907).

[2] [This should be repeated. It seems improbable that we have a full statement of the facts. W. D. B.]

ammonia does not cause an emulsification in presence of gelatine. Bromides cannot peptize a silver bromide precipitated from an ammoniacal silver oxide solution.

"Freshly precipitated silver iodide is quickly converted into an emulsion by the action of ammonia in presence of gelatine; but this does not take place after the silver iodide precipitate has stood for a day or two. An excess of silver nitrate at the time of precipitation has no appreciable effect on the peptizing action of ammonia on either silver bromide or silver iodide. The same thing is true in case the silver iodide is added after the precipitation and is then nearly all washed out of the precipitate."

Lefort and Thibault[1] found that mercuric sulphide precipitates rapidly when mercuric chloride is added to the sulphur springs at Bagnères de Luchon; but if solutions of gum arabic, sarsaparilla, wild cherry, beef tea, albumin, or apple jelly be added to the waters, no precipitation will take place on addition of mercuric chloride. It was thought at first that the non-precipitation of mercuric sulphide was due to the increased viscosity of the solution; but this was disproved by the fact that a precipitate is obtained if gum arabic is replaced by glycerine. Experiments with other sulphides showed that gum arabic prevents the precipitation of the sulphides of lead, silver, iron, manganese, mercury, copper, zinc, antimony, and arsenic, provided the solutions of the salts are dilute and that enough gum arabic is added. In presence of gum arabic, metallic hydroxides behave like sulphides.

"The formation of other precipitates is also prevented, as that of calcium phosphate in neutral solutions, uranium ferrocyanide, and ferric hydroxide when a dilute solution of ferric chloride is treated with ammonia. The alkaloids, quinine, cinchonine, morphine, strychnine, brucine, veratrine, are not precipitated by phospho-molybdic acid, potassium mercuric iodide, or tannin, in presence of gum arabic. . . . . The intense colorations produced on adding the reagent to the

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[1] Jour. Chem. Soc., 42, 1322 (1882).

metallic solutions containing gum, show that a reaction has taken place; it therefore remains to be proved whether the precipitation is soluble in gum arabic or held in suspension in an exceedingly fine state of subdivision. The authors are inclined to think that the latter is the more probable, since concentrated solutions of gum arabic fail to dissolve the precipitated substances even when recently formed." It is probable that the failure to obtain peptization was due to ignorance of the idiosyncrasies of the precipitates; but this matter certainly calls for more study. Wegelin[1] has overcome the cohesion of metals by grinding them with gelatine. So far as one can see this is a general method and can be applied in all cases where agglomeration has been too intense.

Lachaud[2] found that "dextrine is partially precipitated from its aqueous solutions by the addition of magnesia or any of the alkaline earth carbonates; but at the same time a part of the precipitating agent goes into solution. Similar results are obtained when solutions of such salts as aluminum sulphate, chrome alum, ferric sulphate, or lead nitrate are added to a solution of dextrine and then rendered alkaline with ammonia. Extended experiments with dextrine, ferric sulphate, and ammonia showed that the whole of the dextrine can be precipitated if the ferric hydroxide is in large excess; if, however, the dextrine is in large excess, no precipitate is formed, and all the iron remains in solution. Many other organic compounds behave in much the same way as dextrine." This seems to be exactly like the action of an alkaline chromic oxide solution on hydrous ferric oxide, which will be discussed a little later.

Saponin peptizes lead sulphate, barium carbonate, and other salts.[3] Soap peptizes rouge, charcoal, etc.[4] If a suspension of soot in water be filtered several times through filter paper, the water will finally run through clear and soot

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[1] Zeit. Kolloidchemie, 14, 65 (1914).

[2] Bull. Soc. chim. Paris, (3) 15, 1105 (1896).

[3] Schiaparelli: Jour. Chem. Soc., 46, 333 (1884).

[4] Spring: Zeit. Kolloidchemie, 4, 161 (1909); 6, 11, 109, 164 (1910).

will be held back by the filter paper. If a soap solution be poured on the filter, a black filtrate is obtained and the filter paper is no longer black. All the soot has passed through the filter paper. The same thing can be done with rouge except that a red filtrate is obtained instead of a black one. At first sight it seems as though the soap must have broken up the carbon or the rouge into finer particles, which then passed through the filter; but I think that this is erroneous. The filter paper is quite porous enough at first to let the particles of soot or rouge through, as is shown by the fact that some usually does pass through the filter at first. The cellulose adsorbs either carbon or rouge and this clogs the filter to such an extent that the pores are not large enough to let the remaining particles through. The soap removes the rouge or carbon from the paper because of its greater adsorbing power for these substances and everything goes through the paper. That this is the true explanation can be shown in two ways. In the first place the experiment does not succeed if the rouge or the carbon is too coarse. In the second place Spring showed that we are dealing with an adsorption of soot by filter paper. If the black filter paper be reversed and washed with water, only the carbon which is not in immediate contact with the paper is removed.

Aniline dyes which are insoluble in benzene can be peptized by a benzene-soluble colloid such as zinc or magnesium resinate so-called.[1]

It is a little uncertain whether albumin is to be called a water-soluble colloid or one peptized by an ion; but the latter is probably the better way of considering it. In the case of caseine there is no question. It is not soluble in water and is peptized by acids or alkalies. Both have been used as protecting colloids and would undoubtedly act as peptizing agents under favorable conditions. A more interesting case than either of these is that of hydrous chromic oxide, an alkali-soluble colloid.[2] Hydrous chromic oxide adsorbs the

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[1] Soxhlet: Art of Dyeing and Staining Marble, etc., 76 (1902).

[2] Northcote and Church: Jour. Chem. Soc., 6, 54 (1854); Nagel: Jour. Phys. Chem., 19, 331 (1915).

hydrous oxides of iron, nickel, cobalt, manganese, and copper; and consequently peptizes them to a certain extent, making them apparently soluble in caustic potash solution. The converse is also true, of course, that these hydrous oxides adsorb hydrous chromic oxide and consequently tend to make the latter apparently insoluble in caustic potash. When chromium salt is present in large excess relatively to the iron salt, no iron oxide is precipitated; when the iron salt is present in excess, no chromium oxide remains in the water phase, the latter becoming colorless. Colloidal copper oxide peptized by ammonia causes the peptization of hydrous chromic oxide by ammonia.[1] These cases are precisely analogous to that of dextrine and ferric hydroxide previously referred to.

Miss Hitchcock[2] points out that molybdic acid is not precipitated from its salts by uranyl salts while tungstic acid is. In presence of tungstic acid, however, practically all the molybdic acid is precipitated. This is obviously a case of adsorption and the converse is undoubtedly true that no tungstic acid would be precipitated in presence of a sufficient excess of a molybdate.[3]

Hydrous chromic oxide peptized by alkali forms a relatively stable colloidal solution. The ordinary ion-peptized solutions of arsenic sulphide and ferric oxide, for instance, are relatively instable. If a positively charged hydrosol of this type be mixed with a negatively charged one in suitable proportions, the two will be precipitated practically completely but this precipitate is peptized by an excess of either hydrosol.[4]

While I have made no effort to consider all possible cases, I think that I have taken up enough to show that we have a good working theory of peptization which is generally applicable. It is based explicitly on Freundlich's assumption

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[1] Prud'homme: Jour. Chem. Soc., 25, 672 (1872).

[2] Jour. Am. Chem. Soc., 17, 483, 520 (1895).

[3] Cf. Wöhler: Zeit. Elektrochemie, 16, 693 (1910).

[4] Freundlich: Kapillarchemie, 446 (1909).

that adsorption is accompanied by a lowering of the surface tension of the adsorbing phase. This is purely an empirical generalization and may not be true. If it should prove later not to be true, it will be a simple matter to restate this theory of peptization in terms of our wider knowledge; but there is nothing to be gained now by discussing that.

It will be well, however, to consider some points which have been brought out by others. Lottermoser[1] studied peptization by adsorbed ions and formulated the following general rule: "If one adds to an amorphous substance an ion—or a closely allied ion—at a higher concentration than the substance itself can generate in the solution, the substance will be converted back into a hydrosol. The essential condition for the success of this reaction is that the substance shall be in such a state that it is capable of swelling or of a decrease in the molecular complex by peptization or addition of the ion; in other words it must be in a definite physical state." The underlying idea is sound but the wording of it could hardly be worse. If the solid phase sends out ions into the solution up to equilibrium, any addition of a salt with a common ion will mean a higher concentration than the substance can generate and why not say so. If he means something else, why not say that? Of course the substance cannot generate a closely allied ion at all. It is also unfortunate, because inaccurate, to insist that the substance shall be amorphous. What Lottermoser really meant was that addition of a readily adsorbed ion will tend to cause peptization, though this is an empirical statement so far as he is concerned. If we bring in the lowering of the surface tension, we at least make the disintegration seem plausible. What Lottermoser says in regard to the physical state is the same thing as my statement that the agglomeration must not have proceeded too far. Both are non-committal phrases because we have no means as yet of measuring the property in question.

In his work on the stannic acids, Mecklenburg[2] has

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[1] Cf. Jour. Phys. Chem., 14, 17 (1910).

[2] Zeit. anorg. Chem., 74, 260 (1912).

brought out some very important facts in regard to agglomeration. "Adsorption is a surface phenomenon and becomes noticeable only when the adsorbing phase is very finely divided and consequently has a very large surface. The starting-point for a colloid chemical theory of the stannic acids is that under otherwise equal conditions the adsorbing power of a substance increases within certain limits[1] with increasing surface, in other words with increasing degree of dispersion. Since the five stannic acids [prepared at five temperatures] behave qualitatively alike but quantitatively different in regard to the adsorption of phosphoric acid, the five must differ in surface, and the size of grain must increase the higher the temperature of preparation. The 0° acid should have the finest grain and the 100° acid the coarsest; the 25° acid should approximate to the 0° acid and the 75° acid to the 100° acid, while the 50° acid should assume an intermediate position. This view is supported by the way in which the samples react with hydrochloric acid and by the fact that, when dried in air, the five stannic acids hold water more firmly and therefore contain more water, the lower the temperature of preparation.

"The conception of size of grain as here used calls for more discussion. In his classical contributions to our knowledge of colloids,[2] Zsigmondy has pointed out that the precipitation of colloids from solutions may occur either because the single particles agglomerate to complexes in which each particle keeps its identity or because the single particles themselves become larger just as crystals grow in a supersaturated solution.

"The colloid chemist is not unfamiliar with cases of the first sort, instances of which probably occur with stannic acids, as was pointed out in the first paper on the isomerism of the stannic acids. Zsigmondy[3] himself has recently studied

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[1] If this assumption were true without limit, the adsorbing power would be greatest when the substance was disintegrated to the molecules or ions. This seems not to be the case.

[2] Zsigmondy: Zur Erkentniss der Kolloide, 13, 175 (1905).

[3] Zeit. anorg. Chem., 71, 356 (1911).

the silicic acid gel with the ultra-microscope and has come to the conclusion that the particles forming the clear transparent gel are amicrons, in other words, so small that they cannot even be detected by means of the ultra-microscope. This result is not to be reconciled with the conclusion that gelatinization results from the increase in size of the single particles. An additional argument is that red colloidal gold solutions become blue before coagulating, for according to Maxwell Garnett a gold sol which contains very small and widely scattered gold spheres should be red, while it should turn blue if the particles agglomerate to larger complexes. As a matter of fact Steubing[1] has made the observation that, while the particles of a red-gold sol appear round when examined in the ultra-microscope, the particles of the blue-gold sols show peculiar distortions—an observation which fits in well with the theory under discussion.

"If the individuality of the single or 'primary' particles of the stannic acid do not remain when the primary particles agglomerate to secondary particles, it is not easy to see why the relative surfaces of the five stannic acids should depend even after coagulation on the temperatures at which the stannic sulphate hydrolyzed. One would rather assume that the adsorption would depend on the greater or less care with which the solid masses afterwards were pulverized. As a matter of fact direct proof can be given that the microscopic size of the grains of the secondary particles has nothing to do with the surface of the primary particles as measured by adsorption. This proof is given by determining the volume occupied by one gram. Into weighed measuring glasses of 10 cc capacity and graduated to 0.1 cc, there were placed 2 cc portions of the stannic acids in the form in which they were used for the other experiments. By tapping carefully on the tops of the glasses the stannic acids were made to settle to the minimum volume. Then another 2 cc of the powder was added and made to settle; this was repeated until the measur-

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[1] Drude's Ann., 26, 339 (1908).

ing glasses were practically full, after which the volumes were read off and the weights determined. Especial stress was laid on making the experiments as uniform as possible. The [mean of the] data are given in Table I.

TABLE I

Sample	Weight in grams	Volume in cc	Specific volume in cc
0° acid	12.27	9.12	0.74
25° acid	22.58	9.27	0.41
50° acid	16.55	9.52	0.58
75° acid	15.08	9.86	0.65
100° acid	8.56	9.26	1.08

"The figures show that the 100° acid is by far the most bulky, which is the more surprising because it has the largest content of the denser SnO_2 [less water]. The 25° acid, which contains relatively little SnO_2, is the densest. The 50° acid is more bulky and then come the 75° acid and the 0° acid. The bulkiness of the powder as thus measured is a haphazard value depending primarily on the resistance to grinding. Though it may be used as an approximate measure of the microscopic fineness of the powder, it of course has nothing to do with the temperature at which the sample was prepared and has no connection with the size of grain as determined by the behavior towards hydrochloric acid or by the adsorption of phosphoric acid.

"This lack of connection between the microscopic size of grain of fine powders and their activity is confirmed by very interesting experiments in an entirely different field. In Lothar Wöhler's laboratory Pluddeman[1] showed that the catalytic action of the oxides Cr_2O_3, Fe_2O_3, etc., on the reaction $2SO_2 + O_2 \longrightarrow 2SO_3$ does not stand in any relation to the size of the particles even with the same catalytic agent. The surface on which this surface action depends must there-

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[1] Dissertation Techn. Hochschule Karlsruhe (1907).

fore lie deeper, a point which is of great importance for the surface action theory of catalytic agents.[1]

"According to the theory of primary and secondary particles the peptization of the stannic acids consists in the splitting up of the secondary particles into the primary particles. It does not seem necessary, however, that the breakdown of the secondary particles shall be complete; a colloidal solution will be formed whenever the disintegration has gone so far that the products, whether they be primary particles or aggregates thereof, can be kept floating in the liquid under the existing conditions. This conception of the process of peptization makes intelligible a number of phenomena which were difficult to account for on the usual theory which makes no distinction between primary and secondary particles. According to the old conception a stannic acid must be peptized more readily the greater its power of adsorption, a conclusion which is not confirmed by experiment, for the 100° acid is not perceptibly more difficult to peptize than the 0° acid, and the 50° acid is not characterized by a lesser power of adsorption even though it is much less readily peptized than any of the other four standard samples. According to the theory of primary and secondary particles, the readiness with which a substance is peptized varies inversely with the force with which the primary particles are held together in the secondary complex. It has nothing to

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[1] In connection with this the fact may be recalled that the natural inorganic products such as cassiterite, chromite, corundum, etc., even when very finely powdered are much less readily attacked by chemical reagents than the corresponding synthetic compounds. Here also the size of the grain, on which the behavior of these substances depends primarily, seems to be beyond the limit to be reached by mechanical disintegration. The crystal fragments produced by the very best grinding, are still very much larger than the primary particles of the synthetic products. The fact that the laboratory products are not crystalline does not prevent a comparison between the natural and the synthetic products because it has been proved for silver iodide by Tammann [Zeit. phys. Chem., 75, 740 (1911)] and has been made probable for silicon by Wilke [Wallach-Festschrift, 682 (1909)] that these substances which are usually considered amorphous are really "cryptocrystalline."

do with the absolute size of the secondary particles,[1] a value which is not defined in any way."

This statement of Mecklenburg brings out pretty clearly how much we have yet to learn in regard to agglomeration and to cohesion in agglomerated particles. The surface for adsorption depends on the porosity. With a metal, which is not porous, the surface is increased enormously by grinding. With a porous material like charcoal, grinding has an almost negligible effect on the degree of adsorption. A colloidal mass, which has only just agglomerated, can often be peptized without difficulty. If the coalescing surfaces are allowed to set or if the substance is heated so that sintering takes place, peptization becomes extremely difficult.

A theory of peptization has been put forward by von Weimarn.[2] He considers that the solid always dissolves in the peptizing agent, forming instable compounds which then break down, the precipitate forming a hydrosol. According to this view all methods of making sols are really condensation methods, the so-called dispersion methods really involving solution and then condensation. According to von Weimarn the necessary and sufficient conditions for peptization are:

1. The solid crystalline substance must consist of such small crystals that the physical and chemical properties vary with the size of the crystals.

2. The peptizing substance must have the power at sufficiently high concentrations to form a stable, soluble, chemical compound with the substance which is peptized. When the concentration of the peptizing agent is sufficiently low, no such compound must be formed.

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[1] It is self-evident that when secondary particles are hard to peptize they disintegrate slowly and a longer action of the solvent is necessary to produce a colloidal solution. This is not a factor in the present discussion, however. The resistance to peptization of the 50° acid stands in no relation to the specific volume as measured. The 25° acid which is easily peptized is considerably denser (1/0.41 than the 50° acid (1/0.58)). When the 50° acid was ground further in an agate mortar, the specific volume was brought to the relatively high value of 0.87; but the resistance to peptization was not changed perceptibly.

[2] Zur Lehre von den Zuständen der Materie, 1, 60 (1914).

3. The medium in which peptization takes place must have practically no solvent action on the substance to be peptized when no peptizing agent is present.

It is true that soluble compounds may be formed in many cases when the peptizing agent is present in high concentration. Instances of this are alumina and hydrochloric acid, silica and caustic soda, silver bromide and potassium bromide; but there seems to be no reason to assume that soap forms a definite chemical compound with carbon, gold with gelatine, or chromic oxide with the oxides of iron, cobalt, copper, etc. In the cases of mechanical disintegration there is not necessarily any solution and subsequent precipitation. So far as I can see the hypothesis of an intermediate soluble compound does not account for the fact that in alkaline solutions hydrous chromic oxide will peptize a relatively small amount of hydrous ferric oxide; but will be carried down completely by a relatively large amount of ferric oxide. In fact von Weimarn has overlooked the conditions for the stability of a colloidal solution completely and he seems also not to have taken into account the peptizing action of the solvent. For these and other reasons I consider that von Weimarn's theory of peptization is inadequate.

The general results of this paper are as follows:

1. If we adopt Freundlich's generalization that adsorption involves a lowering of the surface tension of the adsorbing phase, a theory of peptization follows at once.

2. If Freundlich's generalization proves not to be universally true, it will be easy to modify the theory of peptization so as to account for the new facts.

3. Any substance which is adsorbed by a second will tend to disintegrate or peptize the latter.

4. We may have peptization by a solvent; by a dissolved non-electrolyte; by an ion; by an undissociated salt; by a colloid.

5. Adsorption decreases in general with rising temperature; but so does the cohesion of the adsorbing substance. We may therefore have peptization by a solvent at high tem-

peratures when we do not get it at lower ones. Instances of this are glass and water, vulcanized rubber and many organic solvents, gelatine and water.

6. Instances of peptization by a dissolved non-electrolyte are sugar or glycerine and hydroxides in water, ether and pyroxylin in alcohol.

7. Typical cases under ion peptization in water are silver bromide and potassium bromide, silica or chromic oxide and caustic potash, alumina and acids, chromic oxide and chromic chloride.

8. No cases of peptization by a soluble undissociated salt have been studied as such. If impure mercury is shaken with water we get peptization by an oxide film.

9. Typical instances of peptization by a colloid in water are silver bromide and gelatine, alkaline chromic oxide and hydrous ferric oxide, gold and stannic oxide.

10. Since the adsorption depends on the surface and since peptization involves breaking down the cohesion of particles, there is no necessary connection between amount of adsorption and ease of peptization.

11. A coarse-grained porous precipitate may be peptized more readily than the same mass in a more dense form.

12. Von Weimarn's theory of peptization is inadequate.

Cornell University

THE EQUILIBRIUM BETWEEN MUCIC ACID AND ITS LACTONES[1]

BY W. A. TAYLOR AND S. F. ACREE

In taking up the study of the mechanism of the reactions involved in the oxidation and reduction of sugars and their derivatives, it became necessary to study the equilibrium between the sugar acids and their dehydration products, including the lactones.

In attempting to determine the solubility of mucic acid in water we found that some lactone was formed in the solution at once and that the amount of lactone was greatly increased if the solution were boiled. We also saw that after some time equilibrium was established between the acid and lactone.

A quantitative study of this equilibrium was then taken up. In this work we made up three different solutions of mucic acid at different temperatures. In all three instances we had an excess of acid present. The first was made up at room temperature, the second was kept at 30° for one hour, and the third at 100° for 30 minutes. All three were placed in a constant temperature bath at 25° and shaken from time to time. Measured quantities were withdrawn from each for titration after definite time periods. A piece of filter paper was tied over the end of the pipette to keep the solid particles of acid from being drawn up. It was found that if the solution were poured into ice water the mucic acid could be titrated with standard alkali without affecting the lactone. To determine the amount of lactone present in the solution an excess of standard alkali was added, the solution boiled for a few minutes, and the excess alkali tritated with $N/10$ hydrochloric acid. Phenolphthalein was used as the indicator.

In the following table we give the time t in hours, the

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

amount of *N*/10 alkali necessary to neutralize the free acid and the amount necessary to neutralize the lactone. The amount of the solutions withdrawn for titration was, in each case, 25 cc.

Solution Made Up at Room Temperature

t	Cc alkali necessary to neutralize acid	Cc alkali necessary to neutralize lactone
2	1.63	0.25
4.5	1.70	0.68
28.5	1.65	0.81
52	1.60	1.00
100	1.62	1.16
172	1.64	1.46
258	1.55	1.85
720	1.55	2.13
1440	1.65	3.39

Solution Kept at 30° for 1 Hour

t	Cc alkali necessary to neutralize acid	Cc alkali necessary to neutralize lactone
3	1.90	0.80
26	1.82	0.78
50	1.70	0.90
74	1.68	1.20
146	1.67	1.42
242	1.65	1.69
1440	1.65	3.21

Solution Kept at 100° for 30 Minutes

t	Cc alkali necessary to neutralize acid	Cc alkali necessary to neutralize lactone
3	20.93	19.07
5	19.63	18.95
27	11.12	19.50
51	8.46	17.02
99	7.12	17.62
171	6.00	16.75
267	5.40	14.55
1440	3.76	9.99
2880	1.66	3.42

From these data it is seen that practically the same equilibrium is reached in all three experiments, the first two solutions taking 1,440 hours, while for the third it required 2,880 hours, because of supersaturation phenomena. At equilibrium it required 1.65 cc of alkali to neutralize the free acid and an average of 3.34 cc to neutralize the lactone, so that there are almost exactly twice as many lactone groups as of the carboxyl groups in the solution. It will also be seen from the table that the amount of acid in the first two solutions remains nearly constant throughout, while the amount of lactone steadily increases. In the third solution both the acid and lactone gradually decrease in amount. Whether this lactone is the mono- or di-lactone, or both, we cannot tell from the data but we shall investigate the reaction velocities of the mucic acid, its mono-lactone, and its di-lactone, and shall study some of the monobasic acids to follow the rate of formation of the lactone in those cases in which we can have only the mono compound resulting.

Mr. B. A. Beatty is continuing this investigation under our joint direction, by the use of both conductivity methods and those outlined above, in order to learn whether acids catalyze these changes through the action of the hydrogen ions, or the nonionized molecules, or both.

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THE EFFECT OF TEMPERATURE ON THE FORMATION OF BENZENE, TOLUENE, XYLENE, NAPHTHALENE, AND ANTHRACENE FROM PETROLEUM AT ATMOSPHERIC PRESSURE

BY GUSTAV EGLOFF AND THOMAS J. TWOMEY

Up to the present writing numerous investigators[1] have shown only in a general manner the effect of temperature at atmospheric pressure on the individual aromatic formation from petroleum. It has been pointed out that low temperature "cracking" processes produce either gasoline or the low boiling aromatics—benzene, toluene and xylene—mixed with gasoline with the major portion of the original high boiling oil changed but slightly, and no naphthalene or anthracene formation. Moderately high temperatures resulted in a "cracked" oil containing benzene, toluene, and xylene, relatively free from gasoline, but with the amount of benzene predominating. Naphthalene and anthracene occurred but in quantities less than that of benzene and its homologues. High temperatures, according to experimental evidence, gave relatively large yields of naphthalene and anthracene with a lesser production of the lighter aromatic compounds. These facts, covering a period of the last sixty or seventy years, are to be found generally in the literature.

Due to the European war, which has increased tremendously the demand for benzene and toluene for the manufacture of explosives, attention has been concentrated on the production of these compounds either directly from the cracking of petroleum or indirectly as by-products in the making of gas from petroleum, and coke and gas from coal. Thus it is extremely important that knowledge of the effect of the various factors on the individual aromatic formation be found. With definite data of this kind it would be possible to obtain a max-

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[1] References in Historical Review.

imum yield of the desired aromatic from a given amount of oil.

With one or two exceptions aromatic compounds have been made by the cracking of petroleum at atmospheric pressure either in experimental research or as by-products in the manufacture of gas. Under this condition the factors which influence the formation are (1) temperature, (2) rate of feed, (3) nature of the oil, and (4) the size of the cracking area. Of these factors temperature has the largest effect on the individual aromatic formation. *Hence, the object of this paper was to find the effect of temperature on the formation of benzene, toluene, xylene, naphthalene,* and *anthracene* from petroleum with all other factors held constant.

It is hoped that the data obtained in this research will furnish further evidence for the theory of cracking, and that it will encourage the manufacturers of gas from petroleum to develop the by-product production of their tars and liquid hydrocarbons to a maximum.

Historical

In this historical sketch a review of the research on the production of aromatics from the cracking of petroleum and other mineral oils will be given. The object in mind is to show that this formation as influenced by the various factors has been indicated but slightly by any one investigator. From an analysis of the data which has come to our notice certain regularities in the relationship between the individual aromatics in the cracked oil, depending on the conditions of production, will be brought forth.

The Philosophical Transactions of the Royal Society of London for 1825, page 440, contains a paper "On New Compounds of Carbon and Hydrogen and On Certain Other Products Obtained during the Decomposition of Oil by Heat" by Michael Faraday, which will ever be memorable due to the fact that one of the new compounds described was benzene. In 1825 the Portable Gas Company of London prepared gas by decomposing a mixture of fish and vegetable oils. Faraday states that in the operation of the company when the oil gas was compressed, a fluid deposited which could be drawn off and preserved in the liquid state. Nearly one gallon of oil was obtained from 1,000 cu. ft. of gas compressed. The pressure used was 30 atmospheres. By fractional distillation of this fluid and by freezing the portion boiling between 185° and 190° F (85° and 88° C) a compound was separated which he called "Bi-Carburet of Hydrogen." It had a specific gravity of 0.85 at 60° F (15.5° C), freezing point at 32° F (0° C), and in fact the main properties by which benzene is identified at the present day. The recovered fluid from the gas, specific gravity 0.821, was attacked by sulphuric acid with the evolution of much heat forming a black acid sludge as the lower layer, in a two-layer system which resulted. This action with sulphuric acid is very characteristic of a cracked oil. The work of Faraday's besides resulting in the discovery of benzene is also very important in the history of oil cracking because it demonstrated for the first time that aromatic compounds may be obtained by the cracking of a fish or vegetable oil.

No further work was conducted until 1864, when papers by H. Tuttschew[1] and Vohl[2] appeared, giving the results of passing oil vapors through red-hot tubes. The production of a permanent gas was noted but no attempt was made to analyze the recovered tar.

The first publication of importance was that of Letny.[3] He passed Baku petroleum residue, specific gravity 0.870 and boiling above 270° C, through an iron tube seven feet in length and one foot in diameter, and recovered a tar having a specific gravity of 1.015 to 1.200. The analysis of the tar is given in Table 1.

Besides the tar a liquid was also obtained, specific gravity 0.904, which began to boil at 70° C and consisted of ben-

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[1] Jour. prakt. Chem., 93, 394 (1864).

[2] Dingl. poly. Jour., 177, 58 (1865).

[3] Ibid., 229, 353 (1878).

zene, toluene, xylene, cumene, and naphthalene. It was free from any higher boiling compounds.

TABLE I

Below 200° C	2.3 percent water 4.6 percent benzene 5.2 percent toluene
200°–270° C 270°–340° C	naphthalene and unchanged petroleum
The portion distilling above 340° C was collected in three fractions.	
(*a*) 12.0 percent	9.3 percent petroleum 2.7 percent crude phenanthrene 0.76 percent pure phenanthrene
(*b*) 7.5 percent	5.2 percent petroleum 2.4 percent crude phenanthrene 0.8 percent pure phenanthrene
(*c*) 8.0 percent	6.04 percent petroleum 1.94 percent crude phenanthrene

Two experiments were quoted with tubes four feet in length, one being two and the other one inch in diameter. Using the former, 100 grams of petroleum gave 23.9 grams of tar, specific gravity 0.880, and 30.1 liters of gas; whereas with the latter, 100 grams of petroleum yielded 46.4 grams of tar, specific gravity 0.890, and 54 liters of gas. When the tube was packed with platinized carbon, 100 grams of petroleum gave 66.0 grams of tar, specific gravity 0.890, and 75.2 liters of gas. The analysis of these tars showed the presence of benzene, toluene and xylene, but no naphthalene or anthracene. One distillation record in which no gravities were given indicates, however, that slightly more toluene than benzene was formed in the recovered tar.

Letny's results cannot be compared directly because there is no statement that the rate of flow of the oil into the tube was constant in each case, and that the same temperature was employed. Moreover, different size retorts were used. On the assumption that the specific gravities represent the combined effects of temperature, rate of feed, and size of retort and that these gravities could have been obtained by temperature effect alone—an assumption we know to be true from our own work—it is possible to point out some interesting facts from his data. High gravity of the tar, meaning a high temperature employed, gave naphthalene and phenanthrene, while low gravity corresponding to low temperature used did not result in the formation of these compounds. And with low temperatures there was greater toluene than benzene formation.

That same year Atterburg[1] passed Swedish wood tar through an iron tube filled with coke heated to a dull redness in one case and to a bright redness in another. "At a bright red heat a tar was obtained which contained all of the products to be found in coal tar. The tar was rich in naphthalene and contained much anthracene. The recovery was about 25.0 percent. At a dull red heat, 50–60 percent recovery was obtained consisting of a light oil which began to boil at 58.0° C. It contained 10.0 percent toluene with trace of benzene, no naphthalene and 0.3 percent anthracene." In a general way these results are quite similar to those obtained by Letny. They show in two distinct instances the effect of temperature on benzene, toluene, naphthalene and anthracene formation.

Two other papers—by Salzmann and Wickelhaus[2] and by Lieberman and Burg[3]—the former on the preparation of benzene from lignite tar oil which corresponds to shale oil, and the latter on the decomposition of lignite tar oil at white heat, appeared at this time. The tars were passed through heated iron tubes, and cracked tars were obtained containing aromatic compounds. As the distillation cuts were taken between very wide temperature limits, they cannot be made to show the relationship existing between the individual aromatics.

In 1884, in England, attention was turned toward the analysis of tar and "hydrocarbon" oil produced as a by-

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[1] Ber. deutsch. chem. Ges., 11, 1222 (1878).

[2] Ibid., 11, 1431 (1878).

[3] Ibid., 11, 723 (1878).

product in the manufacture of Pintsch gas, an industry which had been in vogue only a few years. Pintsch gas is made by decomposing petroleum or shale oil with heat, contains a high percentage of illuminants, and is used extensively in the lighting of railroad coaches. Armstrong[1] found that the "hydrocarbon" oil—the liquid deposited in a chamber immediately attached to the pumps and also in the gas containers—and the tar contained benzene, toluene, xylene, trimethyl benzene, pseudocumene, mesitylene and naphthalene. Benzene was present in the largest quantities. Only traces of paraffins, traces of pseudoolefins, large amounts of amylene, hexylene, heptylene, crotonylene and similar compounds of the last type were found to be present. Among one of Armstrong's conclusions was that high temperatures are necessary for the formation of benzene and anthracene.

In the making of Pintsch gas the temperature has a big effect upon the composition of the "hydrocarbon" oil and tar produced. This is brought out by Williams[2] who analyzed several samples of the hydrocarbon oil. The results follow in Table 2:

TABLE 2

No. sample	Specific gravity	Percent benzene and toluene
A	0.850	65.6
B	0.835	54.2
C	0.840	52.0
D	0.830	45.2
E	0.840	44.4
F	0.800	37.8
G	0.760	24.6

While Williams did not give the temperatures under which the oils were obtained, we know that the gravity of the samples represents the relative heats to which the oils were subjected. The analysis brings out that the amounts of benzene and toluene increase with temperature. Very inter-

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[1] Armstrong and Miller: Jour. Chem. Soc., 49, 74 (1886).

[2] Chem. News, 49, 197 (1884).

esting data indeed would have been obtained if the separate quantities of benzene and toluene had been determined in each sample.

Due to economic conditions, the first attempt to commercialize the production of aromatics from petroleum occurred in Russia. Since oil is obtained in large quantities, it is used in the place of coal for the manufacture of gas, and hence scarcity of coal-tar products result. For this reason Russian chemists have concentrated much attention on the manufacture of benzene and allied products from petroleum. The development in Russia which began about 1885 has continued to the present time.

Before mentioning the work of the Russian chemists, the publication of Lewes[1] will be taken up. Lewes cracked Russian petroleum in an iron retort, 10 feet in length and four inch diameter, at 500°, 700°, 900° and 1,000° C, the temperature being judged by the color of the retort. A distillate oil, specific gravity 0.864, was used. The results follow in Table 3:

TABLE 3

Temp.	500° C	700° C	900° C	1000° C
Percent recovered oil	59.1	22.7	12.7	11.8
Sp. gr. recovered oil	0.866	0.908	0.926	1.019
Distillation				
110° C	—	—	1.6	—
120°	—	—	5.0	—
125°	—	9.0	3.3	—
130°	—	1.0	3.3	—
135°	—	2.0	5.0	—
140°	—	1.3	3.3	—
150°	4.0	9.5	6.6	10.0
160°	3.5	4.0	5.0	1.0
170°	0.5	1.5	6.6	2.5
180°	2.5	3.5	5.0	2.0
190°	3.0	3.0	—	—
200°	2.0	2.0	—	1.0

As would be expected the gravity of the recovered oil increased with temperature, while the percent of recovered

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[1] Jour. Soc. Chem. Ind., 11, 584 (1892).

oil decreased. The maximum decrease in the latter occurred between 500° and 700° C, beyond which point the percent of recovered oil decreased at a much slower rate with increase in temperature. As an analysis of the cracked oil, the distillation record with no description of the method and with no gravities means practically nothing, except to show that the higher the temperature employed the greater the extent of the cracking reaction. It is mentioned that the distillate up to 200° C did contain a large percentage of aromatics. From this statement and from the distillation record it seems that the lower temperatures give more xylene than toluene and more toluene than benzene.

The measurement of temperature by eye is not accurate and to all appearances the temperatures indicated for the experiments were lower than was given.

The Russian chemists, although they have published considerable concerning the commercial processes developed have disclosed but little data which can be used to illustrate the desired points in this paper. The method of Nikiforoff[1] is the most important. A typical analysis of a cracked oil obtained by that process yielded 12.0 percent benzene, 2.0 percent naphthalene and 0.5 percent anthracene. Using the same method, but on a larger scale, Zelinsky[2] obtained from cracking a Russian petroleum a cracked oil, of which 14.1 percent distilled up to 180° C. This fraction contained 58.0 percent benzene and 28.0 percent toluene. Dzwienwonski[3] analyzed a gas tar obtained from a Galician mineral residue and found "1.2 percent benzene, 0.88 percent benzene and toluene, some xylene, 6.0 percent naphthalene, and considerable amounts of anthracene." According to Redwood,[4] the Nobel plant at Baku, Russia, obtained by cracking petroleum, from which the kerosene and lighter constituents had been removed, 30-40 percent tar which contained 15 to 17

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[1] Chem. Ztg., 20, 8 (1896).

[2] Ibid., 26, 68 (1902).

[3] Naphtha, 385, 405 (1901).

[4] Jour. Soc. Chem. Ind., 4, 75 (1885).

percent fifty percent benzene. On cracking, this tar, after the benzene had been removed, gave 7 to 10 percent benzene, 16 percent naphthalene, and 2 to 3 percent anthracene. In the manufacture of gas from petroleum at Kasan, Russia, W. Rudnew[1] states that a tar was obtained containing 10–12 percent benzene and 5.0 percent naphthalene.

The Russian processes for the production of aromatics from petroleum either directly or indirectly from gas manufacture seem to give uniformly more benzene than toluene, and also naphthalene and anthracene. No definite data were found concerning the temperature of the cracking, or the rate of feed. Judging from the percent of tar recovered in a few instances, one would expect more benzene than toluene to be produced.

Pamfilow[2] passed petroleum through a hot tube. He states generally that low temperatures yield large quantities of tar containing aromatic compounds mixed with large amounts of paraffins and olefins. Under the same conditions high temperatures produced considerable yields of naphthalene, little anthracene, and but little benzene.

The paper by Dvorkovitch[3] delivered before a group of British gas engineers is valuable in relation to the present communication. Different Russian distillate oils were passed through two horizontal pipes, one above the other and connected together. At the end of one pipe was a condenser in which the cracked oil was collected. The results are given in Table 4.

From the distillation records it is difficult to determine the quantitative relationship between the individual aromatics. The cut 79° to 83° C does not contain all of the benzene, neither does the cut 109°–113° all the toluene. Although stating that the gravities of the cuts did show the presence of aromatics, he neglected to give them. The data, however, are interesting, because they show in a measure the effect of temperature on the cracking reaction.

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[1] Dingl. poly. Jour., 239, 72 (1881).

[2] Chem. Ztg., 1069 (1897); Russ. Priv., 13, 322, Sept. (1897).

[3] Jour. Soc. Chem. Ind., 12, 5, 403 (1893).

TABLE 4

Temp.	1600° F	1300° F	1300° F
Sp. gr. oil used	0.863	0.885	0.899
Percent of rec. oil	32.0	37.5	38.0
Cu ft. gas	126.0	69.8	69.0
Distillation			
60°–79° C	7.0	5.9	2.05
83°	1.7	1.2	1.02
109°	10.0	7.0	16.44
113°	2.66	2.56	1.88
135°	11.0	9.06	9.41
143°	2.33	3.17	2.23
215°	21.66	14.95	13.69
225°	2.66	3.17	4.45

The modern era has witnessed the first complete comprehensive study of the cracking of petroleum. Dr. W. F. Rittman, chief of the petroleum section of the Bureau of Mines at Pittsburg, Pa., published in the November issue of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY a paper entitled "Thermal Reactions of Petroleum Hydrocarbons in the Vapor Phase,"[1] in which are given the data obtained by cracking petroleum from different sources at different temperatures and under different pressures. In this review we are only interested in his results in so far as they show the individual aromatic formation at different temperatures and at atmospheric pressure. These results are tabulated in Table 5.

The data in this table are the best that have ever been published from which the individual aromatic formation may be pointed out. While the quantitative amounts of benzene, toluene, xylene and naphthalene are not given, the distillation cuts with the gravities may be safely used for this purpose. The distillations were conducted using an efficient fractionating column. This method resulted in the separation of the aromatics from each other. As is seen from the table, the cracked oil was distilled making cuts to 100° C, and then every 50° C up to 300° C. The gravities of each

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[1] Jour. Ind. Eng. Chem., 7, 945 (1915).

TABLE 5

Temperature of "Cracking"—500° C

Oil used	Pennsylvania		Oklahoma		California	
Oil recovered (per cent)	94.5		99.0		91.3	
Sp. gr. of oil recovered	0.799		0.872		0.939	
Distillation Temperature	Per cent	Sp. gr.	Per cent	Sp. gr.	Per cent	Sp. gr.
100°	1.0	0.718	2.3	0.724	3.2	0.727
150°	6.7	0.761	2.7	0.766	4.5	0.785
200°	42.5	0.787	4.2	0.802	5.3	0.824
250°	38.0	0.814	11.8	0.835	8.8	0.865
300°	—	..	11.2	—	13.2	0.891

Temperature of "Cracking"—600° C

Oil used	Pennsylvania		Oklahoma		California	
Oil recovered (per cent)	59.9		50.8		46.6	
Sp. gr. of oil recovered	0.840		0.906		0.966	
Distillation Temperature	Per cent	Sp. gr.	Per cent	Sp. gr.	Per cent	Sp. gr.
100°	8.7	0.759	10.3	0.769	8.3	0.767
150°	18.5	0.803	15.0	0.817	14.5	0.831
200°	36.5	0.815	10.5	0.840	8.0	0.861
250°	23.5	0.850	11.2	0.872	12.0	0.902
300°	5.7	0.901	14.0	0.894	15.5	0.937

Temperature of "Cracking"—750° C

Oil used	Pennsylvania		Oklahoma		California	
Oil recovered (per cent)	16.5		17.5		20.9	
Sp. gr. of oil recovered	1.012		1.039		1.092	
Distillation Temperature	Per cent	Sp. gr.	Per cent	Sp. gr.	Per cent	Sp. gr.
100°	16.8	0.876	13.7	0.873	13.4	0.870
150°	14.3	0.878	13.4	0.876	10.8	0.875
200°	8.9	0.922	5.1	0.917	3.6	0.917
250°	20.7	Solid	19.1	Solid	17.5	Solid
300°	8.2	..	6.9	0.994	—	—

Table 5—(*Continued*)

Temperature of "Cracking"—850° C

Oil used	Pennsylvania	
Oil recovered (percent)	9.7	
Sp. gr. of oil recovered	1.026	
Distillation Temperature	Percent	Sp. gr.
100°	18.0	0.875
150°	7.0	0.859
200°	10.0	0.885
250°	Solid	—
300°	—	—

cut are also given. It is very safe to assume that the method of distillation gave the majority of the benzene in the cut to 100° C, and the major portions of the toluene and xylenes in the cut 100° to 150° C.

When the cracking was conducted at temperatures 500° and 600° C, the recovered oil, irrespective of the source, gave on distillation a less amount up to 100° C than it did in the cut from 100° to 150° C. This is positive indication that the amount of benzene is less than the combined amounts of toluene and xylene. At 750° C there is again uniformly a larger percent in the cut to 100° than was found in the fraction from 100° to 150° C. At this temperature, which is relatively high, this fact proves that benzene is formed in larger amounts than either toluene or xylene, or than the combined quantities of toluene and xylene. A similar phenomena is found at 850° C in the recovered oil from the Pennsylvania crude petroleum, although it is more pronounced. It should also be noted sharply that the amounts of toluene and xylene at this temperature are less than were obtained at 750° C. In other words, the toluene and xylene formation reached a maximum, and at 850° C is beginning to decrease.

The solid appearing in the distillation cuts from 200° to 250° C at a cracking temperature of 750° and 850° C is partly naphthalene. As the distillation was not carried above 300° C, there is no means of estimating the anthracene formation. The conclusion may again be drawn, however, that a relatively high temperature, 750° C, or above, is required for the formation of naphthalene.

This paper of Dr. Rittman's shows better than any of the previous ones, the effect of temperature on the individual aromatic formation, and that with the type oils used, the formation is independent of the nature of the oil.

Other investigators[1] have also brought out in a measure the effect of temperature, but a discussion of their work adds nothing to what already has been said.

From the history of the production of aromatic compounds by cracking petroleum at atmospheric pressure, the following conclusions may be drawn:

1. There has been no clear cut attempt to follow the individual aromatic formation with increase of temperature.

2. Interpretations of the analysis of cracked oils obtained by distillation and by chemical methods point out the following:

(*a*) Low temperatures produce more toluene and xylene than benzene, and no naphthalene or anthracene.

(*b*) Moderately high temperatures yield more benzene than toluene and xylene, with appreciable amounts of naphthalene and anthracene.

(*c*) High temperatures result in large quantities of naphthalene and anthracene, and still relatively smaller quantities of benzene, toluene and xylene.

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of passing a weighed amount of oil at a definite rate of feed through an electrically heated furnace. When a run was completed the cracked oil

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[1] Veith: Das Erdöl, Braunschweig, 435 (1892). Adiasiewitsch: Chem. Centralbl., I, 401 (1896). Ogloblin: Chem. Centralbl., 79, 2, 830 (1904). Rosenfeld: Osterr. Chem. Tech. Ztg., 27, 1 (1909). Schutzen and Jonine: Comptes rendus, 91, 825 (1880). Edeleanu: Intern. Pet. Kongr. Paris, 78 (1900); Osterr. Chem. Tech. Ztg., 8, 20 (1902). Boissieu: Bull. Soc. chim. Paris, (3) 9, 2 (1893). Meffert: Chem. Centralbl., I, 159 (1899). Lermontowa: Tech. der Naphtha nach Veith. Ljubawin: Chem. Centralbl., II, 118 (1899); Jour. Russ. Phys. Chem., 31, 358 (1899).

was tapped from the condenser and weighed, and the volume in the gasometer noted.

Oil Used

The oil employed for the cracking experiments was what is commercially termed a distillate or gas oil. It was obtained in refining Pennsylvania crude petroleum and analyzed as follows:

Sp. gr. 0.817

Temp. °C.	Percent	Sp. gr.
200°	2.0	—
200°–250°	7.3	0.792
250°–300°	57.0	0.818
300°–350°	28.0	0.827
Residue	5.5	—

In each experiment 574 grams of oil, filtered through filter paper previous to use, was run through the furnace.

Electrically Heated Furnace and Apparatus

The furnace and apparatus similar to that employed by W. F. Rittman[1] has been described completely.

Experiments

As the object of this paper was to follow the individual aromatic formation with change of temperature, the oil was cracked in the furnace at temperatures 450°, 500°, 550°, 600°, 650°, 700°, 750°, 800° and 875° C. During the procedure the temperature was the only factor which was changed for the respective runs. The same oil was used, and was admitted to the cracking area at the rate of 246 grams per hour. As a very slight variation in the rate would have affected materially the amount and composition of the end products, great care was exercised in keeping this factor constant.

For each temperature, three or more runs were made, first with the object of obtaining checking results, and secondly, for the purpose of receiving enough oil for accurate analysis.

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[1] Jour. Ind. Eng. Chem., 6, 472 (1914).

Analysis of Oil

The oil as it came from the condensers, especially when the result of high temperature cracking reaction, was found to contain appreciable amounts of carbon. For this reason it was filtered before the specific gravity was determined. If not removed, the suspended carbon in the oil would have made the specific gravity of the oil abnormally high in value. The analysis of the cracked oil for benzene, toluene, and xylene was conducted according to the method devised by the authors.[1] The first step in this method of analysis is a distillation of 170° C. This fraction was then analyzed for benzene, toluene, and xylene. The residue above 170° C was distilled in a manner usually adopted for coal tar. The following cuts were made: 170° to 230° C; 230° to 270° C; and 270° C to tar. When naphthalene and anthracene[2] were found present, the respective fractions were chilled in an ice-salt mixture, and these solid aromatics separated from the oil in the fraction by pressing and drying with filter paper. The results are expressed as crude naphthalene and anthracene.

Specific gravities were taken by means of a Westphal balance at 15.0° C.

EXPERIMENTAL DATA

The experimental results are brought out by means of tables and graphs in the following order:

Table 6 and Fig. 1. The effect of temperature on the percent of recovered oil, on the gas formation, and on the specific gravity of the recovered oil.

Table 7 and Fig. 2. The effect of temperature on the percent of benzene, toluene, xylene, naphthalene and anthracene in the recovered oil.

Table 8 and Fig. 3. The effect of temperature on the percent of benzene, toluene, xylene, naphthalene and anthracene on the basis of oil used for their production.

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[1] Rittman, Twomey and Egloff: Met. and Chem. Eng., 13, 682 (1915).

[2] Holde: Examination of Hydrocarbon Oils, p. 257.

Table 9 and Fig. 4. The effect of temperature on the distillate to 170° C, on the specific gravity of the distillate to 170° C, and on the percent of benzene, toluene, and xylene in the distillate to 170° C.

Table 10. The effect of temperature on the specific gravity of the benzene cut 0° to 95° C, on the specific gravity of the toluene cut 95° to 120° C. and on the xylene cut 120° to 150° C.

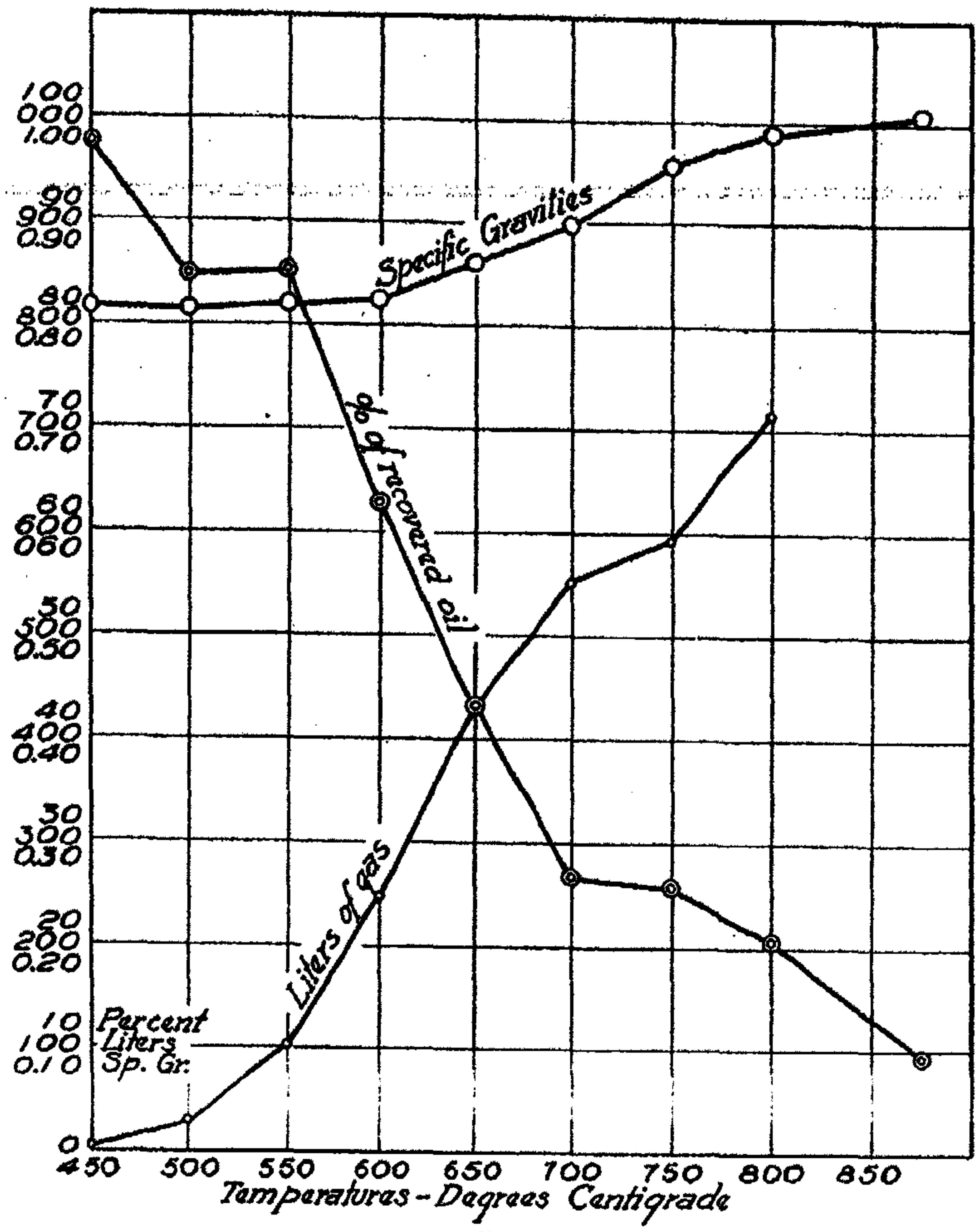

Fig. 1

Table 6—Rate = 246 grams per hour. Atmospheric pressure

Table 11. The effect of the temperature on the residue above 170° C of the recovered oil, as shown by distillation and specific gravities.

TABLE 6

Rate = 246 grams per hour; amount of oil used = 574 grams.
Atmospheric pressure

Temp.	Percent of rec. oil	Av.	Liters of gas per Kg	Av.	Sp. gr.	Av.
450	98.6		6.0	6.0	0.820	
	96.1	97.4	6.0		0.818	0.819
500	85.8		28.0		0.812	
	85.0		34.0		0.813	
	83.4		26.0		0.814	
	85.4	84.9	28.0	29.0	0.814	0.813
550	83.0		102.0		0.819	
	85.0		113.0		0.820	
	86.1		88.0		0.819	
	86.4	85.1	99.0	101.0	0.823	0.820
600	61.5		246.0		0.823	
	64.0	62.8	249.0	248.0	0.825	0.824
650	44.6		427.0		0.851	
	40.3		425.0		0.854	
	44.3	43.1	439.0	430.0	0.876	0.860
700	25.1		552.0		0.894	
	27.2		546.0		0.899	
	27.7	26.7	558.0	552.0	0.904	0.899
750	27.6		558.0		0.964	
	23.0		606.0		0.940	
	24.9		612.0		0.967	
	27.6	25.8	595.0	593.0	0.960	0.958
800	19.0		725.0		0.989	
	19.6		730.0		0.982	
	21.6		705.0		0.990	
	22.2		700.0		0.995	
	21.1	20.7	—	715.0	0.989	0.989
875	6.5		—		1.060	
	6.0		—		1.060	
	13.0		—		1.045	
	8.0		—		1.060	
	13.5	9.4	—	—	1.030	1.050

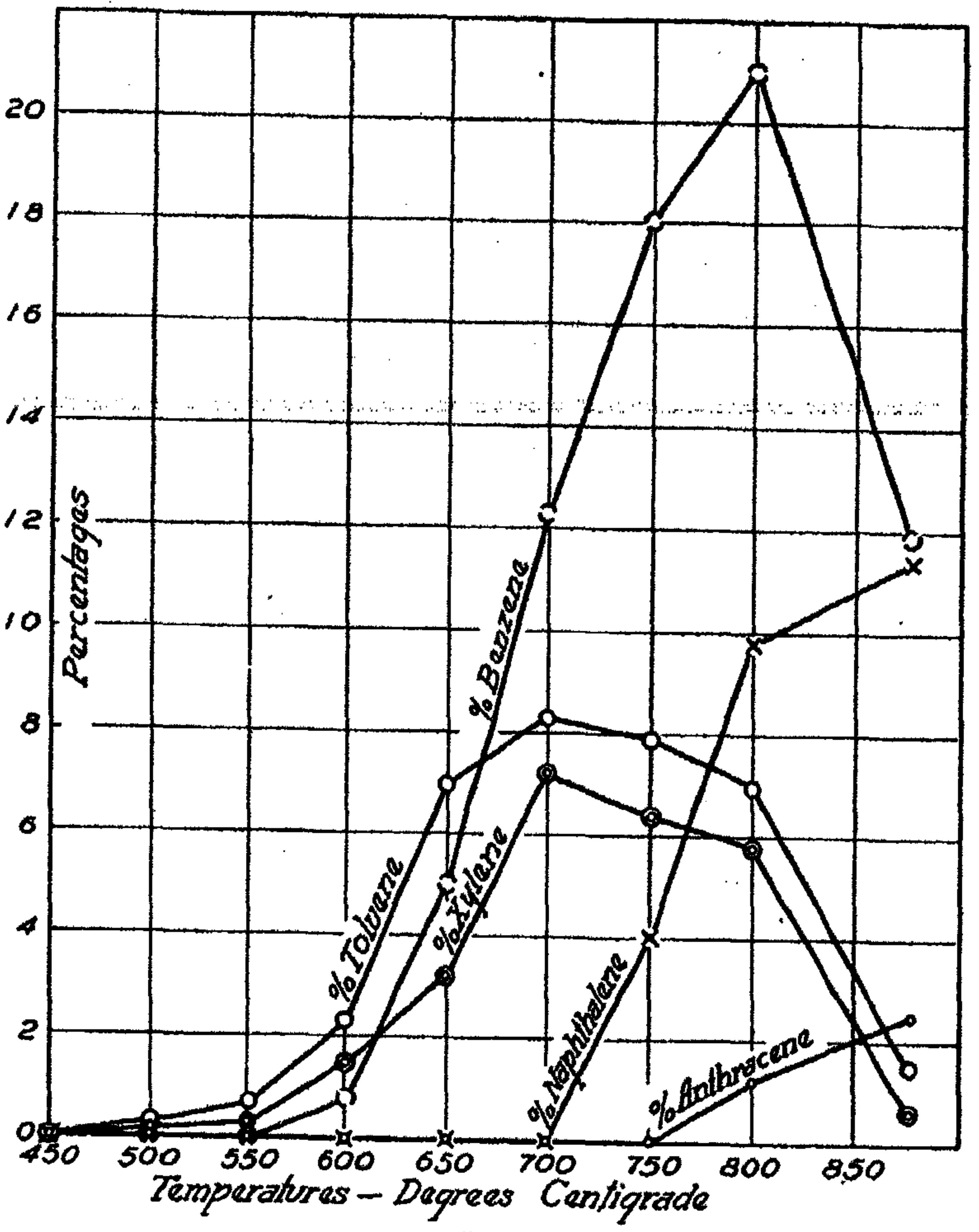

Fig. 2
Table 7—Analysis of recovered oil

TABLE 7
Analysis of Recovered Oil

Temperature	Percent benzene	Percent toluene	Percent xylene	Percent napthalene	Percent anthracene
450	0.0	0.0	0.0	0.0	0.0
500	0.0	0.3	0.2	0.0	0.0
550	0.0	0.7	0.3	0.0	0.0
600	0.8	2.3	1.5	0.0	0.0
650	5.0	7.0	3.2	0.0	0.0
700	12.3	8.3	7.2	0.0	0.0
750	18.1	7.9	6.4	4.0	0.0
800	21.0	7.0	5.8	9.8	1.2
875	11.9	1.5	0.6	11.4	2.5

TABLE 8
Analysis on Basis of Oil Used

Temp.	Percent benzene	Percent toluene	Percent xylene	Percent naphthalene	Percent anthracene
450	0.0	0.0	0.0	0.0	0.0
500	0.0	0.2	0.2	0.0	0.0
550	0.0	0.6	0.3	0.0	0.0
600	0.5	1.4	0.6	0.0	0.0
650	2.5	3.1	1.4	0.0	0.0
700	3.3	2.2	1.9	0.0	0.0
750	4.7	2.0	1.6	1.3	0.0
800	4.4	1.5	1.2	2.0	0.3
875	1.1	0.1	0.06	1.5	0.2

TABLE 9
Analysis of Distillation Cut to 170° C

Temp.	Percent to 170° C	Sp. gr.	Percent benzene	Percent toluene	Percent xylene
450	2.6	0.742	0.0	0.0	0.0
500	7.3	0.745	0.0	2.4	2.1
550	14.8	0.742	0.0	4.7	2.1
600	26.2	0.766	3.1	8.6	5.7
650	31.9	0.806	15.6	22.0	10.0
700	42.7	0.841	28.8	19.3	16.9
750	39.6	0.866	45.8	20.0	16.0
800	38.4	0.876	54.5	18.2	15.1
875	17.6	0.884	67.8	8.6	3.2

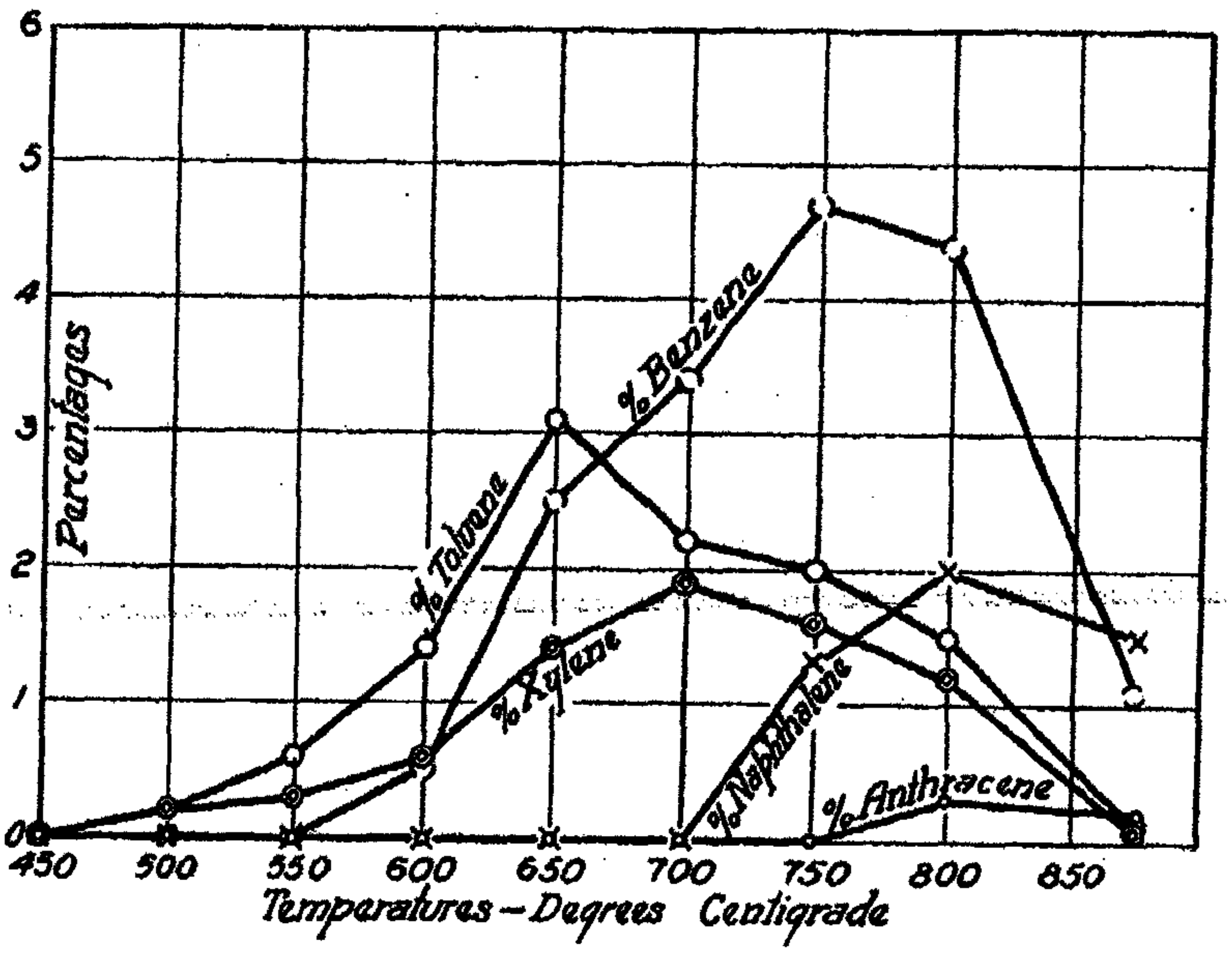

Fig. 3
Table 8—Analysis on basis of oil used

TABLE 10
Specific Gravity of Benzene, Toluene and Xylene Cuts at 15°/15° C

Temp.	Benzene cut 0–95° C.	Toluene cut 95–120° C.	Xylene cut 120–150° C.
450	0.711	0.762	0.771
500	0.711	0.762	0.771
550	0.711	0.762	0.771
600	0.733	0.786	0.792
650	0.784	0.824	0.825
700	0.828	0.850	0.850
750	0.862	0.870	0.880[1]
800	0.875	0.870	0.887[1]
875	0.881	0.870	0.870

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[1] These values are questionable.

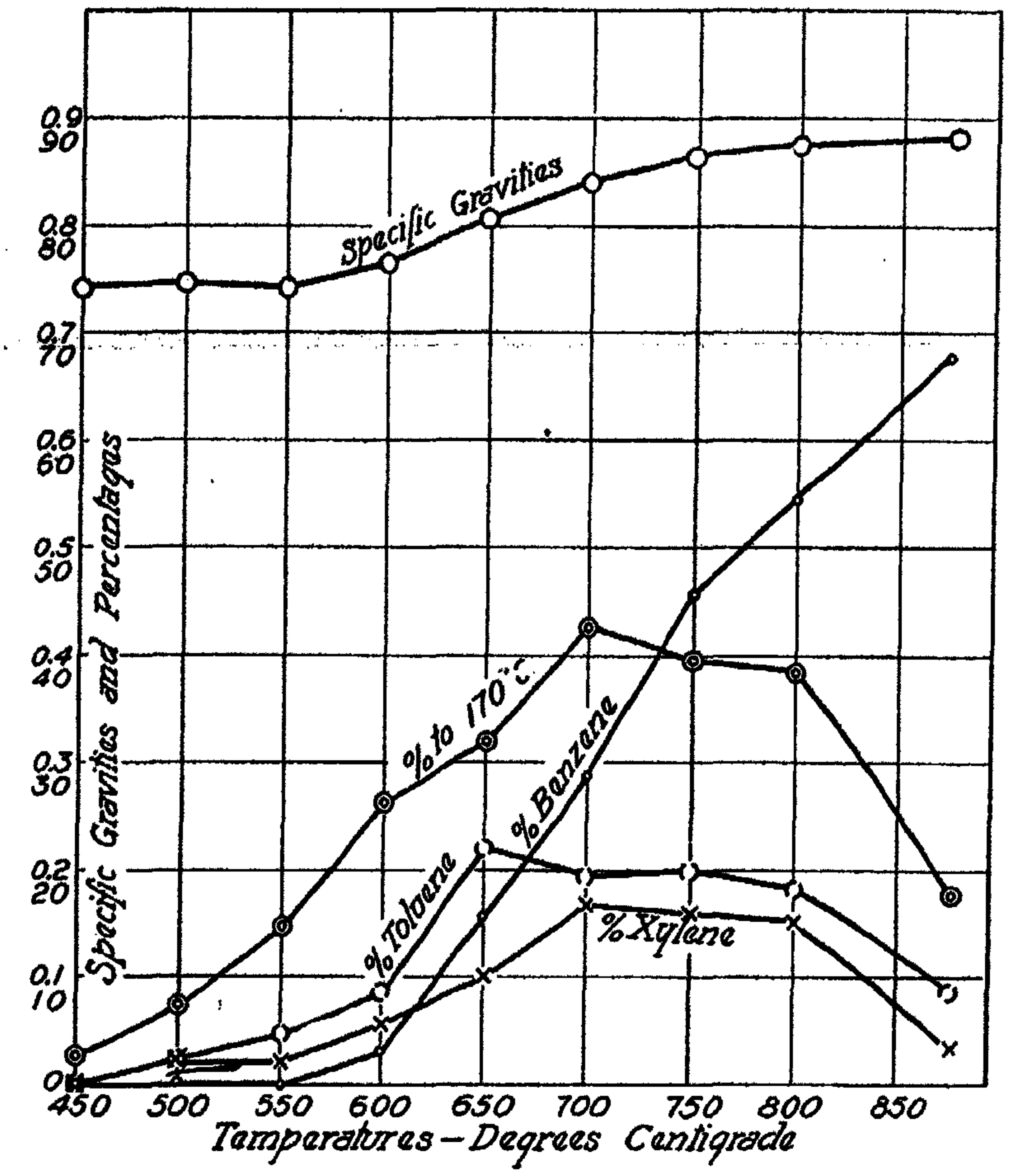

Fig. 4
Table 9—Analysis of distillation cut to 170° C

TABLE II

Analysis of Residue above 170° C

	170-230		230-270		270-Tar		Tar
	Per-cent	Sp. gr.	Per-cent	Sp. gr.	Per-cent	Sp. gr.	Per-cent
Original oil	—	—	21.4	0.798	78.6	0.826	—
Sp. gr. of coal tar[1]		1.000		1.040		1.100	
Temp.							
450	0.6	—	20.2	0.803	72.0	0.820	—
500	1.9	—	27.0	0.804	60.5	0.825	—
550	7.7	0.807	30.0	0.812	50.7	0.830	2.5
600	7.4	0.819	25.1	0.825	33.4	0.846	4.4
650	10.4	0.840	17.6	0.849	26.8	0.869	4.8
700	9.5	0.879	18.2	0.890	22.8	0.938	7.8
750	10.2	solid	14.7	solid	18.5	1.014	18.0
800	11.9	solid	14.4	solid	14.4	solid	21.0
875	—	solid	—	solid	—	solid	—

DISCUSSION OF EXPERIMENTAL DATA

A. The Effect of Temperature on the Percent of Recovered Oil, the Specific Gravity of the Recovered Oil and the Gas Formation

When oil is heated in a vapor state to temperatures above its vaporization point, it decomposes to permanent gases, carbon, and another oil which has a different composition than the original. This action is called "cracking." The oil produced as the result of the cracking is generally called the "cracked" or recovered oil.

The furnace was so constructed that the oil on entering was vaporized and then the vapors were cracked by the heat.

From the temperature graph, it will be noted that temperature has a marked effect on the amount of recovered oil obtained in each case. The natural result expected is that this would decrease proportionally with change in temperature. This, however, was not found to be the case. But little change occurred in the percent of recovered oil when the temperature was raised from 450° to 550° C. The maximum decrease occurred between 550° and 700° C, while be-

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[1] Holde: Examination of Hydrocarbon Oils, p. 257, 1st Eng. Edit., 1915.

yond the latter temperature the rate of decrease was much slower.

The small change produced by the first 100° C is readily explained on the grounds that a definite temperature above the vaporization point of the oil is absolutely necessary to produce any cracking. Once this temperature is reached, however, there occurs a rapid decomposition of the original oil resulting in the formation of much gas and decreasing the percent of recovered oil. Finally that temperature is reached, 700° C, where the reaction has produced a cracked oil in the vapor state in the furnace which contains a large percentage of aromatic compounds, relatively more stable at 750° to 875° C than is the original oil used at the lower temperatures. For this reason the percent of recovered oil decreased at a much slower rate beyond 700° C than it did at lower points.

These results are in agreement with what has been found by other investigators. W. F. Rittman[1] found that the percent of recovered oil obtained at 750° C differed but slightly from the value at 850° C, and that the rate of decrease between these two points was much slower than at 500° and 600° C. Lewes'[1] data also show that a maximum decrease occurred at 500° to 900° C, while from 900° to 1000° C this was much slower.

The gas formation exhibits the same characteristics as the percent of recovered oil but in the reverse direction. As the temperature rose, the amount of gas increased. The maximum again occurred between 550° and 700° C. While at the present time we are not so interested in the gas formation, theoretical considerations[2] and knowledge of the cracking reaction justify the course of the gas formation. If the percent of cracked oil obtained follows certain lines, then the gas formation must also develop along these same lines in the reverse direction to a certain extent. The larger the decomposition of the oil, the greater the gas formation and the less the percent of recovered oil.

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[1] Loc. cit.

[2] Rittman: Jour. Ind. Eng. Chem., 6, 383 (1914).

The specific gravity of the cracked oil increased with temperature. It changed from 0.819, the gravity of the original oil, to 1.050, a gravity generally associated with aromatic tars. Due to the cracking reaction, the original oil has been transformed more or less into an oil containing aromatic compounds which have a higher specific gravity[1] than the aliphatic compounds boiling at the same temperatures. This formation of aromatic compounds accounts for the change of gravity up to a certain point, beyond which the increase must be due to the tar which has been made. These points are brought out in the analysis of the oil.

The percent of recovered oil, the gas formation, and specific gravity of the recovered oil are the three important factors by which the extent to which the cracking reaction has proceeded may be judged.

B. The Effect of Temperature on the Formation of Benzene, Toluene, Xylene, Naphthalene and Anthracene in the Recovered Oil

The data and the curves showing the effect of temperature on the formation of benzene, toluene, xylene, naphthalene and anthracene are by far the most important of all the results in this paper from a scientific standpoint.

It should be noted that xylene and toluene are formed before benzene, and that up to 600° C occur in larger amounts. At 650° C the percentage has increased with the result that there is more benzene than xylene, but still less than toluene. At 700° C the benzene formation has increased to such an extent that the percentage is now greater than either that of toluene or xylene. Toluene and xylene have increased but slightly. The effect was still more noticeable at 800° C, where the cracked oil obtained contained 21.0 percent benzene, 7.0 percent toluene and 6.0 percent xylene. At this temperature, however, the amount of toluene and xylene formed is less than was found at 700° C. At 875° C, the percent of benzene dropped to 11.9, toluene to 1.3 and xylene to 0.6.

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[1] Rittman and Egloff: Jour. Ind. Eng. Chem., 7, 481 (1915).

Coincident with a fairly large quantity of benzene at 750° C naphthalene is formed, but no anthracene, and with still higher temperatures both the percentages of naphthalene and anthracene increased.

These results are directly in accord with what has already been pointed out from the combined publications of other investigators. They are important in that they show (1) the course of the individual aromatic formation with change of temperature and (2) the temperature limits which determine the maximum production of each aromatic in the cracked oil.

The experimental evidence indicates that toluene and xylene are formed before benzene. Most likely, the higher homologues of benzene, such as ethyl benzene, mesitylene, pseudocumene, and hemimellitene, for which analysis was not made in this paper, were formed first during the cracking reaction, and decomposed into xylene and toluene, and toluene into benzene, benzene into naphthalene, and naphthalene into anthracene.

This chain of reactions outlined for the explanation of the formation of the individual aromatics in the cracking of petroleum has been partially substantiated by a study of the decomposition[1] of benzene, toluene and xylene where it was found that the following reaction took place:

xylene ⟶ toluene ⟶ benzene ⟶ naphthalene ⟶ anthracene

C. The Effect of Temperature on the Formation of Benzene, Toluene, Xylene, Naphthalene and Anthracene on the Basis of Oil Necessary for the Production

From a commercial viewpoint the percent of benzene, toluene, xylene, naphthalene, and anthracene is very important on the basis of oil used for the production, since the cost of the starting oil is a factor in the expense of production.

There are two factors which determine the type of curve

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[1] Rittman, Byron and Egloff: Jour. Ind. Eng. Chem., 7, 1019 (1915).

obtained on the basis of oil used, first the percent of aromatic in the cracked oil, and secondly, the percent recovery of the cracked oil. For this reason all the curves show a maximum. This fact is very readily explained. As the temperature of the cracking is increased, the percent of aromatics in the recovered oil increased while the percent recovery decreased. Up to a certain point represented in this case by the temperatures for the different maxima shown, the percent of the former increased at a faster rate than did the percent of the latter decrease. With this factor more than counterbalancing the other, the percent of aromatics on the basis of oil used increased. Then, there arise conditions produced by higher temperatures where the percent recovery decreased at a much faster rate than did the increase of aromatics. These conditions cause a decrease of the percentage on the basis of oil used. The mean of these two cases just decribed will result in a maxima in the curves.

Benzene, toluene, xylene, naphthalene and anthracene occur in different amounts in the cracked oil and exhibited different rates of increase formation with increase of temperature. For this reason the maxima would occur at different temperatures. For toluene, a maximum of 3.1 percent is had at 650° C; for xylene, 1.9 percent at 700° C; for benzene, 4.7 percent at 750° C; for naphthalene, 2.0 percent at 800° C; and anthracene, 0.3 percent at 800° C.

This curve is valuable in showing the conditions which will give the maximum production of individual aromatics on the basis of oil used. For example, under conditions similar to those which produced the cracked oil obtained by the authors, 650° C gave the maximum production of toluene; 750° C, the maximum production of benzene.

Applied to other oils under different conditions of feed and size of cracking area, it is expected that the actual values would change. However, the same type of curves would undoubtedly be obtained, exhibiting maxima for each individual aromatic at temperatures depending on the other conditions which may effect the cracking.

D. The Effect of Temperature on the Percent, Specific Gravity and Percents of Benzene, Toluene and Xylene in the Distillate to 170° C

The distillate to 170° C corresponds to what is known in coal-tar practice as the light oil. The relation between benzene, toluene and xylene, as well as the gravity of the cut and the percent which it was of the original, are of value.

The data show specifically the extent to which temperature influences the breaking up of the original high boiling oil to lower boiling aromatics and aliphatic compounds. The results are very similar to those brought out by the previous set of curves. They go into further detail, however, in indicating that the cracking at the lower temperatures produces mixtures of aliphatic and aromatic compounds. The gravity of the cut shows this to be true. The gravities of the aliphatic compounds produced by the cracking of petroleum range close to 0.65 to 0.76, while those of the aromatics are: benzene, 0.881; toluene, 0.871; and xylene, 0.869; all at 15°/15° C. As the temperature of the cracking increases, the gravities of the cuts point out that the composition changes gradually from mixtures of aliphatic and aromatic hydrocarbons to practically pure aromatic compounds. The wide difference between the gravities of the two sets of hydrocarbons makes it possible to differentiate the effect of temperature on the composition of the distillate to 170° C.

The relations between benzene, toluene and xylene are similar to what has already been shown. Indications seem to point out that temperatures higher than were used in these sets of experiments would produce only benzene, and no toluene or xylene in this distillation cut.

There is one practical use to which these values may be put. A certain gravity of the cut to 170° C corresponds to a definite content of benzene, toluene, and xylene. In view of this it is possibie to distil the cracked oil to 170° C, find the percent and gravity, and from the gravity read off the percent of the different aromatics in the cut. These percents multiplied by the percent of which the cut is of the original gives the amounts of benzene, toluene and xylene in the oil.

Different oils, of course, will give somewhat different relationships between benzene, toluene and xylene in this cut. Once this relationship has been found for a particular oil, the method outlined offers an easy, quick and fairly accurate method of analysis of a cracked oil. It is especially accurate when aromatics are produced commercially under practically the same conditions day by day.

E. The Effect of Temperature on the Specific Gravity of the Benzene Cut 0° to 95° C; the Toluene Cut 95° to 120° C; and the Xylene Cut 120° to 150° C

In order to show the purity of the benzene, toluene and xylene the specific gravities of the cuts in which they occur are given. From previous work[1] the specific gravity of the impurities may be safely assumed to be as follows:

	Sp. gr. impurities	Sp. gr. aromatics
Benzene cut 0° to 95° C	0.72	0.881
Toluene cut 95° to 120° C	0.73	0.871
Xylene cut 120° to 150° C	0.76	0.869

For comparison the gravities of the pure aromatics are also given. The data again show the changes produced by temperature, and that the higher temperatures produce benzene, toluene and xylene, almost free from aliphatic compounds such as paraffins and olefins.

F. The Effect of Temperature on the Residue Above 170° C of the Recovered Oil as Shown by Distillation and Specific Gravities

With increase of temperature the composition of the original oil changes until it is almost all aromatic in character. In order that the change in composition may be fully appreciated the distillation of the original oil with cuts similar

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[1] Rittman, Twomey and Egloff: Loc. cit.

to those adopted for the cracked oil are given, also the gravities of the cuts and gravities of similar cuts from a typical coal tar.[1]

Application to the Distillation of Coal

According to Lunge[2] and Allen,[3] when coal is distilled at a high temperature for the manufacture of coal gas, the condensable hydrocarbons consist chiefly of benzene and its homologues, naphthalene and anthracene. At a somewhat lower temperature most of the naphthalene disappears and a larger proportion of benzene is formed. At a dull red heat such as employed for the distillation of bituminous shale, the liquid products are almost free from benzene and naphthalene.

The distillation of coal is too extensive a subject to be treated in this paper. It should be noted, however, that temperature seems to have the same effect on the distillation of coal, as was shown in the cracking of petroleum.

A study of the effect of temperature on the distillation of coal would undoubtedly show that the individual aromatic formation resulting from the distillation follows the same lines as have been shown for petroleum.

Summary

In the investigation of the effect of temperature on the cracking of petroleum at atmospheric pressure experimental data were obtained which may be summarized as follows:

1. The percent of cracked oil obtained decreased slowly with increase of temperatures—450° to 550° C; drops sharply from 550° to 700° C; and changed at a much lower rate from 700° to 875° C.

2. The gas formation increased proportionally with temperature change similarly to the percent of cracked oil obtained.

3. The specific gravity of the cracked oil increased with temperature.

4. Temperatures 450° to 600° C produced in the cracked

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[1] Holde: Loc. cit.

[2] G. Lunge: Coal Tar and Ammonia, 3rd English Edition.

[3] Allen: Commercial Organic Analysis, Vol. III, p. 22.

oil more toluene and xylene than benzene, and more toluene than xylene. No naphthalene or anthracene was formed.

5. At 650° C more toluene than benzene, and more benzene than xylene were formed. No naphthalene or anthracene occurred.

6. Temperatures 700° to 875° C yielded uniformly more benzene than toluene or xylene, but more toluene than xylene.

7. Naphthalene formation began at 750° C, anthracene at 800° C, and both increased then with temperature.

8. Benzene formation in the cracked oil attained a maximum of 21.0 percent at 800° C; toluene, 8.3 percent at 700° C; and xylene, 7.2 percent at 700°. Beyond these respective temperatures the formation of each decreased fairly rapidly with rise in temperature.

9. The largest percentage of naphthalene obtained was 11.4 percent at 875° C, and anthracene, 2.5 percent at the the same temperature.

10. Temperatures 450° to 700° C produced benzene, toluene, and xylene mixed with aliphatic compounds. The higher temperatures, 750° to 875° C, yielded aromatic compounds practically free from aliphatic compounds.

11. On the basis of oil used, a maximum of 4.7 percent benzene was obtained at 750° C; 3.1 percent toluene at 650° C; 1.9 percent xylene at 700° C; 2.0 percent naphthalene at 800° C; and 0.3 percent anthracene at 800° C.

12. The experimental evidence indicates that the individual aromatic formation with change of temperature follows the following lines:

$$\begin{matrix}\text{Higher}\\ \text{Homologues}\end{matrix} \longrightarrow \left\{\begin{matrix}\text{Toluene}\\ \text{Xylene}\end{matrix}\right\} \longrightarrow \{\text{Benzene}\} \longrightarrow \{\text{Naphthalene}\} \longrightarrow \{\text{Anthracene}\}$$

13. A study of the temperature effect on the distillation of coal would undoubtedly give similar results to those obtained in this paper.

14. The results of the experiments agree with the combined results of other investigators.

Pittsburg Division
Aetna Chemical Co.
Pittsburg, Pa.
Dec. 1, 1915

THE REDUCTION OF LEAD SULPHATE

BY G. A. PERLEY AND C. W. DAVIS

While studying methods of regenerating sulphated storage cells, one of the authors[1] discovered that the normal charging current caused a satisfactory reduction of any lead sulphate on either the spongy lead plate or the peroxide plates if sodium sulphate were substituted for sulphuric acid. A further test of the method was made by Bennett and Cole.[2] During the experiments it was noticed that when sodium hydroxide, lead, and lead sulphate were all in contact simultaneously, very beautiful crystals of lead were deposited, whereas no crystals of lead were formed from any combination of two of the substances. When one of our sulphated lead grids was immersed in a solution containing 500 g NaOH per liter, the lead sulphate disappeared completely and splendid crystals of lead were found deposited on the lead grid.[3] This reaction was so unexpected and so interesting that a thorough investigation of it seemed desirable.

Chemically pure lead was purchased from Eimer & Amend. Analysis, by estimation as the sulphate, showed that it was of 99.7 percent purity. Other grades of less pure lead were also utilized, and in all cases the reaction appeared to be the same. For the most accurate experiments, the sodium hydroxide was made in the absence of air by the action of pure barium hydroxide upon pure sodium sulphate. The lead sulphate was prepared carefully from C. P. chemicals.

Experiments were first made to see whether crystals of lead could be obtained in any way by a reaction between sodium hydroxide and lead or between sodium hydroxide and lead sulphate. When proving the existence of plumbous acetate in aqueous solution, Denham and Allmand[4] showed

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[1] Perley: Jour. Phys. Chem., 15, 489 (1911).

[2] Trans. Am. Electrochem. Soc., 21, 303 (1912).

[3] Perley: Jour. Phys. Chem., 15, 498 (1911).

[4] Jour. Chem. Soc., 93, 424 (1908).

that metallic lead reacted with a hot solution of lead acetate to form plumbous acetate and that this reaction reverses in the cold, crystalline lead being deposited in the cold parts of the apparatus. It is precisely similar to the formation of cuprous sulphate from metallic copper and cupric sulphate in hot solution and the precipitation of metallic copper when the solution is cooled. The reversible equilibrium may be indicated by the equation

$$Pb + Pb^{\cdot\cdot} \rightleftharpoons 2\ Pb^{\cdot}$$

Since no pains had been taken to keep the temperature constant in the first experiments, there was a possibility that the precipitation of lead crystals was due to temperature changes involving the formation and decomposition of a plumbous compound. To test this, the experiments of Denham and Allmand were repeated, substituting a solution of sodium hydroxide alone as well as a solution of lead sulphate in sodium hydroxide for the lead acetate solution. Several runs were made varying in time from three hours to three days. In one experiment slight traces of a black substance were seen in the cold tube but negative results were obtained in all the other experiments. It seems certain, therefore, that the slight temperature variations during the first experiments did not cause the formation of the lead crystals.

In the literature on lead we were unable to find anything very satisfactory in regard to the action of sodium hydroxide upon metallic lead; but Stolba[1] has shown that granulated lead (of doubtful purity) decomposes boiling water slowly with evolution of hydrogen. The liquid in the flask was cloudy with lead hydroxide and reacted alkaline. It seemed possible that lead might react with caustic soda forming sodium plumbite and hydrogen. Even assuming that this reaction took place vigorously, the hydrogen could hardly reduce the sodium plumbite again to lead unless we were dealing with a case of small crystals increasing to larger ones. On

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[1] Jour. prakt. Chem., 94, 113 (1865).

the other hand, Gladstone and Tribe[1] have shown that spongy lead, free from occluded hydrogen, reduces nitrates to nitrites and to ammonia. They state that spongy lead has no action upon an aqueous solution of potassium chlorate, but that the addition of one percent of sulphuric acid causes a slow reduction to the chloride. Lead filings act similarly but to a lesser extent. There was a bare possibility that the roughened lead left by the corrosion might react with the plumbite, giving crystals of lead either directly or indirectly. While one must always consider the possibility of occluded hydrogen playing some part in a slow reduction, Shields[2] states that "lead belongs to that group of metals which does not occlude hydrogen, and as all the other evidence is in agreement with this fact, we are compelled to reject the hypothesis, which is sometimes advanced, that hydrogen is occluded by lead."

A series of experiments was carried out in order to determine the action of a solution of sodium hydroxide on pure lead. A long capillary was fused to a small glass bulb, and the whole was treated with an alkaline solution for some time. Lead shavings were placed in the glass bulb. The lower end of the capillary tube was attached to a pure rubber tube fitted with a levelling bulb. The bulb and capillary tube were filled with a three normal sodium hydroxide solution by alternate heating and cooling. The levelling bulb was filled with mercury. As a result, there was no air space within the apparatus. The shavings of pure lead in contact with the sodium hydroxide solution were heated and cooled a great number of times under reduced pressure, yet no extensive evolution of gas resulted. It is possible that a mere trace of gas was formed. A very small bubble of gas remained in the capillary tube; but it was so minute that not even a spectroscopic examination was attempted. No crystals of lead were formed during the heating and cooling. The shavings had the appearance of being somewhat etched, the solution

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[1] Jour. Chem. Soc., 43, 347 (1883).

[2] Chem. News, 65, 195 (1892).

gave a slight test for lead, and there was a small quantity of a flocculent white substance, apparently lead hydroxide. Even when heated and cooled, pure lead is therefore attacked but slightly by sodium hydroxide solution. In so far as it is attacked, there is necessarily an equivalent quantity of hydrogen to be accounted for. It would have required a special investigation to determine whether there had been hydrogen adsorbed, dissolved, or oxidized. Since these experiments show that we do not get crystals of lead by the action of caustic soda on lead, the question of the missing hydrogen was not studied further.

The next step was to see whether crystals of lead can be obtained by the action of caustic soda on lead sulphate. Wichmann[1] has shown that lead monoxide is formed when lead sulphate is made into a paste with water and is added to a boiling sodium hydroxide solution. We repeated the experiments and confirmed these results. With hot concentrated sodium hydroxide red crystals are formed and yellow crystals with hot dilute sodium hydroxide. When lead sulphate is treated with cold dilute sodium hydroxide yellowish green crystals are obtained These have the general appearance of the crystals obtained by using a hot dilute sodium hydroxide, but it was found impossible to separate the yellow crystals from the remaining undecomposed lead sulphate and so no analysis was made. One of the authors has made a study of all the possible sulphates and basic sulphates of lead from the standpoint of the phase rule; and it is interesting to notice that no solid phase of a yellowish green color has been in evidence. The colors of the solid phases varied from yellow to red. This is to be reported on in a separate paper as it was found to have no bearing on this problem.

Under no conditions has it been possible to obtain any crystalline lead either by the action of sodium hydroxide on lead or on lead sulphate. It is therefore evident that the reduction of lead sulphate to metallic lead in the presence of sodium hydroxide necessarily involves the presence of some

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[1] Chem. Centralblatt, 1860, 334.

form of lead. The experiments with pure materials confirm the conclusions drawn from the earlier work.

Very pure lead was cut into strips in which grooves were made and filled with pure lead sulphate made into a paste with distilled water. The dried grid was placed vertically in a three normal sodium hydroxide solution. After a short time the lead sulphate turned to a light greenish yellow color, which was succeeded in time by a black deposit. In every experiment the black deposit always formed first near the top of the grid and only where the lead sulphate was in direct contact with the lead. After a time all of the white sulphate was replaced by a finely divided black material which on examination proved to be lead. After a long time lead leaflets formed on the bottom corners of the original lead strips grew in some cases to the length of nearly one-half inch. This appeared to be a secondary reaction, dependent upon a different set of conditions. This crystalline lead was distinct from the finely divided form. A dilute sodium hydroxide solution reacts with extreme slowness, and an excess of lead sulphate always prevented the completion of the reaction. It was observed that the lead sulphate was dissolved by the sodium hydroxide. In order to determine whether the lead obtained by the reduction was equivalent to the lead sulphate dissolved by the sodium hydroxide solution, the data in Table I were obtained, from which it appears that there

TABLE I

	I Gram	II Gram	III Gram
Weight of lead at start	33.345	28.141	61.600
Weight of lead at end	33.317	28.121	61.512
Weight of lead dissolved	0.028	0.020	0.088

is actually a loss of lead in spite of the fact that finely divided lead has been precipitated. In each experiment the original lead strip had been corroded.

To ascertain whether there was any concentration of sodium hydroxide solution in which no intermediate yellow substance was formed, the following strengths of sodium hydroxide were tried: 12 N; 6 N; 3.5 N; 2.5 N; 2 N; 1.5 N; 0.75 N. With the 12 N sodium hydroxide solution an intermediate red substance resulted, while with all other concentrations yellow crystals always appeared before the reduction was complete.

Since it was difficult to formulate any series of chemical reactions, to account for the observed facts, an experiment was made with zinc so as to see whether the phenomena were general or were peculiar to lead. Zinc was coated with zinc oxide and placed in a solution of sodium hydroxide. The zinc oxide was reduced rapidly to spongy zinc and there was an evolution of gas. Except for the evolution of gas this is exactly what happens with lead. If one had a concentration cell of some sort, one would expect just this difference between zinc and lead. In the previous paper[1] the assumption had been made that the lead crystals were due to the action of a concentration cell; but this hypothesis was discarded because reduction took place when a cylindrical lead grid, coated with lead sulphate, was rotated. It was thought at the time that the rotation must do away with all concentration differences. In order to test the previous work more experiments were made. Small cylindrical lead grids, coated with lead sulphate, were made to revolve in 3 N sodium hydroxide solution. When the speed of the grid was 50 R. P. M., reduction occurred uniformly over the whole grid and took place more rapidly than when the grid was stationary. A speed of 1400 R. P. M. increased the rate of reduction still more. In all instances it was noted that reduction takes place uniformly over the rotated grids, whereas the reduction always takes place faster at the top of the stationary grids. Rotating the grids increases the speed of reaction and makes the reaction uniform.

Though these experiments confirm the previous ones, the fact that reduction takes place on a revolving grid does not

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[1] Perley: Jour. Phys. Chem., 15, 499 (1911).

necessarily disprove the hypothesis of a concentration cell. The solution in the grooves of the grid is not affected by the stirring to anything like the same extent as the solution on the projecting surfaces. Paradoxical as it seems, rapid stirring may increase instead of decrease the differences of concentration. While this is a possible explanation, it is not one to be accepted without further proof. Some measurements of potential difference were therefore made to determine approximately what solutions constituted the hypothetical concentration cell. The experimental cell consisted of an electrode of lead encased in a glass tube and one of lead sulphate enclosed in another glass tube of equal size, Fig. 1. The lead sulphate electrode was connected to the external circuit by means of a lead strip inserted at the top. A three normal sodium hydroxide solution was used. No deflection of the voltmeter was observed until the solution had risen in the lead sulphate electrode as far as the lead connector. A reading of 0.06 volt was obtained, the lead sulphate being cathode. A cell was made up like the preceding one except that the lead sulphate electrode was replaced by a lead strip running to the same depth as the lead connector. No appreciable voltage was obtained. This was to be expected because the cell was now Pb | NaOH | NaOH | Pb, the only lack of symmetry being in the depths to which the two electrodes were immersed.

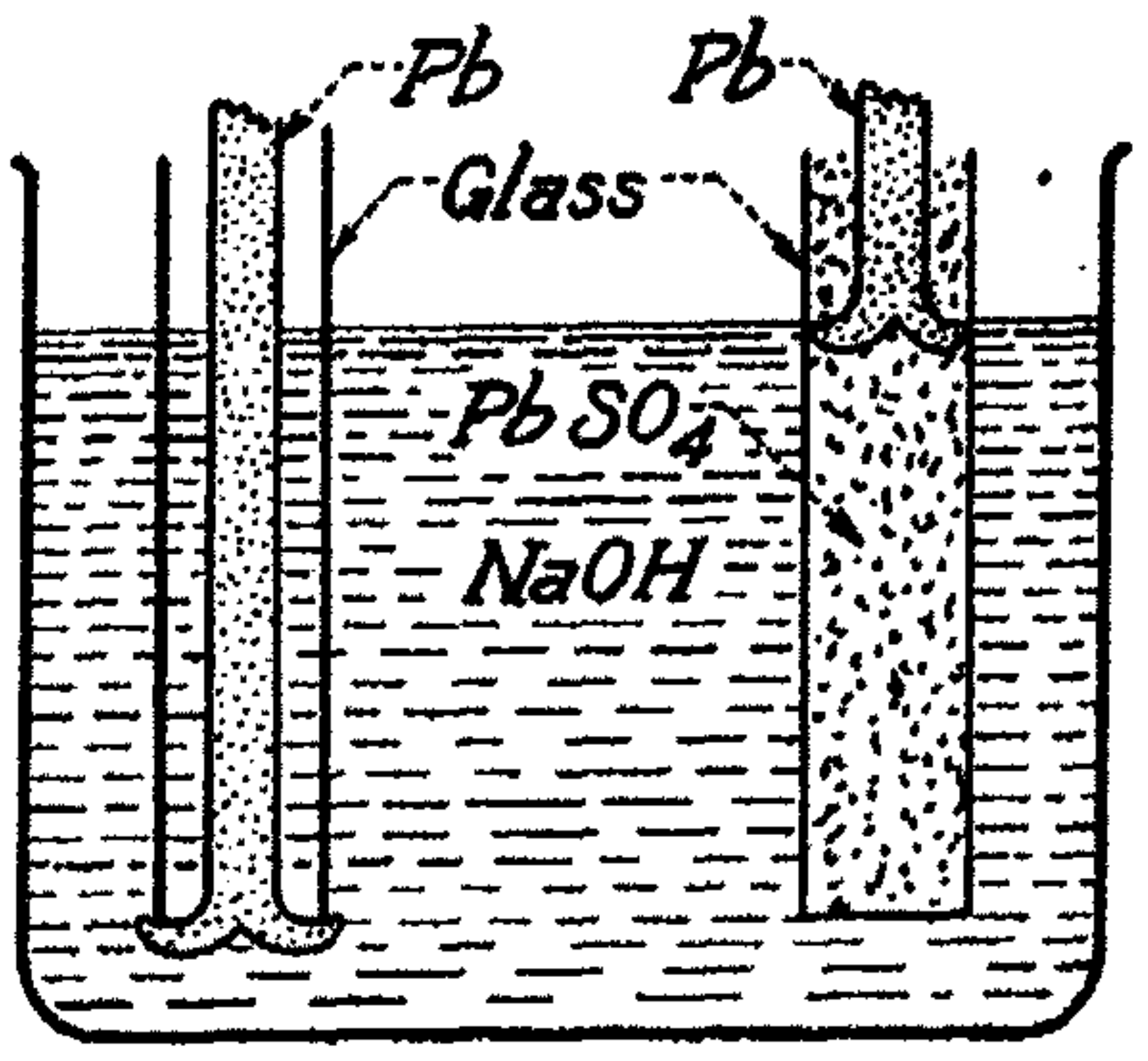

Fig. 1

A cell was made up similar to the first one, except that platinum was used instead of lead in the lead sulphate electrode. A reading of 0.06 volt was obtained, which is the same as when lead was used. From these experiments it is clear that the concentration of lead ions is less in a caustic soda solution in contact with lead than in a caustic soda in contact with lead sulfate; but it is not clear whether this is a result of the formation of sodium plumbite. A series of experiments was therefore made by means of a "salt bridge" cell. Two containers were connected by a large tube filled with the same sodium hydroxide solution that was to be used in both containers. With two lead electrodes, no voltage reading could be obtained. In a second experiment, lead in a glass tube was used as one electrode and lead sulphate in another glass tube as the other. A reading of 0.05 volt was obtained which is practically identical with 0.06 volt when one considers the differences in the internal resistance of the cells. This voltage remained constant for five days while the cell was on closed circuit. Some of the lead sulphate was reduced to lead but only that portion in direct contact with the lead connector. A similar cell, made up at the same time and left on open circuit, showed no appreciable reduction. It seems probable that it is the dissolved lead sulphate which is reduced to finely divided lead, and not the sodium plumbite. When phenolphthalein was added to the lead sulphate electrode at the end of the experiment, the deep coloration due to excess of alkali was evident at the bottom of the electrode, whereas the top zone, where the reduction occurred, remained neutral.

A relatively large amount of finely divided lead can be obtained in a short time by filling a platinum cone with lead sulphate and resting it on wires attached to the sides of a lead dish filled with three normal sodium hydroxide. Of course the cone must be completely covered by the solution.

To show that the sodium plumbite played no important part, a cell was made up of four normal sodium hydroxide solution on one side and of an unsaturated solution of lead sulphate in sodium hydroxide on the other. With lead electrodes this cell showed a difference of potential of 0.01 volt. When a solution of sodium sulphate is substituted for the solution of lead sulphate in sodium hydroxide, the voltage jumps to 0.05 volt. A cell consisting of a lead electrode in a four normal sodium hydroxide solution on one side and a lead sulphate electrode in sodium sulphate on the other side gave a reading of 0.05 volt. The lead sulphate was reduced in a comparatively short time when the cell was left on closed circuit.

The results of the salt bridge experiments are given in Table II.

TABLE II

Anode side is lead in 4 *N* NaOH

No.	Cathode	Solution	Volt
1	Pb (small)	4 *N* NaOH	0.00
2	$PbSO_4$	4 *N* NaOH	0.05
3	Pb	$PbSO_4$ in NaOH	0.01
4	Pb	Na_2SO_4	0.05
5	$PbSO_4$	Na_2SO_4	0.05

Single potential determinations were obtained by making readings with a standard calomel electrode. The results are given in Table III.

TABLE III

Single potential difference	Concentration	Volts
Pb H_2O	—	—
Pb Na_2SO_4	4 normal	0.035
Pb NaOH	4 normal	0.085
Pb $PbSO_4$ in NaOH (dissolved)	4 normal	0.080

It may be noted that the difference between the single potential readings for lead in the sodium hydroxide solution and for lead in the sodium sulphate solution is 0.05 volt. This is the same reading that was obtained in the first cells.

The voltage reading of about 0.05 volt must be due to a lead concentration cell and yet it can hardly be due to lead ions from sodium plumbite because we get only 0.01 volt when the cathode solution consists of an unsaturated solution of lead sulphate in caustic soda. The reaction between lead sulphate and caustic soda may be written tentatively as

$$PbSO_4 + 4NaOH \rightleftharpoons Na_2PbO_2 + Na_2SO_4 + 2H_2O.$$

Writing this as an ion reaction and cancelling the terms common to both sides, we have

$$Pb^{\cdot\cdot} + 4OH' \rightleftharpoons PbO_2'' + 2H_2O.$$

If we assume that the change of lead ion and hydroxyl ions to plumbite ion and water takes place slowly, everything becomes fairly simple. If we pour a caustic soda solution over lead sulphate, we shall have a gradual conversion of some or all of the lead sulphate into plumbite; but the amount of lead sulphate dissolved as such, and consequently the concentrations of lead ions, will always be greater than the value corresponding to equilibrium up to the moment when equilibrium is actually reached. The two elements of the concentration cell are therefore lead in caustic soda with a very low concentration of lead ions, and lead with lead sulphate in sodium sulphate. If we start with lead sulphate and caustic soda, we have the sodium sulphate and the sodium plumbite as minor complicating factors. It is the lead ions from the lead sulphate which are reduced to metallic lead rather than the lead ions from the sodium plumbite. When a grooved grid coated with lead sulphate is dipped into a caustic soda solution, the lead sulphate disappears first from the projecting portions of the grid because the coating is thinnest there. Since the resulting solution is more dense than the caustic soda solution, it flows down over the plate more or less rapidly and the projecting portions of the grid become bathed in a nearly pure caustic soda solution, thus setting up important differences of concentrations. Since the plumbite solution flows down over the grid, the caustic soda solution will flow to the plate at the surface; the concentration difference will be more marked there than elsewhere and consequently the reduction will start there provided the solution is not stirred. If the solution is stirred the concentration differences between the projections and the grooves will be greater and consequently the reduction will be more rapid; the concentration differences will be set up uniformly over the plate and consequently the reduction will be uniform. What happens with the larger grooves and hollows takes place, though less markedly with the minor, almost microscopic differences in the surface of the lead plate. A very instructive experiment shows that reduction takes place only with a caustic soda solution which has not reached equilibrium. If a sulphated grid is dipped into a saturated solution, no lead crystals are formed so long as the temperature is kept constant and provided the lead is pure.

It has previously been mentioned in this article that after grooved lead strips coated with sulphate had stood for a long time in a sodium hydroxide solution, beautiful lead crystals grew at the lower edges of the lead strips. Since a comparatively long time was required for this action and since the presence of solid lead sulphate did not seem necessary throughout the experiment, another explanation seemed called for. Since the sodium plumbite solution is always flowing down to the bottom of the beaker, and since the caustic soda is flowing to the plate at the surface of the liquid, there will be gradually formed a concentrated solution of sodium plumbite near the bottom of the vessel and a more dilute one above. We therefore have a concentration cell, Pb | dil. plumbite | con. plumbite | Pb. Since the difference of potential is small the current will be small and the lead will be precipitated slowly in relatively large crystals. This was shown experimentally in two ways. A four normal sodium hydroxide solution was saturated with lead sulphate. The resulting solution and a concentrated sodium hydroxide solution were made into a "salt-bridge" cell with two lead electrodes and the cell short-circuited. Many large crystals of lead were formed in an exceedingly short time on the electrode dipping into the solution containing the plumbite. The other method of showing the same thing is to place a concentrated solution of sodium hydroxide in a cylinder and to pour carefully upon it a solution of lead sulphate in a more dilute caustic soda, then passing a lead strip down so that it is in contact with both layers. Fine crystals of lead grow in the upper lead solution. This arrangement is like that to show the principle of the concentration cell with tin and stannous chloride. No effect is obtained if two different concentrations of pure sodium hydroxide are taken. The presence of the dissolved lead salt is essential.

The general results of this paper may be summarized as follows:

1. Pure lead dissolves slowly in a pure sodium hydroxide solution, but experiments under reduced pressure and in the absence of air failed to show any appreciable evolution of gas. Experiments were not made to determine whether the missing hydrogen was dissolved, adsorbed, or oxidized.

2. The formation of lead crystals when lead, lead sulphate and caustic soda are in contact is not dependent on impurities in the lead. All three substances are necessary and crystals of lead are not obtained by the action of caustic soda on lead or on lead sulphate.

3. While the lead crystals are forming, the lead plate is being corroded and the net result is a decrease in the total amount of metallic lead.

4. The formation of lead crystals in alkaline solution is not due to temperature fluctuations with the intermediate formation and decomposition of a lead salt with a lower valence though this is what happens in Denham's experiments with lead and lead acetate.

5. The rapid formation of fine lead crystals is due to a concentration cell consisting in principle of Pb | NaOH | Na_2SO_4, $PbSO_4$ | Pb. The caustic soda dissolves the lead sulphate and the denser solution thus formed flows to the bottom of the container, while fresh caustic soda flows in from above to replace it, thus setting up concentration differences.

6. It seems necessary to assume that the conversion of lead ions into plumbite ions takes time and that the amount of lead sulphate dissolved as such is greater than it should be until equilibrium is reached.

7. Rotating the sulphated lead strip makes the reduction more rapid and more uniform. This is not an argument against the reaction being due to a concentration cell. Rotating the electrode increases the removal of plumbite solution from the projecting portions of the electrode but has less effect on the sunken portions where there is more lead sulphate. We thus have the paradox that stirring increases the concentration differences, causing more rapid and more uniform reduction.

8. On long standing large crystals of lead are formed at the lower edge of the grid. These continue to grow after all the lead sulphate has disappeared. These crystals are due to the action of a concentration cell consisting in principle of Pb | dil. Na_2PbO_2 | conc. Na_2PbO_2 | Pb. This can be duplicated by placing a lead strip in a test-tube, pouring in a concentrated solution of caustic soda, and superposing a solution of lead sulphate in more dilute caustic soda. Beautiful crystals of lead are formed in the upper portion of the tube.

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THE REGENERATION OF SULPHATED STORAGE CELLS

BY G. A. PERLEY AND C. W. DAVIS

In the preceding paper[1] it was shown that the formation of lead crystals, when a sulphated lead strip is dipped into caustic soda solution, is due to the action of myriads of concentration cells. From these experiments it follows that it should be possible to regenerate a sulphated storage cell after a fashion by standing it in a caustic soda solution without using any external source of current. This can be done but the method is not satisfactory, because the lead is not precipitated in a suitable form and because the caustic soda solution dissolves a large amount of lead sulphate, which is a complete loss.

Some years ago, one of the authors[2] showed that sulphated storage cells could be regenerated satisfactorily if the battery acid were replaced by a solution of sodium sulphate. Upon the passage of a normal charging current, the lead sulphate is reduced within sixty hours even on badly sulphated grids. This method has since been tried by various people, always with good results. One great advantage of the method was that no new acid radical was introduced into the cell and that there was no need of a laborious and possibly ineffective washing before putting the cell in commission. On the other hand, it was conceivable that some other salt might give deposits that were enough better to justify its use, and accordingly some experiments have been made with other sodium salts. The comparative data are given in Table I. In all of these experiments 4″ × 5″ badly sulphated storage battery grids were used. The current density was 6.5 amperes per square foot. Normal solutions of all of the electrolytes were taken. All the solutions except those of

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[1] Perley and Davis: Jour. Phys. Chem., 20, 151 (1916).

[2] Perley: Jour. Phys. Chem., 15, 489 (1911); Bennett and Cole: Trans. Am. Electrochem. Soc., 21, 303 (1912).

the salts plus alkali were clear at the start. At the end of the run the sulphite solution was turbid and brown while the solutions containing caustic soda were turbid and yellow; all the others were clear.

Table I

Solutions	Acidity		After 2 hours	
	Start	End	Cathode	Anode
$NaOH$	Alkaline	Alkaline	Yellow coating	Brown PbO_2
Na_2SO_4	Neutral	Acid	Partly reduced	Brown PbO_2
Na_2SO_3	Alkaline	Acid	Brittle lead buckling	Gray brown PbO_2
Na_2CO_3	Alkaline	Alkaline	White reduced at edges	Brown PbO_2
Na_2HPO_4	Alkaline	Neutral	Partly reduced	Gray coating
$NaClO_3$	Acid	Acid	Spongy lead	No change
Na acetate	Slightly alkaline	Neutral	Mass of crystals	Gray yellow
Na oxalate	Acid	Acid	Basic salts	Basic salts
Na tartrate	Acid	Acid	Basic salts	Basic salts
Above salts plus $NaOH$	Alkaline	Alkaline	Yellow coating	Brown PbO_2

From the experiments it appears that a sulphated grid may be reduced in whole or in part with solutions of sodium sulphate, sodium carbonate, sodium phosphate or sodium sulphite. The rate of reduction is the fastest and the cathode and anode corrosion the least in the sulphate solution. The only solutions which give a good deposit of lead peroxide from sulphated anodes are the sulphate, carbonate, and hydroxide. The phosphate is converted slowly to lead peroxide at the anode. Insoluble salts (chiefly lead hydroxide) form as a sludge in the case of the hydroxide, acetate, and tartrate solutions.

When using the sodium sulphate method, we found that far better reduction occurred if two outer dummy positive grids were employed in addition to the usual number of positives. If not, the two outer negative surfaces require a much longer time for regeneration. This alone saves much time in the reduction. There is no question but that a badly sulphated grid may be brought to a high state of efficiency if sufficient time be allowed, approximately sixty hours at the normal charging rate. The chief objection—and possibly not an over serious one—is the fact that the concentration of acid increases with the duration of the run, and this tends to neutralize the alkali formed at the cathode. It is possible to prevent the diffusion of acid by wooden partitions, or to neutralize the acid from time to time, yet both of these methods are awkward.

Off-hand it seemed as though a very dilute solution of sodium hydroxide might prove a fairly efficient electrolyte. In all of the experiments, however, in which sodium hydroxide was used as the electrolyte, either alone or combined with other salts, a yellow precipitate of lead oxide was formed after the current had been flowing for about an hour. This precipitate clouded the solution and caused no end of trouble by settling on the electrodes and containers. This is due to the corrosion of the lead anode, sodium plumbite being formed which afterwards hydrolyzes. With sodium sulphate as electrolyte there is no excess of alkali at the anode and consequently no appreciable formation of plumbite.

Lead carbonate is much less soluble in sodium carbonate and hydroxide than lead sulphate is in sodium sulphate and hydroxide. Consequently when sodium carbonate is used as electrolyte, the sulphate is converted at the cathode into an insoluble basic carbonate which is reduced much more slowly than is lead sulphate. The regeneration therefore takes place at a very slow rate. A very fine anode deposit of lead peroxide is always obtained from a sulphated grid in a carbonate solution.

The rate of reduction of lead sulphate is quite rapid in a sodium phosphate solution; but there is a perceptible anode corrosion, so that active material is removed from the grid. There is apparently a tendency also to form a basic salt of some sort at the anode, as evidenced by the formation of a gray coating in a few spots where lead sulphate had existed. The chief difficulties with this solution are the high anode corrosion and the slowness with which the lead sulphate is converted at the anode to lead peroxide. The lead which results at the cathode from the reduction in a sulphite solution differs decidedly from that obtained in all of the other solutions. A very hard crystalline metal is deposited which causes more or less severe buckling of the grids. In the acetate, oxalate, and tartrate solutions the sparing solubility of the basic lead salts formed in presence of alkali causes so much trouble through crystallization of the salts on the electrodes that these solutions are valueless.

The experiments point to the following general conclusions:

1. Sodium sulphate is the best salt to use in regenerating positive and negative storage battery grids.

2. Dummy positive grids on the outside of the negative plates cut down the time of reduction.

3. Hydrolysis of the lead salts formed in sodium hydroxide solution yields large and troublesome quantities of lead monoxide. The active material of the grids is removed to a considerable extent.

4. With sodium sulphite solutions a hard crystalline lead is deposited at the cathode which causes buckling of the grids.

5. Reduction in whole or in part of a sulphated grid results by the use of a solution of sodium sulphate, carbonate, phosphate, or sulphite.

6. Good anode deposits from sulphated grids can be obtained only with sulphate, carbonate, and hydroxide solutions. This relatively high anode corrosion with sodium hydroxide solutions makes these useless.

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NEW BOOKS

Physiological Chemistry. *By Albert P. Mathews. 24 × 17 cm; pp. vi + 1040. New York: William Wood and Company, 1915. Price: $4.25 net.*— In the preface the author says: "I hope that this book may raise in the minds of those who read it more questions than it answers. Enormous as the science of physiological chemistry, or biochemistry, has grown to be, covering as it does the whole of the chemical and physico-chemical phenomena of living nature, only a beginning has as yet been made in it. To few of its fundamental questions can we now give an answer. The great discoveries remain for the future. To arouse interest in the subject, to stimulate interest and inquiry, are the main objects of every teacher. I hope that in the pages which follow I have not hit too wide of the mark."

The subject is divided into three parts: the chemistry of protoplasm and the cell; the mammalian body considered as a machine—its growth, maintenance, energy transformations and waste substances; practical work and methods. In the first part the special chapters are entitled: the general properties of living matter; the carbohydrates; the lipins—fats, oils, waxes, phosphatides, sterols; the proteins; the physical chemistry of protoplasm. In the second part the headings of the single chapters are: animal heat; the raw materials or foods; salivary digestion; digestion in the stomach; digestion in the intestine; absorption; the circulating tissue—the blood; the master tissue of the body—the brain; the contractile tissues—muscle; the connective, or supporting, tissues—the bones, cartilage, teeth, connective tissue; the cryptorhetic tissues—the thyroid, parathyroid, suprarenal, hypophysis, reproductive glands; the excretions of the body—urine; the metabolism of the body considered as a whole—carbohydrates; protein metabolism of the body; metabolism under various conditions —respiration, vitamines.

The author says, p. 215: "that the molecular size of colloidal particles is large is shown not only by their non-diffusibility, but also by the fact that they may at times be seen in the ultra-microscope; that they scatter light and the light so reflected from their surfaces is polarized (Tyndall phenomenon); and by the fact that they may be centrifugalized out of solution." The author is—perhaps unconsciously—treating colloidal solutions as true solutions. He never would consider that the molecular weight of a kilogram of platinum was very high because the platinum does not diffuse and can be seen. The mere fact of grinding the lump of platinum into small particles cannot increase its molecular weight; but apparently it is permissible to assign all sorts of new properties to finely divided platinum. On p. 228 the author speaks of the sodium salt of the colloid and throughout prefers to talk of indefinite compounds rather than of adsorption. From the reviewer's point of view the author's treatment of colloids, though interesting and consistent, is the weak part of the book.

While the book is primarily technical, there are a great many passages in it of great general interest. One of these is the definition of a living thing, p. 3.

"The various objects on the surface of the earth may be divided into two great classes, the living and the lifeless, the former being characterized by the possession of certain properties which the latter lack. The first of the distinctive properties of living matter is the power of movement; and of movement having an internal rather than an external origin. These movements are either from place to place as in animals; or movements of growth and foliage as in plants. It is by the property of movement that we instinctively distinguish living and lifeless. A second property is that of growth; growth not by the apposition of particles to the outside of the living thing, but growth from within, by the intercalation of substances within the organism. Another, the most characteristic, and the only property it is certainly known that some of the simpler organisms possess, organisms too small to be seen, is that of reproduction. Such organisms are called living because they are capable of indefinite multiplication. Finally we have two properties which often require special apparatus for their detection, but which are, none the less, fully as fundamental as the others, the properties, namely, of respiration and irritability. All living things respire, that is they consume oxygen, liberate energy by combustion or oxidative changes, and they give off a gas, carbon dioxide; and they are irritable; that is they respond in some way, either by a change in the rate of reproduction, in movement, in growth, or in some other of their functions when their surroundings change. We cannot directly observe that many of the smaller forms of life are irritable, but we believe from analogy that they must be so.

"These five properties, movement, growth, reproduction, respiration and irritability, are, hence, those properties possessed by living things, and not possessed, or at least not all of them, by any non-living thing. Their possession defines a living thing. When we speak of life we mean this peculiar group of phenomena; and when we speak of explaining life, we mean the explanation of these phenomena in the terms of better known processes in the non-living."

On pp. 67–69 the author discusses the resemblance of the chemistry of painting to some biological processes. "It is interesting to consider the many curious resemblances of the chemical processes involved in painting with protoplasmic respiration, memory and growth. The use of linseed oil in painting depends on the fact that it oxidizes spontaneously in the air, especially in the light, and decomposes, the decomposition products forming a resinous hard mass of a composition still largely undetermined. Linseed oil has the power, then, of spontaneous oxidation; it respires. It takes up oxygen and it gives off carbon dioxide and other volatile substances. Light, and particularly ultra-violet light, accelerates this respiration just as it does that of protoplasm. Moreover, growth, or rather synthesis, occurs; for, in the condensation following the decomposition, substances are formed more complex than the linolenic acid. Heat moreover is set free. It is, in other words, a veritable metabolism which the linseed oil undergoes. But the relationship to protoplasmic metabolism does not end here. In living matter there are substances which hasten the oxidation, catalytic substances, or oxidases as they are called. In the presence of these substances oxidation goes on much more rapidly than in their absence. Cells use various substances as oxidative accelerators. Manganese salts are used by some; copper or iron salts by others; or organic oxides and peroxides, like the quinones, by others. The painter uses similar substances to accelerate the decomposition and drying of the oil. The oil is sometimes boiled in iron or copper vessels and dryers of various kinds are added to help the oxidation, such as manganese dioxide, litharge, manganous borate or iron salts; or he uses an organic oxidizer, turpentine, which in the light picks up oxygen with great ease and carries it over to the oil. In this respect, then, the metabolism of paint resembles that of protoplasm.

"But most remarkable of all is the fact that the oil may be taught to oxidize itself and it remembers its lesson for some time. If linseed oil is exposed to light, or ultra-violet rays, in the presence of air in a closed flask provided with a mercury manometer, for the first 24 to 36 hours nothing seems to happen; but then slowly the oil begins to oxidize and oxidizes at a constantly accelerating pace so that the oxygen is used up in the flask and the negative pressure may be measured by the mercury manometer. The curve of the rate of absorption of oxygen is at first convex downward, not, like most chemical reactions, concave. It is the curve of an autocatalysis. It is as if the oil had to be taught by the light to oxidize itself and learned to oxidize better and better. Now it may be shown that the oil remembers. If after 60 hours' illumination when the oil is oxidizing let us say at fairly rapid rate, the illumination is discontinued and the oil put in the dark, the oxidation goes on at a slower pace. If after a period of a few hours in the dark the oil is again illuminated by the light, it will be found that the oxidation no longer waits 24 hours before beginning, but now the stimulation by the lamp is effective within an hour or more; the oil acts as if it remembered the teaching by a previous illumination and now oxidizes at a more rapid rate. However, oil can also forget. If left in the dark 24 hours or more after being taught to oxidize, it has forgotten and now teaching must be done all over again, a long illumination being necessary before the oxidation begins. We do not usually speak of the long latent period of the oxidation as a period of teaching, but it is called in chemistry a period of 'inductance;' and we do not say that the oil is learning to oxidize itself, and doing it better and better, but we say that it shows phenomena of autocatalysis; nor do we say that it forgets again in the dark, but that the intermediary, autocatalytic agent has disappeared; but when organisms show the same kind of phenomena we speak of teaching, of latent periods, of stupidity, of good or bad memories. And it is not impossible by any means that the phenomena of memory, shown in greatest perfection by the mammalian cerebrum, may have at the bottom some such basis as this, and the persistence within certain cells of substances of an autocatalytic nature which have remained from a previous stimulation. Perhaps the brain cells remember longest because they most carefully maintain intact, or preserve, these labile autocatalytic substances. It may be mentioned that the whole of growth is an autocatalytic process. There are always left over in the cell, at the close of a period of feeding, substances, enzymes, derived from the metabolism of the foods, which hasten the metabolism of the next succeeding feeding and hasten growth. It is because of the presence of these autocatalytic substances that foods change into protoplasm so much more rapidly in cells than outside of them."

On p. 222 there is an interesting paragraph in regard to soap.

"Perhaps one of the most interesting and instructive cases of a colloidal solution is that of soap in water. In alcohol a soap solution is quite normal, the molecules being monomolecular and not colloidal; but in water there is a true colloidal solution. The explanation of this throws light on many puzzling colloidal phenomena. In water soap is hydrolyzed: that is, some of the soap molecules react with the water to form sodium hydrate and the free fatty acid, the fatty acids being very weak acids.

"Stearic acid is not by itself soluble in water, but just as atoms unite readily in a physical or chemical union with other atoms of the same kind, so stearic acid unites with the stearic ion of that portion of the soap which has not been hydrolyzed. Every sodium atom has, therefore, attached to it one stearate ion, but united with this stearate ion, in either a physical or a loose chemical union, are two or three molecules of stearic acid. If now the soap is salted out of the solution, this mixture of sodium stearate and stearic acid separates in the form of soap. The soap thus forms an electro-negative colloidal particle consisting of several molecules of palmitic, or stearic, acid, and this is held in solution because of the great attraction of the sodium ion for water. The alcoholic soap solution is normal, and not colloidal, for the reason that hydrolysis does not occur in the alcohol and the stearic acid, if formed, has so much greater an affinity for alcohol than for water that it does not form molecular complexes. The cleansing power of soap depends upon this same principle of affinity between the palmitic or stearic acid colloidal particle and the fatty acids of the neutral fats. When soap is put on the skin, the fats of the skin, like the palmitic acid of the soap, adhere to the latter, and the whole is suspended in water because of the attraction of the sodium for the water and the electro-static affinity between the sodium and the palmitate or stearate ion. Very large, loose physico-chemical aggregates may be built up in this way. Thus vaseline, a hydrocarbon, does not readily combine with soap, but it does have an affinity for oil and oil for soap. Thus by rubbing vaseline with oil it is easily removed by soap, the oil acting as an intermediate body. Probably such unions as these contribute to the formation of protoplasm; the union between fat, phospholipin and cholesterol may be of this nature."

From the chapter on digestion in the intestine we quote the following paragraphs, p. 443:

"It has been suggested that substances having the property of raising blood pressure may be produced from tyrosine in putrefaction and that these substances are active in causing arteriosclerosis and the ills which follow from this. Since a man is said to be as old as his arteries it would appear possible that intestinal putrefaction may be a factor in the production of the decrepitude of old age, as Metchnikoff has suggested. To what extent putrefaction produces premature decrepitude cannot be stated without more investigation.

"There can, however, be no question of the importance of these putrefactive substances in the general well-being of the individual. We are all constantly exposed to food poisonings, which, when slight, are generally overlooked as the true cause of inefficiency, depression, sluggish mental processes, dissatisfaction or abnormal irritability. Particularly chicken, veal and pork are liable to contamination from some person handling these meats in the kitchen, who may carry a peculiar race of bacteria. Such food poisonings may come from infected meat-choppers, so that hashed meat is more apt to be a source of trouble than unhashed. If the bacteria are not killed in the subsequent cooking, and the hash is kept, as it is in restaurants, it may give rise to symptoms of food poisoning more or less marked. These symptoms generally come on in 1–5 hours after a meal, if they are due to ptomaines or toxic substances already formed in the meat before eating; but the bacteria themselves may develop in the intestine and form toxic substances. In such cases the onset of the symptoms is delayed coming 12–48 hours after the meal, varying with different individuals. If the symptoms are not well marked so as to lead to cramps, prostration and diarrhoea, by which the bacteria are swept out of the system, only feelings of drowsiness, headache, migraine, lassitude or depression often preceded by mental or sexual excitement are produced, and the real cause of the trouble is overlooked. The symptoms are often baffling and are referred to the nervous system, the ductless glands or any other rather than the true cause. Moreover, when once such a bacterium is lodged in the canal it may persist for a long time and the effect of a single food poisoning in an experiment on human metabolism was found to be clearly perceptible for a month or longer. These facts make it desirable, in case of headache, drowsiness or depression, even though there may be no symptoms of deranged digestion or constipation, to try the effects of a good purge. The effect on the mentality is often remarkably prompt."

The paragraphs on the clotting of blood, pp. 513–520, are very important but too long to quote. Some of the paragraphs in the chapter on the brain must be given, however, p. 584. "In the brain three fundamental properties of living matter are brought to their highest perfection, *i. e.*, conduction, irritability and memory. One function on the other hand is practically in abeyance from an early age, that is, the function of growth. The brain early reaches its full development and thereafter division of the nerve cells does not occur, although there may be some increase in complexity and growth of the dendritic processes. We have before us, therefore, in the brain, in as pure a form as we can find it, a tissue specially built for the functions just mentioned, and we may infer from a study of its composition and a comparison with those tissues which are specialized for growth, or movement, what kind of protoplasm, or what substances in protoplasm, are particularly concerned in irritability. The fact which at once strikes us when we undertake such a study is that the nerve fibers, which are preëminently conducting, are surrounded by medullary sheaths which consist chiefly of phospholipins, glycolipins (cerebrosides) and sulphatides. While it is undoubtedly true that conduction takes place in the axis cylinder, which is of the nature of gray matter, yet the gray matter also is unusually rich in these same constituents or some of them, such as the phosphatides and cholesterol........

"A second very striking and interesting fact in the chemistry of the brain, and one which may perhaps be correlated with the provision of reserve food in the medullary sheath, is the absence of reserve carbohydrate food in the brain and the entire absence of neutral fat. Glycogen, which is found in so many tissues and which occurs in the young, undifferentiated nervous system, is absent in the adult brain. When medullation appears, it disappears and no other carbohydrate is present in the adult brain, except inosite and galactose. The function of inosite is unknown, but it readily combines with phosphoric acid to make phytin and similar esters. Inosite is readily destroyed when taken by the mouth. The absence of neutral fat while the phospholipins and other compound lipins are so abundant is indeed remarkable......

"A third fundamental property of the human cerebrum is memory. It is possible to make some kind of an impression on the human brain of so persistent a nature that when made at from 4–6 years of age it may persist for from forty to eighty years. Of the physical-chemical basis of memory very little is known. When an impulse strikes into the brain something remains there, some trace, perhaps an enzyme. Something happens to the brain, with every impulse fed into it. We may perhaps picture the process as follows in a tentative way, although the evidence is extremely meager that this picture at all represents the real process. There is a growing number of facts which indicate that when nerve impulses impinge on cells they do not at once arouse the peculiar activity of that kind of cell. There is always a latent period. It seems that under the influence of the nerve impulse a substance is produced which in its turn acts as the excitant of the cell activity. This would explain the latent period of muscle and other cells. We may regard the gastric hormone or the secretin of the cells of the intestinal mucosa as such a substance. In muscle possibly lactic acid is the hormone. By a hormone is meant a substance which rouses to activity. Now in the nerve cells it may be that such memory hormones are produced and accumulate, or persist in the cells. There are only two facts of the chemistry of the brain, so far as the author sees, which may be brought into relation with this extraordinary power of memory. One of these facts is the great reduction of autolytic power of the brain tissue as compared with that of any other tissue of the body. If the stomach, the liver, the spleen, the muscles are finely hashed and kept sterile in water at 37° C, their proteins undergo rapid changes of autolytic digestion. The brain under similar conditions undergoes very little autolysis. In fact, the autolysis was at first overlooked, it is so slight; a very little alkali apparently checks it completely. What autolysis there is seems to occur in the first few hours after death. This great reduction of the brain's autolytic power points toward a stability of the brain's proteins, of an absence of wear and tear in the brain, which possibly, but only possibly, for in reality the matter is guesswork, but which involuntarily recalls the stability of impressions and memories in the brain. When autolysis does occur, or when nerve cells are destroyed in injury or by toxins, then memories disappear also, showing that there is some substantial basis of the memories. The stability of the nerve cells, the absence of autolysis, of cell division, all would appear to favor the stability of impressions of whatever kind which are made on the brain by the events about us. It is possible, also, that this absence of autolysis is correlated with the fact that the brain does not lose weight in starvation, but lives on those organs which autolyze the most readily.

"The second fact of interest, although it may be simply a parallelism and not fundamentally connected with the process of memory, is the presence in the cephalin of the brain of very unsaturated acids of the type of linolenic acid. It has already been pointed out that, in the spontaneous oxidation of linolenic acid, phenomena closely paralleling memory and learning occur. These are autocatalytic processes. In the case of linseed oil the memory, if it may be so called, consists in the persistence in the oil of an intermediary, catalytic oxidation product. If this substance could in any way be made stable, so that it would persist for a long period in the dark, linseed oil once illuminated would remember that illumination forever and would always respond differently, when exposed with oxygen to the light, from linseed oil which had not had the experience of a previous illumination. If it were possible that an impulse coming into certain cells caused in those cells the formation of a persistent autocatalytic, intermediary oxidation product, a physical basis of memory might be given. Our ignorance is so profound, however, that at present we can do hardly more than guess at this interesting problem and we must be on our guard against assuming that the basis of memory is in reality that sketched above. All experience shows how often we may be misled by seductive parallelisms of this nature into the conclusion that Nature is working in the manner we imagine her to be. To quote an old and homely, but true, saying: 'Nature knows more than one way to kill a cat.'"

The final chapter on metabolism under various conditions should be read by everybody interested in the subject. Two quotations from it are given, pp. 832, 834.

"The general effects of fasting are extremely interesting. There is no doubt that in many cases fasting is very beneficial to the general health. Chronic diseases, such as catarrhs, and pimples, boils, etc., are said often to have been permanently cured by this simple expedient. The first few days of the fast may be, and generally are, trying; there is not infrequently considerable nausea for a few days; but thereafter the deprivation of food does not appear to cause any very painful sensations beyond great hunger. The total effect on the body is to sweep out of the protoplasm all the deposited waste or reserve material. At least half of the muscle substance has to be regenerated and, according to Child, fasting is, in its essence, of the nature of a regeneration or rejuvenation. This is certainly the case in some of the lower animals, in particular in the flat worms, Planaris, and other animals upon which he worked. In these forms, it is possible to show the fasting animals are in reality rejuvenated and emerge from the fast with all the characteristics of young animals, including a stimulated metabolism, heightened respiration and so on. Whether the human being is capable of a certain degree of rejuvenation by this same process is not yet certain, but there are some indications that some rejuvenescence is possible. It seems generally true that the deposition of colloidal matter in protoplasm is one of the conditions of senescence. It is possible that such depositions increase the difficulty of passage of certain substances into and out of cells, or they interpose barriers in the way of a free exchange of material between the different parts of cells and so ultimately break down the coördination of cell metabolism. If this explanation of senescence, which has been proposed by Child, is true, then fasting would appear to be a means of combating the process to some degree.......

"As has been so often remarked, nearly all of the really fundamental facts in nutrition remain still to be determined. This is illustrated in no more striking fashion than by the discovery in the past few years of the specific action of foods in nourishing the body quite apart from their protein, carbohydrate and fat content. A great field has thus been opened which promises to yield many valuable discoveries. It seemed a few years ago as if with the discovery of the fuel value of a food, of how many calories of energy it contained which were available to the body, and with the estimation of the grams of fat, carbohydrates and protein in it, all that was necessary to determine its food value was known. How far that was from being the truth will appear from what follows. We now know that the character of the fat, protein and carbohydrate is of as great importance as the amount. It is by no means the same whether one eats cane sugar or lactose, although they resemble each other so closely in calories and composition. It has been found, for example, that there is in the brain a large amount of the sugar, galactose. This occurs in the cerebrosides in the medullary sheaths of the nerves. We do not know whether the body, particularly in youth, has the power of making galactose from other carbohydrates. We see, in fact, that Nature, which has had charge of the rearing of children for millions of years, has provided in the mammary glands an organ for the manufacture of galactose, so that the child during the period of the medullation of the nerves of the cerebrum, when cerebrosides may be produced in great abundance, that is in the third to sixth month, may have a nourishment which contains quantities of galactose. The sugar of milk is not cane sugar; it is not maltose; it is not dextrose or levulose, or ribose; but lactose, a sugar containing half its weight of galactose, that important sugar of the brain. It may be almost stated as a truism that had it been more advantageous to have dextrose in milk than lactose, the sugar found there would have been dextrose. The suggestion, therefore, advocated by some physicians, to substitute for the lactose of the milk either cane sugar or dextrose, in artificial feeding of children can only be regarded with misgivings. It is wiser to accept the conclusions of nature which has tried, no doubt, many thousands of experiments of which we are ignorant, and which has provided lactose in the food of infants only after a prolonged research."

This is not only a good and a timely book; it is an interesting one.

Wilder D. Bancroft

Elementary Chemical Microscopy. *By Émile Monnin Chamot. 23 × 15 cm; pp. vi + 410. New York: John Wiley & Sons, 1915. Price: $3.00 net.*—In the preface the author says: "The American chemist, usually ready to accept with alacrity all time, labor and money-saving devices, has been strangely backward in taking advantage of the benefits to be gained through the intelligent application of chemical microscopic methods in the industries and in research. He has also failed to grasp the fact that the modern microscope is, in reality, a more important adjunct to his laboratory than spectrometer, polarimeter, or refractometer; in fact, it may be said that the microscope is entitled to as important a place as the analytical balance. No other instrument can perform so many functions and do them all well . . . .

"The failure of the chemist to obtain from the microscope all that the instrument is capable of yielding is, perhaps, largely due, first, to the fact that few of them are given an opportunity of becoming sufficiently familiar with the instrument and its accessories; second, they are not aware of the great variety of problems which are solvable through the microscope, nor of the specific sort of problems for the investigation of which this is *the* instrument *par excellence;* third, there has been a lack of elementary manuals covering the field, and for this reason the microscope has been looked upon as an instrument peculiar to the biological laboratory."

The headings of the chapters are: objectives and oculars; microscopes for use in chemical laboratories; illumination of objects and illuminating devices; ultramicroscopes and apparatus for the study of the ultramicroscopic particles; the examination of opaque objects, vertical illuminator, metallurgical microscopes; useful microscope accessories, laboratory equipment, work tables, radiants; micrometry and micrometric microscopes; polarized light, the simple polarizing microscope, crystals under the microscope; the determination of refractive index by means of the microscope; quantitative analysis by means of the microscope; the determination of melting and subliming points; methods for handling small amounts of material; the methods of microchemical qualitative analysis; characteristic microchemical reactions of the common elements and acids when in simple mixtures; preparing opaque objects for the microscopic study of internal structure.

The reviewer has had some experience in the use of the microscope in alloy work and elsewhere, and he is glad to bear witness to the great and increasing importance of the microscope to the chemist. Since mental inertia makes most of us very slow to take up a new technique, no matter how important or how simple it may be, it is very fortunate that we now have an excellent book to aid the chemist. It is much to be hoped that the chemical laboratories of the country will lay more stress on chemical microscopy in the future.

The reviewer has only noticed one slip and that is merely a casual matter. On p. 55 the author says that the presence of disintegrating or so-called "digestive" colloids increases the Brownian motion. What the author means is that these substances keep the particles from agglomerating. It might have been well to point out that a homogeneous alloy may seem markedly inhomogeneous because certain crystal faces are in shadow. This can be distinguished from true inhomogeneity by rotating the stage. The dark portions remain dark if one has two phases which have etched differently, while the dark and the light portions reverse if the alloy is homogeneous. For this reason a photomicrograph may be hopelessly misleading. *Wilder D. Bancroft*

Handbuch der Mineralchemie. *By C. Doelter. Vol. II, Part VIII. 25 × 18 cm; pp. 160. Dresden: Theodor Steinkopff, 1915. Price: 6.50 marks.*—This number deals chiefly with the sodium and potassium aluminum and iron silicates, including albite, leucite, and muscovite. The methods for distinguishing the zeolites are admittedly bad, p. 374. A page is given to permutite, p. 375, as being a technically important synthetic zeolite. On p. 400 the author says that "in consequence of the great viscosity of its melt, albite has no definite melting point, but fuses gradually, a phenomenon which is to be noted with many silicates. The interval between the beginning of fusion and point of complete liquefaction is especially large with this silicate and amounts to 60°-80°." What the author really means is that owing to the high viscosity of the melt it is very difficult to determine the actual melting-point of albite.

Wilder D. Bancroft

VAN DER WAALS' EQUATION—A SUPPLEMENTARY PAPER

BY W. V. METCALF

In a recent paper[1] I tried to make it clear that van der Waals' equation is an expression of an equilibrium between opposing pressures. It may be written $P_1 + \frac{a}{v^2} = \frac{RT}{v-b}$ (Equation A) or $P_1 + P_2 = P_3$. P_1 is the external pressure applied to the substance. $P_2\left(=\frac{a}{v^2}\right)$ is the cohesive pressure due to the attraction between the molecules. These two pressures act together in tending to decrease the volume. $P_3\left(=\frac{RT}{v-b}\right)$ is a pressure which tends to increase the volume of the mass. It is due, according to the kinetic theory, to the total effect per unit area of the blows of the individual molecules. I have called it the elastic pressure. As shown in the previous paper, this term has the dimensions of a pressure, since from the ideal gas equation RT has the dimensions of pv and $v - b$ expresses a volume. It seems therefore to be a necessary deduction from the kinetic theory and from the nature of the terms themselves that van der Waals' equation is an expression of an equilibrium between opposing pressures, which determines the volume of the mass.

By the term "volume coefficient" of a pressure in this paper I shall mean $\frac{1}{P}\cdot\frac{dP}{dv}$, that is, the rate of change of the pressure with volume relative to its own value. By the "rate of change with volume" of a pressure I mean $\frac{dP}{dv}$, that is, its absolute rate of change. In the former paper the terms "density coefficient" and "rate of change with density" were used instead of volume coefficient and rate of change with volume. The relation between the two is evident, since v is the reciprocal of D if unit mass is taken. In the present

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[1] Jour. Phys. Chem., 19, 705 (1915).

paper it is found more convenient to express the relations in terms of volume instead of pressure.

The principal conclusions of the previous paper, expressed in terms of volume instead of pressure, were as follows:

1. The volume of a gas or liquid is determined by an equilibrium of pressures, as above.

2. In a stable liquid the *volume coefficient* of the pressure P_3 is greater than that of the pressure P_2. As the liquid increases in volume along a volume-temperature curve however, the ratio of the volume coefficient of P_2 to that of P_3 increases; it becomes equal to unity at a certain definite volume; and thereafter the coefficient of P_2 is increasingly greater than that of P_3.

3. In a stable liquid the *rate of change with volume* of $P_1 + P_2$ is less than that of P_3. As the liquid increases in volume along the volume-temperature curve however the ratio of the first rate to the second increases; it becomes equal to unity at *c*, the maximum point of the curve; beyond *c* it continues to increase to a maximum at *d*, after which it decreases, passing through the value unity again at the minimum point *e*, and beyond *e* it is a decreasing proper fraction.

4. The points *c* and *e* therefore are points at which the rate of change with volume of $P_1 + P_2$ is equal to that of P_3; at which therefore the coefficient of expansion becomes infinite; and at which therefore the nature of the equilibrium changes from stable to unstable and *vice versa*. On curves plotted at successively higher constant external pressures, these two points must, as a necessary result of pressure equilibrium concept, approach nearer and nearer to each other until they finally coincide at the critical temperature.

In the previous paper I tried to show in a purely qualitative way, and largely from physical considerations, that the above propositions are necessary deductions from the kinetic theory, as applied to van der Waals' equation and to the phenomena in question, and that they offer a simple mechanical explanation of all the phenomena. I called attention also to the fact that this pressure equilibrium concept gives a clear insight into the mechanical cause of various phenomena that are not otherwise easily explained. As examples, the explanation of osmotic flow, and of the fact that the vapor tension of a liquid is decreased by dissolving in it a non-volatile substance, were cited.

It is not difficult to explain, in a concrete qualitative way from physical considerations, the mechanical cause of the curious relations described above. In doing this we would have to keep in mind that the cohesive pressure is only a part of the pressure on the left of the equation, while the elastic pressure is the entire pressure on the right; also the fact that the cohesive pressure $\left(\frac{a}{v^2}\right)$ varies inversely as the square of the whole volume, while the elastic pressure $\left(\frac{RT}{v-b}\right)$ varies inversely as the first power of the volume $v - b$, and directly as the absolute temperature, and the physical reasons for this. This is connected with the fact that the cohesive force between the molecules is a function of the average distance between the *centers* of adjacent molecules, while the elastic force, depending at any given temperature on the mean free path, varies as some function of the average distance between the *surfaces* of adjacent molecules. We should bear in mind also that in liquids the average distance between the surfaces of adjacent molecules (on van der Waals' assumption that the molecules are perfectly elastic, incompressible spheres) is ordinarily less than one-half the diameter of the molecule. (See Boynton's "Kinetic Theory," Chapter 8.) We will not elaborate this point at present.

It is possible to prove the above propositions to be rigid mathematical deductions from van der Waals' equation, and it is the purpose of the present paper to do this. As in the former paper, the discussion will be practically confined to the series of volume-temperature curves plotted at successively higher constant external pressures. (See Fig. 1.) An entirely similar analysis applies to the volume-pressure curves plotted at constant temperatures.

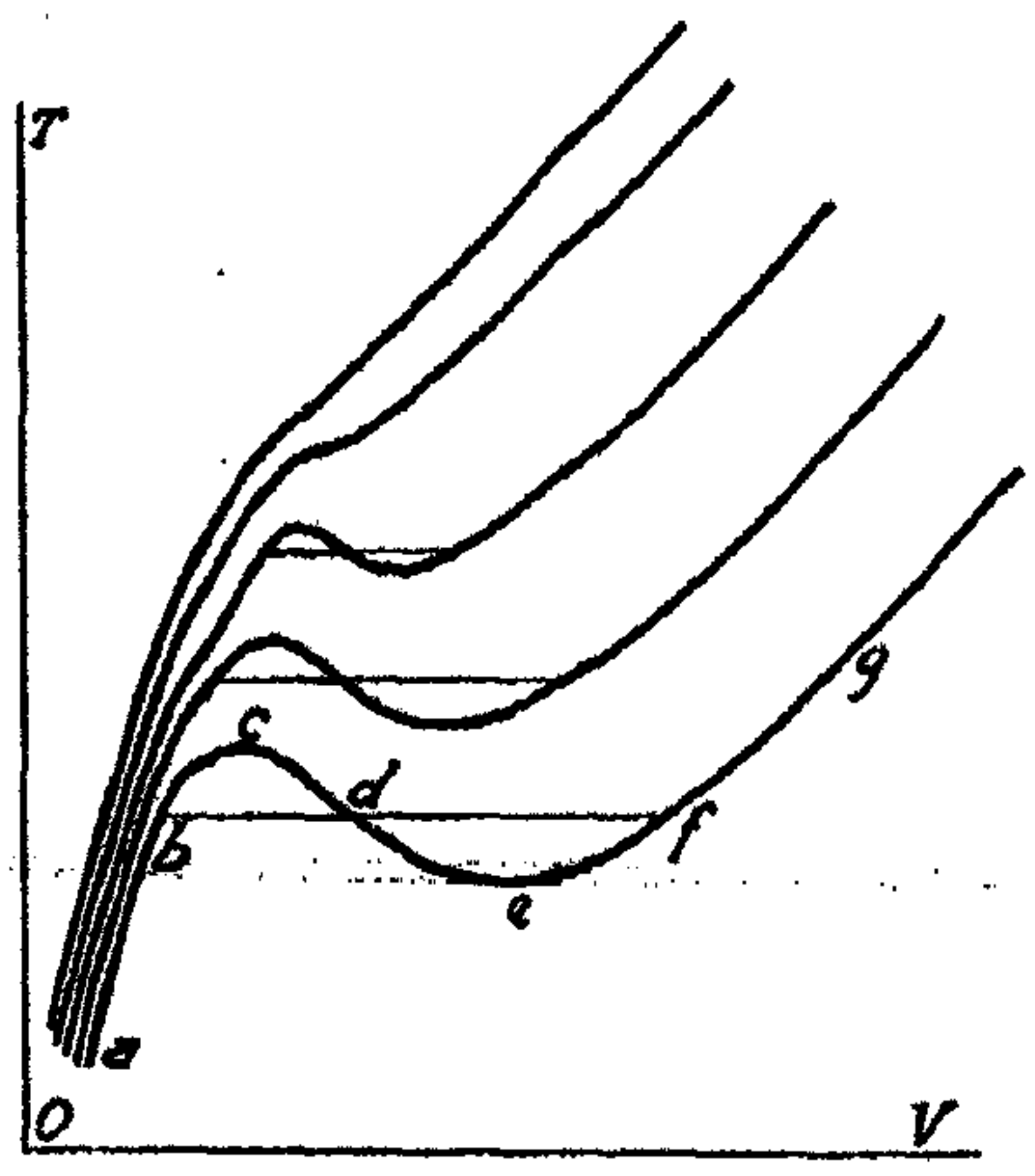

Fig. 1

(1) From Equation A,

The *rate of change with volume* of $P_2 = \frac{d}{dv}\left(\frac{a}{v^2}\right) = -\frac{2a}{v^3}.$

The *rate of change with volume* of $P_1 + P_2 =$

$$\frac{d}{dv}\left(P_1 + \frac{a}{v^2}\right) = -\frac{2a}{v^3}. \quad (P_1 \text{ constant.})$$

The *rate of change with volume* of $P_3 = \frac{\partial}{\partial v}\left(\frac{RT}{v-b}\right) = -\frac{RT}{(v-b)^2}.$

The *volume coefficient* of $P_2 = \frac{1}{P_2} \cdot \frac{dP_2}{dv} = -\frac{2a}{v^3} \cdot \frac{v^2}{a} = -\frac{2}{v}.$

The *volume coefficient* of $P_1 + P_2 =$

$$\frac{1}{(P_1 + P_2)} \cdot \frac{d(P_1 + P_2)}{dv} = -\frac{2a}{v^3} \cdot \frac{v_2}{(P_1v^2 + a)} = -\frac{2a}{(P_1v^2 + a)v}.$$

The *volume coefficient* of $P_3 =$

$$\frac{1}{P_3} \cdot \frac{\partial P_3}{\partial v} = -\frac{RT}{(v-b)^2} \cdot \frac{v-b}{RT} = -\frac{1}{v-b}.$$

It is to be noted that the *rates of change with volume* of $P_1 + P_2$ and of P_3 are the same, since P is constant, but their *volume coefficients* are different.

(2) Equating the expressions in Paragraph 1 for the

volume coefficients of P_2 and P_3, $-\frac{2}{v} = -\frac{1}{v-b}$, or $v = 2b$. Therefore

When $v < 2b$, the volume coefficient of $P_2 <$ the volume coefficient of P_3 (numerically).

When $v = 2b$, the volume coefficient of $P_2 =$ the volume coefficient of P_3

When $v > 2b$, the volume coefficient of $P_2 >$ the volume coefficient of P_3 (numercially),

and as v increases this excess increases. Stated differently,

When $v < 2b$, the ratio of the volume coefficient of P_2 to that of $P_3 = \left(\frac{2(v-b)}{v}\right) < 1$

When $v = 2b$, the ratio of the volume coefficient of P_2 to that of $P_3 = \left(\frac{2(v-b)}{v}\right) = 1$

When $v > 2b$, the ratio of the volume coefficient of P_2 to that of $P_3 = \left(\frac{2(v-b)}{v}\right) > 1$, and

as v increases the ratio $\frac{2(v-b)}{v}$ increases, approaching the limit 2, as v becomes infinite. This proves the second proposition above, and determines the volume at which the two coefficients are equal.

(3) The ratio of the *rate of change with volume* of $P_1 + P_2$ to that of P_3 is $-\frac{2a}{v^3} \cdot \frac{(v-b)^2}{-RT} = \frac{2a}{RT}\left(\frac{1}{v} - \frac{2b}{v^2} + \frac{b^2}{v^3}\right)$. If we should take T as a constant, the first derivative of this expression with respect to v would be $\frac{2a}{RT}\left(-\frac{1}{v^2} + \frac{4b}{v^3} - \frac{3b^2}{v^4}\right)$, and the second derivative would be $\frac{2a}{RT}\left(\frac{2}{v^3} - \frac{12b}{v^4} + \frac{12b^2}{v^5}\right)$. Placing the first derivative equal to zero and solving for v, we get $v = 3b$ or b. Substituting the value $v = 3b$ in the second derivative, we get a negative result. This means that on any volume-pressure curve, the maximum excess of the rate of change of $P_1 + P_2$ over that of P_3 occurs when $v = 3b$, which is the volume of the mass at the critical temperature. This point of maximum excess is the point of inflexion on the curve, and it therefore follows that on any series of volume-pressure curves all the points of inflexion are on the same

vertical line as the critical point. Substituting the value $v = b$ in the second derivative gives a positive result. This means that the algebraic expression has a minimum value when $v = b$, but this has no physical significance, since the condition that $v = b$ is physically impossible on the assumptions from which the equation is deduced.

On the volume-temperature curves, T varies as well as v, and it is not so easy to locate the point at which the maximum ratio between the two rates of change occurs. I have not yet obtained an expression for the volume at this point. It is easy however to prove that such a maximum exists on the curve somewhere between the points c and e, as will be shown later.

(4) Differentiating the original equation,

$$P_1 + \frac{a}{v^2} = \frac{RT}{v - b},$$

we get

$$-\frac{2a}{v^3} = \frac{R}{v-b} \cdot \frac{dT}{dv} - \frac{RT}{(v-b)^2}, \text{ or } \frac{RT}{(v-b)^2} - \frac{2a}{v^3} = \frac{R}{v-b} \cdot \frac{dT}{dv}.$$

From the original equation,

$$T = \frac{1}{R}\left(P_1 v - P_1 b + \frac{a}{v} - \frac{ab}{v^2}\right), \text{ and } \frac{dT}{dv} = \frac{1}{R}\left(P_1 - \frac{a}{v^2} + \frac{2ab}{v^3}\right).$$

Substituting this value of $\frac{dT}{dv}$ in the expression $\frac{R}{v-b} \cdot \frac{dT}{dv}$, we get

$$\frac{P_1}{v-b} - \frac{a}{(v-b)v^2} + \frac{2ab}{(v-b)v^3},$$

therefore

$$\frac{RT}{(v-b)^2} - \frac{2a}{v_3} = \frac{P_1}{v-b} - \frac{a}{(v-b)v^2} + \frac{2ab}{(v-b)v^3}.$$

From Paragraph 1,

$$\frac{RT}{(v-b)^2} - \frac{2a}{v^3}$$

is the rate of change with volume of $P_1 + P_2$ minus that of P_3, and therefore

$$\frac{P_1}{v-b} - \frac{a}{(v-b)v^2} + \frac{2ab}{(v-b)v^3}$$

is equal to the same difference of rates. When the two rates are equal, each of these expressions equals zero, and we get

$$\frac{\mathrm{RT}}{(v-b)^2} - \frac{2a}{v^3} = 0, \text{ or } v^3 = \frac{1}{\mathrm{RT}}(2av^2 - 4abv + 2ab^2),$$

also

$$\frac{\mathrm{P}_1}{v-b} - \frac{a}{(v-b)v^2} + \frac{2ab}{(v-b)v^3} = 0, \text{ or } v^3 = \frac{av}{\mathrm{P}_1} - \frac{2ab}{\mathrm{P}_1}.$$

Equating these two values of v,

$$v^2 - \left(2b + \frac{\mathrm{RT}}{2\mathrm{P}_1}\right)v + b + \frac{b\mathrm{RT}}{\mathrm{P}_1} = 0.$$

Solving for v, we get

$$v = b + \frac{\mathrm{RT} - \sqrt{\mathrm{R}^2\mathrm{T}^2 - 8b\mathrm{RTP}_1}}{4\mathrm{P}_1}. \quad \text{(Equation B) and}$$

$$v = b + \frac{\mathrm{RT} + \sqrt{\mathrm{R}^2\mathrm{T}^2 - 8b\mathrm{RTP}_1}}{4\mathrm{P}_1}. \quad \text{(Equation C.)}$$

(5) Equations B and C give two values of v, at which the rates of change with volume of $\mathrm{P}_1 + \mathrm{P}_2$ and of P_3 are equal. As explained in the previous paper, these two values are those of the maximum and minimum points *c* and *e* on the curve.

In Equation B, when $\mathrm{P}_1 = 0$, $v = 2b$.[1] This value corresponds with the conclusion drawn under Paragraph 2, since when $\mathrm{P}_1 = 0$, $\mathrm{P}_2 = \mathrm{P}_3$ and hence their rates of change with volume must be equal when their volume coefficients are equal. In Paragraph 2 it was shown that the two coefficients are equal when $v = 2b$.

In Equation C, when $\mathrm{P}_1 = 0$, v is infinite, which means that on the limiting curve on which the external pressure is zero, there is no second value of v for which the rates of $\mathrm{P}_1 + \mathrm{P}_2$ and of P_3 are equal. In the nature of the case, no minimum point corresponding to *e* would be possible on this

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[1] $\left.\frac{\mathrm{RT} - \sqrt{\mathrm{R}^2\mathrm{T}^2 - 8b\mathrm{RTP}_1}}{4\mathrm{P}_1}\right]_{\mathrm{P}_1 = 0} = \frac{0}{0} = \left.\frac{b\mathrm{RT}}{\sqrt{\mathrm{R}^2\mathrm{T}^2 - 8b\mathrm{RTP}_1}}\right]_{\mathrm{P}_1 = 0} = b$ (taking the derivative of numerator and denominator). Therefore $\left. v\right]_{\mathrm{P}_1 = 0} = b + \left.\frac{\mathrm{RT} - \sqrt{\mathrm{R}^2\mathrm{T}^2 - 8b\mathrm{RTP}_1}}{4\mathrm{P}_1}\right]_{\mathrm{P}_1 = 0} = b + b = 2b$, as stated above.

curve. At c, P_2 would be equal to P_3. After passing c, P_2 would decrease with increase of volume more rapidly than P_3 and would therefore remain permanently less than P_3. There being no external pressure to produce equilibrium, the condition would be unstable from this point on, and the mass would continue to expand indefinitely.

In Equation B again, when $P_1 = 0$, $v = 2b$, and as P_1 increases from 0 to $\frac{RT}{8b}$, v increases from $2b$ to $\left(b + \frac{RT}{4P_1}\right)$. Therefore, on the successive volume-temperature curves plotted at successively higher constant external pressures, the maximum point c occurs at successively greater volumes (that is, further and further to the right) up to the limit $v = b + \frac{RT}{4P_1}$, beyond which it can not go since beyond this point the expression becomes imaginary.

In Equation C, as P_1 increases from 0 to $\frac{RT}{8b}$, v decreases from infinity to $\left(b + \frac{RT}{4P_1}\right)$, that is, the minimum point e occurs further and further to the left on the curves plotted at successively higher constant external pressures. It can not move further to the left than this, since beyond this point the expression is imaginary. The two points c and e therefore coincide when $v = b + \frac{RT}{4P_1}$. This is of course the critical point, and the critical volume is $b + \frac{RT}{4P_1}$. Substituting for P_1 in this expression its value at this point $\frac{RT}{8b}$, the value of v reduces to $3b$. Substituting these values of P_1 and v in the original equation (A), and solving for T, we get $T = \frac{8a}{27Rb}$; and substituting this value of T in $P_1 = \frac{RT}{8b}$, we get $P_1 = \frac{a}{27b^2}$. These are the well-known critical constants, $\phi = 3b$, $\theta = \frac{8a}{27Rb}$, and $\pi = \frac{a}{27b^2}$, obtained from van der Waals' equation by an entirely different line of argument.

In Paragraph 4 it was proved that on any volume-temperature curve, the rate of change with volume of $P_1 + P_2$ minus the rate of change with volume of P_3 is equal to zero when $v = b + \frac{RT - \sqrt{R^2T^2 - 8bRTP_1}}{4P_1}$, and also when $v = b + \frac{RT + \sqrt{R^2T^2 - 8bRTP_1}}{4P_1}$. These two points are the maximum and the minimum points *c* and *e* on the curve. Since at these two points the excess of the rate of $P_1 + P_2$ over that of P_3 is equal to zero, it is evident that somewhere between *c* and *e* this excess must have either a maximum or a minimum. It is evident from what precedes that at *c* the ratio of the rate of $P_1 + P_2$ to that of P_3 is an increasing function of v, and therefore the excess of the rate of $P_1 + P_2$ over that of P_3 has a maximum rather than a minimum between *c* and *e*.

We have now shown that the propositions stated at the beginning of this paper are mathematical deductions from van der Waals' equation. But the accuracy of the propositions is not dependent on that of the equation. The equation is only an approximation to the truth. It varies materially from the facts of experiment, especially in the case of liquids. The propositions in question however, as shown in the previous paper,[1] are an expression of the way liquids actually behave. The equation describes qualitatively, in a remarkable way, the behavior of a substance in the gaseous and the liquid states. This fact makes it one of the important generalizations of modern science. It establishes the probability, in my judgment, that when the more accurate law is found, it will prove to be a more general expression of which van der Waals' equation is a limiting case, just as the ideal gas law is a limiting case of van der Waals' equation.

Van der Waals' equation describes qualitatively the behavior of liquids and gases *because* the truth of the propositions in question is necessarily involved in it. Quantitatively it is inaccurate because of something else in the equation, or

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[1] For an exception to this statement see Bridgman's work referred to in the previous paper.

some lack in the equation, which causes its variation from the facts of experiment. The various attempts to improve the equation, that have been made from the theoretical and from the empirical standpoints, do not seem as yet to have produced results of much value. I suspect that the inaccuracy of the equation is due, in part at least, to its failure to take into consideration the elastic force arising from the compression of the molecules and the atoms. If so, the expression for the elastic pressure will have to be modified, and perhaps a new term added to it which will represent a pressure that is powerful in liquids but practically zero in gases. It may be, if Bridgman is right in his analysis of this kind of elastic pressure,[1] that in liquids the new force will replace rather than supplement that due to the vibrations of the molecules, there being an intermediate stage in which the two elastic pressures act together. In this case van der Waals' expression for elastic pressure will have to be so modified that it reduces to zero in the case of liquids, leaving the added term to express the entire elastic pressure in this condition. And these changes must be so made as to leave the equation in harmony with the propositions at the beginning of this paper.

In the previous paper it was suggested that it may prove possible, through the pressure equilibrium concept and a comparison of its necessary deductions with the physical properties of liquids, to determine the values of the internal pressures of liquids and the laws of their variation. The law of the variation of the elastic pressure may well prove exceedingly complex, if it depends on the compressibility of the molecules and the atoms. The idea is suggested of pressure equilibria within the individual molecules and atoms, by which their volumes are determined.

Such speculations, however, are of little value until they materialize into a definite form that can be tested experimentally.

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[1] For reference, see previous paper.

In conclusion, I call attention to the fact that the pressure equilibrium concept has a bearing on many other phenomena than those represented by van der Waals' equation. As examples we may cite the vaporization of liquids and the melting of solids and the reverse processes; the solubility of a solid in a liquid; the mutual solubility of two liquids, with all its variations from complete miscibility, through the various cases of partial mutual solubility, to complete mutual insolubility; the change from one allotropic modification to another. Finally the course of chemical reactions must be vitally affected by the changes involved in internal pressures.

I desire to express my thanks to Professor F. Anderegg for checking over with me the mathematics of this paper.

The following corrections should be made in the previous paper:

(1) Page 713, line 7, omit "not of the cohesive pressure alone, but" (2) page 714, line 2, omit "approximately that of the critical point" (3) page 714, line 7, omit "rate of change of the cohesive pressure," and insert in its place "excess of the density coefficient of the cohesive pressure over that of the elastic pressure."

THE ADSORPTION OF ACIDS BY CELLULOSE

BY ALAN LEIGHTON

In 1875 Girard[1] noticed that 55 percent sulphuric acid changed cotton wool inside of twelve hours into a material which crumbled between the fingers. The same brittle product can also be obtained with more dilute acid if the cotton is heated to 60°–70°, and also with other acids than sulphuric acid. Girard[2] called this product hydrocellulose. The reasons for considering it a new substance are the brittleness and the fact that basic dyes are taken up more strongly by it than by the original cotton. This latter fact is no argument because mercerized cotton takes up dyes more readily than the untreated fiber and yet has not been changed chemically. The brittleness is not conclusive as to the occurrence of a new substance any more than is the lustre of mercerized cotton or the varying apparent solubility of beryllium hydroxide. Girard[3] found that hydrocellulose was not soluble in hot one percent caustic potash. This makes it seem probable that hydrocellulose is really cellulose and is not a new compound at all.

As a preliminary to a possible future study of hydrocellulose, Professor Bancroft requested me to make some measurements on the adsorption of acid by cellulose. The cellulose used was surgeon's cotton purified by treating with one percent caustic soda as previously described.[4] About one gram of cotton was shaken with 100 cc acid for three hours and then centrifuged for one hour, after which the amount of acid retained in the cotton was determined by suitable gravimetric or volumetric means. The limiting concentrations of the acids were those at which the cotton could still be centrifuged completely. The data obtained by the anal-

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[1] Comptes rendus, 81, 1105 (1875).
[2] Ann. Chim. Phys., (5) 9, 116 (1876).
[3] Ibid., (5) 24, 366 (1881).
[4] Leighton: Jour. Phys. Chem., 19, 32 (1915).

ysis of the cotton form the gravimetric curve when plotted. The acid that was centrifuged from the cotton was also titrated. When there was any change in concentration, the apparent amount of acid adsorbed was calculated. As shown in the paper on the adsorption of caustic soda, the "titration curve" thus obtained is not accurate, because water is also taken up by the cotton and this fact is ignored deliberately in making the calculations. All measurements were made at room temperature.

The first acid studied was sulphuric acid. After the cotton had been centrifuged, it was treated with alkali to fix the acid as sodium sulphate and the whole ignited in platinum. The sodium sulphate was leached from the residue and the sulphate determined as barium sulphate. The liquor from the cotton was titrated with standard alkali using methyl orange as indicator. The data are given in Table I and are plotted in Fig. 1, the scale of abscissas for the titration curve being one hundred times that for the gravimetric curve. There is no evidence for the existence of a compound on either curve. Up to a concentration of 400 g sulphuric acid per liter the solution is adsorbed as such within the limits of error of the titration. There is nothing in my work to show whether

TABLE I

Solution g H_2SO_4 per liter	Adsorption	
	Gravimetric g H_2SO_4 per 100 g cellulose	Titration g H_2SO_4 per 100 g cellulose
50.0	—	0
101.2	4.65	0
151.7	5.77	0
202.3	7.35	0
252.3	10.00	0
302.3	12.55	0
352.3	15.36	0
413.9	20.99	0
459.2	—	0.12
521.7	23.70	1.53
747.7	—	2.04

acid more concentrated than 400 g per liter produces any irreversible change in the cellulose or not. It would have been a good plan to have treated the cotton with acid of about 700 g per liter and then to have diluted the solution carefully to about 400 g per liter, to see whether the titration curve dropped back practically to zero again; but unfortunately this was not done. Vignon[1] found that there was no perceptible change in concentration when cotton was treated with one percent sulphuric acid. This is in accord with my results which show the same thing to hold true up to a concentration of 400 grams per liter. Schwalbe[2] states that Koechlin found that sulphuric acid is readily washed out of cotton. This is in accord with my results, because the acid will wash out readily when the ratio of acid to water in the solution is the same as in the fiber.

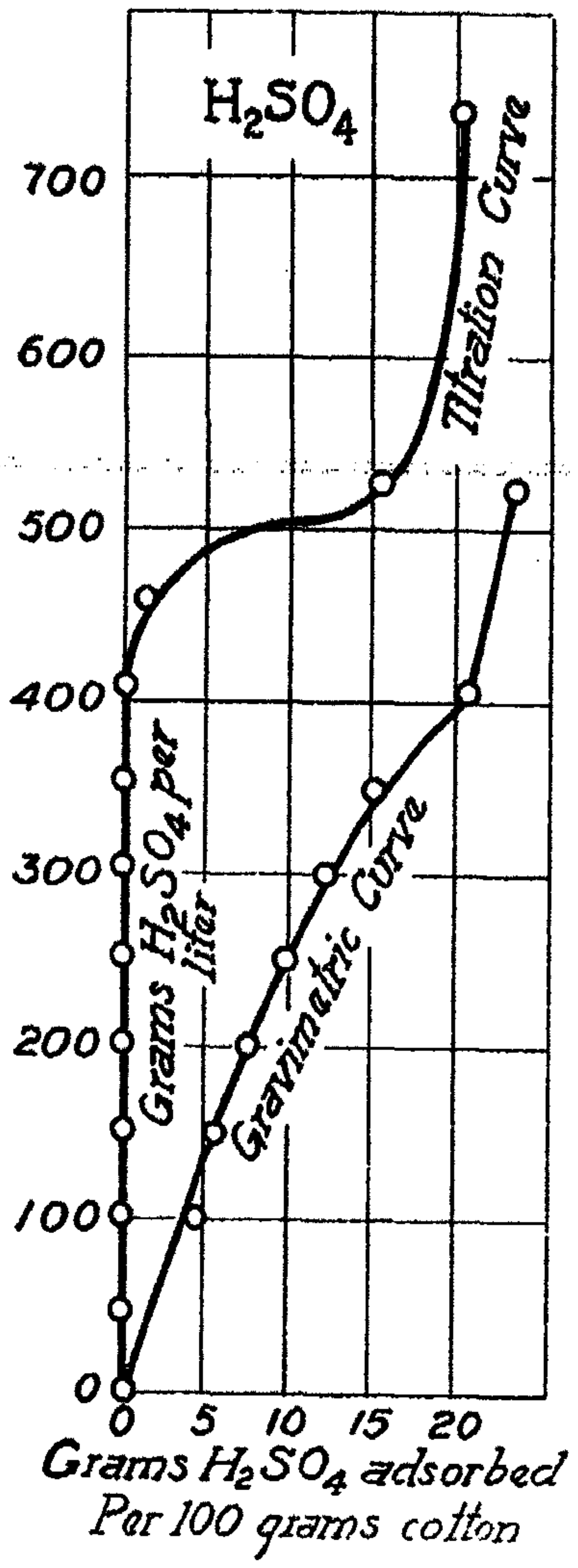

Fig. 1

One rather surprising thing follows from these figures. If we calculate the amount of water adsorbed per gram of cotton, we find that it is about 0.3–0.4 g for concentrations up to 400 g H_2SO_4

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[1] Comptes rendus, 143, 550 (1906).

[2] Die Chemie der Cellulose, 57 (1911).

per liter whereas it worked out to four grams with concentrations of caustic soda up to 75 g NaOH per liter and is 0.8 gram for a concentration of 475 g NaOH per liter. In other words, the presence of sulphuric acid in the solution cuts down enormously the amount of water taken up by the cotton even though the solution is adsorbed without change. To word it somewhat differently, cotton is much dryer when immersed in sulphuric acid solution than when in caustic soda solution.

The next acid studied was the tribasic phosphoric acid. The cotton was burned off and the phosphoric acid determined as magnesium pyrophosphate. Fewer points were determined because it was merely desired to get a general idea of the relative form of the curve. In concentrated solutions the cellulose went completely into solutions. The data are given in Table II and are plotted in Fig. 2.

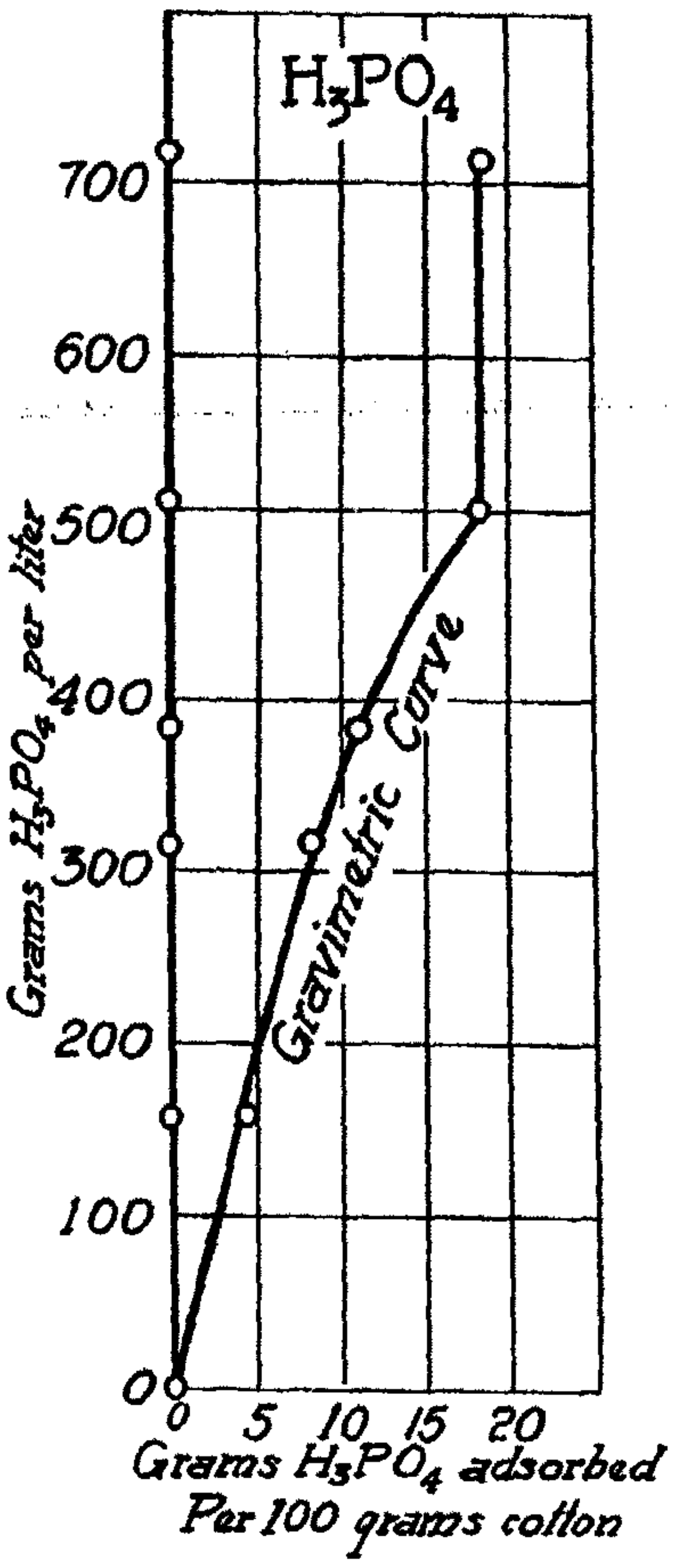

Fig. 2

The gravimetric curve is a smooth one. At all concentrations the solution is apparently adsorbed as such and consequently there is no titration curve. The adsorption of phosphoric acid is somewhat less than that of sulphuric acid. The amount of water adsorbed by the cotton is less, only about 0.2–0.3 g H_2O per gram of cotton.

Hydrochloric acid was then studied as a typical mono-

TABLE II

Solution g H_3PO_4 per liter	Adsorption	
	Gravimetric g H_3PO_4 per 100 g cellulose	Titration g H_3PO_4 per 100 g cellulose
158.0	4.53	0
318.8	8.57	0
382.9	11.53	0
514.4	18.43	0
715.2	18.68	0

basic acid. After centrifuging, the acid in the cotton was fixed as sodium chloride and the whole mass was ignited at a low heat. The sodium chloride was dissolved from the residue and determined volumetrically as silver chloride, using chromate as indicator. The curve thus obtained is still the "gravimetric curve." The few points on this curve are the averages of many determinations, since it proved difficult to get concordant results, presumably owing to the volatility of the acid. There was no difficulty in determining the titration curve. The data are given in Table III and are plotted in Fig. 3.

TABLE III

Solution g HCl per liter	Adsorption	
	Gravimetric g HCl per 100 g cellulose	Titration g HCl per 100 g cellulose
45.8	2.0	0
114.5	3.1	0
209.2	6.2	2.34
288.9	6.9	7.00
331.3	7.3	9.28
373.6	9.1	11.63
414.0	—	13.97

It will be noticed that the titration curve cuts the gravimetric curve. It seems certain that this is an experimental error. It is probable that some hydrochloric acid volatilized from the cotton during centrifuging. The time at my disposal was too short to allow me to test this point further.

On comparing the three tables we see that sulphuric acid is adsorbed more than phosphoric acid, and phosphoric acid more than hydrochloric acid when the concentrations are expressed in grams. There is no selective adsorption with phosphoric acid, some with sulphuric acid, and a good deal with hydrochloric acid. Curiously enough, the selective adsorption becomes marked only at the high concentrations. This is not in accord with what has been noticed in experiments on adsorption by filter paper. Thus Bayley[1] says: "Taking a strong solution of copper sulphate and diluting portions of it (and dropping on filter paper), I found that at one degree of dilution the metal spread outwards just as far as the water, and that with solutions more dilute than this, the water is separated from the metal, which remains in the center. The more dilute the solution the broader is the external water-ring." This result has been confirmed by Gordon.[2] It is quite possible that I would have obtained different results with more dilute solutions. These experiments should be made.

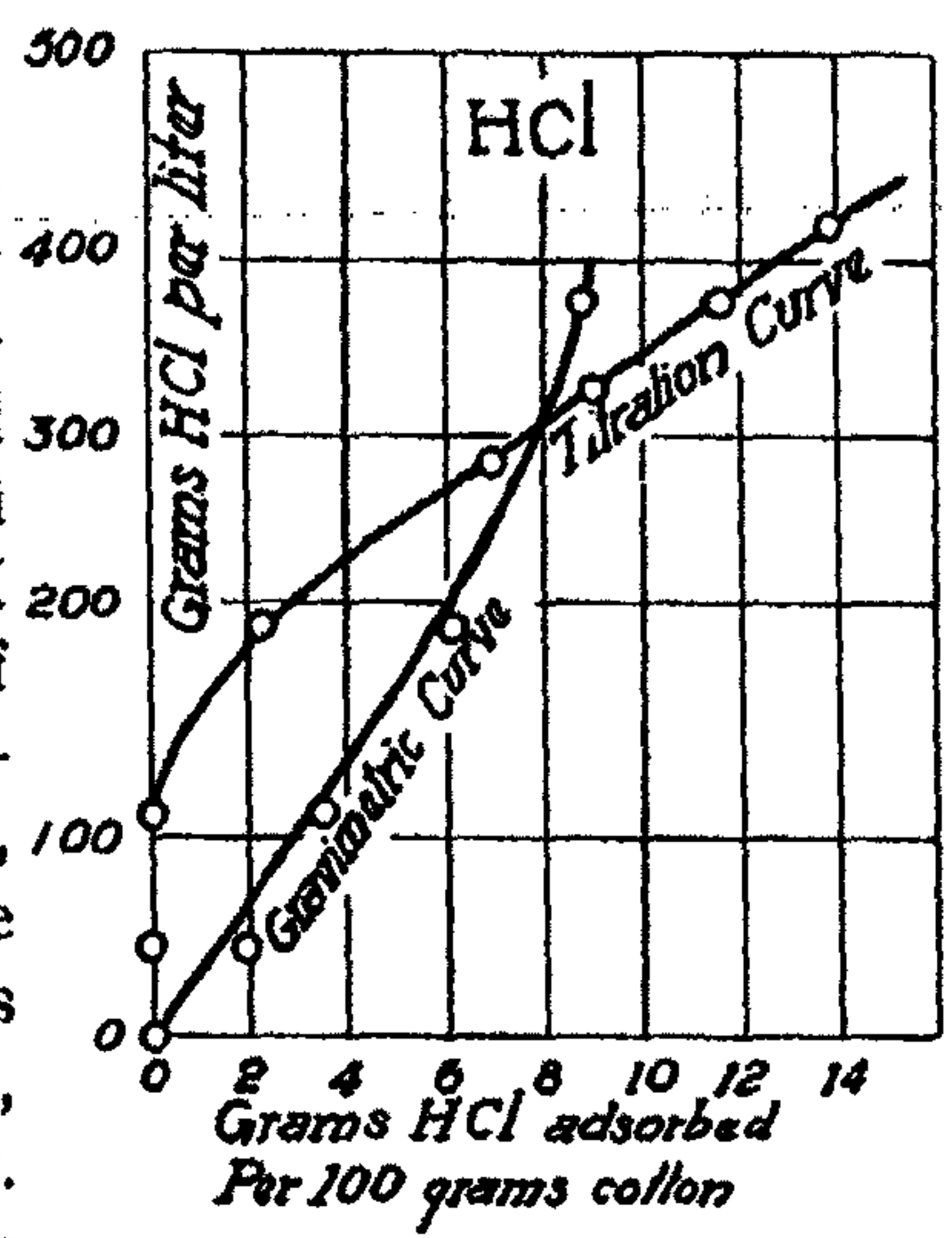

Fig. 3

The general results of this paper are:

1. Hydrochloric, sulphuric, and phosphoric acids form no compounds with cellulose at ordinary temperatures.

2. Hydrochloric acid is least adsorbed and sulphuric acid the most.

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[1] Jour. Chem. Soc., 33, 304 (1878).

[2] Jour. Phys. Chem., 18, 337 (1914).

3. Presence of any one of these three acids cuts down markedly the amount of water adsorbed by the cotton.

4. Selective adsorption is most marked with hydrochloric acid; it is less with sulphuric acid; and does not occur at all with phosphoric acid.

5. In my experiments selective adsorption was noticed only with the higher concentrations. From the work of others it seems probable that selective adsorption would also have been found with more dilute solutions.

6. The differences between the titration method and the gravimetric method are large because the first method gives merely the selective adsorption.

Cornell University

THE VELOCITY OF SAPONIFICATION OF FATS AND OILS BY POTASSIUM HYDROXIDE IN DIFFERENT SOLVENTS[1]

BY ERNEST ANDERSON AND H. L. BROWN

There has been considerable controversy as to the exact reactions which take place during the saponification of glycerides.[2] The theory usually accepted is that the alkali acts as an accelerating agent, and that no saponification can take place in the absence of all traces of water.[3] All investigators agree that such reactions as that between ethyl acetate and aqueous potassium hydroxide are bimolecular, but the various investigators hold different views as to the order of the reaction in the saponification of glycerides. The majority hold that this reaction is bimolecular,[4] some, however, hold that the saponification of certain glycerides is a tetramolecular reaction.[5]

In this investigation the points studied were: (1) The order of the reaction. (2) The relative velocity of saponification of different fats and oils under the same conditions. (3) The influence of the solvent on the velocity of the reaction. (4) The temperature coefficient for the reaction. In addition to the above points the investigation throws light upon the influence of variation in the concentration of alkali and oil; upon the equilibrium finally reached, and other minor points.

Method of Procedure

There are two accurate methods by which the velocity of saponification may be determined. In this investigation

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[1] Contribution from the Massachusetts Agricultural College.

[2] See Lewkowitsch: Oils, Fats and Waxes, 1913 Ed., 76, for a list of references to these controversies.

[3] Lewkowitsch: Am. Chem. Jour., 43, 432 (1910).

[4] Geitel: Jour. prakt. Chem., 55, 429 (1897); 57, 113–131 (1898).

[5] Kellner: Chem. Zeit., 33, 453, 662, 993 (1909); Jour. Chem. Soc., 96, 357, 548, 759; Balbiano: Ber. deutsch. chem. Ges., 36, 1571 (1903); 37, 155 (1904); Marcusson: 39, 3466 (1906).

the volumetric method was used. It is very accurate though possibly not so accurate as the conductivity method used by Walker,[1] Stieglitz and Derby.[2]

The exact procedure followed in the investigation is given below. A certain volume of oil, usually 5 cc or 10 cc, was made up to 100 cc with the desired solvent,[3] and placed in the thermostat. At the same time an equal volume of potassium hydroxide in the same solvent was placed in the thermostat. After the two solutions had reached constant temperature, they were mixed. At suitable intervals, which depend upon the velocity of the particular reaction, 10 cc of the reaction mixture were withdrawn, and run into an excess of $N/10$ hydrochloric acid, the time being accurately noted. The excess hydrochloric acid was then titrated with $N/10$ barium hydroxide, using phenolphthalein as indicator. This titration was made in 50 cc of ethyl alcohol so that the final mixture would, in all cases, be clear, thus making possible a delicate end point.

The Results Obtained in the Investigation

I. The saponification of fats and oils by potassium hydroxide is a bimolecular[4] reaction under the conditions of this investigation.

The velocity of saponification of five different oils was determined as follows: Five cubic centimeters of the oil were saponified by 200 cc of 2/10 normal amyl alcoholic potassium hydroxide at 25° C. Substitution of the velocity data

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[1] Chem. News, 94, 238 (1906).

[2] Am. Chem. Jour., 31, 449 (1904).

[3] The solvents used were methyl alcohol, ethyl alcohol and amyl alcohol. In each case they were purified by treatment with a small amount of silver nitrate and considerable solid potassium hydroxide. After standing 24 hours they were filtered and distilled. Lewkowitsch (Oils, Fats and Waxes, 1913 Ed., Vol. I, 103-4), gives the various methods used in purifying alcohol for use in work such as described in this article.

[4] Geitel: Jour. prakt. Chem., 55, 429 (1897); 57, 113-131 (1898), studied the hydrolysis of triacetin by dilute hydrochloric acid and the saponification of cottonseed oil by alcoholic potassium hydroxide, and decided that they were bimolecular reactions.

in the various reaction formulas gave constant values with only the bimolecular formula, hence the reactions were all bimolecular. See Table 1. Two cubic centimeters of methyl acetate were saponified under the same conditions, and gave a similar constant. This is a well known bimolecular reaction.

Table 1[1]

Evidence that the Reaction is Bimolecular. The constants in this table were obtained by substituting the experimental data from 5 cc oil and 200 cc 2/10 normal alkali (amyl alcohol) in the bimolecular reaction formula

	Butter fat	Cottonseed	Castor	Olive	Croton	Methyl acetate
	0.001750	0.001529	0.001720	0.001633	0.001789	0.005496
	0.001801	0.001537	0.001711	0.001616	0.001658	0.005363
	0.001746	0.001635	0.001633	0.001609	0.001611	0.005610
	0.001773	0.001595	0.001614	0.001552	0.001575	0.005357
	0.001756	0.001572	0.001627	0.001606	0.001503	0.005303
	0.001769	0.001555	0.001798	0.001521	0.001464	0.005335
	0.001798	0.001556	0.001744	0.001535	0.001445	—
	—	0.001579	—	0.001768	—	—
	—	0.001466	—	—	—	—
Average	0.001770	0.001557	0.001698	0.001605	0.001578	0.005411

The average saponification value of the oils used is about 200. Therefore, although it would require only 0.91 gram of potassium hydroxide to completely saponify the average oil, there were 2.24 grams of potassium hydroxide present. Determinations were also made in which 5 cc of oil were saponified by 200 cc of 4/10 normal amyl alcoholic potassium hydroxide. In this case there were 3.57 grams of potassium hydroxide in excess of the 0.91 gram actually required to saponify the 5 cc. of oil. The results are given in Table 2. The reaction proceeds quite rapidly, but the results are as nearly constant as could be expected.

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[1] The experimental data and method of calculation for each table are given under the corresponding heading at the close of the paper.

Table 2

Evidence that the Reaction is Bimolecular. The constant in this table was obtained by substituting the experimental data from 5 cc castor oil and 200 cc 4/10 normal amyl alcoholic potassium hydroxide in the bimolecular reaction formula

Castor oil
0.002175
0.002222
0.002052
0.002034
0.002125
Average 0.002149

When 10 cc of castor oil were saponified by 200 cc of 2/10 normal amyl alcoholic potassium hydroxide, there was present about 0.42 gram of potassium hydroxide in excess of the amount actually required by the oil. The constant obtained in this case is given in Table 3.

Table 3

Evidence that the Reaction is Bimolecular. The constant in this table was obtained by substituting the experimental data from 10 cc castor oil and 200 cc 2/10 normal amyl alcoholic potassium hydroxide in the bimolecular reaction formula

Castor oil
0.001549
0.001541
0.001557
0.001581
0.001554
0.001532
0.001517
0.001536
Average 0.001546

The results given in Tables 1, 2 and 3 seem to show conclusively that the reactions are bimolecular under the three concentrations investigated. The constants for the glycerides compare favorably with that obtained for methyl acetate which is without a doubt a bimolecular reaction.

II. The fats and oils investigated are all saponified at approximately the same rate.[1]

The data given in Table 4 are the average of the constants obtained by saponifying 5 cc of the oil or fat in 200 cc of 2/10 normal amyl alcoholic potassium hydroxide. It is evident that butter fat is saponified a little more rapidly than the other four glycerides.

TABLE 4

The Saponification Constants for Different Oils and Fats under the Same Conditions are Approximately the Same

Butter fat	Cottonseed	Croton	Olive	Castor
0.001770	0.001550	0.001578	0.001605	0.001692

The mean molecular weights of the fatty acids present in the above four vegetable oils are approximately the same. If arranged in the order of their molecular weights it will be seen that the velocity increases with the molecular weight.

TABLE 5

The Velocity of Saponification Increases with the Molecular Weight of the Acid in the Glyceride[2]

Oil	Cottonseed	Croton	Olive	Castor
Mol. wt.	274	279	291	293
Vol. const.	0.001550	0.001578	0.001605	0.001692

The relation indicated in Table 5 may or may not be due

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[1] So far as the authors are aware, no one has compared the velocity constants of saponification of different fats and oils up to the present time. The results obtained here would be expected from the work of Thum: Zeit. angew. Chem., 1890, 482, and Henriques: Jour. Soc. Chem. Ind., 1898, 673 and 853; Urbain, Saigon and Feige: Bull. Soc. Chim., 31, 1194, derived the conclusion from their experiments with the castor bean ferment, that the saponification of the various glycerides proceeds at the same rate. On the other hand, Haller: Comptes rendus, 143, 660 (1906), is of the opinion that glycerides of the lower fatty acids are more readily hydrolyzed than those of higher fatty acids.

[2] See preceding note for the conclusions of Haller.

to a coincidence. It would of course be possible that experimental error was the cause of this apparent relation.

III. The velocity of saponification reactions is different in different solvents.[1]

The evidence supporting this statement was obtained by saponifying castor oil in three different alcohols. Three different concentrations of oil and potassium hydroxide were used in each alcohol. The proportions were as follows:

(*a*) Five cubic centimeters of oil with 200 cc of 4/10 normal alcoholic alkali.

(*b*) Five cubic centimeters of oil with 200 cc of 2/10 normal alcoholic alkali.

(*c*) Ten cubic centimeters of oil with 200 cc of 2/10 normal alcoholic alkali.

The constants obtained when using 5 cc of oil with 200 cc 4/10 normal alcoholic potassium hydroxide are given in Table 6.

TABLE 6

Relative Speed of Saponification of Castor Oil by 4/10 Normal Alkali in Different Alcohols

	Methyl	Ethyl	Amyl
	0.0001079	0.001173	0.002222
	0.0001051	0.001135	0.002034
	0.0001104	0.001165	0.002052
	0.0001002	0.001179	0.002034
	0.0001010	0.001214	0.002125
	0.0001010	0.001166	—
	—	0.001205	—
Average	0.0001020	0.001177	0.002149
Ratio	1	11.5	21

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[1] The influence of the solvent on the speed of chemical reactions in general is very great. Menschutkin: Zeit. phys. Chem., 6, 41; Patterson and Montgomerie: Jour. Chem. Soc., 101, 2100; Dimroth: Liebig's Ann., 399, 91; Halban and Kersch: Ber. deutsch. chem. Ges., 45, 2418; Halban: Zeit. phys. Chem., 67, 129; Jour. Chem. Soc., 96 II, 722. Some investigators vary the composition of the solvent in the saponification of fats by the addition of other solvents. Thus Geitel, Hehner, Duclaux, and others, have added ether to the mixture. Henriques: Jour. Soc. Chem. Ind., 1896, 299 and 476, dissolves the fat in petroleum ether, and mixes this solution with alcoholic soda solution.

When 5 cc of oil were saponified by 200 cc of 2/10 normal potassium hydroxide, the constants given in Table 7 were obtained.

TABLE 7

Relative Speed of Saponification of Castor Oil by 2/10 Normal Alkali in Different Alcohols

	Methyl	Ethyl	Amyl
	0.00006333	0.0008125	0.001623
	0.00006384	0.0007865	0.001605
	0.00006218	0.0007894	0.001615
	0.00006357	0.0008039	0.001665
	0.00006244	0.0008044	0.001645
	0.00006301	0.0008044	0.001603
	—	—	0.001607
Average	0.00006322	0.0008002	0.001623
Ratio	1	12.6	25.6

When 10 cc of oil were saponified by 200 cc of 2/10 normal potassium hydroxide, the results given in Table 8 were obtained.

TABLE 8

Relative Speed of Saponification of Castor Oil by 2/10 Normal Alkali in Different Alcohols

	Methyl	Ethyl	Amyl
	0.00007046	0.0008002	0.001549
	0.00007115	0.0008119	0.001541
	0.00006864	0.0007939	0.001557
	0.00006958	0.0007987	0.001581
	0.00007194	0.0007991	0.001532
	0.00006918	0.0007943	0.001554
	0.00007074	0.0007968	0.001517
	—	—	0.001536
Average	0.00007023	0.0007993	0.001546
Ratio	1	11.3	20.1

The average ratio obtained from the above tables is

1 : 11.8 : 22.8.

The reaction is much slower in methyl alcohol than in either of the other alcohols and the ratios obtained are fairly constant. If the constants for ethyl and amyl alcohols are compared, the ratios are more nearly constant as is shown in Tables 9, 10 and 11.

Tables 9, 10 and 11. Relative Speed of Saponification of Castor Oil in Different Alcohols

TABLE 9

Five Cubic Centimeters of Castor Oil in 4/10 Normal Alkali

	Ethyl	Amyl
Average constant	0.001177	0.002149
Ratio	1	1.83

TABLE 10

Five Cubic Centimeters of Castor Oil in 2/10 Normal Alkali

	Ethyl	Amyl
Average constant	0.0008002	0.001623
Ratio	1	2

TABLE 11

Ten Cubic Centimeters of Castor Oil in 2/10 Normal Alkali

	Ethyl	Amyl
Average constant	0.0007993	0.001549
Ratio	1	1.9

As a check on the influence of the solvent upon the velocity of saponification the results obtained by saponifying 2 cc of methyl acetate by 200 cc of 2/10 normal potassium hydroxide in the different alcohols is given in Table 12. If the ratio of the constants in ethyl and amyl alcohol are determined the result is the same as for castor oil. See Table 13.

Tables 12 and 13. Relative Speed of Saponification of Methyl Acetate in Different Alcohols

TABLE 12

	Methyl	Ethyl	Amyl
Average constant	0.0001769	0.002795	0.005339
Ratio	1	15.8	30.1

TABLE 13

	Ethyl	Amyl
Average constant	0.002795	0.005339
Ratio	1	1.9

From the various data it would seem that the velocity of saponification is about ten times as great in ethyl alcohol as in methyl alcohol, and about twice as great in amyl alcohol as in ethyl alcohol.[1] It might, therefore, be possible to calculate the velocity of any saponification reaction in these alcohols if the velocity of that reaction in one of the alcohols is known. However it will be seen later that the water content of the alcohol is a factor which would have to be considered when calculating a velocity constant.

IV. An increase of approximately one percent in the amount of water present causes an increase of about four percent in the velocity of saponification of castor oil at 25° C.

The evidence supporting statement IV lies in the results obtained with methyl and ethyl alcohols of different strengths. Only one strength amyl alcohol was used because that alcohol dissolves only a small amount of water. The results of methyl and ethyl alcohol check each other as closely as could be expected. The results are given in Tables 14 and 15.

Tables 14 and 15. Relation between the Percent Water in the Alcohol and the Speed of Saponification of Castor Oil

TABLE 14

Methyl alcohol	Constant
$92^1/_2$% by weight	0.0001620
$91^1/_2$% by weight	0.0001757

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[1] The velocities of other chemical reactions in these three solvents would not have the same ratios found here. See Patterson and Montgomerie: Jour. Chem. Soc., 101, 2100 (1912).

TABLE 15

Ethyl alcohol	Density of alcohol	Constant
91½% by weight	0.8171	0.000952
89½% by weight	0.8238	0.001022
87½% by weight	0.8289	0.001031
84½% by weight	0.8370	0.001298

The data in Table 14 show an increase of 4.4 percent in the velocity constant for an increase of one percent in the water content of methyl alcohol. More data were obtained for ethyl alcohol than for methyl. The data in Table 15 show an average increase of 3.8 percent in the velocity constant for every increase of one percent in the water content of the alcohol.

V. Doubling the concentration of alkali causes an increase in the velocity of reaction, but the increase is not the same in alcohols of different strengths.

The evidence supporting Statement V was obtained by using two different concentrations of alkali in the three solvents, methyl, ethyl and amyl alcohol. It is evident that the water content of the alcohol is connected with the effect produced by variation in the strength of the alkali.

TABLE 16

Relation between the Strength of the Alkali Used and the Speed of Saponification of Castor Oil in Different Alcohols

Methyl Alcohol

Strength of alcohol	Constant with 2/10 normal alkali	Constant with 4/10 normal alkali	Increase in velocity due to doubling alkali
95%	0.0000632	0.0001020	61.2%
92½%	0.0001401	0.0001682	20%
91½%	0.0001338	0.0001517	13%
Ethyl Alcohol			
91½%	0.0008002	0.001177	47.1%
89½%	0.0009487	0.001031	7.7%
Amyl Alcohol (Density 0.8140)			
—	0.001623	0.002149	32.4%

From the foregoing data it would seem that the stronger the alcohol the greater the acceleration caused by doubling the quantity of alkali. The fact that the velocity is not doubled by doubling the quantity of alkali must be due to the degree of ionization of potassium hydroxide in the alcohol. Therefore it would not be expected that the increase caused by doubling the alkali would be the same in the three solvents because the degree of ionization of potassium hydroxide in the three alcohols is probably quite different.[1]

The effect of increasing the amount of oil gave varying results. It was found, as in the case of increasing the amount of alkali, that the water content seemed to have some influence on the effect produced by the oil.

TABLE 17

Relation between the Amount of Oil Used and the Speed of Saponification

Methyl Alcohol

Strength of alcohol	Constant with 5 cc castor oil	Constant with 10 cc castor oil	Increase in velocity due to doubling the oil
95%	0.00006322	0.00007032	11.2%
$92\frac{1}{2}\%$	0.0001682	0.0001809	7.6%
$91\frac{1}{2}\%$	0.0001517	0.0001540	1.5%
Ethyl Alcohol			
$91\frac{1}{2}\%$	0.0008002	0.0007993	0.11% Increase
$87\frac{1}{2}\%$	0.001049	0.001078	2.7% Increase
Amyl Alcohol (Density 0.914 at 16°)			
—	0.001623	0.001538	5.5% Decrease

These results are conflicting, but might be explained as follows: In the case of methyl alcohol the velocity constants are very small, and therefore the experimental error would be large. On the other hand, they follow the same order as in the variation of the amount of alkali. In the case of amyl alcohol the results were carefully checked, and there is, without a doubt, a marked decrease in the velocity when

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[1] Jones: Zeit. phys. Chem., 31, 114 (1899), has shown that the ionization of salts is different in different alcohols.

the amount of oil is increased. This fact is possibly due to the formation of considerable glycerol during the reaction, which might cause a decrease in the velocity due to the change in solvent. It is well known that products of reactions do occasionally influence the velocity of the reaction. The glycerol might increase the velocity in one solvent and decrease it in another solvent.

VI. An increase of 10° C in the temperature at which the reaction is carried out causes castor oil to be saponified 2.36 times as fast by ethyl alcoholic potassium hydroxide.[1]

Castor oil was saponified by ethyl alcoholic potassium hydroxide at 15° C and 25° C, all other factors being exactly the same. The results are given in Table 18.

TABLE 18

Relation between the Temperature and Speed of Saponification of Castor Oil by Ethyl Alcoholic Potassium Hydroxide

	Constant at 15° C	Constant at 25° C
	0.0004527	0.001073
	0.0004456	0.001077
	0.0004538	0.001056
	0.0004450	0.001054
	0.0004478	0.001062
	0.0004479	0.001018
	0.0004424	0.001047
	0.0004479	0.001069
	0.0004386	0.001066
	0.0004437	0.001047
	0.0004482	0.001015
	—	0.001013
Average	0.0004417	0.001053

The temperature coefficient, K 25°/K 15°, for this reaction is 2.36, which is about the average coefficient for ordinary reactions.

VII. The reaction does not go to completion but only to equilibrium.

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[1] Trautz and Volkmann: Zeit. phys. Chem., 64, 53; Jour. Chem. Soc., 94 II, 824 (1908); Harcourt and Esson: Jour. Chem. Soc., 102 II, 923 (1912).

The correctness of Statement VII is easily seen from the difference in the end titrations when oil is saponified by varying amounts of alcoholic potassium hydroxide. The more concentrated the alkali, the further the reaction is carried along. The figures given in Table 19 are the number of cubic centimeters of tenth normal potassium hydroxide absorbed by 10 cc of the reaction mixture.

TABLE 19

Relation between the Concentration of Alkali Present in the Solvent and the Amount Used up at Equilibrium

Solvent	Cubic centimeters of 2/10 normal KOH used up by oil in 10 cc of the mixture	Cubic centimeters of 4/10 normal KOH used up by oil in 10 cc of the mixture	Difference
Amyl alcohol	7.64	9.48	1.74
Ethyl alcohol	7.51	9.07	1.56
Methyl alcohol	8.64	10.23	1.59

Summary of Results

1. The saponification reactions under all conditions studied are bimolecular.

2. The glycerides studied are saponified at approximately the same rate.

3. An increase of 1% in the water content of the alcohol causes an increase of about 4% in the velocity of the reaction.

4. The velocity of saponification of glycerides in amyl alcohol of density 0.8140 (15.50°) is about twice as great as it is in ethyl alcohol of density 0.8171 (15.50°), and about ten times as great in this ethyl alcohol as it is in methyl alcohol of density 0.8100 (15.50°).

5. The temperature coefficient of the reaction K 25°/-K 15° is 2.36 in the case where castor oil is saponified in ethyl alcohol.

6. The velocity is greatly accelerated by increasing the

amount of alkali, but no definite ratios could be determined from the data.

7. When amyl alcohol of a density 0.8140 is used as the solvent, an increase in the amount of oil causes a decrease in the velocity of reaction. While in the case of methyl and ethyl alcohols there seems to be an increase in the velocity due to the increase in amount of oil.

Experimental Data and Calculations

As described above, in carrying out a determination, the oil dissolved in the solvent is mixed with the alkali dissolved in the solvent. At intervals, the volume of 1/10 normal alkali remaining in 10 cc of the mixture is determined as follows:

Ten cubic centimeters of the mixture are run into excess, either 20 cc or 40 cc of 1/10 normal HCl. The excess acid is then titrated with 1/10 normal $Ba(OH)_2$. The difference between the volume of 1/10 normal HCl used and 1/10 normal $Ba(OH)_2$ used gives the volumes 1/10 normal alkali present in 10 cc of the mixture. This value is given in the second column in the experimental tables below.

The second order reaction formula used in all of the calculations is

$$K = \frac{2.3025}{T_e t} \log \frac{T_t(T_o - T_e)}{T_o(T_t - T_e)}.$$

K = Velocity constant.

T_o = Volume of 1/10 normal alkali present in 10 cc of the mixture at first titration.

T_e = Volume of 1/10 normal alkali present in 10 cc of the mixture at the end of the reaction.

T_t = Volume of 1/10 normal alkali present in 10 cc of the mixture at time t.

t = Time in minutes after the first titration.

In the experimental data below T_o is the first value and T_e the last value under the second column.

DATA[1] FOR TABLE 1

Five cubic centimeters of fat or oil were saponified by 200 cc of 2/10 normal amyl alcoholic potassium hydroxide at 25° C

Butter fat			Cottonseed oil		
t	T_t	K	*t*	T_t	K
0	17.42	—	0	17.52	—
12	15.19	0.001750	9	16.14	0.001529
20	14.11	0.001801	16	15.31	0.001537
29	13.31	0.001746	23	14.52	0.001635
40	12.48	0.001773	31	13.95	0.001595
49	12.01	0.001756	41	13.37	0.001572
56	11.68	0.001769	51	12.92	0.001555
71	11.13	0.001798	62	12.51	0.001556
E	9.70	—	72	12.36	0.001579
			87	11.98	0.001466
			E	10.83	—

Olive oil			Croton oil		
t	T_t	K	*t*	T_t	K
0	2.39	—	0	17.50	—
19	4.68	0.001633	11	15.82	0.001789
27	5.28	0.001616	19	15.03	0.001658
36	5.81	0.001609	26	14.47	0.001611
44	6.13	0.001552	36	13.83	0.001575
52	6.51	0.001606	46	13.40	0.001503
62	6.73	0.001521	55	13.13	0.001464
71	6.98	0.001535	65	12.76	0.001445
78	7.36	0.001768	E	11.08	—
E	8.15	—			

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[1] The experimental data on castor oil were lost after the result had been tabulated. Another determination of the same is given in Table 7.

Methyl Acetate. Two cubic centimeters in 200 cc of 2/10 normal amyl alcoholic potassium hydroxide at 25° C

t	T_t	K
0	16.68	—
6	14.55	0.005496
12	13.42	0.005363
18	12.64	0.005610
23	12.33	0.005357
30	11.98	0.005335
36	11.79	0.005303
E	11.36	—

DATA FOR TABLE 2

Five cubic centimeters of castor oil saponified by 200 cc of 4/10 normal amyl alcoholic KOH at 25° C

t	T_t	K
0	35.73	—
1	35.28	0.002175
4.5	34.18	0.002222
8	33.49	0.002034
11.5	32.85	0.002052
15	32.38	0.002034
18.5	31.92	0.002125
E	30.52	—

DATA FOR TABLE 3

Ten cubic centimeters of castor oil saponified by 200 cc of 2/10 normal amyl alcoholic potassium hydroxide at 25° C

t	T_t	K
0	17.28	—
5	15.89	0.001549
11	14.55	0.001541
15	13.78	0.001557
20	12.93	0.001581
25	12.34	0.001532
32	11.49	0.001554
40	10.82	0.001517
50	10.02	0.001536
E	5.65	—

DATA FOR TABLE 6

Five cubic centimeters of castor oil saponified by 200 cc of 4/10 normal alcoholic potassium hydroxide at 25° C, in the three alcohols, methyl, ethyl and amyl. The data for amyl alcohol are the same as given in Table 2

Methyl alcohol			Ethyl alcohol		
t	T_t	K	*t*	T_t	K
0	36.92	—	0	36.12	—
19.5	36.39	0.0001079	4.5	35.23	0.001173
26.5	36.23	0.0001051	7.5	34.77	0.001135
33.5	36.11	0.0001104	11	34.24	0.001165
51.5	35.70	0.0001002	14	33.85	0.001179
63.5	35.44	0.0001010	17	33.47	0.001214
73.5	35.24	0.0001010	20.5	33.21	0.001166
E	29.77	—	24	32.86	0.001205
			E	30.93	—

DATA FOR TABLE 7

Five cubic centimeters of castor oil saponified by 200 cc 2/10 normal alcoholic potassium hydroxide at 25° C, in the three alcohols, methyl, ethyl and amyl

Methyl alcohol			Ethyl alcohol		
t	T_t	K	*t*	T_t	K
0	18.94	—	0	18.68	—
8	18.87	0.00006333	17	17.32	0.0008125
20	18.76	0.00006384	23	16.98	0.0007865
59	18.43	0.00006218	32	16.47	0.0007894
117	17.97	0.00006357	42	15.96	0.0008039
148	17.76	0.00006244	54	15.47	0.0008044
211	17.32	0.00006301	68	15.00	0.0008044
E	11.36	—	E	12.49	—

	Amyl alcohol	
t	T_t	K
0	18.10	—
10	16.70	0.001623
14	16.28	0.001605
18	15.89	0.001615
23	15.42	0.001665
33	14.79	0.001643
41	14.42	0.001603
52	13.96	0.001607
E	12.40	—

DATA FOR TABLE 8

Ten cubic centimeters of castor oil saponified by 200 cc of 2/10 normal alcoholic potassium hydroxide at 25° C, in the three alcohols, methyl, ethyl and amyl[1]

Methyl alcohol			Ethyl alcohol		
t	T_t	K	*t*	T_t	K
0	18.85	—	0	17.30	—
46	18.01	0.00007046	15	15.10	0.0008002
59	17.79	0.00007115	27	13.72	0.0008119
74	17.58	0.00006864	33	13.23	0.0007939
89	17.30	0.00006958	39	12.70	0.0007987
119	16.85	0.00007194	45	12.24	0.0007991
172	16.18	0.00006918	52	11.78	0.0007943
188	15.95	0.00007074	59	11.33	0.0007968
E	4.76	—	E	4.79	—

DATA FOR TABLES 12 AND 13

Two cubic centimeters of methyl acetate saponified by 200 cc of 2/10 normal alcoholic potassium hydroxide at 25° C in the three alcohols, methyl, ethyl and amyl[2]

Methyl alcohol			Ethyl alcohol		
t	T_t	K	*t*	T_t	K
0	18.48	—	0	18.14	—
15	18.09	0.0001841	8.5	15.92	0.002800
33	17.69	0.0001766	15	14.77	0.002808
41.5	17.51	0.0001755	18	14.39	0.002786
47.5	17.21	0.0001693	22.5	13.92	0.002753
55	17.20	0.0001806	33	13.10	0.002734
64	17.04	0.0001773	E	11.33	—
73	16.89	0.0001752			
E	10.59	—			

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[1] Data for amyl alcohol same as Table 3.

[2] Data for amyl alcohol same as Table 1.

DATA FOR TABLE 18

Five cubic centimeters of castor oil saponified by 200 cc of 2/10 normal ethyl alcoholic KOH at 25° C and 15° C (alcohol was 87½%)

Constant at 15° C			Constant at 25° C		
t	T_t	K	t	T_t	K
0	19.18	—	0	18.66	—
21.9	18.00	0.0004527	8.7	17.66	0.001073
32.6	17.54	0.0004456	14.7	17.08	0.001077
41.3	17.16	0.0004538	22.2	16.50	0.001056
51.7	16.81	0.0004450	29.7	15.99	0.001054
62.8	16.43	0.0004479	36.5	15.57	0.001062
75.55	16.05	0.0004478	45	15.23	0.001018
85.2	15.82	0.0004424	63	14.46	0.001047
95.4	15.54	0.0004479	70.5	14.18	0.001069
107.8	15.31	0.0004386	84.2	13.82	0.001069
121.4	15.01	0.0004437	92.2	13.65	0.001066
148.6	14.52	0.0004482	100.7	13.52	0.001047
E	12.15	—	109.2	13.43	0.001015
			117.7	13.27	0.001034
			E	12.24	—

It was thought unnecessary to give any data for Tables 14 to 17 except those included in the tables.

Amherst, Mass.
Dec. 15, 1915

STUDIES ON SOILS. I.

BY FRANK E. RICE

Basic Exchange

It has long been known that when a portion of soil is shaken with a neutral salt solution, much of the cation of the salt is removed by the soil and other bases are given up to the solution in exchange.[1] This exchange is found to affect the cation only; the concentration of the anion remains the same except where secondary reactions take place.[2] Such extracts have been found to contain most of the bases known to be present in soils: manganese, aluminum, iron, calcium, magnesium, potassium, sodium.

Most of the earlier investigators believed that the quantity of base adsorbed by the soil was equivalent, or nearly equivalent, to that passing into solution. These conclusions were based upon partial or complete analyses of the bases present in solution before and after contact with the soil.[3]

Others have believed that the exchange was not quite equivalent. Henneberg and Stohman[4] were in doubt as to whether substitution in chemically equivalent amounts had taken place. More recently, Parker[5] concluded from analyses of extracts prepared by treating soils with potassium chloride and potassium acetate solutions that the base was adsorbed to a little greater extent than it was liberated by the soil, and that the excess of anion should be accounted for by the presence of the corresponding acid. With some artificial

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[1] Thompson: Jour. Roy. Agr. Soc., 11, 68–74 (1850); Way: Ibid., 11, 313–379 (1850); 13, 123–143 (1852).

[2] Ehrenberg: Landw. Jahrb., 38, 857–861 (1909).

[3] Way: see above; Peters: Landw. Vers. Stat., 2, 113–145 (1860); Rautenberg: Jour. für. Landw., 7, 49–66, 405–554 (1862); van Bemmelen: Landw. Vers. Stat., 21, 135–191 (1877); Sullivan: U. S. Geol. Survey, Bull. No. 312 (1907); and others.

[4] Jour. Landw., 3, 25 (1859).

[5] Jour. Ind. Eng. Chem., 6, 831–835 (1914).

silicates and minerals it has been found there is more base given up to the solution than is adsorbed.[1]

In nearly all cases these extracts react acid to phenolphthalein, and require considerable quantities of alkali to bring them to an endpoint with this indicator.[2] Veitch[3] prepared extracts of soils by shaking with sodium chloride solution, and was led to believe "that there is no setting free of appreciable quantities of hydrochloric acid—but that the acidity of the filtrate (or that acidity which is greater than would be given by water under the same conditions) is due to the solution of alumina or some other acid-salt yielding base." He says further: "It appears that the hydrated neutral silicates or aluminates are quite strongly attacked by the salt solution, resulting in the replacement of aluminum by sodium, or a breaking up of the compound, and a consequent formation of an acid solution of aluminum chloride, the titration of which, with alkali, constitutes the apparent acidity." Many have noted the presence of aluminum and iron in such extracts and generally have reached similar conclusions.[4]

Cameron[5] and Harris[6] disregard this basic exchange, and attribute the acidity of extracts prepared by shaking soils with neutral salt solutions to the predominant removal of the base from the solution leaving the acid free.

Previously, then, it has been generally agreed that there is an exchange of bases between the soil and salt solutions

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[1] Wiegner: Jour. für Landw., 60, 111–150 (1912); Dittrich: Mitt. grossh, bad. geol. Landesanstalt, 4, 341 (1903).

[2] This fact has been made the basis for methods of determining acidity in soils. Hopkins, Knox and Pettit: Bur. of Chem., Bull. No. 73, p. 114 (1903); Loew: Porto Rico Sta., Bull. No. 13 (p. 7); Jones: Am. Fert., 39, No. 11, 28–29 (1913).

[3] Jour. Am. Chem. Soc., 26, 637–662 (1904).

[4] Sullivan: See above; Morse and Curry: N. H. Agr. Exp. Sta., Rept. 1906–1908, pp. 271–293; Abbott, Conner and Smalley: Ind. Agr. Exp. Sta., Bull. No. 170 (1913); Daikuhara: Bull. Imp. Cent. Agr. Exp. Sta., Japan, 2, 1–40 (1914); Ruprecht: Mass. Agr. Exp. Sta., Bull. No. 161 (1915).

[5] The Soil Solution.

[6] Mich. Agr. Coll., Tech. Bull. No. 19 (1914).

in contact. Some have concluded from analyses made, that the exchange is chemically equivalent, and that the acidity of extracts thus prepared is due to aluminum and iron compounds. Others have believed that soils and minerals (those called "acid") adsorb more base from the solution than is given back to it, and that there is free acid in proportion to the excess of anion. Quite recently, Bogue[1] states: "It has been repeatedly proven that the base liberated by the soil is usually not nearly equivalent to the base adsorbed from the solution."

As the total quantity of elements involved in basic exchange is small, and as errors in the chemical analysis of such small quantities are great, it seems impossible to judge in this way how nearly a true basic exchange takes place between soil and solution. It was thought that observations of hydrogen ion concentration of such soils extract might lead to some conclusions in this direction.

Experiments were carried out on a number of soils collected from various parts of New York State. Thirty-three gram portions of soil were shaken with 100 cc of normal potassium nitrate solution, allowed to stand over night, and filtered. Upon the filtrates the following determinations were made: (1) hydrogen ion concentration by the indicator method of Sörensen;[2] (2) a portion of the solution was boiled, cooled, and made up to the original volume with boiled distilled water, and the hydrogen ion concentration determined at once; (3) titration of a 25 cc portion with $N/50$ NaOH; (4) qualitative determination of the bases present; (5) the lime requirement by the Veitch method is recorded in terms of pounds CaO per acre.

Hydrogen ion concentration is expressed as the logarithm of the normality factor of the actual concentration of hydrogen

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[1] Jour. Phys. Chem., 19, 665–695 (1915).

[2] Biochem. Zeit., 21, 131–304 (1909). Walpole [Biochem. Jour., 5, 207–214 (1911); 8, 628–640 (1914)] has gathered the results of Sörensen and others in this connection, and arranged them in the form of charts, which are very useful in this kind of work.

ions, the negative sign being understood. (See Walpole.) Elements present in greatest quantities are indicated by italics. Soils are tabulated in order of hydrogen ion concentration of the unboiled extract.

Soil No.	Exponent of hydrogen ion concentration	Exponent of hydrogen ion concentration after boiling	Cc of N/50 NaOH required by 25 cc	Qualitative tests	Lime requirement
1	7.8	9.0	trace	*Ca*, Mg	none
2	7.1	8.5	trace	*Ca*, Mg	480
3	7.0	9.0	trace	*Ca*, Mg	none
4	6.3	7.3	0.10	*Ca*, Mg	720
5	6.3	6.3	0.15	*Mg*, Ca	720
6	6.3	6.2	0.20	*Ca*, Mg	none
7	6.1	6.0	0.20	*Ca*, Mg	none
8	6.0	6.0	0.10	*Mg*, Ca	none
9	5.5	5.5	0.15	Mg, Ca	240
10	5.4	5.4	0.20	*Ca*, *Mg*	960
11	5.3	5.8	0.15	*Ca*, *Mg*	960
12	5.3	5.7	0.15	*Ca*, Mg	1200
13	5.1	5.3	trace	*Mn*, Mg, Ca	2400
14	5.1	5.0	0.40	*Ca*, *Mg*	2400
15	4.9	4.5	0.45	*Mn*, *Ca*, Mg	2160
16	4.9	4.0	0.55	Ca, Mg	2400
17	4.7	4.0	0.75	*Mn*, Ca, Mg	1920
18	4.7	4.5	1.00	*Ca*, *Mg*	1920
19	4.7	3.9	1.10	Ca, Mg	2400
20	4.7	3.7	1.60	Ca, Mg	1920
21	4.7	3.5	1.80	Mg, Ca	1680
22	4.5	4.0	0.80	*Ca*, *Mg*	—
23	4.5	3.5	4.10	*Mn*, Al, Ca, Mg	5280
24	4.5	3.0	4.80	Al, Mn, Ca, Mg	4800
25	4.3	3.5	2.10	Al, Mg, Ca	1440
26	4.3	3.0	4.40	Al, Mn, Ca	1680
27	4.2	3.5	2.50	*Mn*, *Al*	3600
28	4.2	3.0	3.70	Al, Ca, Mg	3600
29	4.1	3.6	3.30	Al, Ca, Mg	3840
30	4.0	3.3	8.25	*Mn*, *Al*, Ca	6000
31	4.0	3.0	12.60	*Al*, Ca, Mg	7200
32	4.0	3.0	14.90	*Al*, Ca, Mg	6000
33	3.5	3.3	5.1	*Al*, Mn, Ca, Mg	3360

Calcium and magnesium were found in considerable quantities in extracts from both the more acid and less acid soils. Much aluminum was present in extracts from soils of the highest acidity. Rather large quantities of manganese were found in several cases. Iron was never detected, and sodium was not tested for.

A study was next made of the hydrogen ion concentration of the nitrates of manganese, aluminum, calcium and magnesium in normal potassium nitrate solution, to find if the behavior of the above soils extract could not be accounted for by the presence of these substances alone.

The exponent of hydrogen ion concentration of a normal solution of potassium nitrate in boiled distilled water is about 6.0. (Absolute neutrality is about 7.1.) One-tenth percent of calcium or magnesium in the form of nitrate dissolved in normal potassium nitrate gave hydrogen ion concentations between that of pure distilled water and normal potassium nitrate—about 6.7—when fresh, and upon long standing became slightly more acid. A fresh solution of manganese nitrate in normal potassium nitrate had a similar hydrogen ion concentration, but on long standing it became very much more acid and at the same time a brown precipitate of manganese oxide (?) appears: One-tenth percent manganese nitrate in normal potassium nitrate gave exponents of hydrogen ion concentration: when fresh, 6.5; after three days, 5.8; after five days, 4.8; after eight days, 4.7; after sixteen days, 4.7.

Only traces of alkali are necessary to bring fresh solutions of calcium, magnesium, or manganese nitrates to the neutral point with phenolphthalein, and the hydrogen ion concentrations are greatly affected by the presence of traces of base or acid. Upon boiling and cooling these solutions, the hydrogen concentration is but very slightly changed; they usually change a little towards the alkaline side.

Considering these facts, we must conclude that the high hydrogen ion concentration of soil extracts prepared as above cannot be accounted for by calcium, magnesium or manganese nitrates in solution. Also, there must be another agent present that requires alkali for neutralization to phenolphthalein.

Data obtained from solutions of aluminum nitrate in normal potassium nitrate follow:

Percent aluminum	Hydrogen ion concentration	Hydrogen ion concentration after boiling	Cc of *N*/50 NaOH required by 25 cc
0.05	3·4	3·4	68.0
0.025	3·7	3·7	33·7
0.0125	3.8	3·0	17·3
0.01	3·9	3·0	13·7
0.005	4.0	3·0	7·0
0.0025	4.2	3·1	3·5
0.002	4·3	3·3	2.9
0.00125	4·5	3·4	1.8
0.001	4·5	3·4	1.45
0.000625	4.6	3·7	1.00
0.0005	4·7	3.8	0.70
0.00025	4.8	4·0	0.35
0.0001	5.1	4·5	0.15
0.00005	6.0	6.0	0.10

Aluminum salts in solution are known to hydrolyze strongly with the formation of hydrated aluminum oxide and the acid corresponding to the anion of the salt. As hydrated aluminum oxide scarcely ionizes, there will be present in solution but little hydroxyl ion, while there will be very much more hydrogen ion, and in quantity depending upon the extent of hydrolysis of the salt and the strength of the acid. Therefore, to indicators, such as neutral red, paranitrophenol, litmus, etc., which indicate end points near absolute neutrality, such solutions react acid.

This hydrolysis proceeds until an equilibrium point is reached, where the acid begins to combine with the oxide again. In the above table the effect of boiling is seen to increase the hydrogen ion concentration of the more dilute solutions. Either the equilibrium is displaced towards the side of greater hydrolysis, or, it is possible that there is some coagulation of the aluminum oxide portion, removing from solution hydroxyl ions, and thus leaving a higher concentration of hydrogen ions. This increased hydrogen ion concentration is not permanent, however, but eventually comes back to the figures obtained on the unheated solution; it was found, too, that the hydrogen ion concentration of the unboiled portions does remain constant. Aluminum nitrate solutions in normal potassium nitrate were prepared, (1) containing 0.01 percent aluminum, (2) 0.001 percent aluminum. Portions of both solutions were boiled and cooled (1*a* and 2*a*). Determinations of hydrogen ion concentration gave the following results:

	1	1*a*	2	2*a*
At beginning	3.9	3.0	4.5	3.4
After five hours	3.9	3.4	4.5	3.6
After one day	3.9	3.7	4.5	3.9
After two days	3.9	3.8	4.5	4.0
After eight days	3.9	3.8	4.5	4.2
After fifteen days	3.9	3.8+	4.5	4.5

Since solutions of salts of calcium, magnesium, and manganese nitrates did not show this phenomenon of increased hydrogen ion concentration by boiling, such behavior in soil extracts must indicate the presence of aluminum. In soils 14–22 it is seen that no test was given for aluminum by the ordinary qualitative methods, yet it must have been present for this reason.

As the acid resulting from the hydrolysis of aluminum salts is neutralized by alkali, further hydrolysis takes place, and the process continues until all the acid is combined with alkali and all the aluminum is in the form of hydrated aluminum oxide. Titrating in this way with standard alkali, using phenolphthalein as indicator, the whole quantity of acid in combination with aluminum may be quite accurately determined. This is the basis for methods determining by titration the quantity of aluminum in solution as salts of aluminum, and is accurate, provided alumina and acid are present in equivalent quantities.[1]

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[1] See Veitch.

If, however, either alumina or acid is present in slight excess, the requirement of alkali varies but little, while the difference in hydrogen ion concentration will be found to be considerable. The following results were obtained upon normal potassium nitrate solutions containing varying quantities of aluminum nitrate with small quantities of acid and base:

Percent aluminum	Solution contains *N*/2000 NaOH		Solution contains *N*/10000 HNO_3	
	Hyd. ion concen.	Cc *N*/50 NaOH required by 25 cc	Hyd. ion concen.	Cc *N*/50 NaOH required by 25 cc
0.05	3.5	67.9	3.3	67.5
0.025	3.9	33.3	3.6	34.0
0.0125	4.0+	16.4	3.7	17.1
0.01	4.2—	12.9	3.8	13.7
0.005	4.4	6.2	3.9	7.0
0.0025	4.6	2.9	4.0	3.6
0.002	4.7	2.3	4.0	2.9
0.00125	4.8	1.2	4.0	1.9
0.001	4.9	0.80	—	—
0.000625	5.0	0.35	4.0	1.0
0.0005	5.6	0.05	—	—
0.00025	9+	alk.	4.0	0.45
0.0001	9+	alk.	—	—
none	—	—	4.0	0.10

The results obtained in all these experiments are plotted in Fig. 1,—cc of sodium hydroxide required against exponent of hydrogen ion concentration. Crosses are used to indicate points of the aluminum nitrate solutions, and circles for soils. Points representing aluminum nitrate solutions are joined in curves: A, containing *N*/2000 sodium hydroxide; B, containing no acid or alkali; C, containing *N*/10000 nitric acid.

In general, the acid soils fall near the curve for aluminum nitrate. With one exception (Soil 33), therefore, the acidity of these extracts may be accounted for by the presence of nitric acid in solution with equivalent quantities of alumina, or aluminum nitrate, alone. In no case could there be present excess acid to the extent of more than $N/10000$, as a solution with this quantity of nitric acid will always have a hydrogen ion concentration of 4.0, and yet more if there are present appreciable quantities of aluminum.[1]

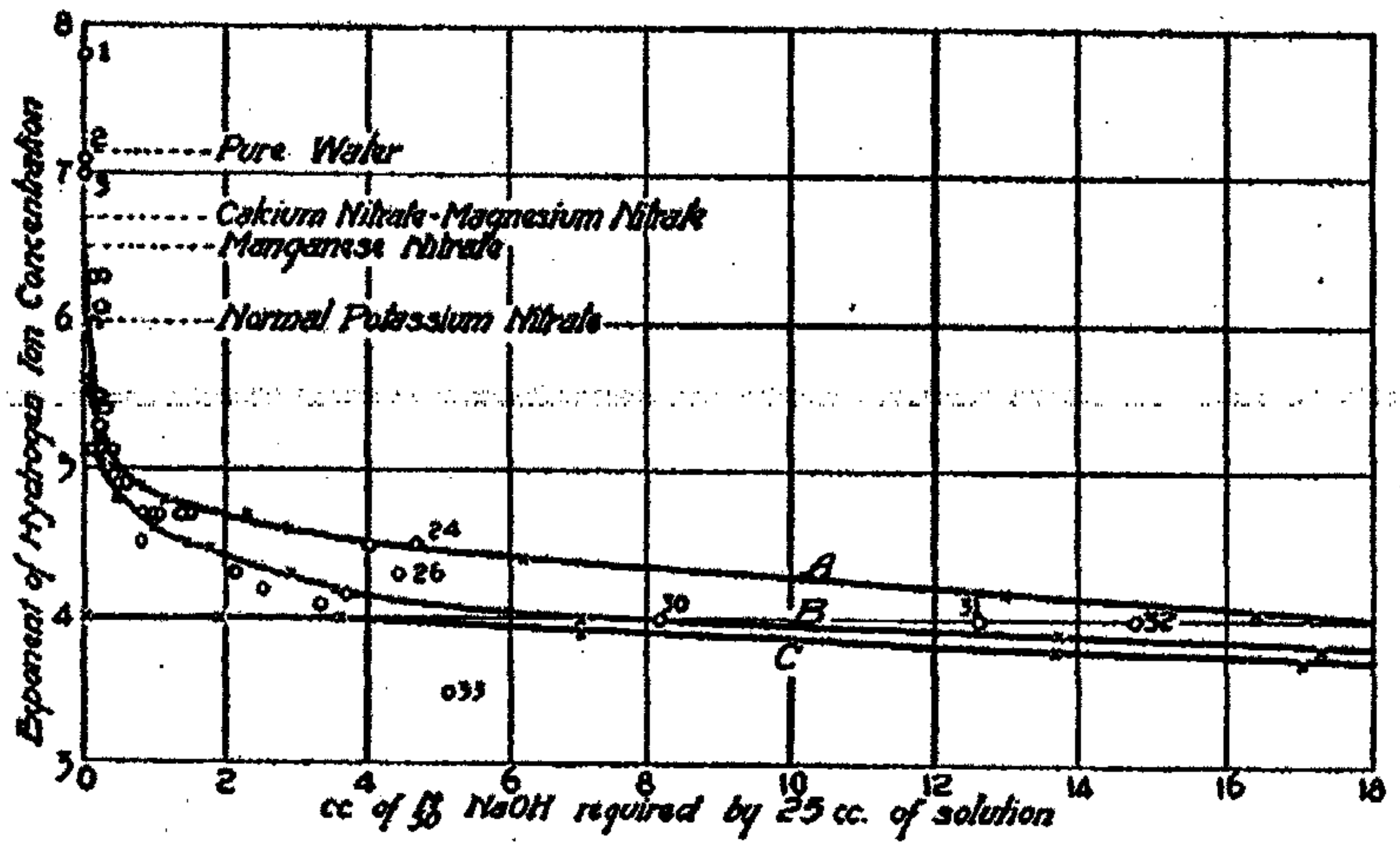

Fig. 1

Extract from soil number 33 was so acid in reaction that the presence of water-soluble acid was suspected. It was found by shaking portions of this soil with water, filtering, and boiling the filtrate to expel carbon dioxide, a decidedly acid extract was obtained. The exponent of hydrogen ion

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[1] The presence of calcium, magnesium or manganese does not disturb the hydrogen ion concentration of aluminum nitrate, neither does it disturb the hydrogen ion concentrations of solutions containing an excess of base or acid along with aluminum nitrate. Solutions were prepared—all containing normal potassium nitrate and 0.001 percent aluminum as aluminum nitrate: (1) contained nothing more; (2) contained one-tenth percent calcium as nitrate; (3) same as (2), but with $N/10000$ nitric acid; (4) same as (2), but with $N/2000$ sodium hydroxide; (5) contained one-tenth percent magnesium as nitrate; (6) same as (5), but with $N/10000$ nitric acid; (7) same as (5), but with $N/2000$ sodium hydroxide; (8) contained one-tenth percent manganese as nitrate; (9) same as (8), but with $N/10000$ nitric acid; (10) same as (8), but with $N/2000$ sodium hydroxide. The exponents of hydrogen ion concentration of these solutions were found to be: (1) 4.5; (2) 4.5; (3) 4.0; (4) 4.9; (5) 4.5; (6) 4.0; (7) 4.9; (8) 4.5; (9) 4.0; (10) 4.9.

concentration was found to be 5.3; 25 cc of the solution required 0.6 cc $N/50$ NaOH. All other acid soils tested in this way gave water extracts with hydrogen ion concentrations differing but little from that of boiled distilled water,—in most cases a little toward the alkaline side. They also required but traces of alkali to make them alkaline to phenolphthalein indicator.

We must conclude that there is at least as much base in these extracts as there is acid. From this it follows that there is as much base given up as is adsorbed by the soil.

On the other hand, it seems that in more cases soils fall on the basic side of the aluminum nitrate curve, though in only one case (Soil 24) is there more base than $N/2000$.

Soil 24 was high in organic matter and yielded an extract of brownish color, evidently due to a partial solution of this organic material. Extracts from other soils were practically colorless.

It seemed possible that this organic material might in some way influence the hydrogen ion concentration results, and from the following experiment, it seems that this is the case: A solution was prepared by extracting 10 grams of muck with 200 cc of boiled distilled water, and filtering. In the filtrate was dissolved enough potassium nitrate to make it of normal concentration. This solution was free from suspended matter, but quite brownish in color. The exponent of hydrogen ion concentration was found to be 6.2. Fifty cc of this solution were mixed with 50 cc of 0.002 percent aluminum as aluminum nitrate. The hydrogen concentration of the resulting mixture was 4.7, while that of a 0.001 percent aluminum solution was 4.5. The organic matter, which is more or less colloidal in nature, may be interfering with the colorimetric method for the determination of hydrogen ion concentration—by adsorbing part of the indicator or by affecting the shade produced in some other way; or, it may be actually decreasing the concentrations of ions—by forcing back the dissociation of the acid or by adsorbing hydrogen ions from the solution.

Some mucks were tested in a manner similar to that used on the mineral soils. Ten to fifteen gram portions were shaken with 100 cc of normal potassium nitrate solution, allowed to stand over night, and filtered. These filtrates were so dark in color that it was impossible to make accurate measurements of hydrogen ion concentration. It was quite evident, however, that there was smaller concentration of hydrogen ions than should be expected from the quantity of alkali required. Should these points be plotted, they would fall well on the basic side of the aluminum nitrate curve. Again, the organic matter is affecting the hydrogen ion concentration determination.

Basic exchange takes place extensively in muck soil, seemingly more so than in mineral soils. Calcium and magnesium, aluminum and manganese, were all found. Calcium and magnesium seemed usually to predominate.[1]

Hydrogen ion concentration of water extracts from mucks were not far from absolute neutrality,—a little on the acid side. One muck was found, differing from other mucks similarly as Soil 33 differed from other soils of that class. The water extract of this one yielded a hydrogen concentration of 4.7, and 25 cc required 2.0 cc of $N/50$ sodium hydroxide for neutralization with phenolphthalein.

The figures for lime requirement by the Veitch method increase with the hydrogen ion concentration results quite regularly. This was hardly to be expected, since the two processes depend upon entirely different factors. Adsorption of lime by soils is occasioned especially by the colloidal organic matter, while acidity yielded to salt solutions by soils involves basic exchange, principally with the mineral part. Yet this may be accounted for by assuming that the organic portion of soil removes preferably calcium and magnesium from the mineral part, leaving the less basic elements, as manganese and aluminum. Basic exchange, then, in soils high in organic matter may necessarily involve the ex-

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[1] Hall and Gimingham [Jour. Chem. Soc., 91, 677–687 (1907)] find calcium passing into solution, similarly, when peat is treated with ammonium salts.

traction of aluminum to a greater extent than soils low in organic matter.

Many soils are found that yield extracts with hydrogen ion concentrations less than that of normal potassium nitrate solution, and even less than that of pure water. (See Soils 1, 2, 3, etc.) Such soils are evidently yielding up to the solutions excess of base; however, it is possible that this excess of base is entirely water soluble, and that, after all, the actual basic exchange is chemically equivalent. Soil No. 1 was shaken with boiled distilled water and filtered. The exponent of hydrogen concentration of the filtrate was found to be 7.8, and upon boiling it became alkaline to phenolphthalein (about 8.5).

Sörensen in his original paper pointed out that the colorimetric method for the determination of hydrogen ion concentration gave more or less erroneous results when other substances were present in the solution. It may be that potassium nitrate, calcium nitrate, magnesium nitrate, manganese nitrate, aluminum nitrate, colloidal (?) aluminum oxide, etc., interfere with accurate measurements to some extent.[1] At any rate, the results may be considered comparatively, for the errors entering into the determination of hydrogen ion concentration of soil extracts will also be found in the solutions made up to approximate them. The conclusions reached, therefore, should not be invalidated on this account.

The way in which soluble organic matter may interfere has been already mentioned.

It is seen that the so-called "acidity" of soils is of a nature different from that usually considered. The infertility of such soils seems not to be occasioned by the lack of bases and the consequent existence of true acid hydrogen, neither should

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[1] However, in a previous experiment, hydrogen ion concentration of solutions containing $N/10000$ nitric acid, aluminum nitrate, and potassium nitrate was found to be 4.0 when only small quantities of aluminum were present. This is, of course, what $N/10000$ nitric acid should run, provided there is complete ionization. It seems, then, that neither aluminum nitrate nor potassium nitrate interfere under ordinary conditions.

it be accounted for fundamentally by a capacity of the soil for strongly attracting base, either free or from neutral compounds, although this latter phenomenon is found; but it is probably due in a great measure to loose combinations (perhaps of the nature of adsorption compounds) of relatively large quantities of the weak bases, as aluminum, compared with the quantities of the stronger bases, as calcium, magnesium, etc. If the stronger bases are present in considerable quantities, the weaker bases are prevented from becoming a factor in determining the character of the soil solution, and the soil is good. If the reverse is true, the soil is probably of low fertility.

Another experiment may be mentioned in this connection: Soils 26 and 30, which respond strongly to all the usual tests for soil acidity, were shaken with three times their quantities of $N/100$ nitric acid. This strength of acid was found to have an exponent of hydrogen ion concentration of 2.0. After contact with the soils both extracts gave as hydrogen ion concentration—3.8; 20 cc of No. 26 required 2.2 cc $N/50$ sodium hydroxide, and of No. 30—3.5 cc. Extract from Soil 26 was found to contain large quantities of aluminum, manganese, and small quantities of magnesium and calcium, and from Soil 30—much aluminum and manganese with a very little magnesium. Hence, even "acid" soils may neutralize acids to some extent. Whether or not, in addition, some of the acid was adsorbed by the soil was not determined.

Further experiments along these lines are contemplated.

Conclusions

When so-called "acid" soils are shaken with salt solutions, part of the cation of the salt is adsorbed, and an equivalent quantity of bases from the soil is given up to the solution.

The extracts, thus obtained, show greater acidity than that of the salt solutions themselves. This can be accounted for by the fact that one of the bases present is aluminum which does not securely hold its share of the acid, but through hydrolysis, hydrated aluminum oxide is formed along with equivalent quantities of free acid. The former being slightly ionized, possibly in a colloidal condition, and the latter more or less strongly ionized, the resultant solution is quite acid.

Acid soils rarely contain water-soluble acid; but one case of mineral soil and one of muck soil was found that did yield an acid to water.

Basic soils (as distinguished from "acid" soils) gave up to salt solutions more base than is adsorbed. But as they are also found to give up to water quantities of base sufficient to produce solutions of alkaline reaction, this should not be considered entirely a phenomenon of basic exchange, but of simple solution of the excess of base.

The writer wishes to acknowledge his indebtedness to Professor Wilder D. Bancroft for valuable suggestions and advice.

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FACTORS AFFECTING THE ELECTROMOTIVE FORCE OF BINARY SOLID ALLOYS

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The great advance in the knowledge of the metallic alloys which has been made in recent years through the application of thermal analysis and micrography has given, in the equilibrium diagrams, a rational basis for the investigation of the properties of these substances, and there appears to be no important property which has remained wholly unstudied.

In nearly every instance certain relations have been found between the property in question and the metallographic structure of the alloy, so that the observation of each property constitutes in principle a method which might be expected to correct and amplify the thermal and micrographic results with regard to constitution. Hence it is at first thought surprising that this expectation can scarcely yet be said to have been fulfilled by even the best-studied of these properties, as is shown by the preference very generally given to the thermal, and particularly the micrographic evidence, where these conflict with the indications of electrical conductivity, electromotive force, thermoelectromotive force, hardness, etc., etc.

The reasons for this state of affairs are, however, not obscure. For in order to obtain accurate values for the measure of any property as a function of composition and structure it is necessary that these be both uniform and accurately known throughout the region observed, while it is notoriously difficult to obtain even apparent uniformity throughout a sample of sufficient size to permit the observation of most of the properties under consideration. Thus the electrical resistance observed for an alloy of such and such composition is in reality a value integrated over a region of considerable size, within which composition and structure vary, and does not correctly represent the resistance of the alloy in question. This involves an error which robs the method of much of the value which it would otherwise have for determining, for example, the limits of a region of solid solutions.

Since it is impracticable to avoid this source of error by observing conditions at a geometrical point in the alloy, the methods which may be expected to give the most accurate information are those in which the observations can be confined to a small area in a single plane, the more so since the causes chiefly responsible for differences of composition, at least in the case of alloys cooled in the crucible, operate in the vertical direction, so that horizontal sections may be obtained of a relatively high degree of uniformity. This advantage of permitting the observation of conditions in a small plane area is possessed by micrography, and undoubtedly is in a measure accountable for the exceptional value of this method of metallographical investigation. It appears to lend particular promise, as an additional method for the study of the solid alloys, to the observation of their electromotive force against electrolytes, and we have been led in consequence to undertake a somewhat detailed study of the factors affecting the potential of a binary solid alloy. In the present paper are given the introductory discussion and methods, with the results of some preliminary experiments.

The general dependence of potential on composition and structure has already formed the subject of numerous investigations for which reference may be made to the bibliographies available.[1] We may therefore confine ourselves to noting some respects in which further development appears to be needed.

In the first place, it would seem to be worth while to devote more attention than has usually been given to obtaining alloys free from oxides. To this end we have melted our samples only under borax, and have avoided casting.

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[1] The fullest is probably that given by W. Broniewski: Thèse, Paris, pp. 138–9 (1911).

The attainment of uniform composition, in order that the electrode surface determining the potential may have, as nearly as possible, the same proportions of the components as are shown by analysis, is a consideration equally important, and has led us to prolong the time during which the alloy was maintained in a state of fusion, with frequent stirring, as well as the duration of annealing. As a control, the entire electrode surface of each test-piece has been subjected to microscopic examination. These precautions, together with the manner of selecting the test-piece, explained elsewhere, give specimens of brass which may reasonably be regarded as exceptionally uniform.

In the next place, the prevailing theory of solid alloy potentials, developed by Nernst[1] and Reinders,[2] is still in need of adequate experimental confirmation.[3] And if the validity of the theory be assumed, certain details of its application in the conduct of measurements remain yet to be worked out. In particular, a method is needed of ascertaining the composition of the equilibrium electrolyte which corresponds to each composition of the alloy. Lacking this knowledge, it has been the usual practice to allow the alloy and an electrolyte of composition not greatly removed from that of equilibrium to interact, the value at which the potential became approximately constant being taken as that of the alloy. This method is known to give inaccurate results because of the change produced in the surface of the electrode, in consequence of which the final potential is in reality that of an alloy of somewhat altered composition. The true potential corresponding to the composition of the alloy at the time of immersion, and hence of analysis, would be obtained only in case the electrolyte possessed, to begin with, the equilibrium composition. It may be noted that experience has

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[1] Nernst: Zeit. phys. Chem., 22, 539 (1897).

[2] Reinders: Ibid., 42, 225 (1903).

[3] See comments of Tammann: Lehrbuch der Metallographie, Leipzig, pp. 338–9 (1914).

led Broniewski,[1] and apparently also Puschin,[2] to views not altogether in accord with this conception.

Finally, there have accumulated, since the earlier studies of solid alloy potentials, various considerations which raise questions as to the reproducibility of the potential, and the possible influences of heat treatment and surface treatment of the alloy. Here it will be enough to mention the dynamic conception of allotropy developed by Smits[3] since 1910, the work of Cohen[4] on the metastability of the metals, including copper and zinc, Beilby's observations, extended by Rosenhain,[5] regarding the nature of polished surfaces and the possible existence of amorphous metal, and certain experiments upon the variability of the electrode potentials of pure metals.[6]

The factors affecting the electromotive force of a binary solid alloy, which are particularly in need of investigation, may therefore be said to be (*a*) the effect of heat treatment and surface treatment of the alloy, and (*b*) the composition of the electrolyte.

Among the most necessary precautions, other than those already indicated, must be reckoned exclusion of air, which is well known to exert a disturbing influence, and the avoidance of changes of concentration in the electrolyte. In the latter connection it is necessary to guard against evaporation, and against local changes due to convection currents or to relative motion of electrode and electrolyte.

Convection currents are not likely to be troublesome in an electrode vessel such as that which we have employed, in which the electrode chamber proper is surrounded by a second vessel with which it connects only through a small

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[1] W. Broniewski: Loc. cit. and Ann. Chim. Phys., (8) 25, 1 (1912).

[2] N. Puschin: Jour. Russ. Phys. Chem. Soc., 39 (1907); through Zeit. anorg. Chem., 56, 1 (1908).

[3] See especially Zeit. phys. Chem., 88, 743 (1914).

[4] E. Cohen: Zeit. phys. Chem., 1913, et seq.

[5] Reviewed by W. Rosenhain: Internat. Zeit. Metallog., 5, 65 (1914).

[6] G. N. Lewis and W. N. Lacey: Jour. Am. Chem. Soc., 36, 804 (1914); F. H. Getman: Trans. Am. Electrochem. Soc., 26, 67 (1914).

opening, especially where the temperature throughout is highly uniform.

As regards the influence of electrode motion, we have observed that, whenever in the midst of a set of readings showing a progressively changing potential, the cell is shaken, the E. M. F. drops back to a value shown some time before, and then gradually recovers, if the system is left undisturbed. It may therefore be supposed that the effect is due to the access to the electrode of fresh electrolyte not yet greatly altered in composition by interaction with the alloy.[1] It is evident that for the present purposes the altered layer of electrolyte in immediate contact with the electrode should not be removed, and that means intended to maintain uniformity in the composition of the liquid, such as stirring, are altogether inadvisable. The method of Kistiakowski, with rotating electrode, would increase the very changes in the alloy which it is here sought to minimize, and should only be employed when these are to be studied separately. We have therefore endeavored to keep the electrolyte as still as possible, even stopping the flow of nitrogen through the apparatus before beginning our observations.

In preparing the alloys Kahlbaum's "Kupfer, elektrolytisch, geraspelt," and "Zink I, geraspelt" were employed. Borax was melted in a 10 gram Battersea fire-clay crucible, which was heated in a Nichrome-wound furnace, and the metals were alternately stirred under in small portions until the calculated quantities had been added. Although rapidly attacked by the flux, stirrers of porcelain were used, as it was thought desirable to avoid the employment of carbon. This procedure is attended by a considerable loss of zinc, amounting to some twenty percent in the case of an alloy which finally contained 64 grams of zinc and 115 grams of copper, but it makes possible the preparation of brasses of

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[1] Compare W. Kistiakowski: Zeit. Elektrochemie, 14, 113 (1908); Nernst Festschrift, 215 (1912); St. Procopiu: Annales de Jassy, 7, 224 (1912), through Fort. der Phys., 68, I, 369 (1912); F. Giraud: Comptes rendus, 157, 586 (1914).

fairly high copper content with a simple furnace not capable of melting pure copper, and yields an alloy free from oxides.

The alloy, which was in every instance remelted and well stirred to increase its uniformity, formed on cooling a slightly conical block, of nearly equal height and diameter, having a volume of approximately 30 cc. From this block horizontal layers were cut, and these in turn were divided into strips of about 30 × 3 × 3 mm, which constituted the test-pieces.

The particular alloy upon which the measurements reported in this paper were made yielded eight layers, the copper content of which varied from 50.67 percent in the uppermost to 49.54 percent in the bottom one, showing a change from layer to layer of about 0.16 percent. That this decrease was quite regular from top to bottom may be inferred from the fact that the fifth layer, counting from the top, showed an analysis of 50.01 percent copper, as compared with the interpolated 50.03 percent.

The analyses were made on one-half gram samples, the copper being deposited electrolytically from a nitric acid solution.

After grinding and polishing and etching with nitric acid, a microscopic examination showed some lack of uniformity and the test-pieces were accordingly annealed for from ninety-six to one hundred and sixty-seven hours at a temperature of 700°–750° C. For this purpose they were enclosed in hard glass tubes which were then evacuated with the water pump. After admitting nitrogen the pressure was reduced to 190 mm of mercury, when the tubes were sealed. These tubes were embedded in sand in an electric furnace and, with the exception of a few which gave way, with consequent destruction of the test-pieces, remained gas-tight throughout the annealing, as was shown by the vacuum found upon opening, and by the entire absence of any evidences of oxidation. The outer layers of the glass, perhaps because of the inoculating action of the sand, were devitrified to some depth.

The annealing temperatures were observed with a Siemens and Halske direct-reading galvanometer, and a platinum

platinum-rhodium thermocouple imbedded in the sand in the midst of the tubes containing the test-pieces.

A microscopic examination of the annealed test-pieces, Nos. 1 and 2 below, after polishing and etching with nitric acid, showed large polygons which appeared to have undergone a transformation resulting in an extremely fine-grained structure, which the highest available magnification of 740 diameters was insufficient to resolve clearly. This is the structure to be expected if the β solid solutions undergo at 470° a eutectoid change into $\alpha + \gamma$, in accordance with the views of Carpenter. That there was no appearance of pitting may be regarded as evidence of the absence of oxides.[1]

As it was desirable because of the ease with which our results under these conditions might be compared with the requirements of the Nernst-Reinders theory, to employ electrolytes 1-normal in copper and zinc combined, but having different very small concentrations in copper, and as it was further advisable to make the liquid-junction potentials between these solutions and those of the reference electrodes either negligible or constant, it was determined to make all solutions 1-normal in sodium sulphate and 1-normal in copper sulphate and zinc sulphate together. It may be supposed that such hydrolysis as occurs in these solutions is practically constant, and that consequently the ion concentrations are very nearly proportional to the equivalent normal concentrations. The sulphate solutions were adopted only after numerous experiments had convinced us that it was impracticable because of hydrolysis to employ chloride solutions 1-normal in potassium chloride in order to eliminate entirely the liquid-junction potential against a normal calomel electrode.

The electrolytes were prepared from Kahlbaum's Brown Label salts, two stock-solutions being made up of which one was 1.4-normal in zinc sulphate and of like concentration in sodium sulphate, while the other was 1.4-normal in both copper and sodium sulphates. The further steps are best

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[1] Cf. Turner: Jour. Inst. Metals, 8, 248 (1912).

explained by giving the procedure used to obtain a solution $1.0.10^{-6}$-normal in copper. For this, 71.4_3 cc of the zinc stock-solution were measured from a burette graduated to 0.1 cc, into a 100 cc volumetric flask, and to this was added 1.0 cc of a solution obtained by diluting 0.71 cc, or ten drops, of the 1.4-normal copper stock-solution to one liter. On filling the flask to the mark there was thus obtained a solution $1.0.10^{-5}$-normal in copper sulphate, approximately 0.999-normal in zinc sulphate, and 1-normal in sodium sulphate. To make the dilution of the copper stock-solution a simple operation it is evidently necessary only that, for a dropping tube giving a drop of volume v cc, the stock-solution have such a normal concentration, c, that $v.c = 1.0.10^{3-x}$, where x is a small integer, and hence 1 drop = $1.0.10^{-x}$ equivalents. Since our dropping tube gave, with the copper stock-solution, a drop of 0.071 cc, 1.4-normal stock-solutions were convenient. All measuring flasks; burettes, and pipettes were calibrated for 20° C, from which the room temperature varied by not more than three degrees.

The half-cell in which the test-piece was placed as electrode for observation of its potential, consisted of a narrow-necked glass cylinder 14 cm in height and 4 cm in diameter, within which was supported an inner vessel, or bell, about 1.2 cm in diameter containing the brass. The outer vessel stood upon a leaden disc, to which it was clamped to prevent floating in the thermostat. The inner bell, which was closed at the bottom by a one-holed rubber stopper secured with platinum wire, narrowed above to a 5 mm tube, or neck, which passed up through the large rubber stopper at the mouth of the outer vessel, and ended just above. Through this neck of the bell entered a narrower, rather closely-fitting tube, the draw-tube, which was sealed at the lower end, and had a small orifice in the side at a point about 1 cm higher up. Both this draw tube and a third tube of similar size, the inlet tube, which passed through the large stopper and ended open near the bottom of the annular space between inner and outer vessels, were connected by black rubber tubing to the forked outlet of the wash bottle through which nitrogen was introduced. The large stopper which closed the outer and supported the inner vessel, admitted also a siphon, which served as salt-bridge to the intermediate vessel, and a small gas-exit tube with a bubble trap to prevent entrance of air.

The test-piece was secured with a drop of marine glue against the inner surface of the bell, and a fine copper wire, firmly wound about the upper end of the test-piece, passed between the neck of the bell and the draw-tube, and thence out to the potentiometer. A short piece of rubber tubing surrounding the draw-tube just above the neck of the bell, could be slipped down to close the opening between the two, and prevent ingress of air after the bell had been filled with nitrogen.

The electrolyte having been placed in the outer vessel, the large stopper bearing the bell, inlet tube, siphon and bubbler was inserted, the draw tube being at this time thrust down into the hole in the small rubber stopper at the bottom of the bell, and so preventing the entrance of electrolyte into the latter, and its access to the brass.

Nitrogen was now admitted, and entered the bell through the orifice in the draw-tube, its passage into the outer vessel through the inlet tube being prevented by the hydrostatic pressure of the electrolyte beneath which the latter ended. When the bell had been filled with nitrogen it was closed from the air by pushing down the short piece of rubber tubing already mentioned, and the draw-tube was thrust down until the orifice near its lower end came within the hole in the small stopper at the bottom of the bell, thus preventing the further passage of nitrogen through the bell, and compelling the gas to make its way through the inlet tube into the outer vessel, and thence out through the bubbler. After the outer vessel also had been filled with nitrogen, the draw-tube was raised until clear of the small stopper, through the hole in which the electrolyte then entered the bell and came in contact with the test-piece.

This type of cell permitted the brass to attain the temperature of the electrolyte before actually coming in contact with it, so that the initial readings were little affected by errors due to differences of temperature.

The nitrogen employed was commercial tank nitrogen, passed through alkaline pyrogallol, and then through a portion of the electrolyte contained in a wash bottle which stood in the thermostat. An appreciable change in the composition of the electrolyte in the cell during the twenty minutes for which the gas flowed was thus avoided, while the fact that at the end of an experiment the part of the brass which had been at the contact of the electrolyte and the gas phase showed none of the corrosion observable when a similar experiment was made in air, indicated that the influence of any residual oxygen in the gas must have been extremely small.

Circuit with the reference-electrode was made through the siphon which contained the cell-electrolyte and thence through an intermediate vessel containing 1-normal potassium chloride, when a normal calomel electrode was in use, and 2-normal sulphuric acid, when the electrode employed was mercurous sulphate with the same 2-normal acid. The reference electrodes were carefully checked against each other and against a hydrogen electrode.

The cell, and the wash bottle designed to saturate nitrogen with the vapor of the electrolyte, were kept, during the observations, in a thermostat containing thirty gallons of kerosene, which was electrically heated and electromagnetically controlled. The temperature was shown by a Beckmann thermometer divided to 0.01° C which had been compared with a certificated standard instrument, and no variation from 25° C could be detected, during or immediately before any set of measurements, which was as great as 0.003° C.

The measurements of E. M. F. were made by means of a Leeds and Northrup potentiometer, using a Broca galvanometer by the Cambridge Scientific Instrument Company as zero instrument. A saturated cadmium cell was employed as standard, which the courtesy of Professor G. A. Hulett allowed us to check against his reference battery of similar cells.

Only in the case of the measurements recorded in Tables 1 and 2 was a less sensitive method employed. For these the E. M. F. was observed by means of a modified compensation apparatus, which permitted the voltage to be read directly on a millivoltmeter to within about three millivolts, a capillary electrometer of closed form being used as a zero instrument. When apparent constancy of the potential was shown by this apparatus, the final potential was measured with the potentiometer. For all later measurements the potentiometer was used throughout.

The twenty minutes or more required for the displacement of air from the cell having already permitted the equalisation of temperature, the potential was read as soon as possible after the admission of the electrolyte, observations being taken twice in the first ten minutes and thereafter at ten minute intervals.

The first experiments relate to the constancy of the potential when the surface is untreated, and to the effect of changes of composition in the electrode surface, produced by the action of the electrolyte.

Test-piece No. 1 came from the middle of the sixth layer of eight, numbering from the top, and may be considered to have had before annealing the composition 49.9 ± 0.1 percent copper. After annealing for 96 hours, and polishing, it was employed for the four series of observations, the results of which are given in Table 1. At the head of each double column is shown the composition of the electrolyte, expressed in terms of the normal concentration in copper. Time is given in minutes from the first reading, and E. M. F. in volts.

In these experiments the surface was not renewed between withdrawal from one electrolyte and immersion in the next, but was merely well washed and dried, and air instead of nitrogen formed the atmosphere above the electrolyte. As was the case also with the measurements immediately following, upon test-piece No. 2, readings were discontinued when a potential constant to within three millivolts had been reached, this being the sensibility of the millivoltmeter. The last reading only was taken with the potentiometer. The bi-normal sulphate electrode was employed in the hope that it would have certain advantages for the special purpose in view, but was abandoned after the first experiments.

TABLE I

Reference Electrode: Hg/Hg_2SO_4, 2-*n* H_2SO_4
Atmosphere in cell: Air
Test-piece: No. 1; copper 49.9 percent
Annealed: Ninety-six hours at 700°–750° C

Electrolyte 1.10^{-5} Cu		Electrolyte 1.10^{-5} Cu		Electrolyte 6.10^{-5} Cu		Electrolyte 4.10^{-6} Cu	
Time	E. M. F.	Time	E. M. F.	Time	E. M. F.	Time	E. M. F.
00	0.48	00	0.46	00	0.50_7	00	0.48_2
11	0.47_1	13	0.46_5	10	0.48	10	0.47_9
23	0.47_1	40	0.47	22	0.47_4	21	0.47_4
44	0.47_1	55	0.47	36	0.47_2	30	0.47_4
67	0.47_1	90	0.4699	48	0.47	53	0.4745
150	0.4700			58	0.46_9		
				69	0.4702		

From these measurements it would appear that a highly uniform, well annealed brass, the surface of which is subjected to no mechanical treatment from one experiment to the next, may give a potential reproducible to within a few millivolts, in spite of slight differences in the copper content of the electrolyte. Such a conclusion would indicate that changes in the composition of the electrode surface play a greater rôle than do changes in the composition of the electrolyte in the attainment of equilibrium between the two. This might indeed be inferred from the fact that changes in the solid phase are doubtless confined to a very thin surface layer, while the ease of diffusion in the liquid distributes the loss or gain of metal through a relatively large volume.

Besides emphasizing the necessity of employing the equilibrium electrolyte, if the potential of a surface of known composition is to be obtained with accuracy, the experiments offer evidence of the high uniformity of the alloy, since the values show in each instance a very gradual steady "drift," the sense of which is determined by the composition of the electrolyte, instead of the highly irregular rise and fall of several centivolts, or even decivolts, observed, for example, by Broniewski[1] with aluminium alloys which had been prepared without special care to secure uniformity.

A similar very gradual variation is shown by test-piece No. 2, which came from the layer below test-piece No. 1 and from the next vertical row, and may be considered to have had before annealing the composition 49.7 ± 0.1 percent copper. With an electrolyte 6.10^{-6}-normal in copper the potential against a mercurous sulphate electrode, with an atmosphere of air, fell from 0.48 volt to 0.465 volt in one-half hour; with an electrolyte 4.10^{-6}-normal in copper from 0.46 volt to 0.45 volt in four hours; and with an electrolyte 2.10^{-6}-normal in copper from 0.51 volt to 0.478 volt in one and one-half hours.

The next experiments were made to determine the effect of surface treatment on the initial value and variation of the potential. The same two test-pieces as in the foregoing experiments were used and the surface was either polished with rouge on a wheel covered with broad-cloth, or rubbed down with No. FF emery-cloth before each set of readings, so that the change of surface produced by former contact with the electrolyte would not, as in the previous instances, affect the potential. Table 2 shows the variation of potential with change of surface, together with the composition of the electrolyte, the initial potential and the change in thirty minutes. From what has been said it will be understood that the electrolyte designated as 0.0-normal in copper was a 1-normal solution of zinc sulphate, 1-normal also in sodium sulphate.

In these experiments an atmosphere of nitrogen was maintained in the cell, and all observations of E. M. F. were made with the potentiometer. Since the potentials are nega-

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[1] Loc. cit.

tive, the minus sign in column four indicates an increase in the values observed, or a rise in potential.

TABLE 2

Reference Electrode: Normal calomel
Atmosphere in cell: Nitrogen
Test-piece: No. 1; copper 49.9 percent
Annealed: Ninety-six hours at 700°–750° C

Surface	Electrolyte	Initial E. M. F.	Change in 30 minutes
Rouge	0.0 Cu	0.289	—0.065
Emery	0.0 Cu	0.257	—0.048

Test-piece: No. 2; copper 49.7 percent
Annealed: 167 hours at 700°–750° C

Surface	Electrolyte	Initial E. M. F.	Change in 30 minutes
Emery	$3 \cdot 10^{-6}$ Cu	0.247	+0.087
Emery	0.0 Cu	0.155	+0.006
Rouge	0.0 Cu	0.103	—0.027
Emery	0 0 Cu	0.180	+0.026
Emery	$1 \cdot 10^{-2}$ Cu	0.091	—0.008
Rouge	$1 \cdot 10^{-2}$ Cu	0.096	—0.014

Two sets of observations, from those the results of which have been summarized in Table 2, are given below in full.

TABLE 3

First Expt. of Table 2				Third Expt. of Table 2			
Time	E. M. F.	Time	E. M. F.	Time	E. M. F.	Time	E. M. F.
00	0.289	20	0.350	00	0.247	20	0.168
5	0.320	30	0.354	5	0.230	25	0.164
10	0.338			10	0.198	30	0.160
15	0.345			15	0.180		

These preliminary experiments appeared to establish the possibility of preparing, by the methods described, brasses of such uniformity as to show very gradual progressive changes of potential, and hence suited to a systematic study of electromotive force. They served also to define clearly the direction which such a study must take.

For from the data of Tables 2 and 3 it is readily apparent that a very marked and as yet undecipherable influence is exerted by surface treatment, producing with a given alloy and electrolyte, "drifts" even the direction of which cannot be foreseen. That these (presumably) mechanical states cannot be obviated by annealing need hardly be said in view of the volatilization of zinc from heated brass,[1] and the consequent alteration of surface composition. If electrode surfaces corresponding to the analysis are to be studied, the exterior of the test-piece must be removed after every annealing, and the influence of sawing, grinding and polishing upon the potential becomes the problem first to be attacked.

Experiments upon these influences are at present in progress.

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[1] Cf. Thorneycroft and Turner: Jour. Inst. Metals, 12, 214 (1914).

A STUDY OF THE HYDROGEN ELECTRODE OF THE CALOMEL ELECTRODE AND OF CONTACT POTENTIAL. V

BY W. F. CLARKE, C. N. MYERS AND S. F. ACREE

I. INTRODUCTION

The increasingly accurate results which have been obtained by various workers who have studied the constancy, reproducibility, and, especially, the applicability of the hydrogen electrode and of the calomel electrode, made the continued study of these systems seem well worth while. With the idea of continuing the work on this subject that was begun in Acree's laboratory by Desha,[1] and continued by Loomis,[2] and Myers[3] with very interesting results, this investigation was undertaken.

The work of Hildebrand[4] in his study of the application of the hydrogen electrode as an instrument for determining the titration curves for various acids, bases and salts, that of Schmidt and Finger[5] in their study of the "Potential of a Hydrogen Electrode in Acid and Alkaline Solutions," and that of Bjerrum[6] in connection with his work on the "Elimination of Contact Potentials" show a few of the important phases of this work along inorganic lines. The hydrogen electrode was used by Denham[7] in measuring the degree of hydrolysis of several inorganic salts, and of aniline hydrochloride.

The chief object of the study of the hydrogen electrode in this laboratory has been to devise a method for allowing us to investigate a number of such catalytic reactions as the following:

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[1] Desha: Diss., Johns Hopkins Univ., 1909; Am. Chem. Jour., 46, 638 (1911).

[2] Loomis: Ibid., 1911; Am. Chem. Jour., 46, 585–622 (1911).

[3] Am. Chem. Jour., 50, 396 (1913).

[4] Jour. Am. Chem. Soc., 35, 847–871 (1913).

[5] Jour. Phys. Chem., 12, 406–416 (1908).

[6] Zeit. Elektrochemie, 17, 389–393 (1911).

[7] Jour. Chem. Soc., 93, 41 (1908).

$$CH_3CONH_2 + \overset{+}{H}\overset{-}{Cl} \rightleftharpoons CH_3CON\overset{+}{H}_3 + \overset{-}{Cl} \rightleftharpoons$$
$$CH_3CONH_3Cl + H_2O \rightleftharpoons CH_3COOH + N\overset{+}{H}_4 + \overset{-}{Cl}$$

It is at once apparent that there are so many unknowns in this reaction that the conductivity and reaction velocity methods together cannot allow us to determine whether the cation or nonionized salt or both are hydrolyzed, but if we could measure at any moment the concentration of the hydrogen ions by means of the hydrogen electrode, we could solve this problem. Conductivity measurements by Nirdlinger showed that there can be at most only a few percent of the amide salt and it is therefore necessary to develop the hydrogen electrode to a high degree of reproducibility, if it is to be of service in this connection.

As an illustration we can choose a solution in which five percent of the hydrogen ions combine with the amide to form the amide salts. In order to show a change of 0.1 percent in the hydrogen ion concentration and hence 2 percent in the concentration of the amide salt, we must make the measurements accurate to 0.000025 volt. Now it is highly desirable in such studies to know the concentration of the amide salts to within 0.1 percent, and hence we must be able to measure e. m. f. with an accuracy of 0.000001 volt. The smaller the percent of hydrogen ions disappearing in such salt-formation, the greater the accuracy demanded in the e. m. f. measurement. We have tried to devise methods to allow us to approach a reproducibility of 0.000001 volt. In studying the hydrogen electrode, the calomel electrode has been used as a standard; consequently the latter needed to be studied with respect to its constancy and ease of reproduction. This involves five lines of study, which, briefly, are:

I. The determination of the average value of the potential of a large number of electrodes, arranged in batteries of ten, which were made up very carefully from chemicals purified by the best known methods, while the apparatus was kept as clean as practicable.

II. The best methods for preparing and keeping the hydrogen electrodes in condition for immediate use.

III. Intercomparisons of different electrodes and systems.

IV. Modifications of the apparatus, especially with reference to the heating system, the bath, new forms of apparatus for calomel electrodes,[1] and new hydrogen electrode apparatus.

V. Measurement of the systems

(*a*) H_2–Pt–0.1 *N* HCl–0.1 *N* KCl–HgCl–Hg.
(*b*) 0.1 *N* KCl–HgCl–Hg.
(*c*) 0.1 *N* HCl–HgCl–Hg.
(*d*) Hg–HgCl–0.1 *N* HCl–0.1 *N* KCl–HgCl–Hg.
(*e*) H_2–Pt–0.1 *N* HCl.
(*f*) H_2–Pt–0.1 *N* HCl–0.1 *N* HCl–HgCl–Hg.
(*g*) Hg–HgCl–0.1 *N* HCl sand filling 0.1 *N* KCl–HgCl–Hg.

II. HISTORICAL

Loomis gave a brief summary of the previous work in the study of calomel and hydrogen electrodes in which he stated that Ostwald[2] was the first to describe the normal calomel electrode, which he found reproducible to within one millivolt and to have the potential $+0.5600 + 0.0006\ (t° - 18°)$ as determined by the drop-electrode method by Rothmund.[3] The study of Coggeshall[4] on the constancy of calomel electrodes; that of Smale[5] on gas elements, in which he showed that the electromotive force of the cell is independent of the material in the electrode, if not acted upon chemically; and that of Wilsmore,[6] Richards,[7] Gewecke,[8] Sauer,[9] and others

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[1] These newest forms are not closed by constricting and sealing the glass at the top as were those designed by Myers and Acree (Am. Chem. Jour., 50, 398, footnote), nor are the ground-glass tops used by Loomis employed. The top of each single electrode has a ground-glass stopper, and a glass cover tube is placed over this and fits down on a small bulb blown in the upper tube of the electrode, to which bulb the cover tube is attached hermetically with sealing wax. A full description appears later in this article.

[2] Ostwald-Luther: "Physiko-chemische Messungen," 3rd Edition, p. 441.

[3] Zeit. phys. Chem., 15, 15 (1894).

[4] Ibid., 17, 62 (1895).

[5] Ibid., 14, 577 (1894).

[6] Ibid., 35, 296 (1900); 40, 385 (1902).

[7] Ibid., 24, 39 (1897).

[8] Ibid., 45, 685 (1903).

[9] Ibid., 47, 146 (1904).

are discussed briefly by Loomis, besides which he gives an extensive bibliography.[1] Wilsmore[2] tabulated the results of the studies of Smale, Neumann, and himself. He found for the potential of the normal calomel electrode the mean value 0.283 volt which was based on his adoption as a zero of potential that of the hydrogen electrode towards a solution normal with respect to hydrogen ions. The elements studied by these workers and from which this result was calculated, included the following systems:

(*a*) H_2–Pt–1 *N* HCl–1 *N* HCl–HgCl–Hg
(*b*) H_2–Pt–1 *N* HCl–1 *N* KCl–HgCl–Hg
(*c*) H_2–Pt–1 *N* HCl–0.5 *N* KCl–0.5 *N* KCl–HgCl–Hg
(*d*) H_2–Pt–1 *N* H_2SO_4–1 *N* KCl–HgCl–Hg
(*e*) H_2–Pt–1 *N* H_2SO_4–0.5 *N* KCl–HgCl–Hg

Especial mention should be made in this brief historical survey, of the work of Schoch,[3] Sauer,[4] Salm,[5] Planck,[6] Palmaer,[7] Nernst,[8] Lorenz and Mohn,[9] Lewis and Sergeant,[10] Abegg and Cummings,[11] and especially that of Bjerrum.[12]

III. THEORETICAL

The potential of the hydrogen electrode toward the solution in which it is immersed is dependent upon the pressure of the hydrogen gas and upon the osmotic pressure of the hydrogen ions in the solution, as was shown by Nernst.

The theory regarding the calculation of the electromotive force between a calomel electrode and a hydrogen electrode is explained by Loomis, as follows:

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[1] Loomis: p. 55, Diss., Johns Hopkins University, 1911.
[2] Zeit. phys. Chem., 35, 296 (1900).
[3] Jour. Phys. Chem., 14, 665 (1910).
[4] Zeit. phys. Chem., 47, 146 (1904).
[5] Zeit. Elektrochemie, 10, 341 (1904).
[6] Wied. Ann., 40, 561 (1890).
[7] Zeit. phys. Chem., 59, 129 (1909).
[8] Ibid., 56, 544 (1906).
[9] Ibid., 60, 422 (1907).
[10] Jour. Am. Chem. Soc., 31, 363 (1909).
[11] Zeit. Elektrochemie, 13, 17 (1907).
[12] Ibid., 17, 58 (1911).

"In the comparison of a calomel electrode against a hydrogen electrode in a solution whose hydrogen ion concentration is $H^{\cdot}$, we find that if π represents the observed electromotive force, π_1 the potential of the calomel electrode against a hydrogen electrode when immersed in a solution with unit concentration of hydrogen ions, F the quantity of electricity necessary to deposit one gram ion of hydrogen and π_2 the contact potential between the solutions of the system, then the equation $\pi = \pi_1 - \frac{RT}{F} \log_e H^{\cdot} + \pi_2$ holds when the hydrogen gas is under atmospheric pressure. From this equation when $T = (25° + 273°)$ we find that

$$\log_{10} H^{\cdot} = -\frac{\pi - \pi_1 - \pi_2}{0.0591}.$$

"The value of π is obtained by actual measurement with the potentiometer, π_1 is calculated from some system in which π_2 and $\frac{RT}{F} \log_{10} H^{\cdot}$ are known and π has been previously measured, and π_2 is calculated. The best system for determining the value of π_1 is: H_2-Pt/0.1 *N* HCl/0.1 *N* KCl/HgCl-Hg in which π can be measured, $\frac{RT}{F} \log_e H^{\cdot} = 0.0591 \times \log_{10} 0.0922$ and π_2 can be calculated by some such formula as that of Planck."

The calculation of π_2 is difficult and methods have been sought for eliminating this contact potential between the two systems. For this purpose there has been interposed between the two solutions in question a saturated solution of a very soluble salt, whose anions and cations have nearly equal migration velocities. Abegg and Cumming[1] used for this purpose ammonium nitrate. Denham assumed they were correct in claiming that the use of ammonium nitrate practically eliminates contact potential. He used it in measuring the hydrolysis of aniline hydrochloride. Desha and Loomis showed that it does not entirely eliminate contact potential.

The sand-filling method of Bjerrum for eliminating con-

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[1] Zeit. Elektrochemie, 13, 17 (1907).

tact potential is much more efficient, as shown by Myers. The apparatus required for it consists of a Peligot tube filled with very pure sand to within an inch and a half of the top of each branch. The one side is tightly stoppered and 0.1 *N* KCl is poured in very cautiously and allowed to soak through thoroughly until it reaches the center line of the small bulb at the bottom of the tube. A siphon carrying a stopcock and filled with 0.1 *N* KCl is now fitted tightly by means of a ground joint into the side of the Peligot tube, which has been soaked with the potassium chloride solution. The stopper is removed from the other side and 0.1 *N* HCl is introduced with care, so that the hydrochloric acid and potassium chloride solutions come in contact in a sharp line in the middle of the lowest bulb of the Peligot tube. A siphon of 0.1 *N* HCl is attached in the manner described above to the hydrochloric acid side. When a hydrogen electrode battery is to be connected to a 0.1 *N* KCl calomel battery for intercomparison, the siphon of potassium chloride is introduced into the calomel battery and the siphon of hydrochloric acid is connected with the hydrogen electrode battery. In case the calomel battery is made up with 0.1 *N* HCl for an electrolyte and sand-filling device is not necessary; the hydrogen battery can be connected directly to the calomel battery, as illustrated at J, in Fig. 1.

IV. EXPERIMENTAL

1. Apparatus

The use of the potentiometer for measuring electromotive force; of the Weston cells as primary standards; of an oil bath for maintaining constant temperature, the oil eliminating electric leakage currents far better than water; and of the electrodes themselves, is in the main the same as that described by Loomis with the exception of such modifications and additions as are described below.

There are now in use five Weston standard cells loaned by the Bureau of Standards. The use of the potentiometer and Weston cells as arranged at present permits an accuracy of within 0.00001 volt.

The temperature regulation is correct to within 0.01°, the experiments being carried out at 25°. An especially designed milk-scale thermometer is used. It is made of Jena 59 III glass and consists of a 2 cc bulb and a capillary tube having small bulbs between the fixed points 0°, 5°, 10°, 15°, 20°, 25°, 30° and 35°. On each side of the fixed points the milk scale is graduated in 0.02° over a range of 0.2°. By the use of an especially arranged cathetometer we can easily read the thermometer to 0.0005°. The bulb wall was made rather thicker than usual in order to diminish the errors usually incident to Beckmann thermometers having thin walls. By having the bulbs in the capillary the length of the thermometer is reduced to 16$^1/_2$ inches. This type has proved to be very reliable, the observed temperatures being reproducible to within 0.003° at 25° and 0.005° at 35°.

In place of the electric bulb used by Loomis for heating there has been introduced a heating coil consisting of nichrome wire wound in a spiral upon insulated posts, and divided by lead wires into three sections. The heating capacity of each section is equivalent to that of a 32 candle power light. These sections may be thrown in series or parallel by means of a switch board. It is found that *better regulation of temperature* and electromotive force is obtained by their use for the reason that the coils are exposed directly to the oil and retain the heat for a shorter time than does a lamp.

The thermo-regulation is accomplished by means of the toluene regulator and the master relay system, first devised in Acree's laboratory for maintaining a given temperature constant to within a few thousandths of a degree. In the master-relay system, the toluene thermo-regulator and a two-volt storage circuit actuate a 250 ohm Bunnell relay, or a very sensitive No. 18 Weston relay, which, in turn, operates several other relays acting as short-circuits for the current for the heating coil. Each spark gap is short-circuited by a condenser and a high resistance lamp to prevent sparking or arcing.

The stirring of the oil is accomplished by a fan stirrer which drives the oil down over the heating coil whence it passes under a glass plate supported four inches above the bottom of the bath; the oil flows to the further end of the bath and returns after passing with good contact through the grid-iron toluene thermo-regulator, above the glass plate which supports the apparatus; it is during the last stage of the trip that it comes in contact thoroughly with the apparatus. During the passage of the oil under the glass plate the oil passes over pipes through which cold water is circulated when the external temperature renders it desirable. By means of this system the regulation was constant to within 0.01°.

The stirrer (*c*) circulating the oil is attached to the shaft A in Fig. 1, which also carries, above the surface of the oil, the fan (*b*) for stirring the air. A closely fitting top of wood and glass covers the entire bath. The shaft carries the friction wheel (*d*) which, with the shaft and fans, is revolved rapidly by means of the small friction wheel (*e*) attached to the shaft of the motor. The motor (*f*) is supported just outside the end of the bath by an iron frame work (*g*) which is bolted, through holes in supporting brass plates, to the table on which the bath rests. This arrangement avoids vibrations great enough to interfere appreciably with reading the galvanometer

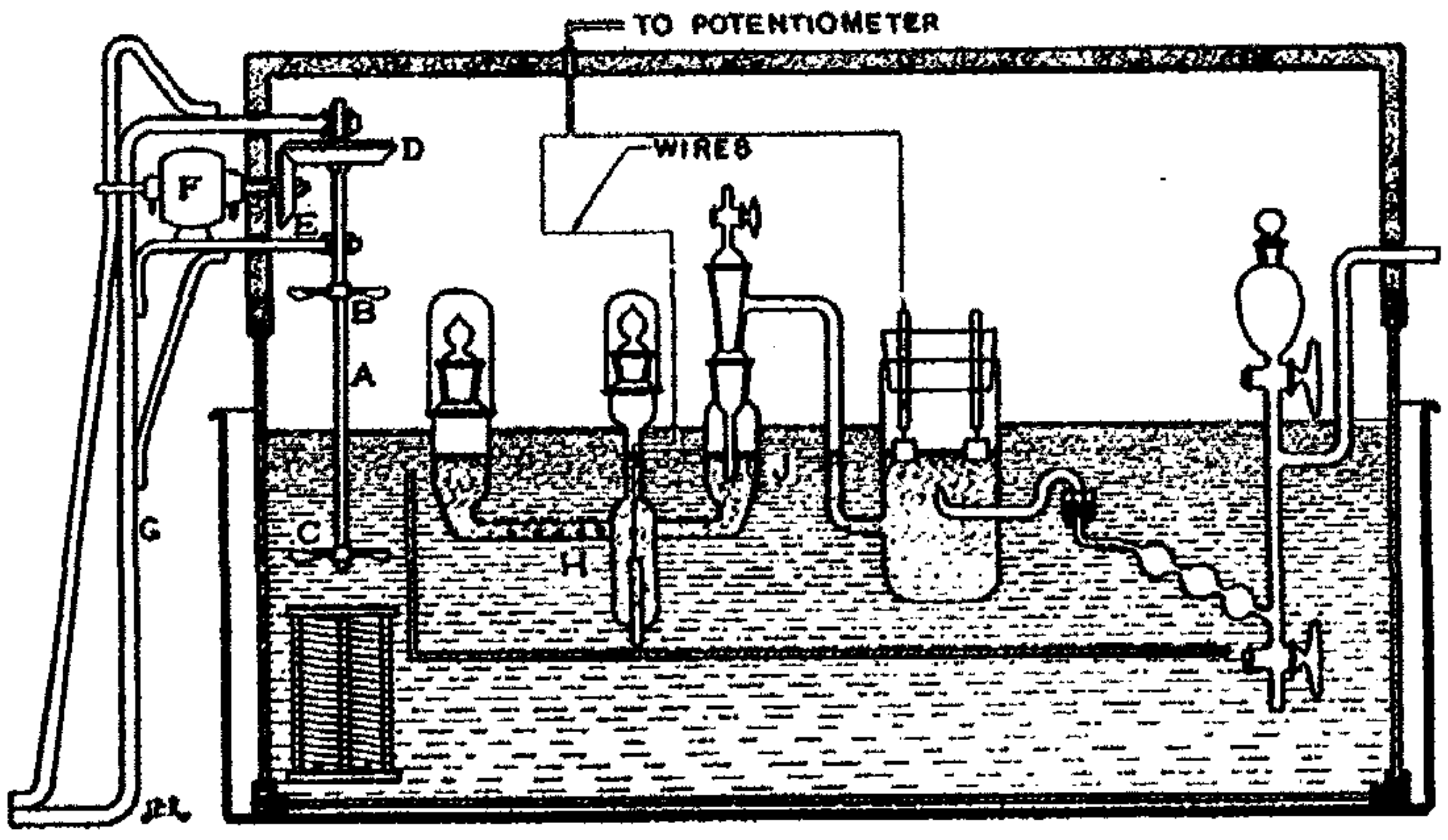

Fig. 1

on the wall at the farther end of the room. *This system avoids the troubles incident to the apparatus used by Loomis, such as the breaking and slipping off of belts, bad vibration and the open bath.*

The galvanometer is supported on a marble slab which is cemented in the wall so as to avoid as far as possible the effect of jarring caused by machinery elsewhere in the building.

The cover consists of a frame work of glass and wood which is held in position over the bath by strips of brass which project for several inches along the outside of the bath at the four corners. It has a top which is as long as the bath and is hinged to the main frame of the cover about four inches from the top back edge. This top consists of two parts hinged together in such a way that it will readily fold back upon itself and permit free access to the interior of the bath. At the end of the bath at which the motor for stirring is located, there are arranged two sliding doors which have had such sections cut from them as will permit the passage of the shaft of the motor. The doors close around this shaft and thus exclude the exterior air. The other end has a hole cut through it for the passage of the glass tube which connects the palladium asbestos tube of the hydrogen purifying apparatus to the hydrogen wash apparatus described by Loomis. Through the top, toward the back, there are three holes for the admission respectively, of the wires used in connecting the cells with the potentiometer, of the wiring for an electric lamp for heating the air when necessary to about 26°, and of the thermometer held by a stopper. *The purpose of the lamp referred to is to heat the air enclosed by the cover to about 26° and thus prevent the condensation, in the upper parts of the calomel electrodes, of the water vapor above the solutions of potassium chloride* and avoid changes in the concentrations and electromotive forces. The air-fan referred to serves to circulate the air and prevent superheating above any one battery. An ordinary thermometer is considered sufficiently accurate for this air space, and no thermo-regulator is necessary as the lamp is not used when the room is warm enough to heat the air of the bath sufficiently to interfere with the regulation of the heating of the oil. The lamp used is blackened with a heavy coating of lamp black and shellac so as to prevent radiation.

For the study of a calomel battery over a period of several years the form used by Myers and Acree is well adapted. It differs from the form used by Loomis in that the upper tubes of the single electrodes are constricted and sealed instead of being closed by means of ground-glass caps containing stopcocks. To study a battery for a short time and to empty and refill seemed highly desirable. *To do this with the form used by Myers and Acree it would be necessary after two or three fillings to seal a new top to each electrode; as such a process incurs considerable risk of breaking an expensive piece of apparatus, it was thought best to modify the form in such a way that it could be used repeatedly without this danger and at the same time without permitting the leaking in of oil as did the form used by Loomis. With this idea in mind the form (H) illustrated in Fig. 1 was devised.* The essential differences consist in the use of ground-glass stoppers for closing each electrode and in using sealing-wax to fasten the glass caps down upon the bulbs shown in Fig. 1. This form of battery and that used by Myers and Acree contain much wider tubes connecting the single electrodes than were used by Loomis. *This decreases the electrical resistance and also permits more rapid diffusion and attainment of equilibrium.*

Several modifications of the hydrogen apparatus used by Loomis are described by Myers and Acree. The use of *pure gum* stoppers, of the device for preventing the hydrogen electrodes from drying while in storage during the summer, and of the short-circuiting "crow-foot" are important changes which they introduced. The storage apparatus for the hydrogen electrodes is illustrated in Fig. 2 and Fig. 3. An ordinary crystallizing dish, A, about half filled with 0.1 *N* HCl is placed in a desiccator, F, which contains enough 0.1 *N* HCl to rise to about $^1/_4$ of the height of the crystallizing dish. The tube D, passing through a stoppered hole, 5, in the side

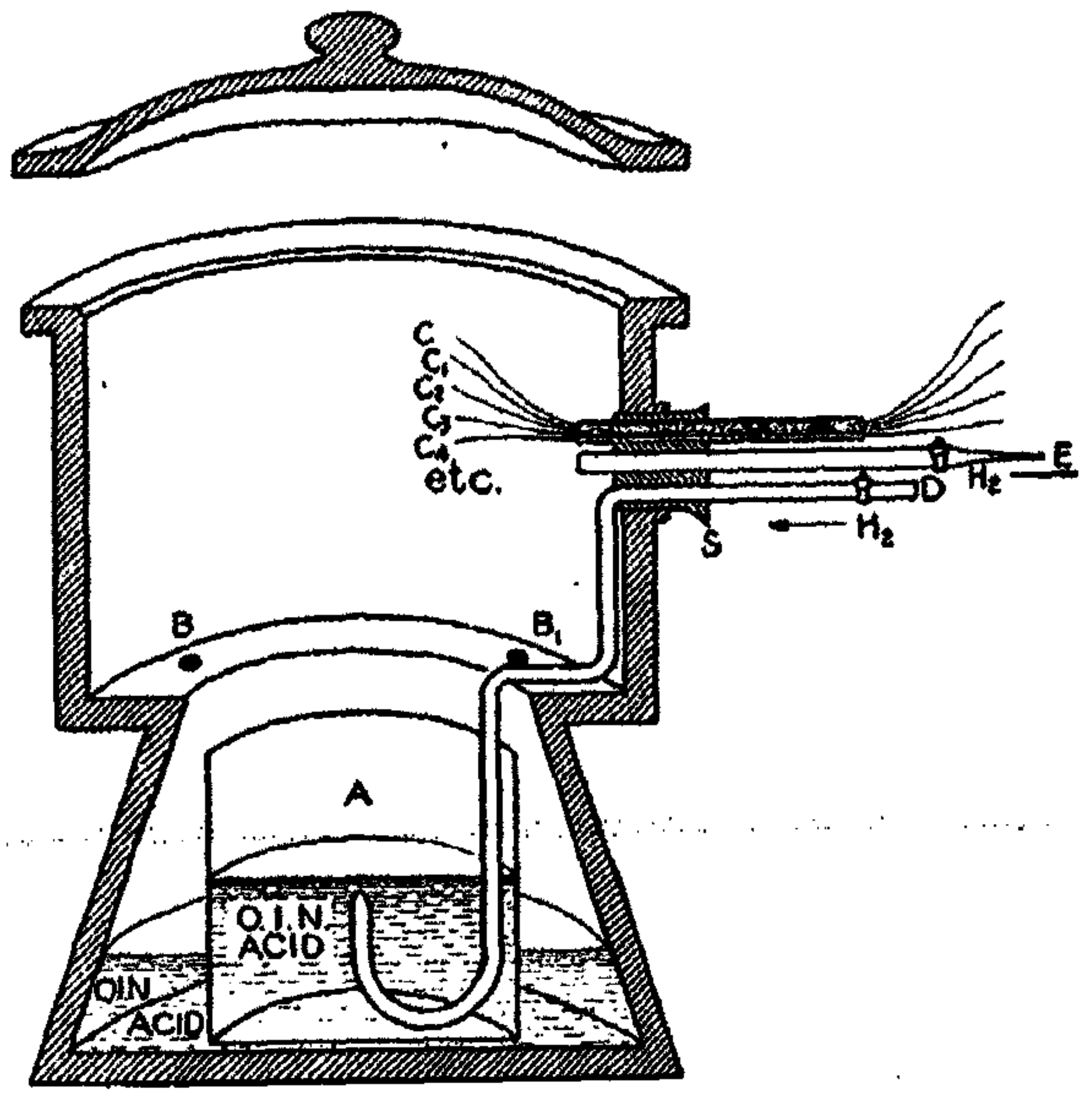
C
C₁
C₂
C₃
C₄
etc.
E
H₂
D
S
H₂
B
B₁
A
0.1 N ACID
0.1N ACID

Fig. 2

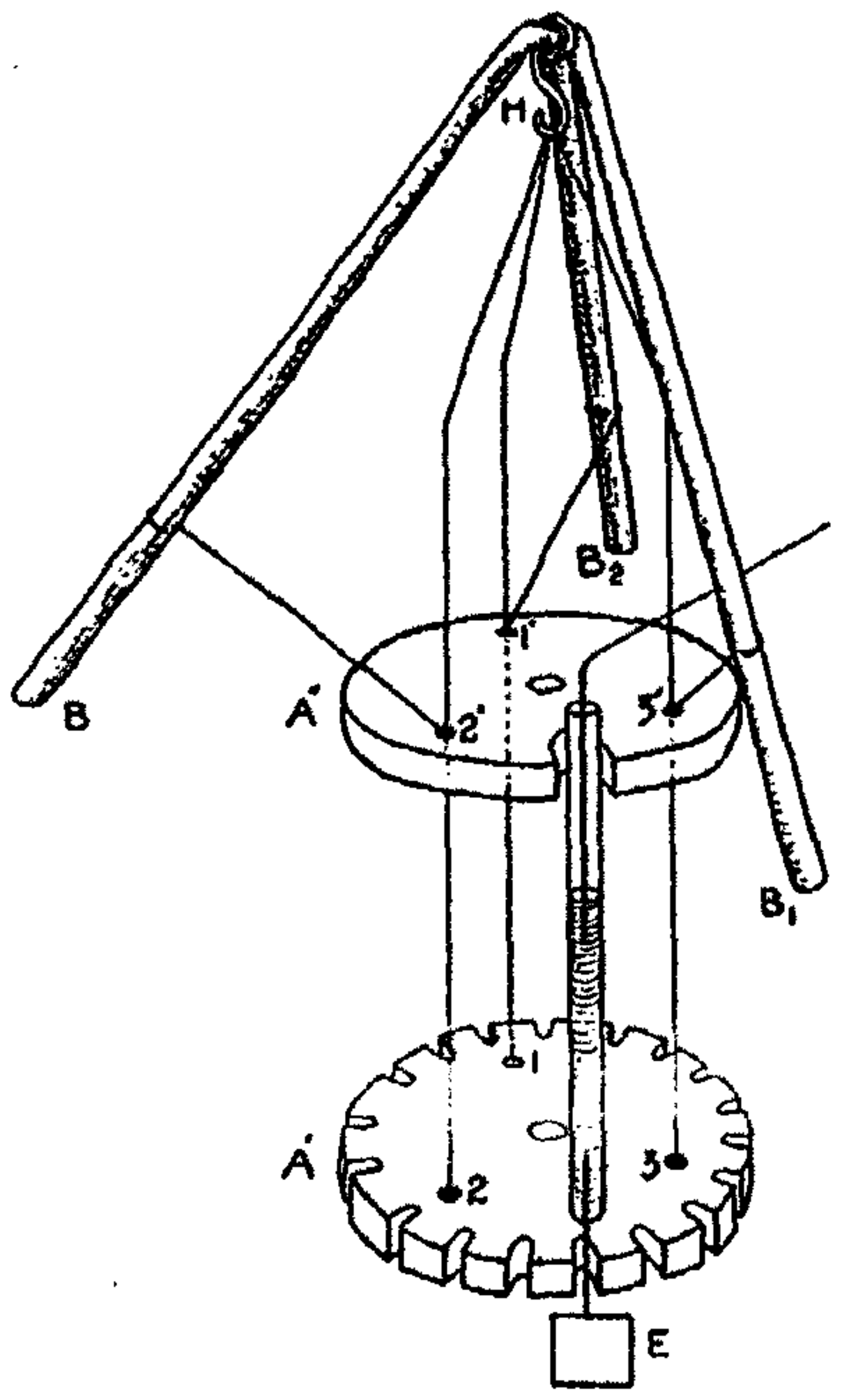
H
B₂
B
A''
2'
1'
5'
B₁
1
A'
2
5
E

Fig. 3

of the desiccator, and so bent as to have an outlet under the surface of the acid in the crystallizing dish, serves as an inlet for hydrogen gas, while the tube E serves for its escape. Fig. 3 shows the framework which supports the electrodes so that they are about half submerged in the acid in the crystallizing dish. B, B_1 and B_2 are the three legs of a glass tripod, upon which, by means of the hook H, and the supporting gold wires 1′–1, 2′–2, 3′–3, are hung the circular glass disks A′ and A″. These disks have cut into their edges indentations suitable for holding the electrodes, as illustrated by E; after the set of electrodes has been placed in position in the disks a gold wire is bound around them in such a way that they will not slip if handled with ordinary care. The tripod is now placed in the desiccator so that the feet rest upon the shoulder B and B_1 in Fig. 2. When the electrodes are not in use, and yet it is desired to keep them active, the wires C, C_1, C_2, C_3, etc., are short-circuited in a cup of mercury outside the desiccator. Inside the desiccator each of these wires is introduced into a different capillary tube carrying a hydrogen electrode. When it is wished to intercompare the hydrogen electrodes, the wires are removed from the cup of mercury; the wire leading to any one electrode (which serves as a standard) is connected by means of a cup of mercury and wiring to the potentiometer; the other wires are similarly, one at a time, connected to the potentiometer and the intercomparison of the potentials of the electrodes is made. Table VI shows that the deviation among a number of electrodes stored in this way for eleven months was generally less than 0.0001 volt. This is highly satisfactory as electrodes left dry even three months vary from 0.0001 volt to 0.06 volt, and cannot be used at all without replatinization.

The barometer is a *Fuess* normal and carries verniers for correcting for capillarity.

The connection between the hydrogen electrode and the calomel is made by means of the sand-filling device of Bjerrum as described later.

With regard to the calomel electrode a little change in the preparation and introduction of the material has been made from the methods used by Loomis. In the preparation of the calomel the precipitation of the mercurous chloride is effected at present by the addition of a dilute solution of potassium chloride to the solution of mercurous nitrate. The form of calomel battery has been modified as described.

Some of this work is concerned with the study of batteries which were made up by Dr. Myers. Two of them designated as B-IV and B-V were made up in May, 1912, while B-II was made up May 1, 1913. The former two have not been refilled during this time and have had a history worth considering at length. Table I shows the data for battery B-IV—0.1 *N* KCl-HgCl-Hg, part of which has been presented by Myers and Acree.

The notations "with wires," "without wires," etc., refer to the readings below; the notations "with wires" means that the crow-foot short-circuit device was in use. "Without wires" means it was not in use. The notation "readings made while storage cell was connected to charging switch" means that wires from the storage cell were connected to the switch leading to the charging current. Although the switch was open there was a leak sufficient to affect the galvanometer, as the readings show. "Changed short-circuit to wood cups" means that in place of the "crow-foot" there was introduced a set of wood cups containing mercury; these were connected by wires to the capillaries in the batteries. The cups of mercury were now short-circuited with one another by means of a frame of brass. "Changed short-circuit to glass cups" means that glass cups of mercury were used in place of wood, it being found that the wood cracked and let the mercury escape. On the whole the figures show that the best system is the "crow-foot" used by Myers and Acree.

Table II shows the data battery B-V — 0.1 *N* KCl-HgCl-Hg; some of the readings were made before this present study was begun. The notes and notations explain some of the variations in the readings.

TABLE I—BATTERY No. IV, 0.1 *N* KCl–HgCl–Hg

Prepared May 2, 1912
The first values recorded were obtained 18 hours after preparation
(Values expressed in millionths of a volt)
Electrode 1 used as standard

Date	2	3	4	5	6	7	8	9	10
With wires									
1912									
May 3	140	41	10	38	26	50	25	55	180
May 4	11	5	12	8	8	80	35	2	4
May 6	15	4	6	11	4	7	2	9	5
May 7	12	7	10	13	2	30	12	15	11
May 9	1	9	9	11	10	16	10	10	30
Without wires									
May 11	50	60	15	70	60	90	45	80	75
With wires									
May 22	8	9	3	7	7	10	1	9	10
1913									
Apr. 11	8	7	6	7	7	7	8	8	5
NOTE.—Readings made while storage cell was connected to charging switch									
Nov. 4	14	24	2	16	24	46	56	56	46
Storage cell disconnected									
Nov. 14	23	2	8	10	6	8	28	1	9
Nov. 20	5	9	9	4	2	14	10	9	4
Changed short-circuit to wood cups									
Dec. 14	16	59	23	20	5	10	11	0	3
Dec. 22	2	11	23	14	14	34	51	26	32
1914									
Feb. 9	29	54	52	59	73	73	61	61	61[1]
Feb. 23	19	1	2	2	34	16	16	26	17
Mar. 2	7	25	11	—[2]	13	8	8	14	14
Mar. 7	2	10	24	12	2	6	2	5	5
Mar. 22	9	9	6	8	15	9	11	20	20
Wire crow-foot replaced									
May 7	3	27	35	33	5	18	—[3]	2	16
May 15	2	27	50	43	23	32	27	29	19

---

[1] Bath had been out of use for a long time. Equilibrium had not been attained when these readings were made.

[2] The wire leading to capillary had broken off from No. 5.

[3] The wire leading into capillary of electrode No. 8 was not amalgamated and did not make contact.

TABLE II—BATTERY B-V—0.1 *N* KCl-HgCl-Hg
Prepared May 2, 1912
First readings recorded 18 hours after preparation
(Values expressed in millionths of a volt)
Electrode 1 used as standard
With wires

Date	2	3	4	5	6	7	8	9	10
1912									
May 3	21	16	28	54	35	142	45	25	15
May 6	4	5	2	5	9	10	1	3	7
May 22[1]	4	2	4	5	1	55	56	15	5
Oct. 17	5	6	8	12	4	9	0	7	2
Oct. 22	1	9	0	7	4	2	5	7	6
Nov. 4	5	0	1	7	9	5	8	5	4
1913									
Jan. 7	2	6	2	4	3	2	3	2	4
Jan. 14	0	0	2	4	2	6	1	4	0
Apr. 11	8	7	6	7	7	7	8	8	5
May 5	0	2	0	1	1	1	1	2	4
Nov. 4[2]	97	82	87	81	96	64	26	20	45
Nov. 5[3]	8	20	4	21	22	3	21	13	38
Nov. 12	0	2	17	2	8	11	34	3	4
Nov. 20	7	0	5	16	16	2	10	8	2
Nov. 25	2	2	2	18	16	16	2	8	2
Dec. 14	5	8	2	2	10	2	7	6	6
1914									
Feb. 11	0	4	0	8	2	3	22	4	0
Feb. 20	2	4	2	2	2	0	15	2	3
Mar. 2	3	3	0	2	2	4	16	6	9
Mar. 17	0	2	0	7	4	3	9	4	3
Mar. 22	1	2	3	3	5	0	5	1	4
May 8[4]	42	63	58	55	58	67	82	67	68

An examination of the values shown in Tables I and II shows that within four days from the time of preparation of

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[1] Battery had been used in making measurements, solution was disturbed.

[2] Readings made while storage cell was connected to charging switch, short-circuiting arrangement was bad.

[3] Better short-circuiting.

[4] Battery had been used to make intercomparisons. Solutions were disturbed.

the calomel batteries, the potentials of the electrodes will differ among themselves by not more than 20 millionths of a volt. The values found in the cases in which the crow-foot short-circuiting was maintained show that this system tends to bring about a closer agreement of the electrodes than is obtained when there is no short-circuiting. The close agreement between the electrodes at the end of two years shows the constancy of the system.

TABLE III (*a*)—COMPARISON OF BATTERIES B-IV AND B-V, 0.1 *N* KCl-HgCl-Hg

	B-IV against Cell I B-V after 18 months	B-IV	B-V
Cell	Without wires	Same date without wires	With wires
1	0.000005	0.000028	0.000001
2	0.000032	0.000031	0.000009
3	0.000029	0.000017	0.000000
4	0.000021	0.000025	0.000007
5	0.000025	0.000012	0.000004
6	0.000012	0.000022	0.000002
7	0.000023	0.000031	0.000005
8	0.000038	0.000014	0.000007
9	0.000010	0.000027	0.000006
10	0.000024	—	—

TABLE III (*b*)—COMPARISON OF BATTERIES B-IV AND B-V, 0.1 *N* KCl-HgCl-Hg

	B-V against Cell I of B-IV	B-IV against Cell I of B-V
Cell		
1	0.000009	0.000001
2	0.000012	0.000007
3	0.000000	0.000004
4	0.000007	0.000002
5	0.000009	0.000000
6	0.000001	0.000001
7	0.000008	0.000000
8	0.000004	0.000001
9	0.000005	0.000000
10	0.000006	0.000003

TABLE IV—BATTERY No. VI, 0.1 *N* KCl–HgCl–Hg

(Values expressed in millionths of a volt)
Electrode 1 used as standard
With wooden cups of mercury

Date	2	3	4	5	6	7	8	9	10
1914									
Feb. 9	43	45	45	118	89	31	31	6	79
Feb. 11	2	46	47	127	94	52	60	56	97
Unblackened 32 c. p. lamp in air space over bath near electrodes 1, 2, 3, 4 and 5 of battery Without wires since Feb. 12th									
Feb. 18	162	181	183	284	276	258	303	293	346
With wooden cups of mercury									
Feb. 23	83	5	108	176	113	127	136	121	157
Mar. 2	108	94	126	182	108	157	180	160	192
Blackened 8 c. p. lamp in air space									
Mar. 17	85	95	95	105	90	85	90	82	71
Mar. 22	95	117	96	109	109	99	110	106	115
With wires									
May 1	11	50	36	29	0	35	35	23	36
May 8	14	30	25	23	30	25	17	12	18

TABLE V—BATTERY No. VII, 0.1 *N* KCl–HgCl–Hg

(Values expressed in millionths of a volt)
Electrode 1 used as standard
With wires

Date	2	3	4	5	6	7	8	9	10
1914									
Feb. 9	2	36	48	70	104	26	7	2	52
Feb. 11	15	20	32	45	77	20	2	2	37
Feb. 13	25	2	6	38	43	10	28	23	54
Unblackened 32 c. p. light placed in air space above bath									
Feb. 18	7	19	35	45	33	31	5	11	17
Feb. 20	5	17	44	55	44	23	14	14	13
Feb. 23	25	28	38	54	51	19	14	8	23
Mar. 2	14	42	38	52	34	1	8	18	2
Blackened 8 c. p. light in air space									
Mar. 8	5	32	28	32	29	33	12	4	13
Mar. 22	6	1	25	30	33	7	11	9	2
May 1	29	12	14	14	22	51	32	0	20
May 8	18	21	15	5	9	35	9	6	31

Table III (*a*) and Table III (*b*) show the comparison of the electrodes of one battery against a single electrode of another. It should be noted that the effect of the use and non-use of the short-circuiting system is marked. The values shown in Table III (*b*) were obtained after the short-circuiting system had been in use for some time immmediately previous.

Tables IV and V give the history of Batteries B–IV and B–VII. These batteries are the latest form, *i. e.*, they have ground-glass stoppers for each electrode and protecting glass covers. The values shown are not so good as those found for batteries B–IV and B–V, but this is due to better technique in preparing the materials for B–IV and B–V. So far as the form of battery is concerned, there seems no reason to believe the forms used for B–IV and B–V are either more or less preferable than those used for B–VII, so far as constancy and reproducibility of the electrodes are concerned. It is interesting to note the effect of the use of unblackened 32 c. p. light and of blackened (to diminish radiation) 8 c. p. light for heating the air-space enclosed by the glass and wood top above the bath. Attention is directed to the fact that in the case of B–VII the crow-foot was used throughout its history, while for B–VI wooden cups of mercury were used. The results in the case of B–VII are rather better than for B–VI. This is believed to be due to the difference in the method of making the reading. In the case of B–VI the readings were made through the cups of mercury, each of which was connected, by means of a screw soldered to a wire, to an electrode. The soldering of the wire to the screw is believed to have brought about resistance differences which affected the readings on the potentiometer considerably. It will be noted that the crow-foot system was made use of in the case of B–VI previous to the last two sets of readings and that the values for the potentials of the different electrodes approached a more constant value.

Table VI shows the history of a set of hydrogen electrodes. Some of the values shown were obtained previous to the time this present study was begun. Whenever the

TABLE VI—H_2-Pt-0.1 *N* HCl. STOPPER I

Electrodes were placed in 0.1 *N* HCl after being left in box three months. H_2 allowed to run about five hours before first record was taken. Electrode 10 chosen as standard

(Values in millionths of a volt)

Date	9	8	7	6	5	4	3	2	1
1912									
Jan. 18	186	820	470	700	62930	956	58810	155	2558
Jan. 19	232	178	168	169	4988	1736	3445	696	820
Jan. 20	175	81	101	195	2654	895	1720	405	525
Electrodes replatinized and treated as described									
Jan. 22	50	75	227	30	636	218	430	97	73
Began use of "Crow-foot" replatinized and electrolyzed									
Jan. 24	15	35	53	40	98	31	15	15	47
Jan. 26	6	10	10	10	46	9	5	25	13
Jan. 27	7	3	0	5	10	6	0	40	2
Jan. 31	10	6	6	3	28	6	6	37	4
Rubber dissolving in acid as shown below									
Feb. 1	42	25	46	14	46	58	44	78	44
Apparatus cleaned. Electrodes and stoppers boiled in distilled water									
Feb. 4	11	15	12	6	10	18	12	25	25
Feb. 6	4	4	1	3	3	8	2	2	5
Stove in bath burned out and temperature drops 6 degrees									
Feb. 9	6	3	3	5	4	2	6	6	1
Without wires									
Feb. 17	25	10	15	15	14	12	9	15	—[1]
Feb. 19	20	3	15	15	26	26	25	34	27
Rubber dissolving in acid									
Mar. 6	50	60	130	55	115	90	50	140	56
Electrodes boiled in distilled water and placed in constant pressure desiccator									
1913									
June 1	20	3	5	2	3	1	1	3	0
Apr. 25	5	3	6	6	7	5	4	1	3
Electrodes stored in desiccator until March 29, 1914, then placed in 0.1 *N* HCl and exposed to stream of H_2									
1914									
Mar. 31	24	20	33	192	105	46	44	70	11
Electrodes replatinized. Placed in bath May 6									
May 8	9	20	12	6	8	25	9	12	25

[1] This electrode was broken and repaired, giving result shown on next date.

TABLE VII—Hg-HgCl-0.1 *N* KCl-0.1 *N* HCl-Pt-H_2
(Bar. in Atms., 1.010; Cor. in e. m. f., —0.00023)

	0.427341		
	0.427342		
	0.427336		
	0.427342		
	0.427335		
	0.427342		
	0.427340		
	0.427335		
	0.427338	Other similar averages	
	0.427340		0.427106 (*a*)
			0.427109 (*b*)
Av.	0.427339		0.427109 (*c*)
Bar. Cor.	0.00023		0.427108 (*d*)
Av.	0.427109	Av.	0.427108
Cor. av.	0.426919	Cor. av.	0.426918

electrodes were replatinized they were boiled with distilled water for several hours after the replatinization.

Table VII shows a comparison of a fresh calomel battery and a hydrogen battery without use of a device for eliminating contact potential. These values were obtained by Myers and are reported here for the sake of comparison with a system in which there was used for elimination of contact potential a saturated KCl solution. The values (*a*), (*b*), (*c*), (*d*) are averages of sets of values obtained at other times. All readings shown were made before the Fuess normal barometer was obtained, and the "Cor. Av." notation means that the readings of the old barometer were not correct, hence the values noted "Av." need the correction applied.

TABLE VIII
0.1 *N* KCl-HgCl-Hg sat. KCl 0.1 *N* HCl-Pt-H_2
B-V-Bar. in atms., 0.990-Bar. Cor. = 0.00026

0.39971	0.39981	Av.	0.39974
0.39972	0.39976	Bar. cor.	0.00026
0.39980	0.39971		
0.39974	0.39972		0.40000
0.39972	0.39973	Cor. av.	0.39982

Table VIII shows the values obtained when saturated KCl is used to eliminate contact potential. The values obtained agree closely with those of Bjerrum.

The results for the system 0.1 *N* HCl–HgCl–Hg were about the same as those obtained by Myers and Acree.

Summary

1. The object of this investigation has been to devise better methods and apparatus for the accurate measurement of the electromotive force of hydrogen and calomel electrodes. Chief among the improvements in apparatus were (1) a new heating and stirring device for the oil bath which permits a more accurate regulation of temperature and electromotive force; (2) an air bath above the oil bath to heat the air and prevent evaporation from the liquids and changes in concentration and electromotive force; (3) a new form of calomel battery which can be filled, emptied and cleaned very quickly and easily without danger of breakage and which gives as accurate values as those used by Myers; (4) a storage reservoir in which hydrogen electrodes can be kept active in hydrochloric acid in an atmosphere of hydrogen and kept constant in electromotive force to within 0.0001 volt. The preparation of very pure calomel by the use of potassium chloride and the use of weight methods in lieu of volume methods for the preparation of the hydrochloric acid have increased the ease of making satisfactory solutions.

2. By the use of these improvements in the apparatus and methods it is possible to obtain much more easily than formerly a reproducibility of 0.01 millivolt with the hydrogen and calomel electrodes.

3. The 0.1 *N* KCl–HgCl–Hg system seems to be constant and reproducible to within 0.01 millivolt. In addition it is a comparatively stable system.

4. The hydrogen electrode has proven to be an easily reproducible and constant system, extremely sensitive to small amounts of impurity, thus indicating its rapidity and accuracy for determining small hydrogen ion concentrations,

which would render it very valuable in determining the hydrogen ion concentration in cases of catalysis by acids.

5. It is found that the system Hg–HgCl–0.1 *N* KCl–0.1 *N* HCl–Pt–H_2 is an extremely accurate and constant element. It undoubtedly gives one of the best intercomparisons that can be obtained.

6. The 0.1 *N* HCl–HgCl–Hg system is found to be rather unsatisfactory over long periods of time. The intercomparison of the individual electrodes indicate that its constancy continues over only a short period of time, due to the formation of $HgCl_2$ and Hg, with a possible further decomposition. The values obtained during the past year support the evidence previously found in this laboratory.

7. An accuracy of 0.01 millivolt was obtained when the following precautions were observed:

a. The materials were most carefully purified. The mercury was purified by washing about five hundred times with three percent nitric acid. It was rinsed with water and let stand under concentrated sulphuric acid. It was distilled three times in a current of air. This was used for making calomel and in the calomel electrode.

The calomel was made by dissolving mercury, purified as indicated, in *N*/5 nitric acid and using an excess of mercury. To the solution of mercurous nitrate a solution of thrice recrystallized potassium chloride was added. The calomel was shaken out with water repeatedly and filtered and washed to get rid of nitric acid and potassium nitrate. It was then shaken with approximately *N*/10 potassium chloride to get rid of the excess of water. Finally it was saturated with carefully standardized *N*/10 potassium chloride prepared from the ignited recrystallized potassium chloride.

The *N*/10 potassium chloride was prepared from potassium chloride recrystallized three times and ignited to constant weight. Conductivity water was used in making up the solution.

The *N*/10 hydrochloric acid was made from redistilled hydrochloric acid. The hydrogen was prepared by electrolysis of dilute sodium hydroxide, using nickel electrodes. The hydrogen was passed through a palladium asbestos tube and a washing apparatus containing *N*/10 hydrochloric acid.

b. A temperature relation in the oil to within 0.01° was maintained for at least two days previous to making readings. The temperature above the bath was roughly kept at 26°. It was intended simply to prevent the condensation of liquid in the upper part of the apparatus which protruded above the oil.

c. When not in use for several weeks the hydrogen electrodes were stored in the container illustrated in Figs. 2 and 3. They were kept saturated with *N*/10 hydrochloric acid and hydrogen.

d. The hydrogen was bubbled through the *N*/10 hydrochloric acid against the electrodes. It was believed that this is more efficient than simply maintaining an atmosphere of hydrogen above the hydrochloric acid.

e. The individual electrodes of the calomel (and hydrogen) batteries were short-circuited together by means of the wire crow-foot. This produced and maintained a very close agreement.

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NEW BOOKS

Unit Photography. *By Morris Steadman. 21 × 15 cm; pp. v + 160. New York: D. Van Nostrand Company, 1914. Price: $2.00.*—The author does not like the f system of numbering the stops of a lens because it is not clear to the untrained mind why an $f/16$ stop calls for four times the exposure of a $f/8$ stop. Instead of using the ratio of the diameter of the opening to the focal length as a basis, the author suggests that we consider the converging beam of light as a cone and use the ratio of the surface of the aperture to the focal length as a basis. Since the $f/64$ stop is as small is often used, the author calls this his unit cone. In the new scale $f/32 = 4$, $f/16 = 16$, $f/8 = 64$, etc., the advantage of this is that the exposures with any two stops is inversely proportional to the ratio of the cone value instead of to the square of the ratio of the f values.

In regard to the absolute actinic unit, the author says, p. 43: "Logically the absolute unit of actinicity must be defined as the rate of emission of radiant energy from a surface just actinic enough to produce the least visible tint on some conventional standard medium in one second when the convergence is one cone unit. As in the case of many other absolute physical units this is impracticable in ordinary use since measured in this manner the surface of the sun itself, when high in the heavens and the atmosphere clear, would have an actinicity of only 128 units and all ordinary intensities would have to be expressed in fractions. A surface as bright as the brightest sky would have only about 1/512 of this unit actinicity. It is evident, therefore, that a much lower actinicity must be chosen as the practical unit. The unit actually chosen is that rate of emission which will produce a least visible tint in one minute (or 64 seconds) when the convergence is $f/1$ (or 4 M cone units). This practical unit of actinicity is called an *actino*. Using the ordinary emulsions as the standard tinting medium, this practical unit gives the brightest sky an actinicity of about 512 actinos and the sun about 32,000,000 actinos. The practical reason for choosing this intensity as the unit is that ordinary surfaces about us, as for example a face when lighted as for making protraits, will have an actinicity of from 8 to 64 units. It is seen, therefore, that the value of the practical unit of actinicity is chosen purely for convenience in practice just as the practical units in other departments of physics have been chosen."

On p. 82 we read that "the latitude of an emulsion is its capacity to render in perfect gradation different degrees of actinicity in the same subject. An emulsion is said to have great latitude when it will register greatly differing intensities and to be 'hard' or contrasty when it will register comparatively little actinic contrast or when a little actinic contrast in a subject suffices to fill, or fully utilize, its gradation capacity.......

"The average and soft emulsions are to be used for the average sunlight view and for portraiture and all subjects having ordinary contrasts. The hard emulsions are used more especially for photomechanical or process work in which it is required to get extreme contrasts in copying flat prints or to obtain effects in black and white as in the production of white lines on a dark ground or the reverse. However, when the illogical desire for speed has run its course among photographic workers and emulsions are selected purely by reason of their quality or latitude, which is simply their adaptability for subjects of certain known contrasts, then these hard emulsions will be used much more for all those subjects which have but little contrast, such as bird's eye views and copies in general."

The author measures accurately the time necessary for an exposure and, after development, intensifies or reduces his negative to suit his taste. He gives illustrations to prove, p. 121, that "it is practically indifferent how long correctly exposed emulsions remain in the developing solution so long as they are afterwards brought to their correct density by reduction or intensification."

The author has written an interesting book and one that is well worth a careful study. It is not clear for what audience the volume is intended. Part of the book is certainly written for the man whose knowledge of physics is negligible while part of it seems to be intended for advanced students.

Wilder D. Bancroft

The Manufacture of Paint. *By J. Cruickshank Smith. Second revised edition. 22 × 15 cm; pp. xiv + 271. London: Scott, Greenwood and Son, 1915. Price: 10 shillings, six pence, net.*—In the preface the author says: "No attempt has been made to provide recipes and manufacturing formulae. To have done so would have altered the nature and intention of the book. The aim of the author has been to set forth in language as simple and concise as the subject permits the fundamental principles involved in the manufacture of modern decorative and protecting paints, an industry which shows no sign of decreasing in importance in the near future."

The headings of the chapters are: scope of subject and definition of terms; storing and handling raw material; testing and valuation of raw material; plant and machinery; the grinding of white pigments; the grinding of earth pigments; the grinding of oxide of iron pigments; the grinding of black pigments; the grinding of chemical pigments; the grinding of pigments in water; the grinding of pigments in turpentine, gold-size, and special mediums; mixed or prepared paints; enamels and enamel paints; modern conditions which affect the selection and application of paint; the designing, matching, and testing of paints; economic and general considerations.

In some cases the author is very explicit, for instance, on p. 5: "Frequently dry-ground pigments fail to give entire satisfaction to the paint grinder because he finds that, however finely a material may be powdered, it is liable to produce a spongy paste-paint when worked up with oil. The difference observable during the grinding in oil in the behavior of pigments which have been ground and separated in the wet way, and of those which have been dry-ground, is usually traceable to one of two causes. The first of these is that the dry-ground pigment is less amorphous in structure, and there is greater variation in the size of the particles. This results in the paste-paint also containing particles whose size varies through wide limits, and the paint consequently lacks coherence. The second reason is that a dry-ground pigment usually contains the same proportion of silica and other indifferent paint-forming substance as did the original material, whereas in the wet-ground and floated pigment these deleterious ingredients have been washed out. For similar reasons finely levigated pigments remain in suspension in mixed paints better than dry-ground pigments."

The account of the way the knives should be set in a pug mill is good, p. 44; the pages on the kind of black pigment to be used in special cases is excellent, p. 142. Those on the lakes, p. 169, are much better than usual in such books. On the other hand it is trying to read, p. 7, that "it is remarkable how the appearance and physical texture of a pigment can be modified by variation in the conditions of drying. A tough or friable or flinty or soft texture may be communicated to some pigments simply by altering the temperature and conditions of drying." This is both interesting and true; but we are not told how to get these different textures and we ought to have been.

On p. 25 we read that "crystalline structure, size of particles, and tendency to fall out of suspension in a liquid medium are among the properties which influence the suitability of a pigment for paint making. The ease with which the particles of a pigment can be reduced in size during grinding is another factor which may render a pigment suitable or the reverse for paint making, for the reason that the cost of reducing a given pigment to the requisite degree of fineness may put it out of court for a specific purpose. The tendency of certain pigments to settle out from the medium with which they are mixed, and the indifferent manner in which others work under the painter's brush are illustrations of defects arising out of poor paint-forming properties. The texture, fineness, and crystalline structure of the particles all influence to a greater or less extent the paint-forming qualities of a pigment, yet these qualities cannot, with any degree of certainty, be predicted from the previously ascertained chemical composition, or from the various physical properties referred to." Depending on one's mood and one's temperament, one will say "How true?" or "How vague?"

The reviewer would like to know something more definite about lithopone, p. 108. "Different brands and makes of lithopone present enormous differences in respect of their behavior when ground in linseed oil. Some prove to be most unsatisfactory, yielding a paste which 'feeds up' and becomes tough and stringy. This is in most cases due to the presence of minute traces of chemical impurity in the pigment, and those who propose to use lithopone largely are advised to make themselves familiar with the nature and properties of the brand they think of adopting before making large purchases."

Wilder D. Bancroft

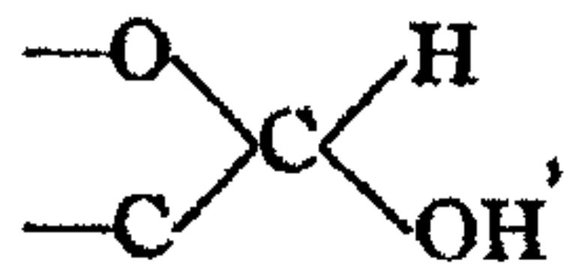
THE ISOMERISM OF THE α AND β FORMS OF THE SUGARS[1]

BY ERNEST ANDERSON

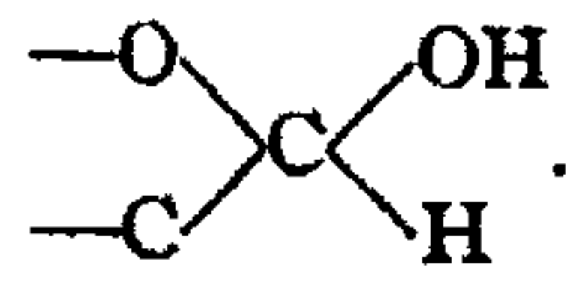
Most chemists now assume that the various crystalline modifications of the pentose and hexose sugars do not possess a free carbonyl group in the molecule but have a 5-atomic lactone of the general type

$$CH_2OH - CHOH - \overset{\frown O \frown}{CH - (CHOH)_2 - C}(OH)H.$$

From this standpoint α and β *d*-glucose have the same lactone and differ only in the space relations about the end asymmetric carbon atom which in one form has the structure



in the other, the structure



This same relation is supposed to hold for the α and β forms of all pentoses and hexoses as well as for the corresponding glucosides.

A careful comparison of the configurations of the sugars with their optical rotations led the author some years ago to conclude that the above-described assumptions may be incorrect and that α *d*-glucose may have a 4-atomic lactone while β *d*-glucose may have a 3-atomic lactone,[2] and, further-

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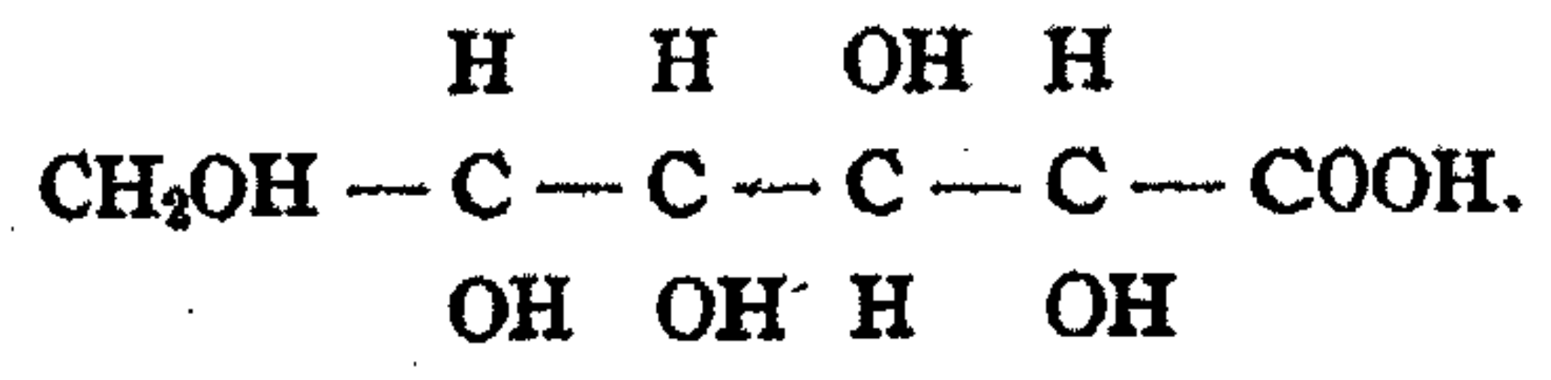
[1] Contribution from the Massachusetts Agricultural College.

[2] Hedenburg: Jour. Am. Chem. Soc., 37, 346 (1915). This requires that there be at least four forms to every sugar, two forms corresponding to the α lactone and two forms to the β lactone. Very probably these different forms will be discovered. Hudson (Jour. Am. Chem. Soc., 37, 1591 (1915)) shows that three penta-acetates of *d*-galactose are known. Fischer (Ber. deutsch. chem. Ges., 47, 1980 (1914) has discovered three monomethylglucosides of *d*-glucose. Nef (Liebig's Ann., 403, 273, 306 (1914)); Jour. Am. Chem. Soc., 37, 345 (1915)) with his assistants and students has isolated two lactones of *d*-gluconic and *d*-mannonic acids. All of this indicates that much work remains to be done in connection with the structure of the sugars and their derivatives.

more, that the same relation may also hold for the α and β forms of all pentoses and hexoses as well as the corresponding glucosides.[1]

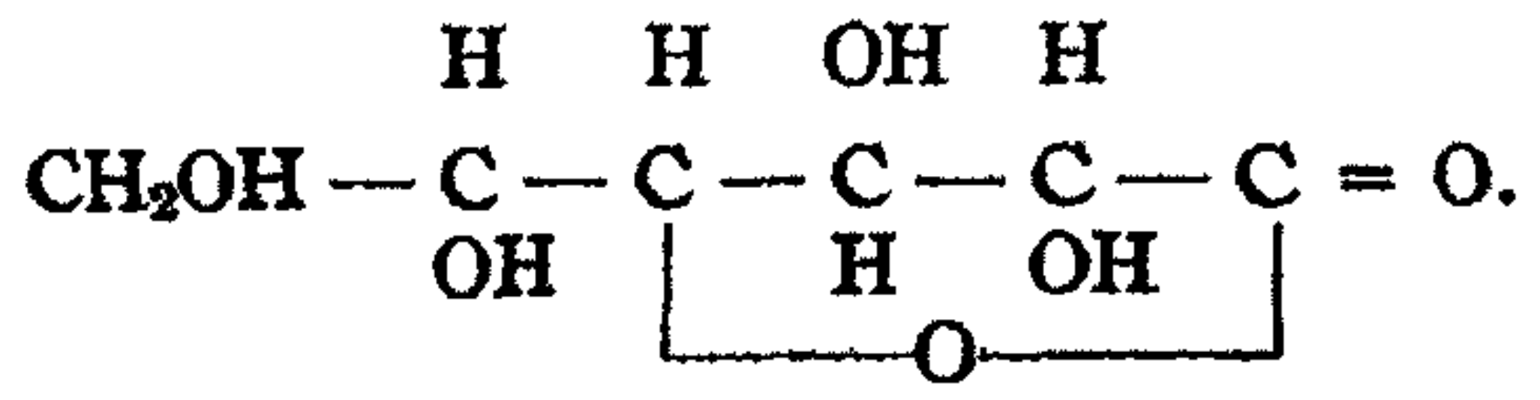
The principal evidence, aside from that given by the work of Nef and his collaborators, in favor of the views presented here lies in the relation between the configuration and rotation of sugars. This is given below together with some other facts that tend to support it.

It has long been known that the monobasic sugar acids form 5-atomic lactones. Hudson[2] has shown that for all monobasic sugars acids forming lactones the position of the hydroxyl group on the γ-carbon atom gives the direction of optical rotation of the lactone. For example *d*-gluconic acid is



$$CH_2OH-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-COOH.$$

The hydroxyl on the γ-carbon atom is below the structure hence the lactone will be



$$CH_2OH-\underset{OH}{\overset{H}{C}}-\underbrace{\overset{H}{C}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-C}_{O}=O.$$

This lactone rotates dextro and the lactone of every other acid having the hydroxyl on the γ-carbon atom below the structure will rotate dextro. If the hydroxyl on the γ-carbon atom is above the structure, the lactone will rotate levo. The same relation holds for the lactones of all monobasic and some dibasic acids in the sugar and saccharinic acid groups.[3]

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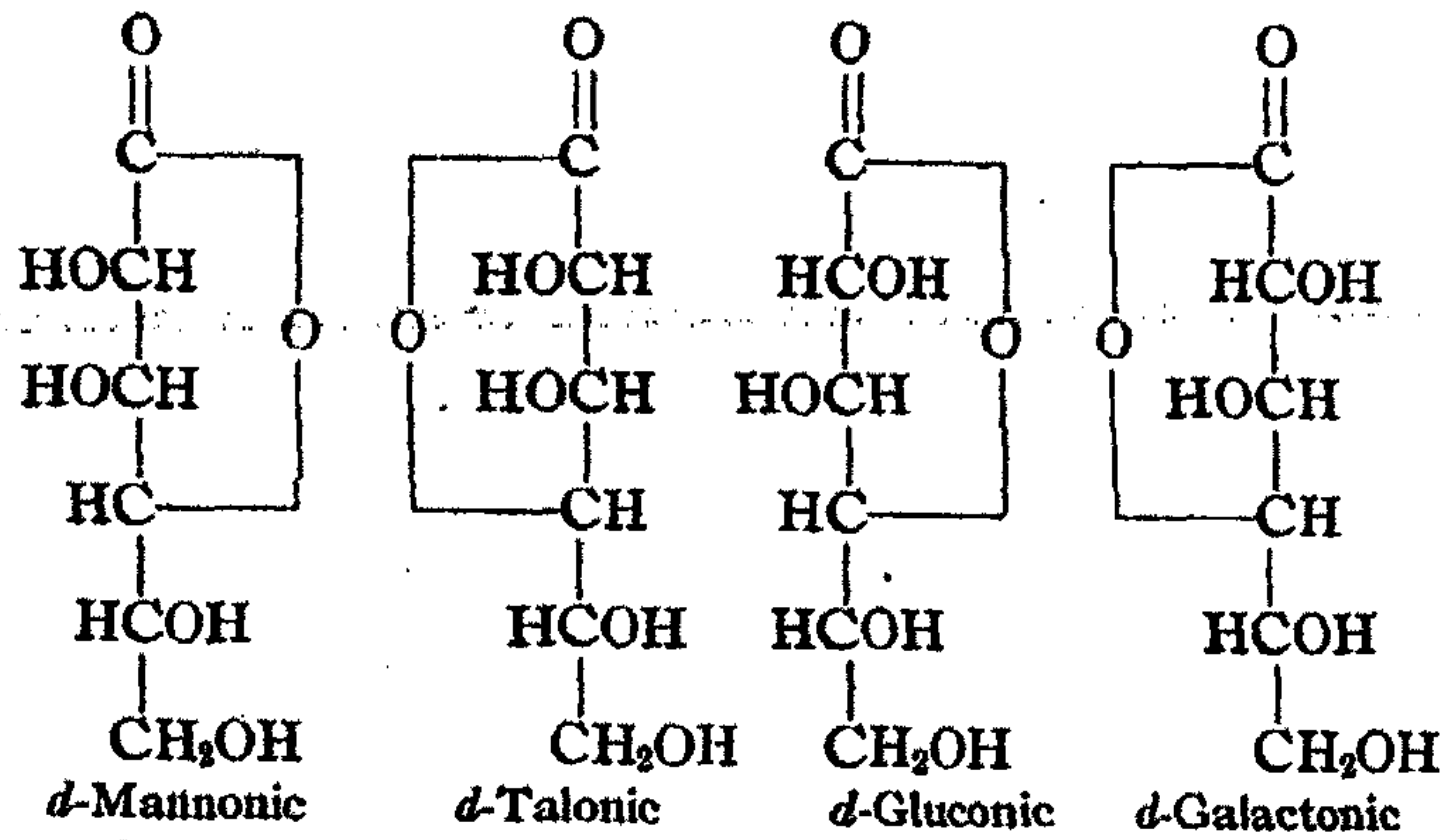
[1] The author pointed out (Jour. Am. Chem. Soc., 33, 1510 (1911)) the close connection between the optical rotation of sugars and the configuration of the α and β carbon atoms. The present explanation was suggested but not given at that time (Loc. cit., 1514). In view of the large amount of theoretical and experimental work being published (Hedenburg, Fischer, Hudson, Nef) showing the insufficiency of the generally accepted views on the pentoses and hexoses, it seems that the relations described in this article, together with the possible explanation, should be considered by chemists.

[2] Jour. Am. Chem. Soc., 32, 338 (1910).

[3] Anderson: *Ibid.*, 34, 51 (1912).

The positions of the hydroxyl groups on the α and β carbon atoms in acid lactones never affect the direction of rotation of the lactone. A comparison of *d*-mannonic with *d*-talonic lactone and of *d*-gluconic with *d*-galactonic lactone will make this clear. These four lactones have, in pairs, the same configuration about the α, β and δ carbon atoms but different configurations about the γ-carbon atom.



d-Mannonic lactone $[\alpha]_D = +56$ *d*-Talonic lactone $[\alpha]_D = -$(strongly) *d*-Gluconic lactone $[\alpha]_D = +68$ *d*-Galactonic lactone $[\alpha]_D = -78$

It is evident that the γ carbon atom determines the direction of rotation of the acid lactone; that the α and β carbon atoms do not affect the direction of rotation of the acid lactone, and that acid lactones having the ring on the same side of the structure rotate in the same direction whereas acid lactones having the ring on opposite sides of the structure rotate in opposite directions.

If sugars have 5-atomic lactones they also should show the same relation between configuration and rotation that the acid lactones show. Such is not the case. For sugars there is no connection between position of the hydroxyl on the γ carbon atom and direction of rotation. On the other hand the positions of the hydroxyl groups on the α and β carbon atoms give at once the direction of rotation of the two forms of the sugars.[1] Thus *d*-glucose and *d*-galactose have the same configurations about the α and β carbon atoms

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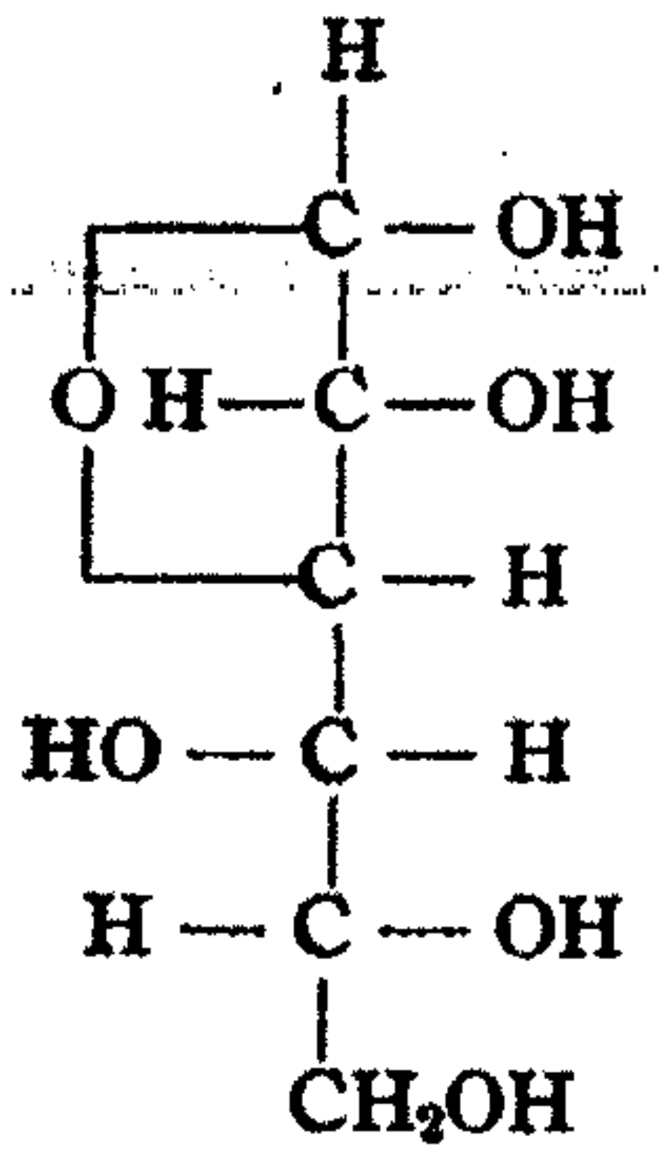
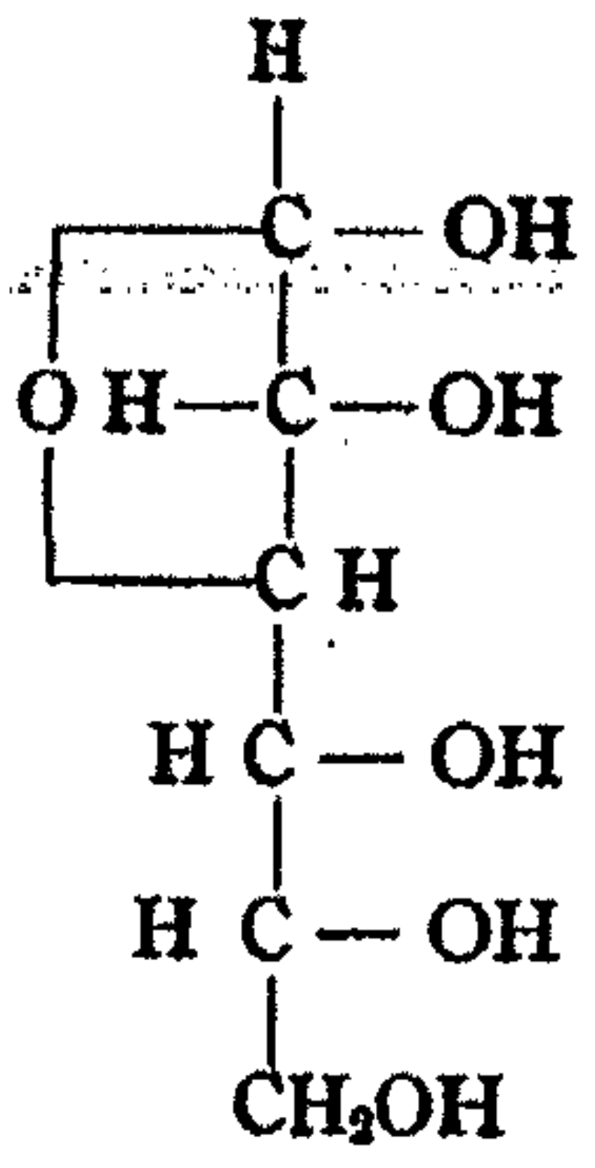
[1] Anderson: Jour. Am. Chem. Soc., 33, 1510 (1911).

but different configurations about the γ carbon atom. All forms of these sugars rotate dextro. If α *d*-glucose and α *d*-galactose are both 4-atomic lactones they have the ring on the same side of the structure and should rotate in the same direction. Also if β *d*-glucose and β *d*-galactose are both 3-atomic lactones they have the ring on the same side of the structure and should rotate in the same direction.[1]

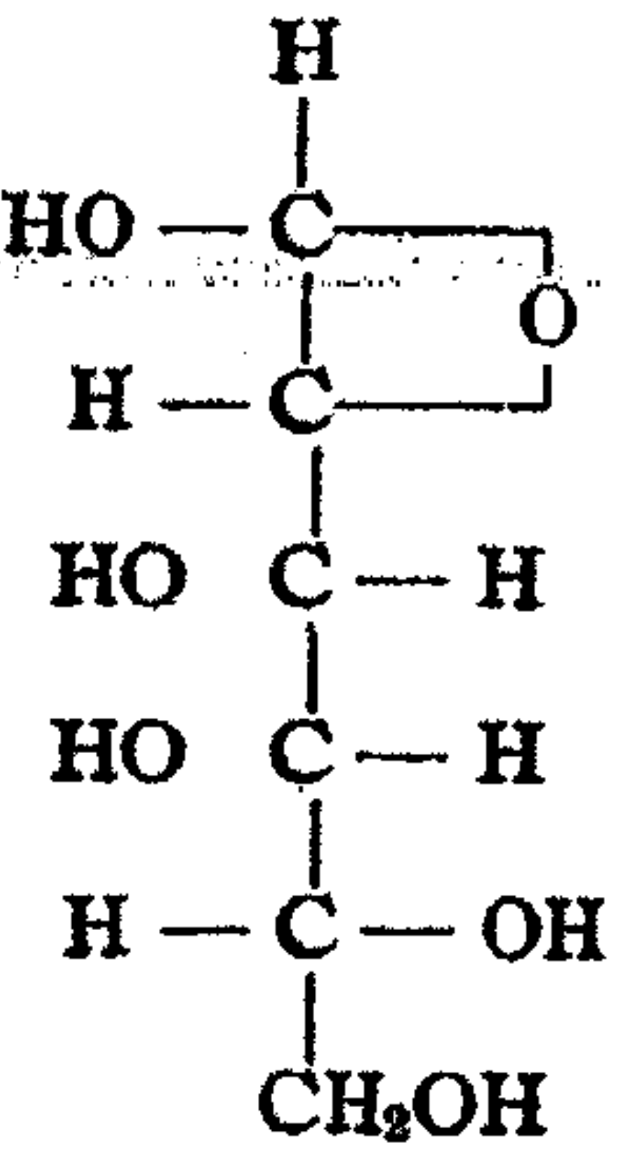
α *d*-Galactose
$[\alpha]_D = +140$



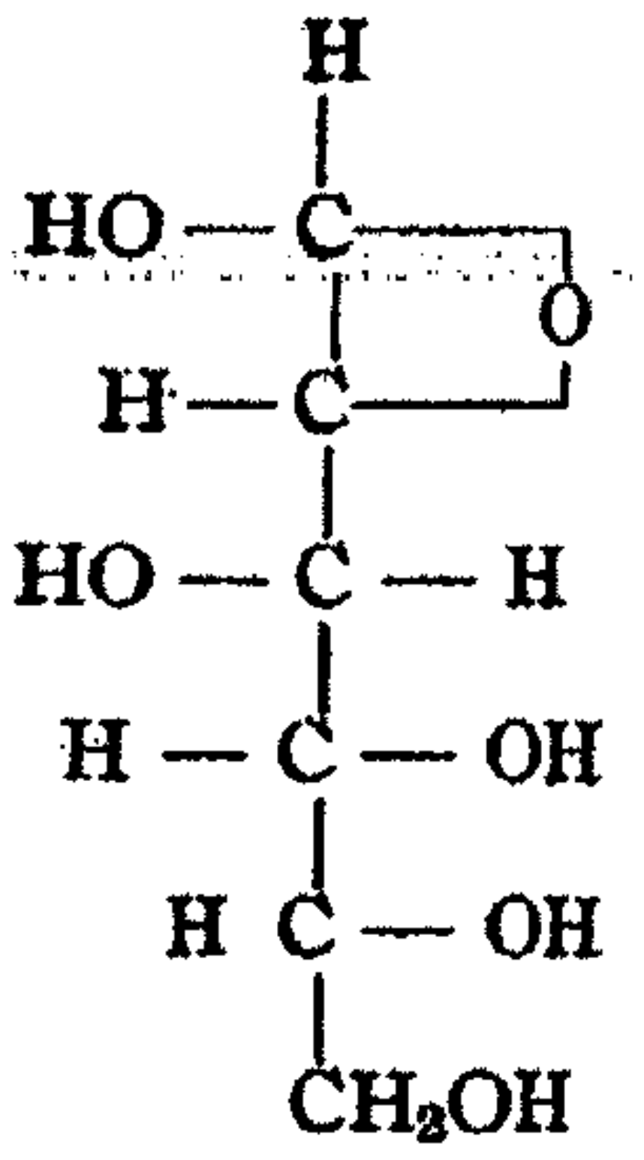
α *d*-Glucose
$[\alpha]_D = +109$



β *d*-Galactose
$[\alpha]_D = +53$



β *d*-Glucose
$[\alpha]_D = +20$



If, however, these sugars have 5-atomic, or γ lactones, *d*-galactose has the ring on one side of the structure and *d*-glucose has it on the other side. Such lactones should rotate in opposite directions. The facts here indicate that the sugar lactones are not the same as the acid lactones.

Furthermore, α *l*-rhamnose rotates levo while β *l*-rhamnose rotates dextro. If both α and β *l*-rhamnose have the γ lactone they should rotate in the same direction. If, however, α *l*-rhamnose has a 4-atomic ring and β *l*-rhamnose has a

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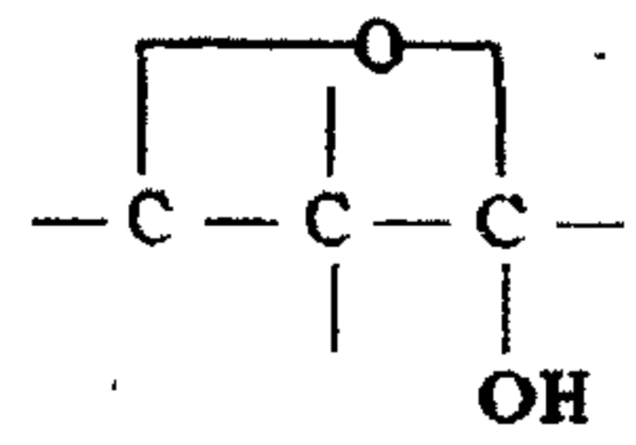
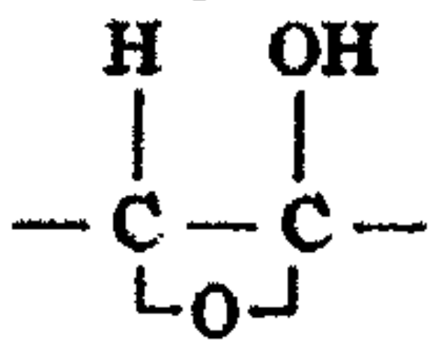
[1] The 4-atomic lactone, or β lactone,



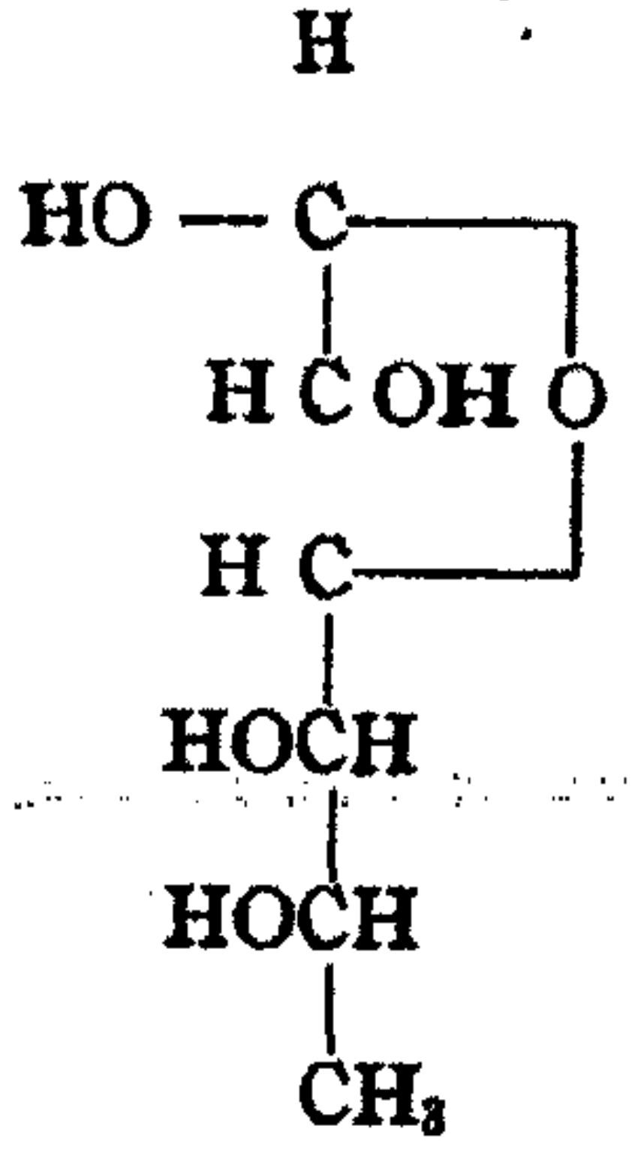
$-C-C-C-H$, rotates dextro and its image rotates levo. On the other hand, the 3 atomic lactone, or α lactone,



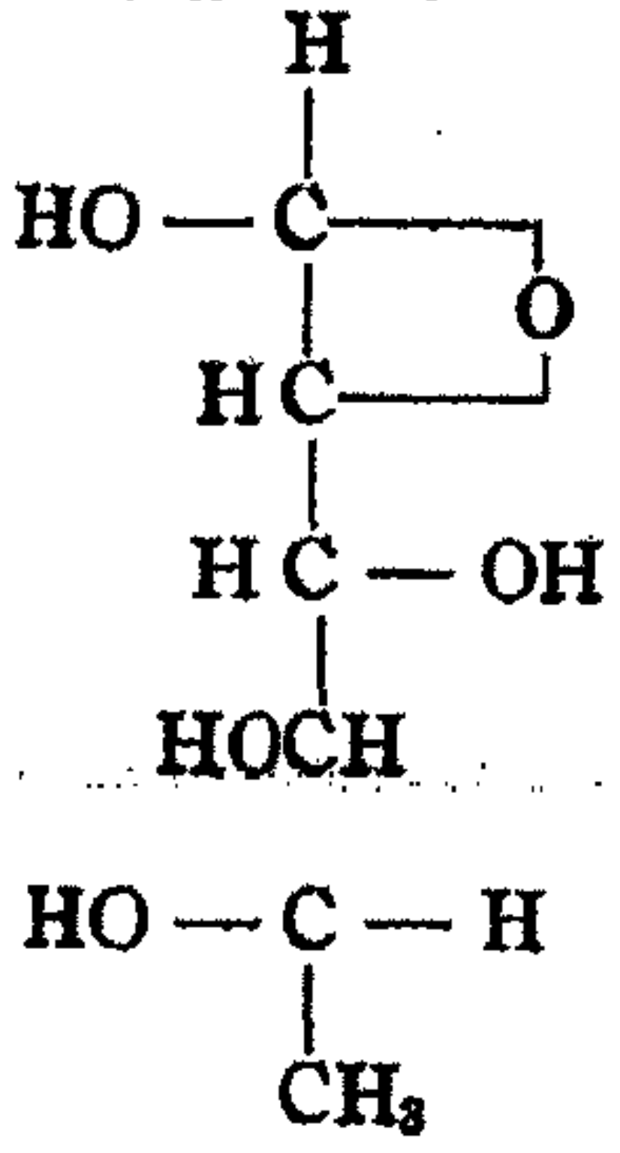
$-C-C-H$, rotates dextro and its image levo.

3-atomic ring the two forms should rotate in opposite directions. The same is true for α and β *d*-mannose.

α *l*-Rhamnose
$[\alpha]_D = -7$



β *l*-Rhamnose
$[\alpha]_D = +31$



If the sugars form γ lactones the ring in any acid lactone will be on the same side of the structure as the ring in the α and β forms of the corresponding sugars. Since *d*-gluconic acid lactone as well as α and β *d*-glucose all rotate dextro it is natural to expect, if they all have the 5-atomic ring, that *d*-galactonic acid lactone, will rotate in the same direction as α and β *d*-galactose. Such is not the case. The acid lactone here rotates levo while the α and β forms of the sugar rotate dextro.

Aside from the relations between rotation and configuration there are other facts indicating that sugars do not have the same rings as the acid lactones.

According to Baeyer's Tension Theory, 3-atomic and 4-atomic rings should be unstable and should open readily, whereas 5-atomic rings should be stable. It is well known that sugar rings are not stable but open with remarkable ease. The 5-atomic lactones of the sugar acids, on the other hand, are much more stable. The new 4-atomic lactones of *d*-mannonic and *d*-gluconic acids, described by Hedenburg and by Nef,[1] are perfectly similar to the sugar lactones in the ease with which they open.

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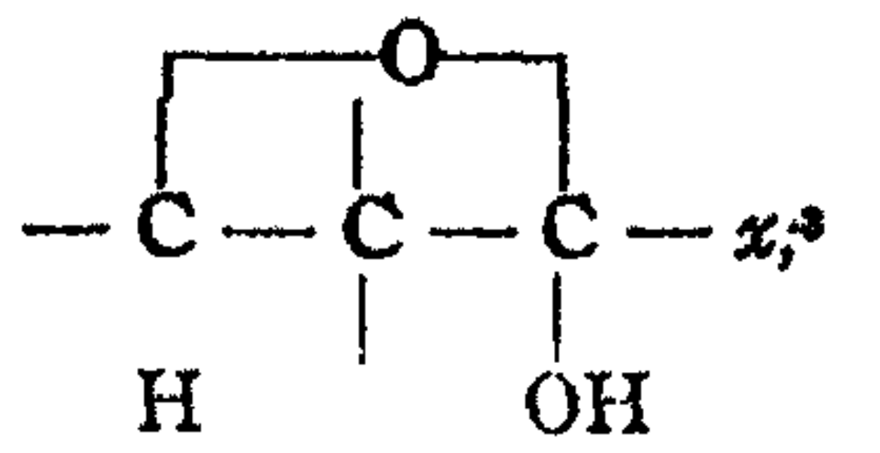
[1] Loc. cit.

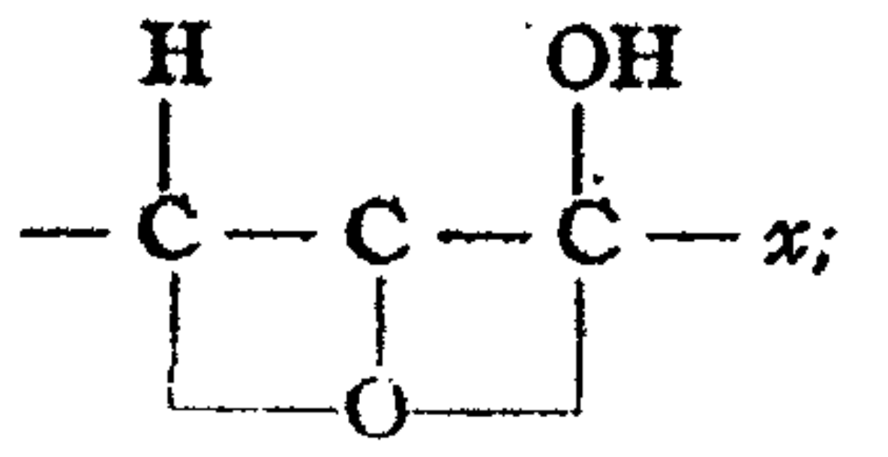
There is a difference in the stability of the α and β forms of the sugars. If the two forms have different rings this would be expected, but if they differ merely in the position of H and OH on the end asymmetric carbon atom they should have the same stability. The same is true for the α and β glucosides.

The difference between the specific rotations of the α and β forms of a sugar is too great to be caused merely by a difference of H and OH on the end carbon atom. This difference between the specific rotations of the α and β forms of a sugar where these are accurately known is usually above 65° and generally 80° to 100°. The difference in the specific rotations of any two acid lactones which differ merely in the positions of H and OH on one carbon atom is never above 56° and usually is about 15° to 20°. Further, acid lactones that differ spatially only in the position of H and OH on one carbon atom never differ in the direction of rotation; α and β *l*-rhamnose differ in the direction of rotation.

The theoretical explanation of the relation between lactone configuration and optical rotation in the sugars is essentially that given by Hudson[1] for the acid lactones. The rotations of the alcohols, free acids and free aldehydes or ketones are so small in comparison with those of the sugars that the rotations of the latter may be assumed as a first approximation to be due entirely to the lactone.[2] There are two possible stereo structures for the 4-atomic or β lactone in sugars, 1 and 2 below, and two for the 3-atomic or α lactone, 3 and 4. The α and β forms of every sugar



(1) Dextro



(2) Levo

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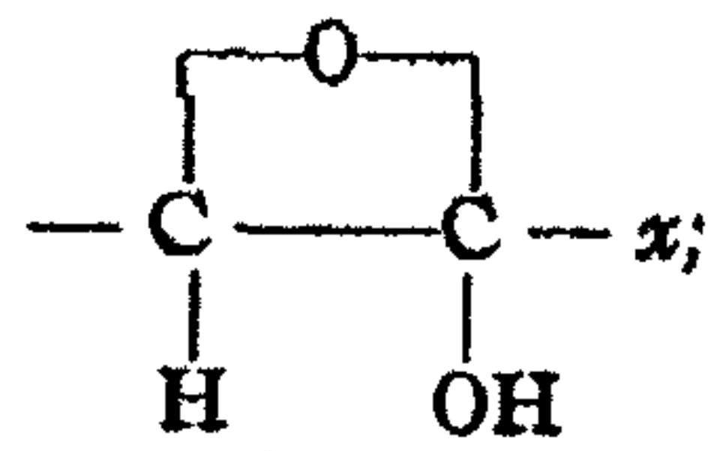
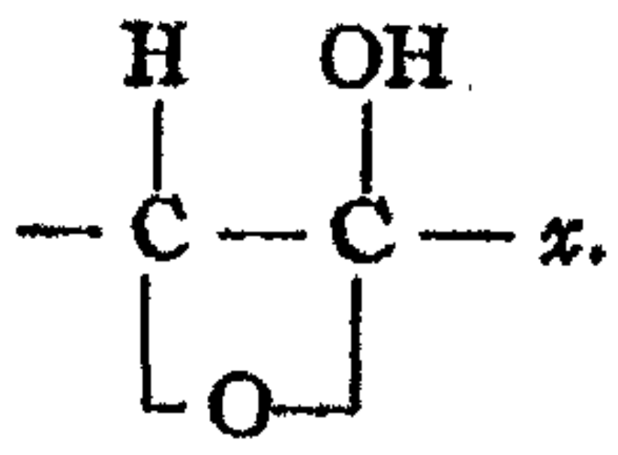
[1] Jour. Am. Chem. Soc., 32, 338 (1910).

[2] This is not entirely correct. In some cases the rotations of the alcohols and free acids are strong and may counterbalance the rotation due to lactone formation (Anderson: Jour. Am. Chem. Soc., 34, 52, note 6).

[3] x may be H or CH_2OH.

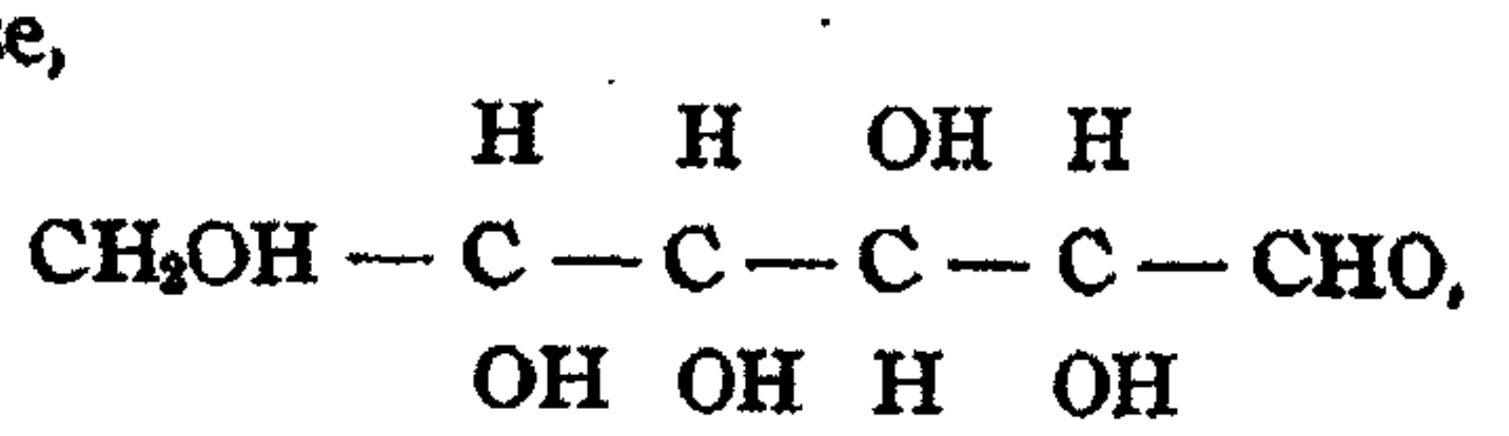


(3) Levo



(4) Dextro

differ in that the α form has ring 1 or 2 while the β form has ring 3 or 4.[1] If the rotation is due entirely to the lactone, rings 1 and 2 make oppositely rotating sugars as do also rings 3 and 4. It is evident that the positions of the hydroxyl groups on the α and β carbon atoms will determine which two of the four possible rings are present. If the hydroxyl on the α carbon atom is above the structure, the β form of the sugar has ring 3 and will rotate levo; if the hydroxyl on the β carbon atom is above the structure, the α form of the sugar has ring 1 and will rotate dextro. It is evident that *d*-glucose,



$$\mathrm{CH_2OH}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CHO},$$

can have only rings 1 and 4. Since both α and β *d*-glucose rotate dextro it is evident that rings 1 and 4 make dextro rotating sugars while rings 2 and 3 make levo rotating sugars.

When either the α or β form of a sugar is dissolved in water it changes rapidly into an equilibrium mixture of these two forms called the γ form.[2]

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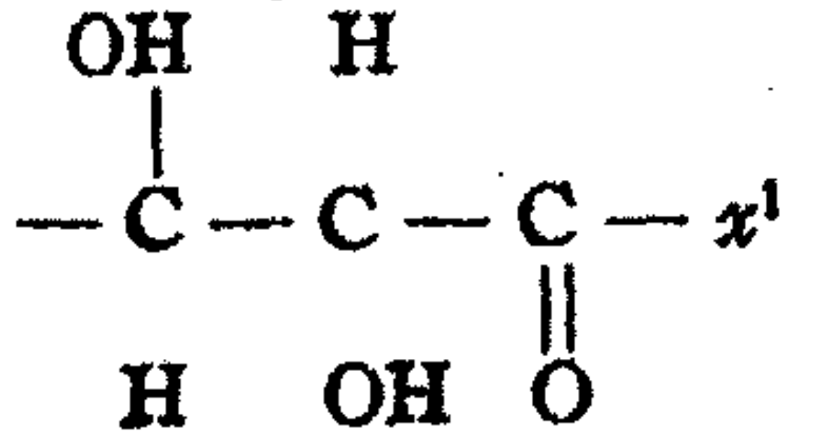
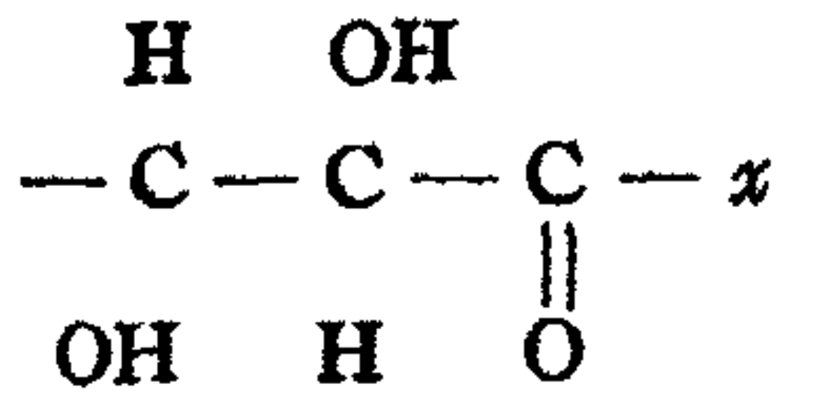
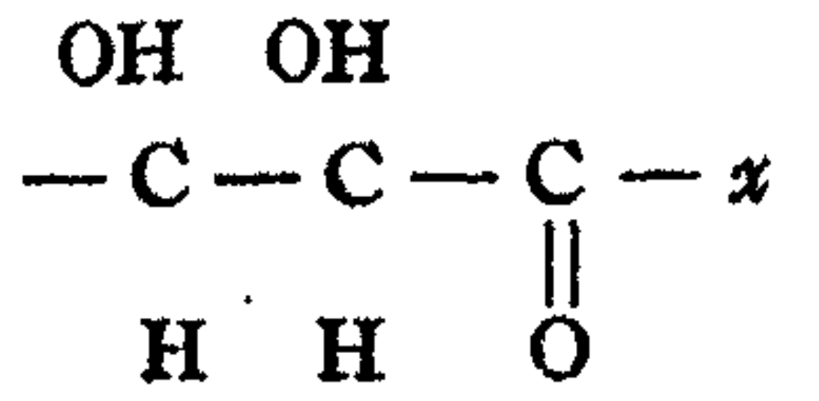
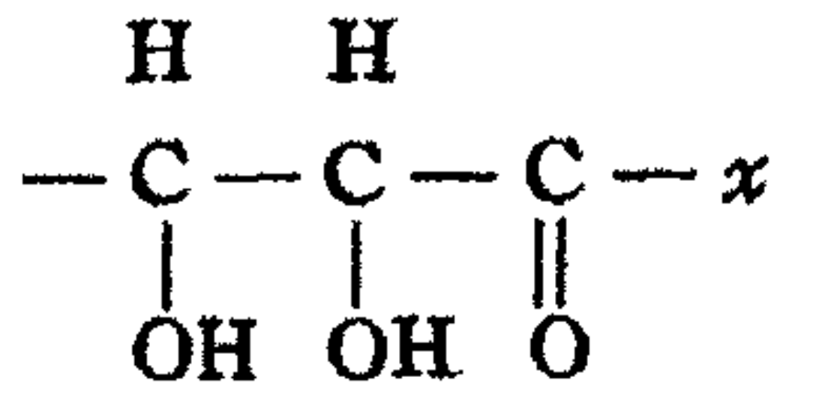
[1] Where the α and β forms of a sugar rotate in the same direction, the α form is defined as the one rotating the stronger. The attempt is made later in this article to show that the α form in such cases has a 4-atomic ring and the β form has a 3-atomic ring. If future investigations prove the correctness of this point which now rests upon very few data, it would seem more correct to reverse the present method of naming the α and β forms of sugars. Hedenburg: Jour. Am. Chem. Soc., 37, 346 (1915).

[2] Armstrong, in "The Simple Carbohydrates and Glucosides," discusses the mechanism of this change. This interchange probably comes about by the lactone opening with water to give the hydrated, lower rotating form which afterwards by loss of water gives the other lactone. When equilibrium is finally reached in the solution, some of the hydrated form with no lactone in it, will be present. This form will rotate but little in comparison with the lactone, which fact explains why the rotation finally reached in solution is usually be-

For most sugars the specific rotation is known only for this equilibrium mixture of α and β forms. However, it is easy to decide from the rotation of this equilibrium mixture in which direction the α and β forms of the sugar will rotate. If the equilibrium mixture rotates strongly dextro or levo, the α form rotates in the same direction as the β form. If, on the other hand, the equilibrium mixture rotates but slightly dextro or levo, then the α form rotates in the opposite direction from the β form.

In brief, where a sugar has any one of the four following configurations about the α and β carbon atoms, the α, β and γ forms of the sugar rotate as indicated.

	Configuration	α rotates	β rotates	γ rotates
(1)	 $-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\underset{\overset{\|}{O}}{C}-x^1$	dextro, strongly	dextro, strongly	dextro, strongly[2]
(2)	 $-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\underset{\overset{\|}{O}}{C}-x$	levo, strongly	levo, strongly	levo, strongly
(3)	 $-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\underset{\overset{\|}{O}}{C}-x$	dextro, strongly	levo, strongly	dextro or levo, slightly
(4)	 $-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\underset{\overset{\|}{O}}{C}-x$	levo, strongly	dextro, strongly	dextro or levo, slightly

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low the mean of the α and β forms, though of course these two forms may not be present in equal amounts. The more concentrated the water solution the higher the rotation at equilibrium. This should be so if there is an equilibrium between lactone and water on one side and hydrated, no lactone sugar, on the other side. The higher the temperature, the lower should be and is, the rotation at equilibrium, since the lactone opens more readily in hot than in cold water.

[1] x may be H or —CH_2OH.

[2] The dividing line between strongly and slightly rotating is about 20 degrees, *i. e.*, those rotating strongly will usually rotate more than 20 degrees

The α and β forms, *i. e.*, the lactone forms, usually rotate strongly;[1] the γ form or equilibrium mixture will rotate strongly or slightly depending upon whether the two lactone forms of which it is composed rotate in the same direction or in opposite directions. It happens that when the hydroxyl groups on the α and β carbon atoms are on opposite sides of the structure, the α and β forms of the sugar rotate in the same direction and the γ form will hence rotate strongly; when these two hydroxyl groups are on the same side of the structure, the α and β forms rotate in opposite directions and the γ form will rotate but slightly.

In order to test out the ideas presented in this paper the configurations and rotations of sixteen sugars are given below. These are all the sugars for which configuration and rotation are accurately known.[2]

All of the following sugars agree with the rules laid down in this paper.

Anderson[3] has already shown that this relation between rotation and configuration of the α and β carbon atoms makes possible the determination of the unknown configurations of some sugars whose rotations are known and furthermore makes possible the prediction of the relative rotations of some sugars whose configurations are known but rotations unknown. This holds true not merely for the γ form as given by Anderson[3] but for the α and β forms as well. This last point is important because in the greater number of cases the rotation of the α and β forms are unknown. However by a glance at the configuration of the α and β carbon atoms in any sugar it is easy to decide in which direction the α and β

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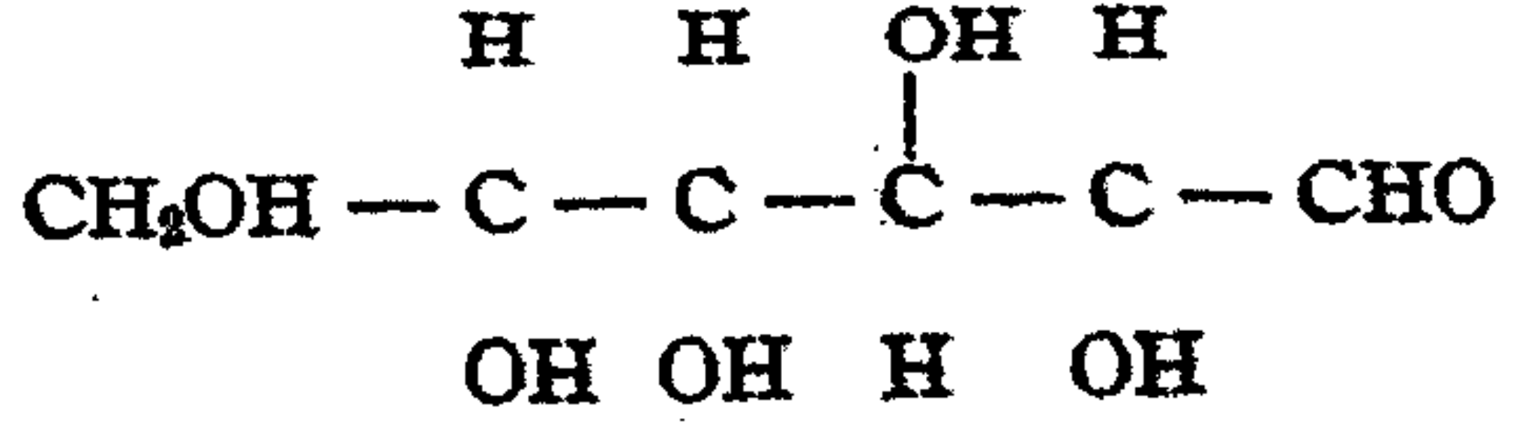
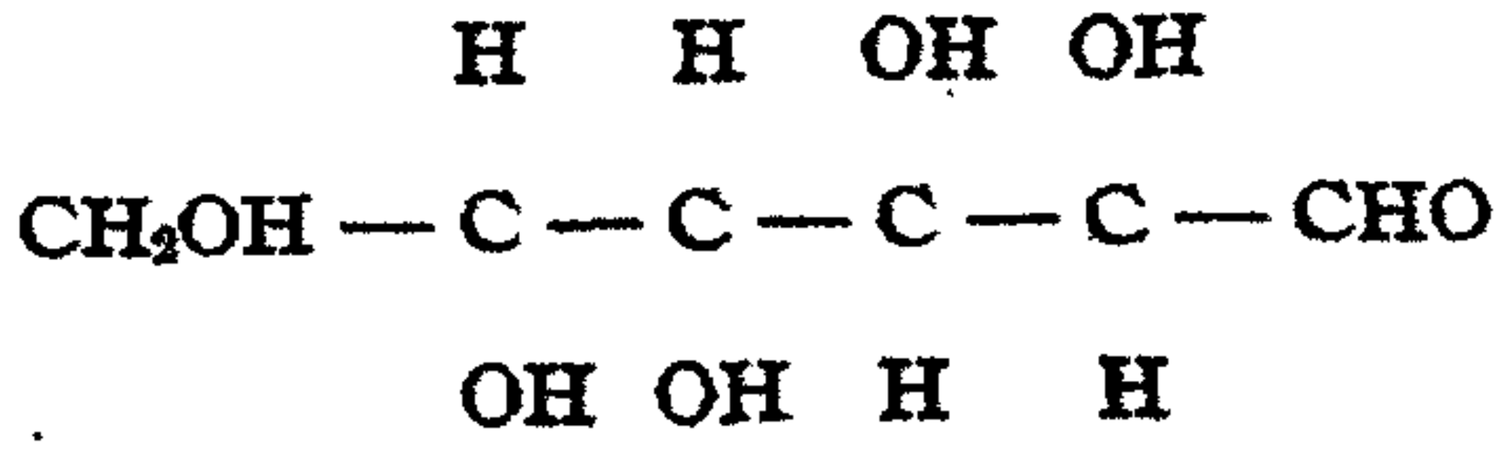
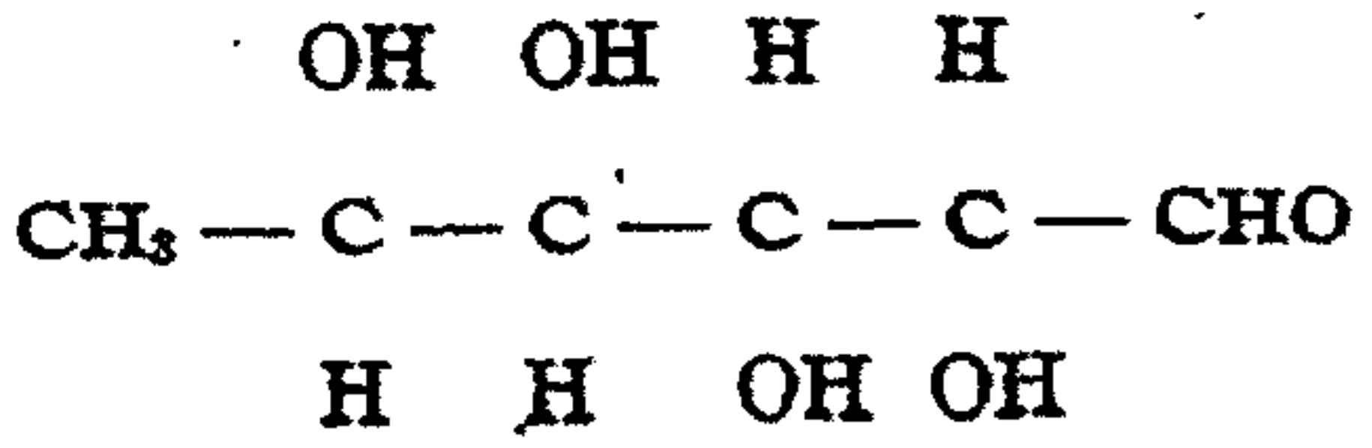
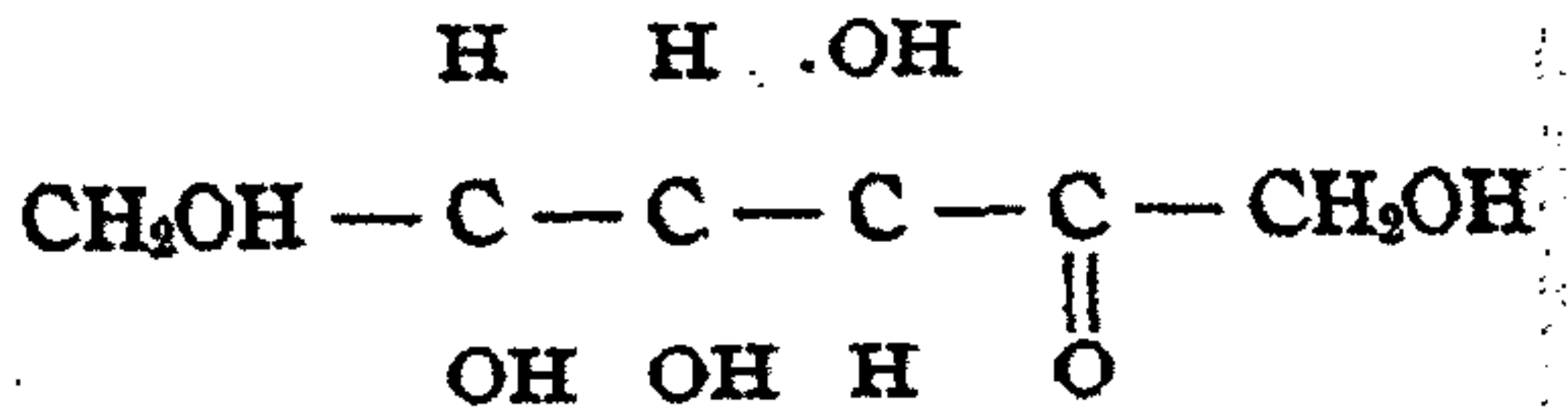
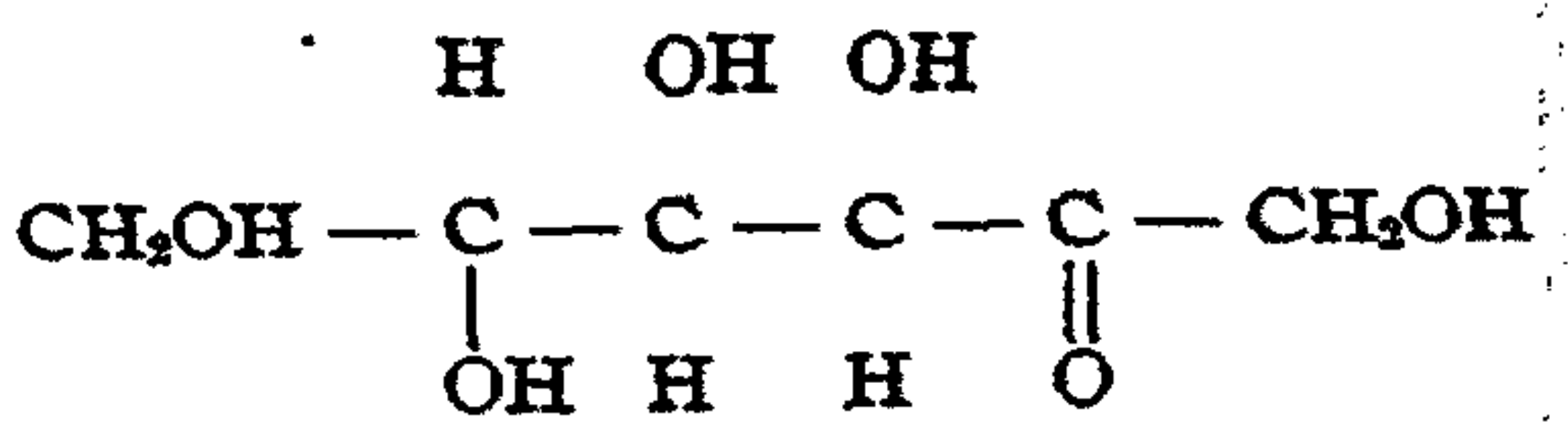
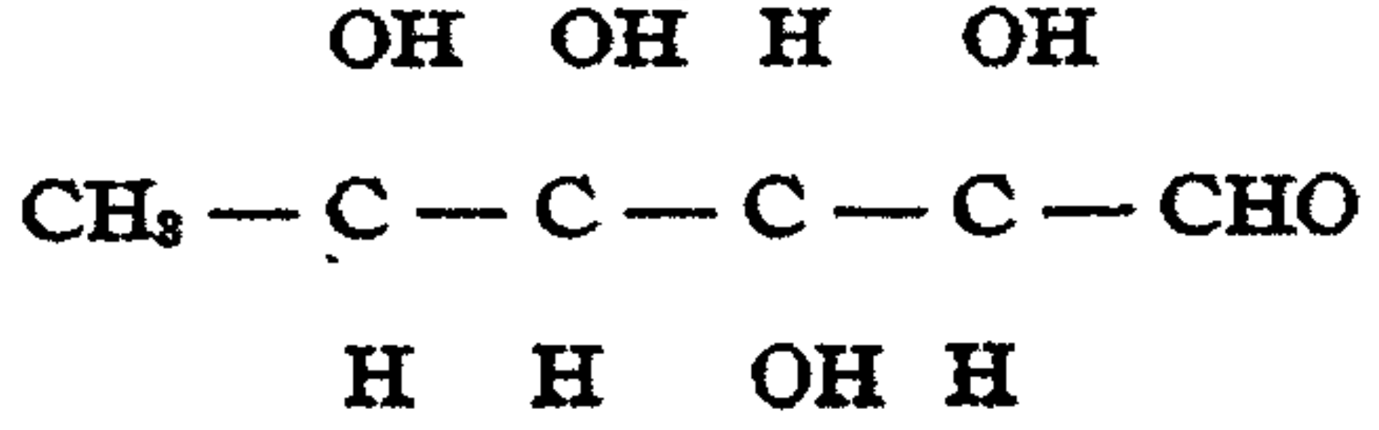
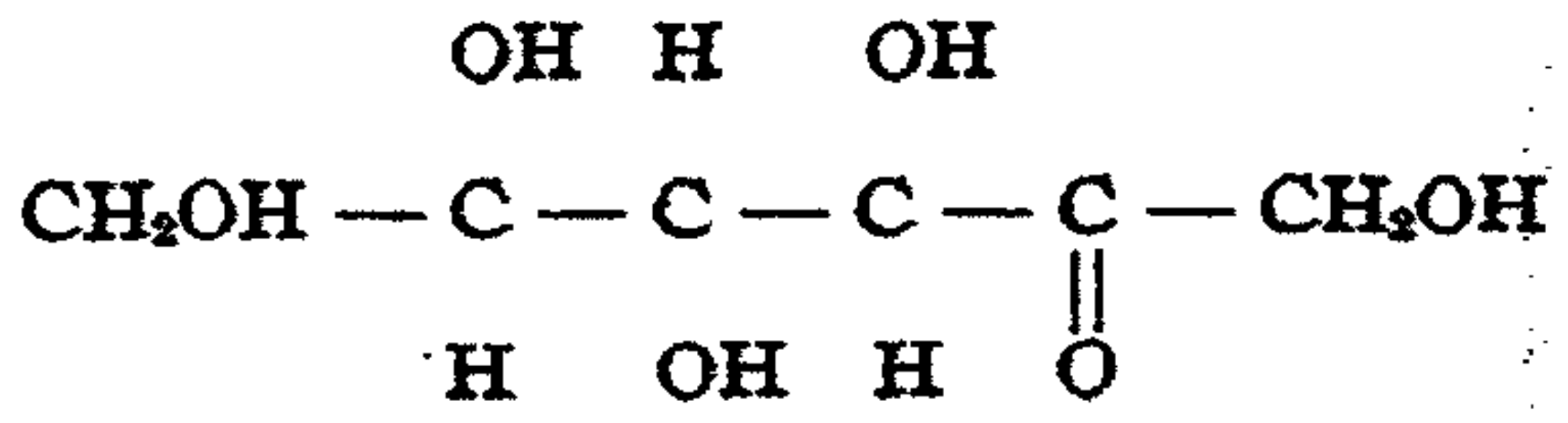
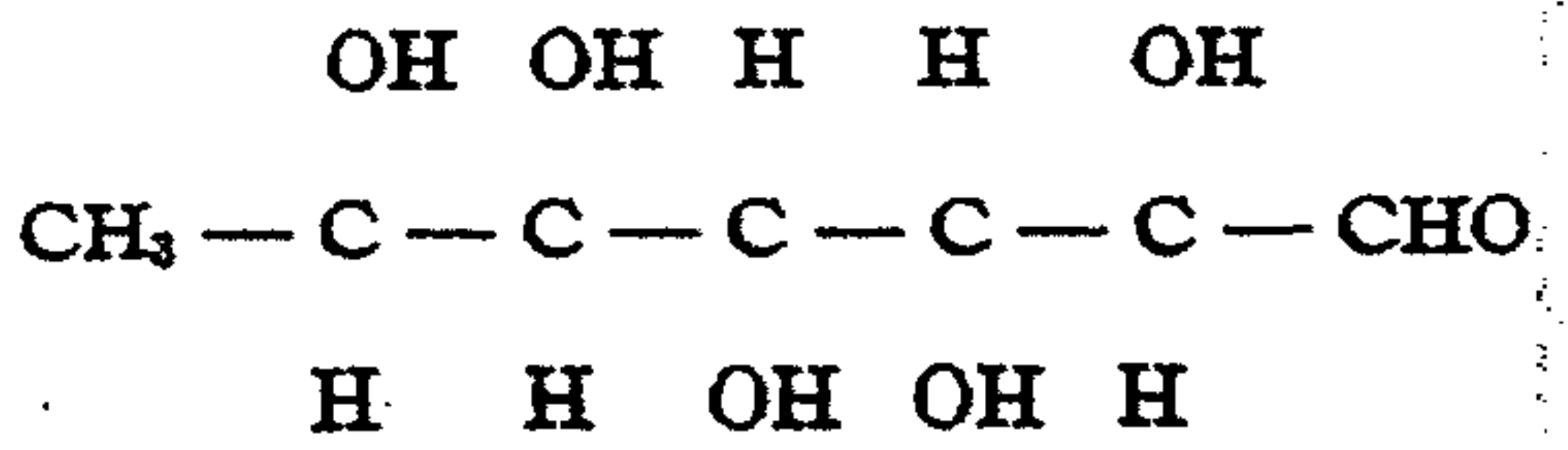
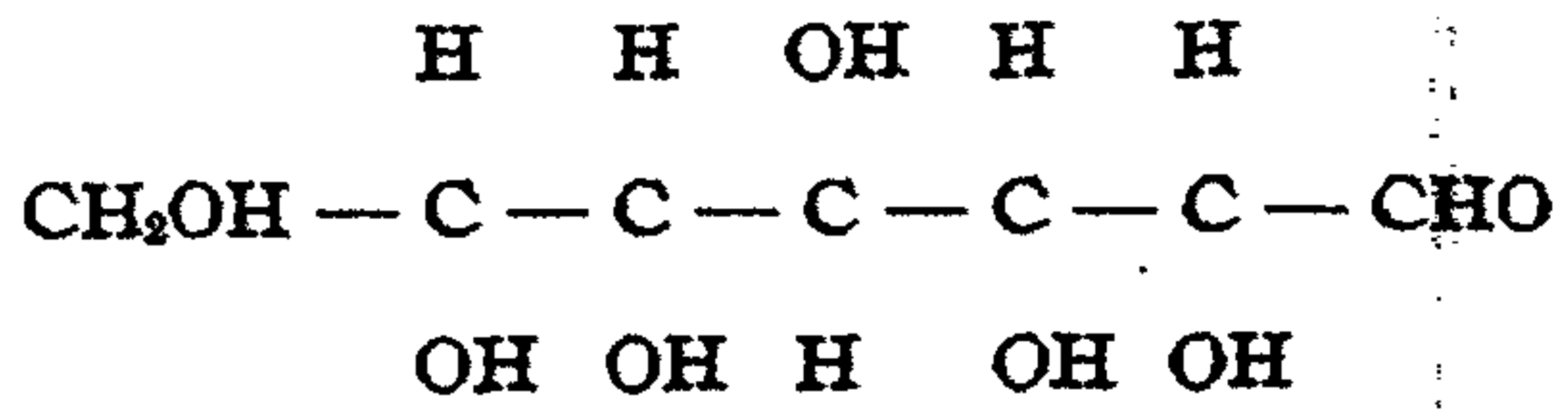
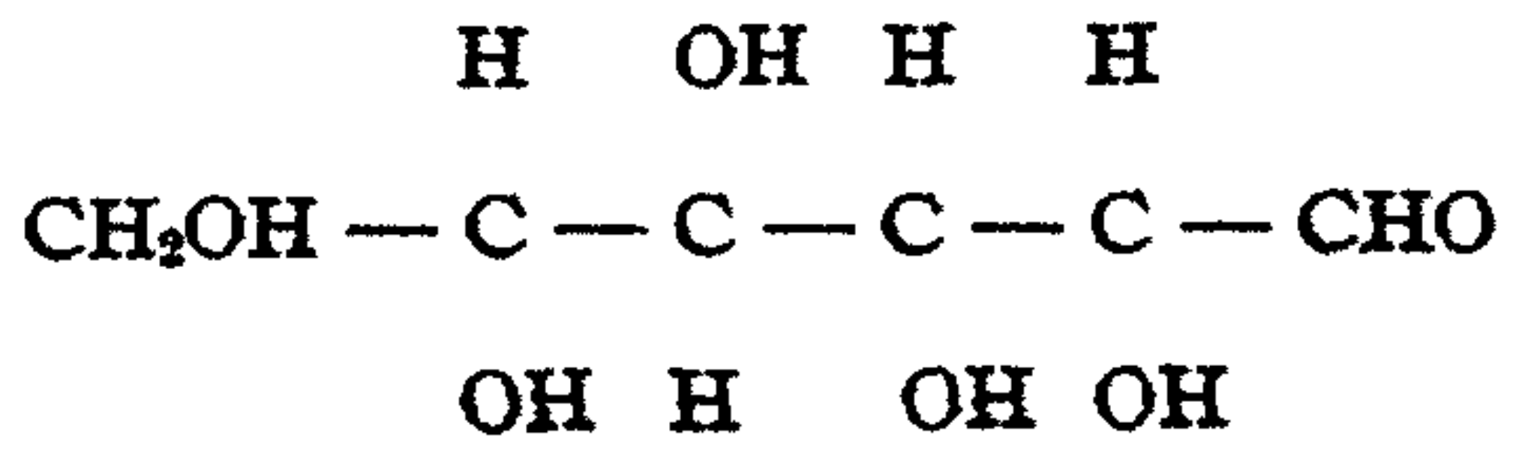
while those rotating slightly will usually rotate less than 20 degrees. This does not hold for one form of the following sugars: *l*-Rhamnose, *d*-mannose and *d*-lyxose. There are two possible explanations for this discrepancy. One is that these sugars have not been obtained pure and the other is that given in Note 2, page 274.

[1] See preceding footnote for exceptions.

[2] This table is given in part, together with references by Anderson: Jour. Am. Chem. Soc., 33, 1511 (1911).

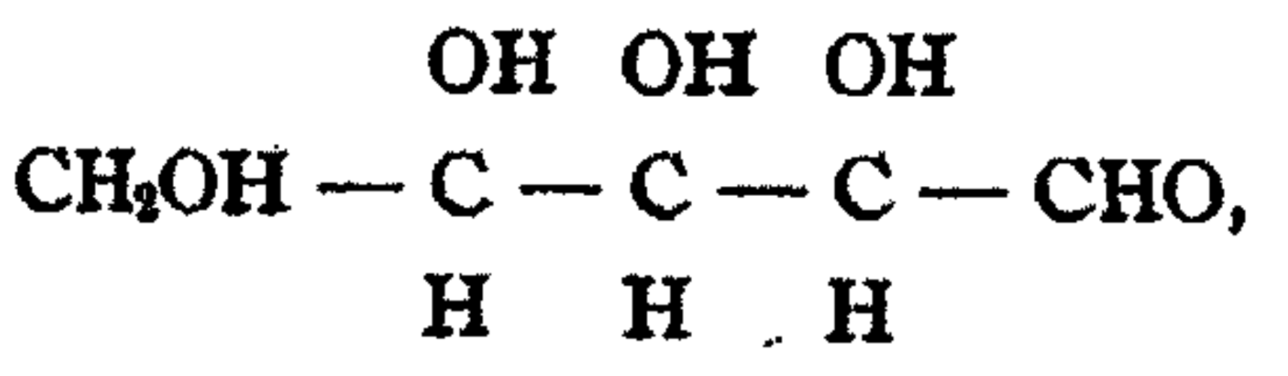
[3] Loc. cit.

Sugar	Configuration	Specific rotation
d-Glucose	 $\begin{array}{c}\text{H}\quad\text{H}\quad\text{OH}\quad\text{H}\\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{CHO}\\ \text{OH}\quad\text{OH}\quad\text{H}\quad\text{OH}\end{array}$	α = +109° Equi. mix. = + 52.5° β = + 20°
d-Mannose	 $\begin{array}{c}\text{H}\quad\text{H}\quad\text{OH}\quad\text{OH}\\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{CHO}\\ \text{OH}\quad\text{OH}\quad\text{H}\quad\text{H}\end{array}$	α = + Equi. mix. = + 14° β = — 14°
l-Rhamnose	 $\begin{array}{c}\text{OH}\quad\text{OH}\quad\text{H}\quad\text{H}\\ \text{CH}_3-\text{C}-\text{C}-\text{C}-\text{C}-\text{CHO}\\ \text{H}\quad\text{H}\quad\text{OH}\quad\text{OH}\end{array}$	α = — 7° Equi. mix. = +9° β = +31°
d-Fructose	 $\begin{array}{c}\text{H}\quad\text{H}\quad\text{OH}\\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{CH}_2\text{OH}\\ \text{OH}\quad\text{OH}\quad\text{H}\quad\overset{\Vert}{\text{O}}\end{array}$	α = —106° Equi. mix. = —92° β =
d-Tagatose	 $\begin{array}{c}\text{H}\quad\text{OH}\quad\text{OH}\\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{CH}_2\text{OH}\\ \text{OH}\quad\text{H}\quad\text{H}\quad\overset{\Vert}{\text{O}}\end{array}$	Equi. mix. = +1°

Sugar	Configuration	Specific rotation
Isorhamnose	 $\mathrm{CH_3}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CHO}$	Equi. mix. = —30°
d-Sorbose	 $\mathrm{CH_2OH}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}-\mathrm{CH_2OH}$	Equi. mix. = —43°
α Rhamnohexose	 $\mathrm{CH_3}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CHO}$	Equi. mix. = —61.4°
α Glucoheptose	 $\mathrm{CH_2OH}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CHO}$	Equi. mix. = —19.7°
l-Gulose	 $\mathrm{CH_2OH}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CHO}$	Equi. mix. = + slightly

Sugar	Configuration	Specific rotation
Rhodeose	$\mathrm{CH_3 - CHOH - \overset{OH}{\underset{H}{C}} - \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{OH}{C}} - CHO}$	Equi. mix. = +86°
Fucose	$\mathrm{CH_3CHOH - \overset{H}{\underset{OH}{C}} - \overset{H}{\underset{OH}{C}} - \overset{OH}{\underset{H}{C}} - CHO}$	α = —112° Equi. mix. = —77°
l-Arabinose	$\mathrm{CH_2OH - \overset{OH}{\underset{H}{C}} - \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{OH}{C}} - CHO}$	α = +184° Equi. mix. = +105° β = +76°
l-Xylose	$\mathrm{CH_2OH - \overset{H}{\underset{OH}{C}} - \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{OH}{C}} - CHO}$	α = 85.7° Equi. mix. = 18.5° β =
d-Lyxose	$\mathrm{CH_2OH - \overset{H}{\underset{OH}{C}} - \overset{OH}{\underset{H}{C}} - \overset{OH}{\underset{H}{C}} - CHO}$	α = Equi. mix. = —14° β = —3°
d-Galactose	$\mathrm{CH_2OH - \overset{H}{\underset{OH}{C}} - \overset{OH}{\underset{H}{C}} - \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{OH}{C}} - CHO}$	α = +140° Equi. mix. = +83° β = +53°

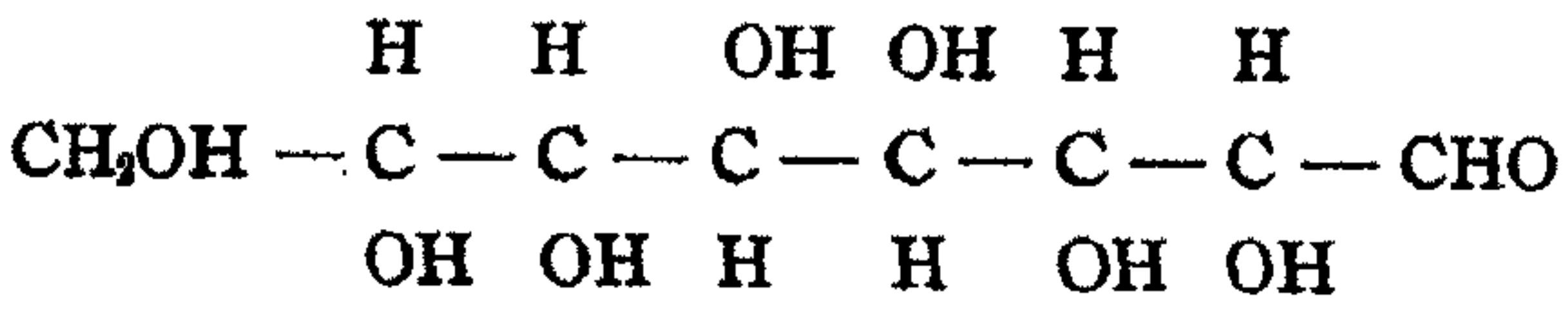
forms of the sugar will rotate and relatively how much they will rotate. For instance, in the case of *l*-ribose,



$$CH_2OH - \underset{H}{\overset{OH}{C}} - \underset{H}{\overset{OH}{C}} - \underset{H}{\overset{OH}{C}} - CHO,$$

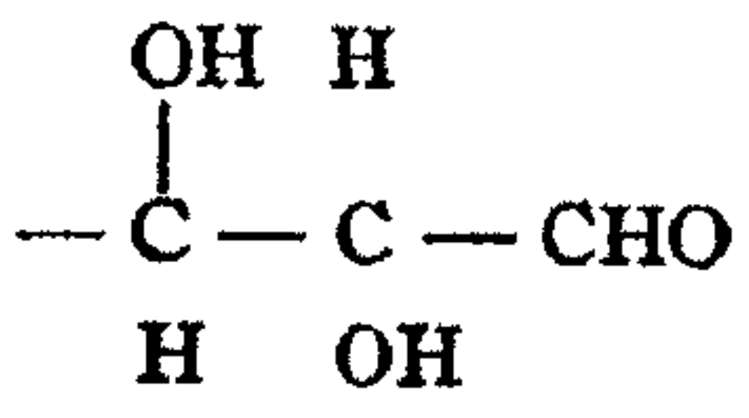
the α form must rotate dextro strongly, the β form levo strongly and the γ form, or equilibrium mixture, either dextro or levo, but in either case it will rotate only slightly.[1]

The ideas presented here enable one to decide upon the probable configuration of the α and β carbon atoms of any of those sugars described by Browne[2] where the rotations are known. They also afford a check upon the correctness of many experimental observations. For example, the rotation —3.3° given by Fischer and Passmore[3] for *d*-manno-octose cannot be correct for the pure sugar because this would lead to the formula[4]



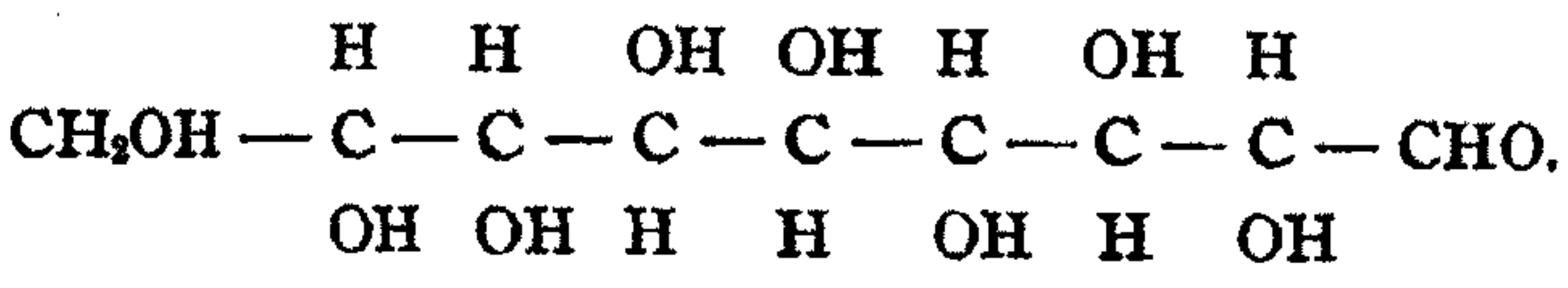
$$CH_2OH - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{OH}{C}} - \underset{H}{\overset{OH}{C}} - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - CHO$$

for this sugar. This formula is incorrect because *d*-manno-nonose[5] $[\alpha]_D$ $+50°$, must have the configuration



$$- \underset{H}{\overset{OH}{C}} - \underset{OH}{\overset{H}{C}} - CHO$$

about the α and β carbon atoms and must therefore be



$$CH_2OH - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{OH}{C}} - \underset{H}{\overset{OH}{C}} - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{OH}{C}} - \underset{OH}{\overset{H}{C}} - CHO.$$

The formula for *d*-manno-octose must be

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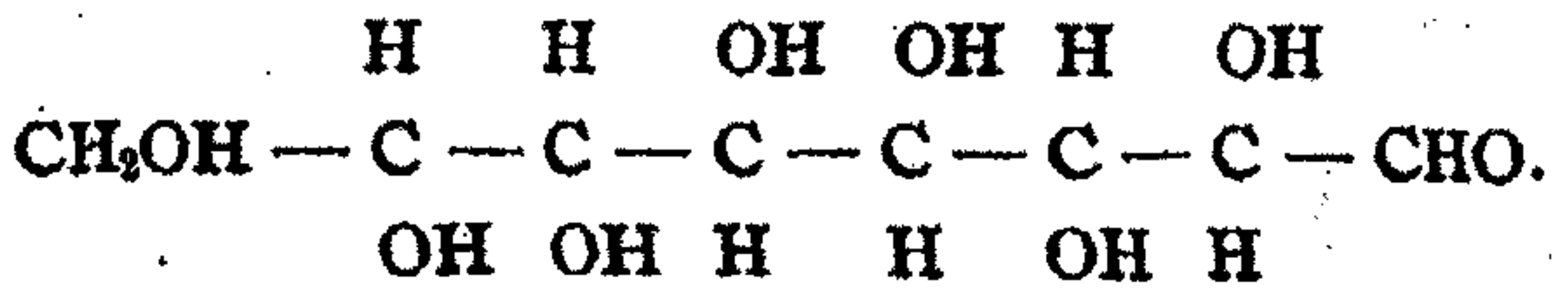
[1] Strongly and slightly here mean respectively above and below 20 degrees.

[2] "Handbook of Sugar Analysis" (1912 Ed., Chap. XIX).

[3] Ber. deutsch. chem. Ges., **23**, 2226 (1890).

[4] Anderson: Jour. Am. Chem. Soc., **33**, 1513 (1911).

[5] Fischer and Passmore: Loc. cit.; Browne: "Sugar Analysis," p. 641.



$$\mathrm{CH_2OH}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CHO}.$$

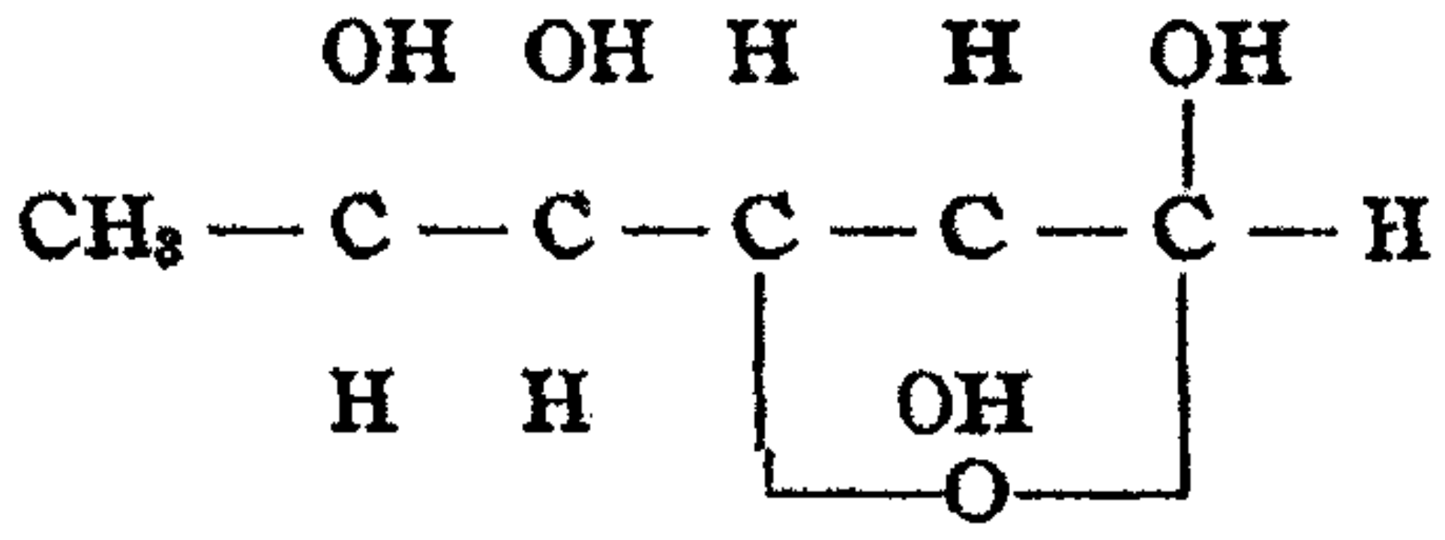
Such a sugar when pure must rotate strongly levo. As a matter of fact, Fischer and Passmore never obtained the pure crystalline form of manno-octose but made their observations on a non-crystalline syrup.

When the hydroxyl groups on the α and β carbon atoms are on the same side of the structure, one form of the sugar will rotate dextro and the other levo. Hence a chemist, having the α and β forms of such a sugar, can easily decide by reference to the lactones on page 275, which form has the 4-atomic ring and which has the 3-atomic ring. On the other hand, when the hydroxyl groups on the α and β carbon atoms are on opposite sides of the structure, the two forms of the sugar rotate in the same direction and a chemist having the α and β forms of such a sugar cannot decide by reference to the lactones on page 275, which form has the 4-atomic ring and which has the 3-atomic ring. It is possible to prove for *d*-glucose and *d*-galactose by a comparison of the rotations of the methyl glucosides with the rotations of the sugars that the α form, *i. e.*, the higher rotating form, of the sugar, has the 4-atomic lactone and the β form or lower rotating form has the 3-atomic lactone.

The following table gives the specific rotations of the α and β forms of three sugars and their corresponding methyl glucosides.

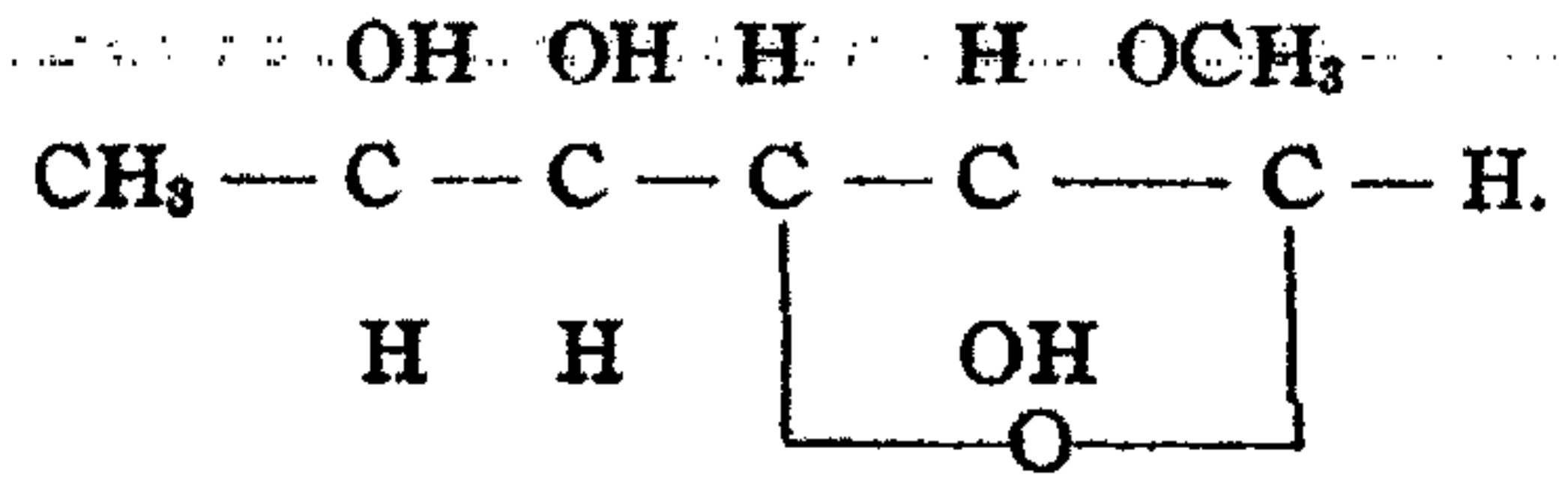
Sugar	Rotation	Methyl glucoside	Rotation
d-Glucose	α +109°	α	+157°
	β +20°	β	−32°
d-Galactose	α +140°	α	+199°
	β +53°	β	0°
l-Rhamnose	α −7°	α	−62°
	β +31°		

From the above table it appears that the $—O—CH_3$ group in place of the OH group on the end carbon atom in one case increases the dextro rotation of the sugar 55° and in the other cases decreases the dextro rotation 55°. The form of *l*-rhamnose rotating —7° must have the configuration



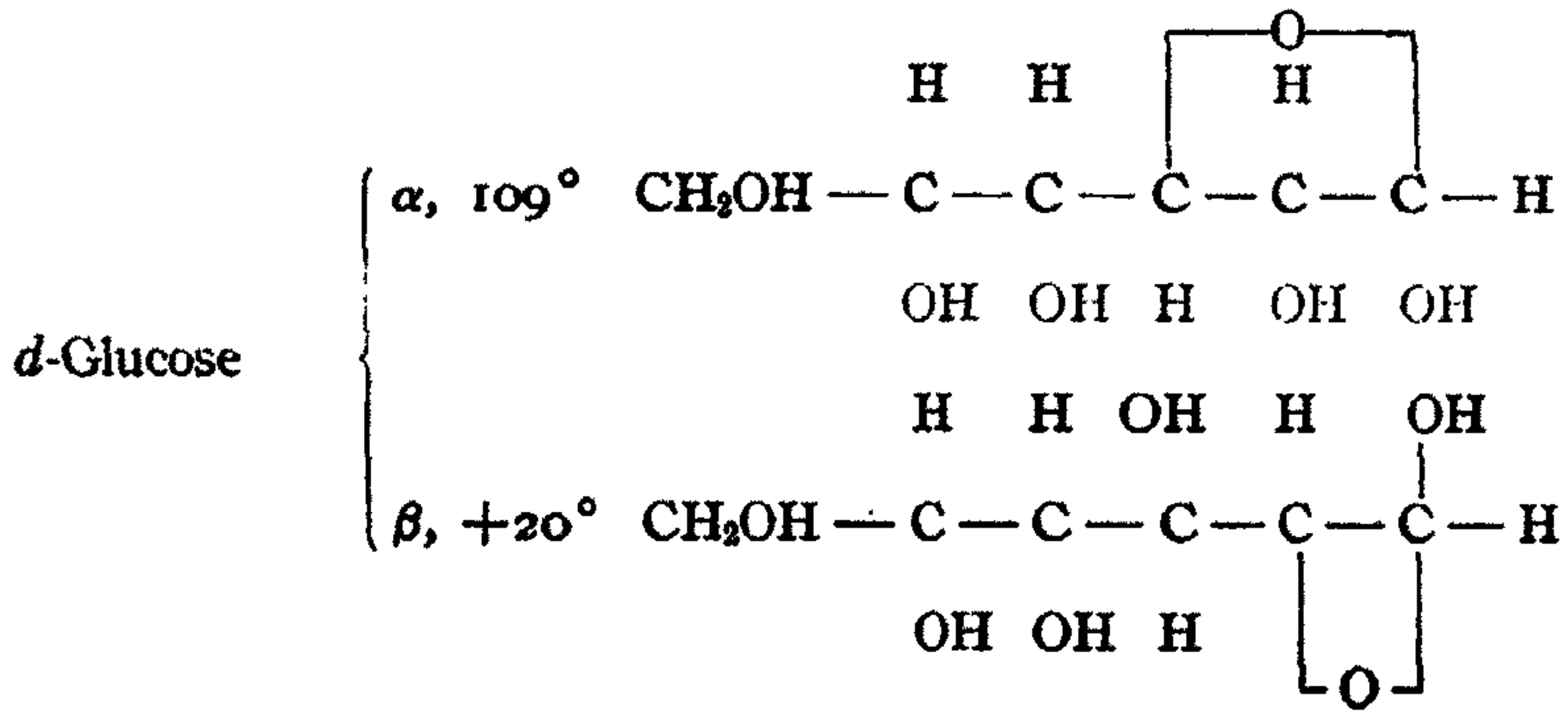
$$\begin{array}{ccccccccccccc} & & OH & & OH & & H & & H & & OH & & \\ CH_3 & — & C & — & C & — & C & — & C & — & C & — & H \\ & & H & & H & & \lfloor & & OH & & \rfloor & & \\ & & & & & & & & O & & & & \end{array}$$

and the corresponding methyl rhamnoside rotating —62° must have the configuration



$$\begin{array}{ccccccccccccc} & & OH & & OH & & H & & H & & OCH_3 & & \\ CH_3 & — & C & — & C & — & C & — & C & —— & C & — & H. \\ & & H & & H & & \lfloor & & OH & & \rfloor & & \\ & & & & & & & & O & & & & \end{array}$$

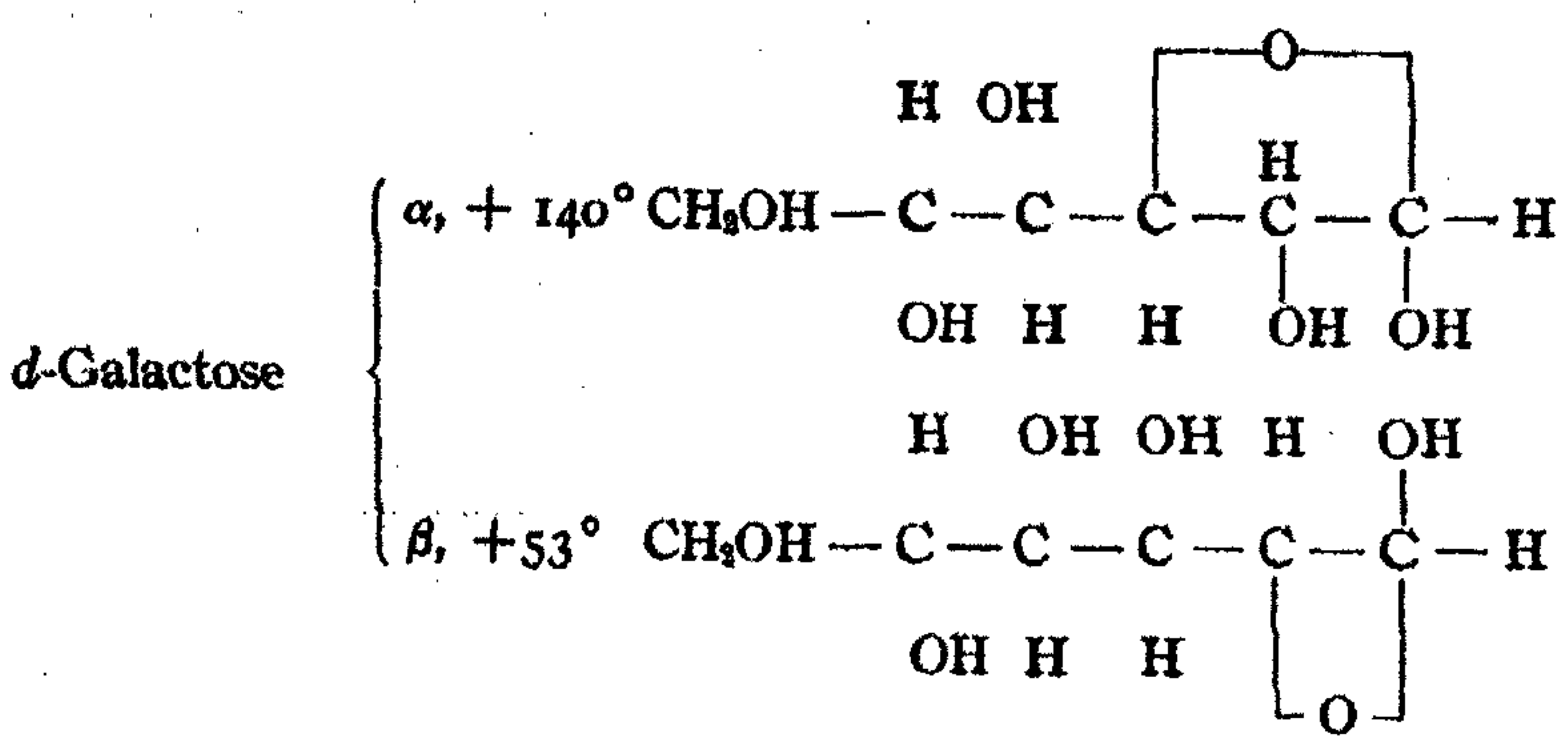
Where the $—O—CH_3$ in the glucoside is above the structure the glucoside rotates roughly 55° levo from the corresponding sugar rotation. Where the $—O—CH_3$ is below the structure the glucoside rotates roughly 55° dextro from the corresponding sugar. Those forms of the sugar then whose glucosides rotate dextro from the sugar rotation have the free OH group on the end carbon atom below the structure while those forms of the sugar whose methyl glucosides rotate levo from the sugar have the free OH group above the carbon structure. The following table gives the configurations of the α and β *d*-glucose and *d*-galactose deduced by the above reasoning:



d-Glucose

$$\alpha,\ 109^\circ\quad \begin{array}{ccccccccccccc} & & & & & & \lceil & & O & & \rceil & & \\ & & H & & H & & & & H & & & & \\ CH_2OH & — & C & — & C & — & C & — & C & — & C & — & H \\ & & OH & & OH & & H & & OH & & OH & & \end{array}$$

$$\beta,\ +20^\circ\quad \begin{array}{ccccccccccccc} & & H & & H & & OH & & H & & OH & & \\ CH_2OH & — & C & — & C & — & C & — & C & — & C & — & H \\ & & OH & & OH & & H & & \lfloor & O & \rfloor & & \end{array}$$



A comparison of *d*-glucose and *d*-galactose shows that the α form rotating the more strongly has the 4-atomic lactone. If then the two lactones rotate in the same direction, the 4-atomic lactone, having three asymmetric carbon atoms in the ring rotates more strongly than the 3-atomic lactone which has only two asymmetric carbon atoms in the ring. The α form of the sugar has then the β lactone, while the β form of the sugar has the α lactone. This last relation has been tested for only the three sugars described because the necessary data are not available for other sugars.

Hudson and his collaborators have published a number of articles dealing with the optical rotatory powers of the sugars and derivatives.[1] In all probability other series of compounds in the sugar group will be found to exhibit similar relations between optical rotation and configuration when they have been investigated systematically and thoroughly.

In conclusion, the author wishes to state that he is familiar with the work of Purdie and Irvine,[2] and E. F. Armstrong,[3] which has been regarded as establishing the γ lactone structure for sugars. In spite of this work and much other of a similar nature the relations[4] pointed out in this article seem

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[1] Jour. Am. Chem. Soc., 31, 66 (1909); 32, 388 (1910); 37, 1264, 1591 (1915).

[2] Jour. Chem. Soc., 83, 1026 (1903); 85, 1049 (1904); 87, 1022 (1905).

[3] Ibid., 83, 1305 (1903).

[4] The relations pointed out in this paper are all between specific rotations.

sufficiently important to warrant their publication, especially since both Fischer[1] and Hudson[2] have suggested the possibility of other lactones in the glucosides in addition to the γ lactone and since Nef[3] has definitely taken his stand against the ordinary accepted view as to the structure of the sugars.

Amherst, Mass.
Dec. 22, 1915

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[1] Ber. deutsch. chem. Ges., **47**, 1980 (1914).
[2] Jour. Am. Chem. Soc., **37**, 1593 (1915).
[3] Ibid., **37**, 345 (1915).

A STUDY OF THE ETHLYENE ELECTRODE[1]

BY W. F. CLARKE, C. N. MYERS AND S. F. ACREE

The constancy and reproducibility of the hydrogen electrode and calomel battery having been shown to be sufficiently accurate, it has seemed advisable to extend its application to other series of measurements even though it has been necessary to study these cases somewhat qualitatively. These studies have been termed qualitative for the reason that many improvements in methods and apparatus will be necessary before accurate results can be obtained. The hydrolysis of aniline hydrochloride, as carried out by Denham,[2] by Desha,[3] and by Loomis,[4] gave values quite satisfactory as compared with the calculated values. In a case of this kind we have a solution of varying composition and increasing complexity. The hydrogen electrode has proved to be very accurate, direct, and rapid in such cases.

Let us examine the hydrolysis of an amide in the presence of hydrochloric acid:

$$RCONH_2 + HCl + \overset{+}{H} + \overset{-}{Cl} + RCONH_3Cl + RCON\overset{+}{H}_3 + \overset{-}{Cl} + H_2O \longrightarrow RCOOH + \overset{+}{N}H_4 + \overset{-}{Cl}, \text{ etc.}$$

After a moment's consideration it is seen that there is no method (*e. g.*, conductivity method) of determining the concentrations of all the constituents of such a system for the reason that too many unknown factors are present. The application to this case of the hydrogen electrode, which furnishes a measure of the hydrogen (hydroxide) ion concentrations would be of great help; the method is best seen in simple organic substances like aniline hydrochloride. This substance is selected for the reason that considerable data

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[1] Contribution from Chemical Laboratory of Johns Hopkins University.

[2] Jour. Chem. Soc., 93, 41 (1908).

[3] Diss. Johns Hopkins Univ., 1909.

[4] Ibid., 1911.

obtained by other methods are at hand and agree sufficiently well when the formula

$$\frac{K_w}{K_b} = \frac{[C_{H^+}]^2 \times \text{volume}}{\left[1 - \frac{\text{Percent hydrolysis}}{100}\right] \times \text{ionization}}$$

is used for calculating this relationship. The reader's attention is called to the work of Loomis, Denham, Desha and Bredig in this connection.

Other cases of applicability are: the hydrolysis of cane sugar,

$$C_{12}H_{22}O_{11} + HOH \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6;$$

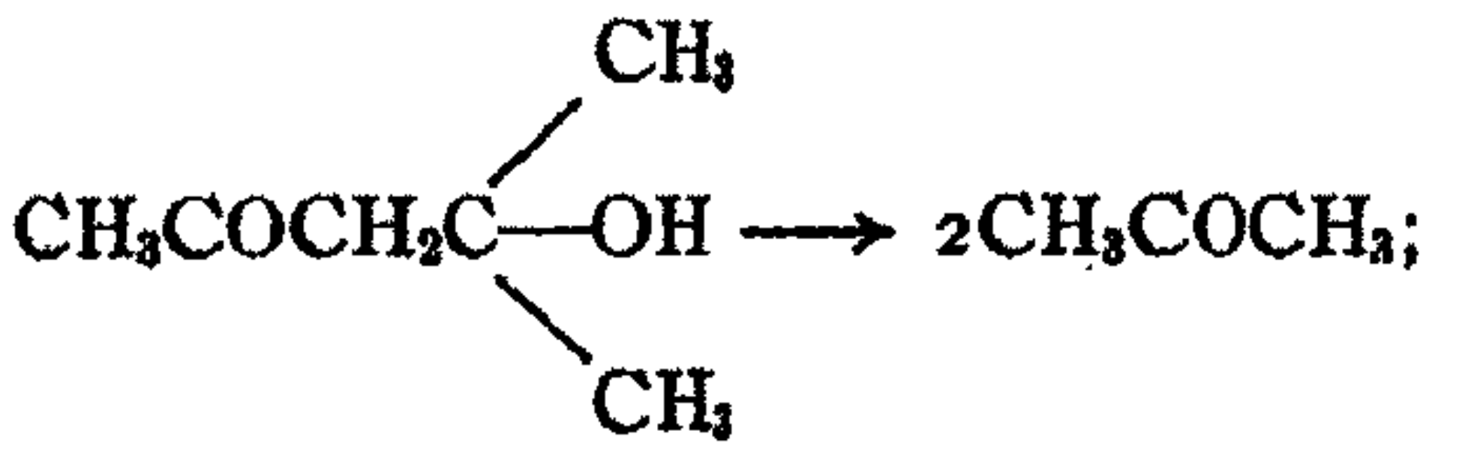
ester and amide catalysis,

$$CH_3COOCH_3 + H_2O = CH_3COOH + CH_3OH$$
$$CH_3CONH_2 + H_2O = CH_3COONH_4;$$

breaking down of diazoacetic ester into glycolic acid ester and nitrogen,

$$N_2CHCOOC_2H_5 + H_2O \longrightarrow (OH)H_2CCOOC_2H_5 + N_2;$$

the change of diacetone alcohol into acetone,



$$CH_3COCH_2C(CH_3)_2{-}OH \longrightarrow 2CH_3COCH_3;$$

and especially cases in which the compounds are weakly dissociated. In cases of this last type the conductivity method presents extreme difficulties.

Ethylene Electrode

The most important investigation carried out under this topic of qualitative experiment consisted in the use of a new electrode which we have termed the ethylene electrode. This consists in the use of ethylene gas on one side and chlorine, hydrogen, oxygen, etc., gas on the other side of the system. Ethylene gas was prepared by the method of Gladstone and Tribe, in which ethylene bromide and copper-zinc couple were used. The copper-zinc couple was prepared by pouring a solution of copper sulphate over granulated zinc several times until a good coating of copper was obtained. Alcohol and ethylene bromide in the proportions 12 : 1 were used and to this mixture water was added to slight turbidity. The mixture was placed in a small balloon flask with a tight stopper and then the copper-zinc couple was added. The gas soon began to be evolved and it was passed through another flask completely surrounded by a freezing mixture in order to condense any ethylene bromide that might be carried along mechanically. The gas is then conducted through a solution of sodium hydroxide, potassium dichromate and water into a third cylinder containing dilute sulphuric acid. From this cylinder the gas is received in a gasometer by the displacement of water. Several liters of the gas were collected in this way and reserved for use in the electrode work. As far as it has been possible to gain any information from the literature nothing has been attempted with an electrode of this kind.

The apparatus necessary for experiments of this kind consists of two platinum electrodes of the same type as described in connection with the hydrogen electrode. In order to make a complete system it is necessary to use some known element whose electromotive force has carefully been worked out. In connection with this phase of the work, the chlorine element has been chosen and reference to the very important work of Lewis and his co-workers is made at this time. The electrolyte chosen for the system was 0.1 *N* hydrochloric acid, which was carefully standardized in this laboratory. This acid was first prepared by the method of Hulett, and then pycnometric measurements were made on the stock solution and these were supplemented by a great many quantitative determinations. A more complete description of this phase of the work will appear in a monograph on this subject. The container used for this study was essentially a U tube with a stopcock between the two halves of the apparatus. A diagram of this apparatus will likewise appear in the above-mentioned monograph.

Method of Experimentation

Emphasis is again laid upon clean apparatus and good chemicals even though the work is only qualitative in this particular case. About three hundred cubic centimeters of tenth normal hydrochloric acid was placed in the U tube. The stopcock between the two halves was closed and the apparatus was ready for the insertion of the electrodes. A three-hole gum stopper was used for each half of the apparatus. One hole was used for holding the electrode in place, the second for the inlet of gas, and the third for the exit of gas. The inlet tube extended below the level of the lower edge of the electrode and thus allowed the gas to bubble against the surfaces of the electrode. The exit tube was drawn to a capillary so that outside air was excluded. The entire apparatus was placed in a constant temperature bath and the gases allowed to flow into each side of the apparatus for fifteen or twenty minutes until saturation was nearly complete. The gas in each case was run through a wash solution of tenth normal hydrochloric acid. The wires leading to the potentiometer were adjusted and the system was in condition to make the ordinary electromotive force measurements. The following tables show the results of three different samples of ethylene:

TABLE I

C_2H_4–Pt–0.1 *N* HCl — 0.1 *N* HCl–Pt–Cl_2

Time	E. M. F.	Time	E. M. F.
12.15	0.850925	3.05[1]	0.741360
12.25	0.856430	3.10	0.723500
12.28	0.857228	3.20	0.714000
12.40	0.874720	3.30	0.708250
12.45	0.873475	3.40	0.704350
12.55	0.864720	3.45	0.696300
1.00	0.864750	3.55	0.693400
2.00	0.821220	4.00	0.691300
2.30	0.816920	4.05	0.688950[2]
2.35	0.817140	4.10	0.487500[3]
2.40	0.817650	4.20	0.874000
2.45	0.819940	4.30	0.747320[4]
2.50	0.824170	4.35	0.647300
2.55	0.823810	4.45	0.420000[5]
3.00	0.822880	5.00	0.448100

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[1] At this stage of the experiment oxygen and ethylene in equal volumes were allowed to flow in against the electrode.

[2] Ethylene stopped for five minutes.

[3] Oxygen stopped for ten minutes.

[4] Oxygen in equal proportions started.

[5] Oxygen in large excess.

TABLE II

C_2H_4-Pt-0.1 *N* HCl — 0.1 *N* HCl-Pt-Cl_2

Time	E. M. F.	Time	E. M. F.
2.35	0.901200	4.00	0.081000
2.40	0.902610	4.05	0.109200
2.45	0.914500	4.15	0.200000
2.47	0.917300	4.20	0.377000[2]
2.50	0.931400	4.25	0.457000
2.55	0.927500	4.30	0.459200
3.20	0.927600	4.40	0.571000
3.25	0.929500	4.45	0.749500
3.30	0.936000	4.50	0.929000
3.35	0.945600	4.55	0.931500
3.40	0.928000	5.00	0.928500
3.50	0.053700[1]	5.05	0.927500
3.55	0.044200		

TABLE III

C_2H_4-Pt-0.1 *N* HCl — 0.1 *N* HCl-Pt-Cl_2

Time	E. M. F.	Time	E. M. F.
10.35	0.887000	12.01	0.967450
10.55	0.923250	12.10	0.964600
11.00	0.951050	12.20	0.962700
11.10	0.961200	12.40	0.963600
11.30	0.943900	1.00	0.962500
11.55	0.964200	1.02	0.961500

The choice of chlorine as a part of this system was brought about by the fact that ethylene and chlorine combine readily and form ethylene chloride. It will be noticed that the initial electromotive force in all three experiments is approximately nine-tenths of a volt. The system remained fairly constant under uniform conditions. In order to find out if this observed E. M. F. was due to the presence of oxygen or hydrogen in the C_2H_4, oxygen was allowed to flow into the system in a volume equal to that of the ethylene and we noticed a dropping off of the potential, as we should expect. This

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[1] The ethylene gas was entirely shut off and only oxygen allowed to flow in.

[2] Oxygen stopped entirely and only ethylene entering.

case is observed in Table I, Note 1. The same table shows the rise and fall of the potential as the amounts of oxygen and ethylene are varied (Notes 2, 3, 4, 5).

The same fact is more distinctly noted in the case of Table II, Note 1, where the E. M. F. becomes very small. It is noticed in this table that the E. M. F. increased as soon as the flow of oxygen was stopped and "pure" ethylene was allowed to bubble in, and that the system returned quite rapidly to its normal value. Table III shows an experiment in which ethylene is used against chlorine, and the E. M. F. remaining fairly constant at approximately 0.9625 volt. These experiments show apparently that ethylene gas when used in a gas electrode sets up an electromotive force of considerable amount and probably proceeds in a manner described below. As analysis of the ethylene showed that it is not absolutely pure, the next phase of our work will be to prepare the pure gas free from hydrogen, oxygen, ethane, etc., in order to prove beyond any question that pure ethylene gives the electrode described above.

The object of these studies is to learn whether ethylene combines with chlorine, bromine, hydrogen, etc., through an electronic transfer which can be used to develop an E. M. F.; as the preliminary study is certainly in harmony with this idea we may interpret the reaction as follows for the present:

$$CH_2 = CH_2 + Cl_2 \longrightarrow \overset{+}{C}H_2 - \overset{+}{C}H_2 + 2\overset{-}{Cl} \longrightarrow CH_2Cl—CH_2Cl$$

Summary

The work which has already been carried out on the study of the ethylene electrode indicates that it is an entirely new system; that it is a system possessing a very high electromotive force; that it is easily reproducible and constant as illustrated by the three separate tables submitted. Furthermore, it is apparent that chemically pure ethylene is difficult to prepare. Finally, the theory of its action as a gas electrode involves the idea that the ethylene loses two electrons to the electrode and then combines with the chloride ions.

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STUDIES IN OXIDATION AND REDUCTION[1]

BY W. F. CLARKE, C. N. MYERS AND S. F. ACREE

The Electromotive Force of the Reaction $HCHO \xrightarrow{O} HCOOH$

Qualitative.—Many of the ordinary reactions which we observe each day serve as excellent examples for the study of electromotive force. The work of Acree and his co-workers leads the student of chemistry to regard the common reactions more carefully in accordance with the theory of ionic and molecular reactivity. The physical chemist should no longer believe that only ions participate in each reaction. The theory of Arrhenius and later workers taught us that the ions were the carriers of electrical charges and that it was their function to bring about chemical change. Accepting this view as a partial explanation and adding to this the newer conception of Acree in which the nonionized salts are regarded as an important factor in reactions, might we not suppose that the nonionized part carries a part of the electrical charge in an equilibrium phase such as:

$$NaOC_2H_5 + IC_2H_5 \longrightarrow \overset{+}{Na}OC_2H_5 + \overset{-}{I}C_2H_5 \longrightarrow$$
$$C_2H_5I.NaOC_2H_5 \text{ or } \overset{+}{C_2H_5} + INa\overset{-}{O}C_2H_5 \longrightarrow NaI + (C_2H_5)_2O$$

Without doubt electromotive force work will aid in studying these rapidly changing systems and complexes, and the accuracy and rapidity of this kind of method will greatly help the investigator to measure these values.

In making a study of this reaction, it is necessary to have a U tube of the type described under the subject of the ethylene electrode. The electrolyte used in this experiment was $N/5$ sodium hydroxide. The oxygen used in the oxidation experiment was obtained by the electrolysis of barium hydroxide. The electrodes consisted of two platinum electrodes of the same type as used in the hydrogen electrode work, one in each arm of the U tube. Oxygen was allowed to bubble against one of

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

the electrodes, and the electromotive force of this element was, therefore, that of a concentration element in which the oxygen on one side is about five times as concentrated as on the other. The concentration pole was positive.

Time	E. M. F.
12.02	0.0305
12.03	0.0300
12.04	0.0298

The above table shows that the E. M. F. for the system is practically constant. The study of the oxidation is now ready. One drop of a forty percent solution of formaldehyde is added to the sodium hydroxide solution on the side opposite to the one into which oxygen is bubbling. The value for the electromotive force immediately increased and reached a constant value.

Time	E. M. F.	Time	E. M. F.
12.05	0.4740	12.09	0.4472
12.07	0.4575	12.10	0.4480
12.08	0.4500	12.12	0.4499

Three drops more of formaldehyde were added and an additional increase of the E. M. F. was observed.

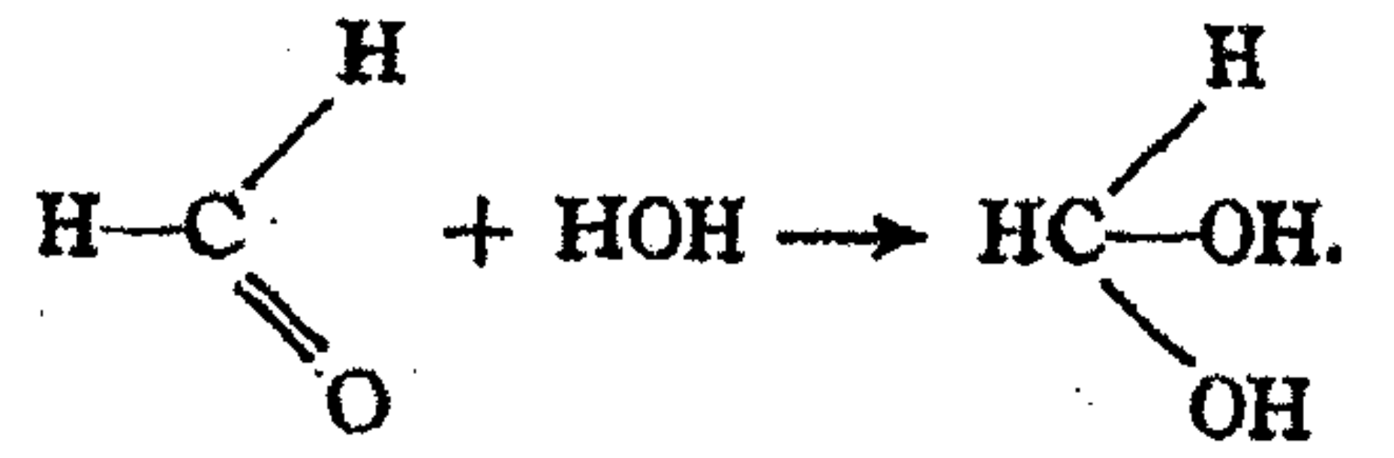
Time	E. M. F.
12.15	0.5270
12.17	0.5240

At this point air and carbon dioxide were blown through the solution, so that an idea of what effect blowing the formaldehyde out of the pipette had on the electromotive force. The reading dropped off to 0.505, showing that the result was not very large.

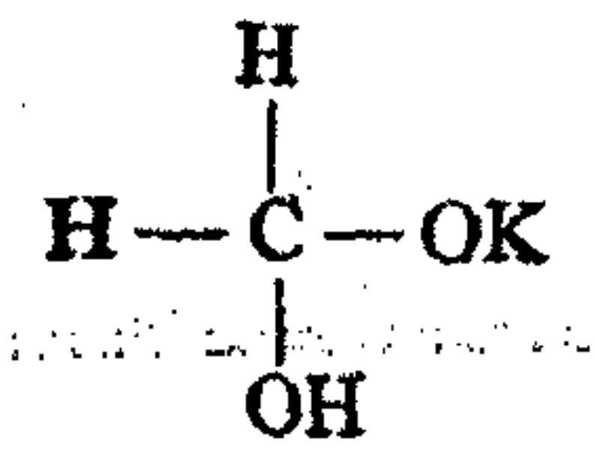
Theory of the reaction:

$$HCHO + O \longrightarrow HCOOH$$

It is well known that aldehydes are easily hydrated and possess acid properties.



In the presence of an alkali, NaOH or KOH, we would have the sodium or potassium salt formed as:

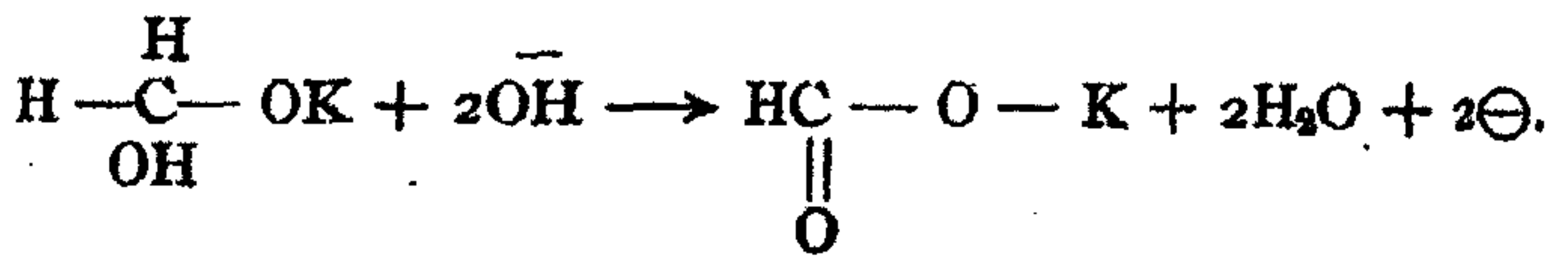


$$H-\overset{H}{\underset{OH}{C}}-OK$$

When oxygen goes into solution at the anode, it reacts with HOH and takes up negative charges from the electrode for each atom of oxygen going over into the form

$$O \longrightarrow 2(\overline{OH}).$$

For every two $(\overline{OH})$ ions that go into solution, two $(\overline{OH})$ ions are discharged at the other pole in the reaction.

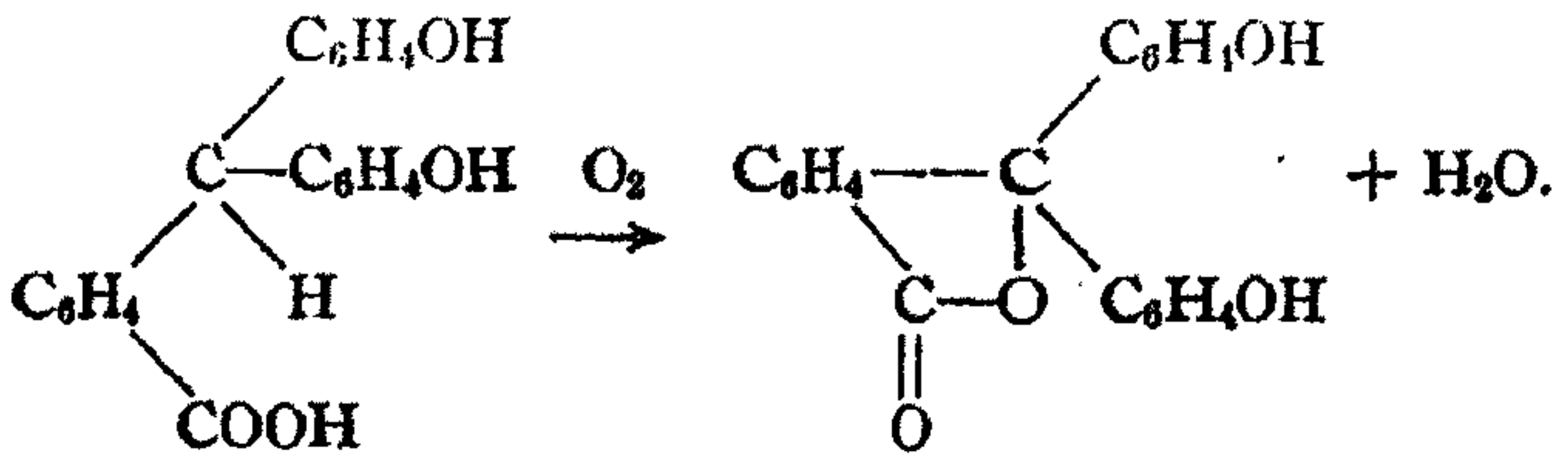
(A) 

$$H-\overset{H}{\underset{OH}{C}}-OK + 2\overline{OH} \longrightarrow H\underset{\underset{O}{\|}}{C}-O-K + 2H_2O + 2\ominus.$$

We do not attempt at this time to give any details of the reaction.

The object of this investigation is to determine whether the anion or molecule, or both, of the salt A is oxidized, and to learn the real mechanism as completely as possible. Now that a constant E. M. F. can be obtained we shall begin these studies quantitatively.

On the Oxidation of Phenolphthalin to Phenolphthalein



A small quantity of the phenolphthalin was dissolved in fifth normal sodium hydroxide, a clear colorless solution resulting. A sufficient amount of this solution was placed in the U tube which has been previously described. The relation between the two electrodes in sodium hydroxide solution was found to be 0.03 volt, when oxygen was passed over one and air over the other. The electromotive force in the presence of the phenolphthalin solution gave a value of 0.176 volt, and no perceptible red or pink color appeared even though the two poles of the cell were connected. The solution was now electrolyzed with an E. M. F. of 4.4 volts and a red color appeared at the anode, a proof that the phenolphthalin is oxidized electrolytically to phenolphthalein. Believing that the reverse reaction might take place we tried the next experiment described under reduction.

Reduction of Phenolphthalein to Phenolphthalin

In one arm of the U tube a *N*/5 sodium hydroxide solution of phenolphthalein (red in color) was placed; in the other fifth normal sodium hydroxide. The platinum electrodes were adjusted and hydrogen was bubbled into the solution continuously. The E. M. F. recorded in this case was 0.845 volt. The color of the solution grew lighter.

These experiments, though qualitative, point out the significance of the study of the electromotive forces of reactions. It leads us to consider that some electronic changes are going on in reactions whether they are organic or inorganic, and these changes should be studied quantitatively.

Summary

These qualitative experiments indicate the extreme importance of the study of the electromotive force of chemical reactions, whether they may be of the oxidation or reduction type, or even reactions involving neutralization. It is hoped that these few qualitative experiments will serve as an incentive to more careful quantitative investigations of these chemical reactions from the point of view of the ion and the molecule and the electronic charges which they may carry.

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OVERVOLTAGE

BY C. W. BENNETT AND J. G. THOMPSON

A large number of measurements of overvoltage have been made and the phenomenon has been characterized many times as very complex. The unsatisfactory state of the published knowledge of the subject may be seen by a consideration of a few of the definitions and theories of overvoltage. The cathode decomposition voltage of sulphuric acid solution with a platinized platinum cathode is a definite value. This value is different if smooth platinum or a zinc cathode be used. These values will all differ depending on whether the voltage drop at the electrode is measured as the voltage is increased, or whether the back electromotive force of polarization is measured.

Overvoltage has been defined in several ways. Caspari[1] considers hydrogen overvoltage, for instance, as the difference between the voltage at a platinized cathode when bubbles of hydrogen form, and at the metal in question under the same conditions. In other words it is the difference in the voltages required to liberate hydrogen at the surfaces of the two metals under the same conditions.[2]

Values for overvoltages of hydrogen and oxygen at several metal electrodes follow in Table I.

The values differ depending on whether the point of gas evolution or whether the break in the voltage current curve is taken. The values also increase with an increase of current density. LeBlanc[3] considers the phenomenon from the standpoint of the electromotive force of the cell after the charging circuit is broken. He considers hydrogen overvoltage as the excess back electromotive force generated at the electrode over that at a platinized platinum electrode. This may be

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[1] Zeit. phys. Chem., 30, 89 (1899); Coehn and Dannenberg: 38, 618 (1901).

[2] See Fuchs: Pogg. Ann., 156, 156 (1875).

[3] Textbook of Electrochemistry, 298 (1907).

TABLE I—HYDROGEN AND OXYGEN OVERVOLTAGES

Electrode material	Overvoltage, volt according to				
	Caspari		Müller[1]	Coehn and Dannenberg	Thiel and Bruening[2]
	Hydrogen	Oxygen	Hydrogen	Hydrogen	Hydrogen
Pt platinized	0.005	0.39	0.01	0.0	0.0
Palladium	0.46	0.39	0.24	—0.26	0.0
Pt polished	0.09	0.62	0.07	—	—
Gold	0.02	0.59	0.06	+0.05	0.016
Silver	0.15	—	0.05	+0.07	0.097
Copper	0.23	—	0.03	+0.19	0.135
Nickel	0.21	—	0.03	+0.14	0.138
Retort carbon	—	—	—	—	0.143
Iron	—	—	—	+0.03	0.175
Iron in NaOH	0.08	—	—	—	0.087
Graphite	—	—	—	—	0.335
Cadmium	0.48	—	—	—	—
Tin	0.53	—	0.43	—	—
Lead	0.64	—	0.35	+0.36	—
Zinc	0.70	—	—	—	—
Mercury	0.78	—	0.42(?)	+0.44	—
Aluminum	—	—	—	+0.27	—

obtained by rapidly closing the charging circuit and as rapidly breaking it, making a new circuit through suitable measuring instruments. This is accomplished by a commutator rotating 1200–1500 revolutions per minute.[3]

It is evident, therefore, that the phenomenon has been considered from the relative standpoint of an arbitrary standard. The significance of this is realized when it is considered that palladium has a "negative overvoltage," which all but gives the impression, especially to the beginner, that there is a gain in the energy of the system when hydrogen is set free at the surface of a palladium electrode.

A new definition of overvoltage will include not only hydrogen, oxygen, and other gases, but also the metals, for

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[1] Müller: Zeit. anorg. Chem., 26, 56 (1901).

[2] Thiel and Bruening: Ibid., 83, 329 (1913).

[3] See LeBlanc: Zeit. phys. Chem., 5, 469 (1890).

the latter have definite overvoltages. It is evident that the definitions of overvoltage in use at the present time are not general, since they, none of them, apply to the metal overvoltage.

Throughout this discussion, therefore, the term overvoltage will be used in the general sense and will denote the excess back electromotive force of the system (cathode or anode as the case may be) under investigation, over the electromotive force of the system consisting of the final product obtained (at anode or cathode) in the solution used.

The overvoltage of hydrogen at a metal electrode would be the excess of the back electromotive force of the metal cathode (containing hydrogen) during electrolysis, over the electromotive force of the reaction

Hydrogen gas ⟶ dissolved hydrogen ion.

This overvoltage varies with the metal used because the metals act differently towards hydrogen. The overvoltage of a metal, zinc, for instance, would likewise be the excess of the back electromotive force of the system:

Zinc ⟶ zinc solution during electrolysis

over the electromotive force of the reaction

Solid zinc ⟶ dissolved zinc ion.

The overvoltage therefore, represents the excess energy required to form a substance over that given by the resolution of the product formed to the original state. It is the amount of energy by which one measures the irreversibility of the process or change.

A number of theories have been suggested to explain overvoltage.

Haber[1] assumed that the electrode adsorbs a film of gas and that the resistance is increased. This is not worthy of consideration when it is realized that a resistance at the electrode would lower the electromotive force of the polarized

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[1] Haber: Zeit. Elektrochemie, 8, 539 (1902); Haber and Russ: Zeit. phys. Chem., 47, 257 (1904).

cell, and also that metals while being deposited have definite overvoltages which must be considered aside from any gas formation.

Nernst[1] ascribed the cause to the slowness with which the electrode gets into equilibrium with the surrounding atmosphere. He considers that before the gas can be liberated the ions must be driven into the electrode. Metals which have only a slight tendency to occlude gases, require energy to force the gas into the electrode, and thus give high overvoltages.

Möller[2] considers that the overvoltage is the energy necessary to give a film of gas thick enough to generate bubbles.

Foerster[3] claims that at a platinum anode, an oxide, probably PtO_3, is formed. This as a solid solution would generate a high back electromotive force, and therefore give a high oxygen overvoltage at a platinum anode. In the case of the other metals where the higher oxide is unstable, it would not accumulate in appreciable quantities and hence the overvoltage would be low. Hydrogen overvoltage would be explained by the assumption of the formation of a solid solution of hydride probably. This theory does not satisfactorily explain the overvoltage of metals.

Tafel[4] takes a view similar to Nernst, in that he considers the forcing of the gas into the electrode takes time, and the excess gas accumulated generates the back electromotive force. He also considers that in the case of hydrogen an intermediate state exists between dissolved ion and gaseous hydrogen. This monatomic hydrogen, forms free hydrogen, more or less rapidly, depending on the catalytic effect of the metal of the electrode. When the reaction is slow and the concentration of the intermediate product high, the overvoltage is high and *vice versa*.

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[1] "Theoretical Chemistry," 766 (1911).

[2] Drude's Ann., 25, 725; Zeit. phys. Chem., 65, 226 (1908).

[3] Zeit. Elektrochemie, 16, 353 (1910); Zeit. phys. Chem., 69, 236 (1909).

[4] Zeit. phys. Chem., 34, 200 (1900); 50, 641, 713 (1905); Brunner: 56, 331 (1906).

This theory was suggested by Ostwald[1] previous to this as a possible explanation and also by E. Müller.[2] This view was accepted by Lewis and Jackson.[3] They say: "The theory of overvoltage, with which the authors began these experiments, was as follows: The reaction, $2H^+ + 2\ominus = H_2$, does not occur in a single stage, but in the two following: $H^+ + \ominus = H$, and $2H = H_2$. The reaction whose slowness causes the polarization is the second of these. In other words, the potential of a hydrogen electrode depends on the concentration of monatomic hydrogen, and this concentration increases rapidly during cathodic polarization on account of the slowness of the reaction by which it is removed. For example, at a polarization potential of 0.7 volt the concentration of this substance at the electrode would be 10^{12} times as great as it would be when in equilibrium with ordinary hydrogen. Nevertheless both of these concentrations might be absolutely very small, and probably are. The difference in polarization with different cathodes would be explained by the different catalytic action of the material at the electrode, the polarization being less the greater the catalysis. This theory, although it has been suggested by Tafel,[4] has had otherwise no place in the numerous discussions which the phenomenon of overvoltage has occasioned. It possesses, nevertheless, a good deal of plausibility. We may in fact cause the electrolytic reaction to proceed in the very two stages which we have written above. When hydrogen is deposited on a platinum cathode, the hydrogen, forming without marked polarization, is absorbed by the metal, where it has been shown by two independent methods[5] to exist in the monatomic condition. If the hydrogen is then withdrawn from the palladium, it appears in the form of ordinary hydrogen, H_2.

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[1] Zeit. Elektrochemie, 6, 40 (1899).

[2] Zeit. anorg. Chem., 26, 11 (1901).

[3] Proc. Am. Acad., 41, 399; Zeit. phys. Chem., 56, 207 (1906).

[4] Zeit. phys. Chem., 34, 200 (1900).

[5] Hoitsema: Zeit. phys. Chem., 17, 1 (1895); Winkelmann: Drude's Ann., 6, 104 (1901).

"But we have more striking arguments in favor of this theory. Those metals, notably platinum and palladium, in whose presence the electrolytic deposition of hydrogen and the reverse reaction, the electrolytic solution of hydrogen progress most readily, are the very ones which we have every reason to believe catalyze the reaction $2H \rightleftharpoons H_2$ (of course, if in one direction, in both). This reaction is doubtless a very slow one under most conditions. Hydrogen at ordinary temperatures is a pretty inert substance, but in the presence of palladium or platinum black it readily reduces a large number of substances. So, also these metals aid the union of hydrogen with other elements, such as oxygen and the halogens. Furthermore, in every known case where hydrogen is produced by a reaction, the reaction is catalyzed by these metals. We may mention the action of metals on acids, the reduction of water by chromous salts, the decomposition of a solution of sodium in liquid ammonia.[1] It is possible that each of those reactions is catalyzed in a specific way; but it is much easier to believe that in every case the metal simply catalyzes the slow reaction, $2H \rightleftharpoons H_2$, and that this is also the explanation of the electrolytic reaction that we are considering. It is to be noted that metals like mercury and lead, on which the overvoltage is highest—that is, which are the poorest catalyzers of the electrolytic reaction—have little influence on any of the reactions mentioned above.

"Although we have laid stress upon the *a priori* plausibility of this explanation, we are nevertheless forced to admit that, while our experiments are in no way opposed to the theory, they fail at the same time to give any evidence in its favor, except in so far as they enable us to exclude certain other explanations and thus limit the field of possibilities. If the main reaction at the basis of polarization is the formation of ordinary hydrogen from monatomic, then our experiments only show that this reaction does not occur in a single homogeneous phase. Since in all probability the monatomic

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[1] The interesting fact that this latter reaction is greatly accelerated by platinum was brought to our notice by Dr. C. A. Kraus.

hydrogen is present in extremely small concentration, this would account for the slowness of any diffusion process in which it enters, even if the diffusion were through a thin film."

Bose[1] considers also that the neutral gas may have its influence in that ions may be formed from it.

Le Blanc[2] assumes that as the ion is discharged the following reaction occurs:

$$\text{Ion hydrate} \rightleftharpoons \text{ion} + \text{water}$$

An equilibrium exists in the solution, and when the ion is set free, this is displaced and polarization is set up, giving back-electromotive forces of different magnitudes, depending on the ions used. Overvoltages occur when the reaction above from left to right is slow.

Reichinstein[3] also considers that the ions as well as the gas formed penetrate the electrode. When this penetration is great, the overvoltage is small, for the electromotive force is low due to low concentration. When the "electrode volume" is small the overvoltage is high, due to high concentration of the ions in the electrode.

The above review presents probably the best known theories for the explanation of the phenomenon. However, Newberry[4] concludes that overvoltage is determined by three factors: first, the metal is permeable to electrified gas, leaving the surface supersaturated with non-electrified gas under high pressure; second, at this surface there may be metastable intermediate products (probably non-hydrated ions) either in deficiency or excess; and lastly, the gas evolved exerts an inductive effect on the electrode.

The striking feature of these theories is that those which are intelligible are obviously inadequate.[5] Not one will ex-

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[1] Zeit. phys. Chem., 34, 701 (1900).

[2] Abh. Bunsen Gesell. No. 3 (1910); Trans. Faraday Soc., 9, 253 (1914).

[3] Zeit. Elektrochemie, 15, 734, 913 (1909); 16, 916 (1910); 17, 85 (1911); 18, 850 (1912); 19, 672 (1913); Trans. Faraday Soc., 9, 229 (1914).

[4] Jour. Chem. Soc., 105, 2419 (1914).

[5] For other papers on overvoltage, see Kaufler: Zeit. Elektrochemie, 13, 635 (1907); 14, 321, 737, 749 (1908); Müller: 13, 681 (1907); Sacerdoti: 17, 473 (1911); Nutton and Law: Trans. Faraday Soc., 3, 50 (1907); Pring

plain metal overvoltages, for instance. The majority of the explanations, however, are unintelligible when it comes to a consideration of the exact mechanism of the reactions.

In view of the fact that several of these theories embody threads of evidence pointing to the explanation of certain parts of the general proposition, it is expedient that the several ideas, be gathered up and unified into a general theory of overvoltage, which explains overvoltages of gases at metal electrodes as well as overvoltage of metals. A discussion of this interesting phenomenon is especially opportune, now that there need be no postulation of the existence of hypothetical intermediate products in the case of the gases. The intermediate products have not only been isolated, but have been found to possess just the necessary properties to be used in the case at hand.

Let us consider some of the known facts concerning hydrogen. The reaction

Hydrogen ion ⟶ hydrogen gas

is not strictly a reversible one, for it is known that "nascent hydrogen" or hydrogen produced when the above reaction proceeds will perform reductions, which do not go on even in the minutest measurable amount, when hydrogen gas is bubbled through a similar solution containing the substance to be reduced. Hydrogen gas even when dissolved is inert.[1] Hydrogen will not reduce hydrogen peroxide or ozone spontaneously when cold, although both of these substances will be decomposed by "nascent hydrogen." It is evident, therefore, that the condition of hydrogen, intermediate between gas and dissolved ion, is many times more active than hydrogen gas (H_2). This form must be a stronger reducing agent than H_2 and probably even stronger than zinc itself. It will be shown below that this "active hydrogen" will reduce phos-

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and Curzon: 7, 237 (1912); Pring: Zeit. Elektrochemie, 19, 255 (1913); Thiel and Bruening: Zeit. anorg. Chem., 83, 329 (1913); Crabtree: Trans. Faraday Soc., 9, 125 (1913); Jour. Soc. Chem. Ind., 32, 521 (1913); Richards: Trans. Faraday Soc., 9, 140 (1913).

[1] See Sackur: Zeit. phys. Chem., 54, 641 (1906); Weigert: 60, 543 (1907).

phorus, zinc oxide, and cadmium sulphate, which will indicate that it is a stronger reducing agent than zinc.

The existence of an intermediate stage, more reactive than either of the end products, is a condition of every day acquaintance. For instance, sodium hypochlorite and sodium chlorate solution will oxidize ferrous salts, but neither sodium chloride nor sodium perchlorate solutions will effect the oxidation. The intermediate products are less stable and more reactive than the end products. Theoretically and practically such a condition is possible.[1] The case of ammonium hydroxide, hydrazine hydrate and hydroxylamine, or ammonia, hydrazine, and hydronitric acid as reducing agents, as well as many others, present themselves.

The active form of hydrogen is produced at the cathode during electrolysis of an acid, during solution of a metal in acid (more active with metals like zinc), by the action of radium emanations, (for these form hydrogen, oxygen, and hydrogen dioxide from water), and lastly, by the action of electrical discharges or by photochemical effects. An extremely active modification of hydrogen has lately been prepared and designated.[2] When a tungsten or platinum wire is heated from 1200°-3500° absolute, in an atmosphere of hydrogen at very low pressures, the hydrogen disappears, and when the containing glass bulb is cooled in liquid air there is condensed on its surface atomic hydrogen (H) which may be kept in this active state for several days. When the bulb is heated and the wire cooled, the hydrogen reappears and the active material is not recondensed until the wire or filament is reheated. This active hydrogen will reduce phosphorus even at room temperature, with the formation of phosphorus hydride. The explanation is given that hydrogen dissolves in the hot metal, dissociates, and on being driven out, passes directly to the walls of the container where it may be condensed.

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[1] Luther: Zeit. phys. Chem., 34, 488 (1900); 36, 385 (1901).

[2] Langmuir: Jour. Am. Chem. Soc., 34, 860, 1310 (1912); Freeman: 35, 931 (1913); Langmuir and Mackay: 36, 1708 (1914); Langmuir: 37, 417 (1915).

It is neutral, that is, it is not electrically charged, for it is not attracted or deflected by electrostatic fields. The quantity or amount of dissociation at 760 mm pressure is shown in the following table where

$$K = \frac{P_1^2}{P_2}$$

in which P_1 is the partial pressure of hydrogen atoms (H) and P_2 that of hydrogen gas (H_2).

Temperature absolute	K
2000°	0.0033
2300°	0.0140
2500°	0.0310
3100°	0.1700
3500°	0.3400

Supplementing the work of Langmuir on the properties of this active material one or two experiments may be given. A filament of molybdenum wire was heated close to the volatilization point in a current of hydrogen over solutions of copper, zinc, and cadmium sulphates. In one case a small amount of copper was obtained, while in a number of cases the cadmium solutions yielded precipitates which after thorough washing gave microscopic tests for cadmium with ammonium mercuric sulphocyanate. This shows that at the temperature used the hydrogen was sufficiently activated to reduce small quantities of cadmium from cadmium sulphate solution.

Another experiment was tried in which ultraviolet light was used to activate the hydrogen. The gas was passed through a quartz tube which held a glass slide, on the side toward the light painted with a paste of zinc oxide and water. A Macbeth printing lamp was used as the source of ultraviolet light. The surface of the paste was readily blackened on exposure to the light. The hydrogen used was first electrolytic hydrogen and finally hydrogen generated by the reaction of sulphuric acid and zinc. It was found that the electrolytic hydrogen produced no blackening in the dark or in the daylight, but produced a blackening due to the reduction of the zinc oxide[1] when exposed to the action of ultraviolet light. A difference in the action of hydrogen generated by zinc and sulphuric acid was found, but this was later shown to be due to impurities in the chemically generated hydrogen. The active hydrogen is sufficiently active to reduce zinc oxide.

The zinc oxide paste slide was exposed to the action of a stream of hydrogen by having a glazed paper placed between it and the source of ultraviolet light. The light, therefore, passed through the hydrogen and this hydrogen later reached the glass slide. It was found that the blackening was most marked at the end next to the incoming hydrogen, and was distinct even after the hydrogen had passed two centimeters from the point of activation. The blackening effect on the slide was graduated from the incoming end, fading out gradually as the hydrogen passed over toward the outlet. This shows without question that active hydrogen will reduce zinc oxide, and that it has a definite period of life, depending upon the conditions under which it exists.

Analogous to hydrogen, oxygen (O_2) is formed from the dissolved ion irreversibly,[2]—nascent oxygen produced by electrolysis, or photochemically, will oxidize substances which are unacted upon by hydrogen dioxide or ozone.

Active oxygen, (presumably O_1) and active chlorine have been prepared[3] by heating oxygen and chlorine under low pressures, with a tungsten or platinum filament. Active oxygen may be condensed by liquid air, and even at that temperature reacts readily with tungsten. Active chlorine may be condensed in the same way. It is also very active.

It may be said, therefore, with all certainty, that these reactive products exist, intermediate between free gaseous

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[1] O'Brien: Jour. Phys. Chem., 19, 130 (1915).

[2] See Coehn and Osaka: Zeit. anorg. Chem., 34, 86 (1903).

[3] Langmuir: Jour. Am. Chem. Soc., 37, 1162 (1915); Bredig and Weinmayr: Zeit. phys. Chem., 42, 607 (1903); Jour. Am. Chem. Soc., 35, 105, 931 (1913).

molecules and dissolved ions. Take the specific case of hydrogen, for instance. When hydrogen (H_2) dissolves in a solution, the first step is to form H_1 neutral. The next step is the formation of $H^{\cdot}_1$ dissolved ion. Hydrogen gas can ionize only through such a series of changes.

A consideration of these reactions in opposite directions will indicate why they are not reversible, statements to the contrary notwithstanding.[1] As hydrogen gas dissolves, it becomes ionized. The concentration of H_1 goes from zero to a maximum value, namely, the equilibrium concentration. Since energy is not added from without, this equilibrium concentration practically cannot be exceeded, otherwise the reaction would reverse. Any variation from this will be in the direction of a lower concentration. Considered from the other side, now, where energy is added, the first step is the formation of H_1 from $H^{\cdot}_1$ dissolved ion. Then gas, (H_2) is formed. The same equilibrium exists here as before, but gas is formed only when the equilibrium concentration of H_1 is exceeded, otherwise the reaction would stop or reverse. The reaction where hydrogen dissolves, becoming ionized through the intermediate stage, is connected with the formation of active hydrogen (H_1) in equilibrium concentration, while the reverse reaction forms active hydrogen (H_1) in concentrations from equilibrium up to values depending on the conditions of the electrolysis. This difference, which will depend on the conditions, is a true measure of the irreversibility of the process.

From the standpoint of the transformation of chemical energy into electricity, the irreversibility becomes even more evident. Hydrogen as H_2 ionizes through this series of reactions,

$$H_2 \text{ dissociates} \longrightarrow 2H_1, \text{ assumes charge} \longrightarrow 2H^{\cdot}.$$

This reaction generates a certain quantity of electricity with a definite intensity, the product of which represents the total chemical energy. In the reverse direction hydrogen gas is

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[1] Neumann: Zeit. phys. Chem., 14, 203 (1894); Westhaver: 51, 65 (1905); Lewis: Jour. Am. Chem. Soc., 28, 160 (1906); Haber: Loc. cit.

not formed until equilibrium is reached or at higher concentrations of active hydrogen if the conditions are not conducive to carrying out the reaction, $2H_1 \longrightarrow H_2$, quickly. When equilibrium is exceeded, at any rate, energy of greater intensity must be required to carry on the reaction. The total voltage or back-electromotive force is that occasioned by the active hydrogen present. The excess back-electromotive force or overvoltage is that occasioned by the active hydrogen present in excess of equilibrium concentration. The energy required to form this excess active hydrogen, is equal, with a change of sign, to the energy yielded by the decomposition of the excess active hydrogen to form gaseous hydrogen. The latter has been calculated and will be mentioned below. The process is irreversible, therefore by the energy, or heat, of formation of active hydrogen in such concentration as it is present above equilibrium.

The process of solution and deposition of a metal cannot be considered reversible. Consider the electrodeposition from solution. The first step is the loss of a positive charge from the ion. This will result in the formation of free atomic metal, in the case of monovalent ions. Suppose we consider the case of zinc without assuming a monovalent zinc ion. The divalent ion becomes free atomic material. Its condition is the same as that of zinc in the vapor state. Zinc vapor, according to vapor density measurements, is Zn. When the ion in solution loses the charge it becomes Zn, and therefore it must be analogous to the vapor, the difference being that the zinc atoms (Zn_1) can come closer together on account of the lower temperature. Analogous to hydrogen when the concentration of Zn exceeds equilibrium values, a complex Zn_x will be found. In other words the material will go into a condition analogous to a "melt,"[1] and from this it will crystallize.[2] Equilibrium concentration value must be exceeded at each stage else the reaction would come to a stand-

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[1] Reichinstein: Zeit. Elektrochemie, 17, 89 (1911); Bennett: Trans. Am. Electrochem. Soc., 21, 256 (1912).

[2] Cf. Ostwald: Trans. Am. Elektrochem. Soc., 6 II, 194 (1904).

still or reverse. Consider the reverse reaction. Crystalline metal breaks down to complexes which then dissociate to Zn_1 which goes into solution with the assumption of two positive charges of electricity. During this change equilibrium concentrations are never exceeded. If they were the reaction would reverse.

Considering the two reactions as proceeding continuously, with zinc of the same crystal structure in both cases, one reaction forms Zn_1 in concentrations up to, and the other above, equilibrium values. This measures the irreversibility of the process.

Zn_1 represents energy of greater intensity than the crystalline zinc, for it has been shown conclusively that the solution pressure, and therefore the voltage varies inversely with the size of the crystals.[1] Zn_1 may be considered as the last stage in the decrease in the size of the crystals or particles of zinc. This consideration shows that more energy will be required to deposit zinc from solution, than is yielded by its resolution and the process is irreversible in that sense.

Suppose we consider the case where ions of intermediate valency may be formed. Copper, for instance, is deposited from copper sulphate solution with the formation of some cuprous ions. This reaction may be irreversible by an amount depending on the quantity of cuprous ions formed and reoxidized either by air or at the anode. It has been shown that copper deposition from copper sulphate solution requires a higher voltage the more rapidly the cathode is rotated.[2] This is higher than that required for a stationary cathode, even though the solution is stirred vigorously. This was shown to be due to the formation of cuprous ions and their removal by rotation from the cathode solution film before they can be re-

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[1] Erskine-Murray: Phil. Mag., (5) 45, 403 (1898); Kenrick: Jour. Phys. Chem., 16, 515 (1912); Bennett: Trans. Am. Electrochem. Soc., 23, 394 (1913); Jour. Phys. Chem., 17, 373 (1913).

[2] Bennett: Trans. Am. Electrochem. Soc., 21, 257; Jour. Phys. Chem., 16, 298 (1912).

duced to copper.[1] Thus the concentration of cuprous ion is kept at practically zero, with a consequent strong tendency to form them. This process, however, is probably reversible, for the solution of copper in copper sulphate, generates a higher voltage when the copper is rotated, the voltage increasing with rotation. This formation of ions of intermediate valency in concentrations above equilibrium differs from the cases considered above in that the intermediate ions are in the solution film, while the free intermediate atoms are in the electrode film. The former substances may decompose, being transformed into electricity, while the decomposition of the latter products cannot yield electricity, since they are in electrical contact with the electrode, and therefore short circuited. The excess energy required to form such products must therefore appear finally as heat.

With reference to the reducing power of the intermediate state of the metals, zinc for instance (Zn_1), it may be definitely said that it has a stronger reducing action than hydrogen liberated at the surface of a zinc electrode, for it has been shown that reductions can be performed during the deposition of zinc from sodium zincate,[2] which are not accomplished or are not carried out with such speed if a zinc cathode and sodium hydroxide as electrolyte be used. For instance, fifteen times more indigo white was formed from indigo blue when zinc was simultaneously precipitated than when hydrogen was liberated at a zinc cathode in sodium hydroxide. This cannot be due to the specific effect of the metal itself on the reaction, for zinc and acid do not reduce indigo blue. This can only mean that some substance is formed during the deposition of zinc which is a stronger reducing agent than massive zinc.

Several other cases of such intermediate action, showing unquestionable irreversibility, are also well known. The most

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[1] See Bennett and Brown: Trans. Am. Electrochem. Soc., 23, 383 (1913); Jour. Phys. Chem., 17, 373 (1913); Reichinstein: Zeit. Elektrochemie, 18, 850 (1912).

[2] Binz: Zeit. Elektrochemie, 5, 5, 103 (1898); Binz and Hagenbach: 6, 261 (1899); Zeit. angew. Chem., 1899, 489; Löb: Zeit. Electrochemie, 2, 532; 3, 42 (1896); 4, 428 (1898); Haber: Zeit. phys. Chem., 32, 258 (1900).

common case[1] is the reduction of nitrates to ammonia. It is claimed by Shinn that it is best to have copper sulphate in the solution throughout the reduction at a copper cathode. The reduction to ammonia will go on, however, without the simultaneous deposition of copper.[2] With a nitrate solution, copper cathode and zinc anode, with a diaphragm, four Grove cells being used, (probably 7–7.5 V) the solution contained one part of ammonia to 20 parts of nitrite after four hours. The zinc copper couple at 15° C gives complete reduction after 24 hours. Smith's analytical method, with copper depositing, is complete after about one-half hour, using 4–5 amperes with a voltage of not over ten volts. It is certain therefore, that copper simultaneously deposited, helps in the reduction.

From what has been said above, it is evident that the intermediate products formed in the passage from dissolved ion to elementary material, as it is commonly known, are more active than either of the materials started with. In other words, in the case of hydrogen and the metals, the products are stronger reducing agents, while in the case of oxygen, chlorine, etc., the products are stronger oxidizing agents.

Let us now consider by how much the processes discussed above are irreversible. Langmuir[3] has calculated that the heat of formation of hydrogen molecules from active hydrogen is 90,000 calories. In passing from the dissolved ion to gaseous molecules if all of the ions went to H_1 which broke down generating heat only, and the reverse reaction generated no H_1 the reaction would be irreversible by 90,000 calories per 2 grams of hydrogen. This in terms of intensity would be

$$E = \frac{90{,}000 \times 4.18}{2 \times 96{,}500} = 1.9 \text{ volts.}$$

In other words, under these conditions of maximum irreversibility, electrical energy of 1.9 volts greater intensity would

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[1] Luckow: Zeit. anal. Chem., 19, 11 (1880); Easton: Jour. Am. Chem. Soc., 25, 1042 (1903); Shinn: Ibid., 30, 1378 (1908); Smith: Electroanalysis, p. 292; Wohl: Ber. deutsch. chem. Ges., 27, 1437, 1817 (1894); Tommasi: Mon. scientifique, (4) Ser. XII, 182 (1898).

[2] Gladstone and Tribe: Ber. deutsch. chem. Ges., 11, 717, 722 (1878).

[3] Jour. Am. Chem. Soc., 37, 457 (1915).

be required to form hydrogen gas molecules than that given by the reverse reaction. As a matter of fact, this maximum value could never be reached for the reverse reaction requires necessarily a definite equilibrium of active hydrogen. This calculation serves to show that the intermediate product, which has been isolated, has an activity of sufficient magnitude to account for differences found experimentally.

Let us next inquire into the case of zinc. Suppose we take the first product of electrolysis Zn_1, as analogous to vapor. The molecular heat of vaporization of zinc from Trouton's law is (950° + 275°) 20 = 24,460 calories approximately, while the molecular heat of fusion is 1840 calories, representing, as assumed above, irreversibility to the extent of 26,300 calories per gram molecule of zinc, or in terms of intensity

$$E = \frac{26{,}300 \times 4.18}{2 \times 96{,}500} = 0.56 \text{ volt.}$$

In other words, electrical energy of 0.56 volt would be used in depositing zinc, over that given by its solution if during precipitation all of the metal went through the Zn_1 stage analogous to vapor, and during the reverse reaction none of the metal went through this stage. This maximum value could not be reached, however, for the same reason as given in the case of hydrogen. If we take platinum or gold, place it in hydrogen gas and heat it to 300–400° C, it is found that the potential of the metal[1] is —1.5 volts, as a maximum at 370°. That for oxygen under these conditions is +0.8 volt, as a maximum. The maximum value is obtained when the gas pressure is lowered. The voltage generated is therefore due to the dissolved gas coming out of the metal into the gas phase.

When hydrogen or oxygen ionizes in a solution at the surface of platinum, for instance, the molecule dissociates, giving H_1 or O_1, which assumes a charge or charges becoming dissolved ion. The process goes on in two steps and equilibrium concentrations are maintained. The process is therefore not reversible as has been pointed out above. When, how-

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[1] Hartley: Proc. Roy. Soc., **90A**, 61 (1914).

ever, hydrogen gas dissolves in gold, it is probably present as H_1; when this comes out into the gas phase, the reaction $H_1 \longrightarrow H_2$ is carried on. This reaction is in one stage, and represents the energy which is lost in carrying out the electrochemical reaction, hydrogen ion to hydrogen gas. There is one case where the maximum value of hydrogen overvoltage may be obtained. In order to measure its value, it is necessary to carry out the reaction $H_1 \longrightarrow H_2$ in one stage without the possibility of conflicting reactions.

It is evident that there are intermediate products between dissolved ions and free gaseous molecules, or solid crystallized metals, the preparation of which requires more energy than is yielded by the opposite reaction. The activity of these substances is wholly sufficient to account for the irreversibilities found experimentally in the case of hydrogen and zinc. It is only necessary to show how the plan may be formulated to explain overvoltage.

In the production or decomposition of one equivalent of zinc, one faraday of electricity is required or formed. The intensity or voltage is greater by about 0.10 volt for the precipitation than that given by the resolution of the zinc. This over or excess voltage is a measure of the irreversibility of the process. Hydrogen requires up to 0.75 volt more to precipitate than is yielded by the reverse reaction, depending on the metal at which it is deposited, and other conditions. Oxygen requires up to about 0.60 volt in excess of that given by the solution and ionization of the gas. This excess voltage is a direct result of an irreversible process, several cases of which have been discussed above. The mechanism of the reaction is just this. The voltage generated during solution is due to molecular material going to atomic material which ionizes. The atomic material is present only in equilibrium concentrations. In the reverse direction the voltage must be sufficient to build the concentration up beyond equilibrium else the reaction would not go on. The over or excess voltage will be low if the reaction

atomic material ⟶ molecular material

is rapid, so that a low concentration of atomic material is had. If this reaction is slow the overvoltage will be high for a high concentration of active material above equilibrium will be obtained. The overvoltage of gases will depend on the building up of concentrations above equilibrium of active or atomic material, while that of the metals will depend on atomic metal (M_1). The former will vary with the metal of the electrode and the nature of the solution, for these must have a catalytic influence on the reaction

atom ⟶ molecule.

The overvoltage should be low where the metal shows strong catalytic action. This is actually found.[1] Overvoltage of metals, however, is simpler since it can exist only at its own surface, since the metal has to be deposited to exhibit this property and have it measured. In fact since overvoltage is dependent on the reaction, ion to molecule, in any case, we should expect to find that when a stationary state is reached, the only factors which can vary overvoltage are factors which change this reaction. We know, for instance, that reactions are hastened by an increase in temperature We should expect an increase in temperature to show a decrease of overvoltage. This has been noted many times and is seen in Table II,[2] which gives the overvoltage of hydrogen at a copper cathode. The current density was 1 milliampere per square cantimeter.

TABLE II

Temperature	Overvoltage
11.5°	0.33
20.0	0.31
30.0	0.28
45.0	0.27
60.0	0.25

Thus when the reaction is hastened by raising the temperature or when catalytic agents are present the overvoltage

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[1] Lewis and Jackson: Zeit. phys. Chem., 56, 193 (1906); Berliner: Wied. Ann., 35, 791 (1888).

[2] Pring and Curzon: Loc. cit.

is low because the concentration of atomic material is kept low.

Conversely, it must be expected that any condition which tends to cause or allow the building up of concentrations of the active intermediate products above equilibrium, would raise the overvoltage by an amount depending on how much the concentration exceeds equilibrium values.

It is plain, too, that when conditions are right for low overvoltage, the reaction $2H_1 \longrightarrow H_2$, for instance, takes place immediately, and therefore at the surface of the electrode, while as the overvoltage increases the sphere of the reaction moves further below the surface of the electrode. In other words, the conception of "electrode volume"[1] varying *directly* with overvoltage, is valid. This, however, has a more important bearing with reference to the ionization of the gas formed, which will be mentioned later.

Let us next consider some of the conditions which should give rise to higher concentrations of intermediate products and therefore higher overvoltage. An increase in current density, other conditions being the same, should increase the concentration of active intermediate products. As a matter of fact the overvoltage increases with the current density, as the following table[2] shows:

TABLE III

Current density milli-amperes per sq. cm	Hydrogen overvoltage at			Oxygen overvoltage at platinum	Zinc over-voltage at zinc
	Lead	Platinum	Mercury		
10	0.62	0.06	0.54	0.56	0.089
20	0.64	0.06	0.45	0.56	0.089
40	0.71	—	—	—	—
50	0.70	0.06	0.40	0.56	0.090
100	0.67	0.07	0.30	0.56	0.091
200	0.66	0.08	0.07	0.56	0.092
300	0.64	0.08	0.08	0.55	0.094
500	—	0.05	0.04	0.55	0.094
1000	—	0.03	—0.01	0.55	0.095
2000	—	—0.03	—0.05	0.54	0.096

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[1] Reichinstein: Loc. cit.

[2] Newbery: Ibid.

The overvoltage increases to a maximum with current density in the case of hydrogen at lead and platinum, and at higher currents decreases. It decreases at the surface of mercury, while oxygen overvoltage decreases slightly at high current densities. Zinc overvoltage increases steadily. If lower current densities had been used, hydrogen at mercury and oxygen at platinum would have shown maxima also. The decrease of overvoltage at high current density is to be explained in part by the rise in the temperature which we have seen lowers the overvoltage, but largely on account of the fact that the concentration of H_1 and O_1 becomes so great that they are forced to break down as soon as formed; namely, at the surface of the electrode. The highest current density used, it may be seen, is 200 amperes per square decimeter, which means that the electrode will all but be covered by a film of gas. In such concentrations it may be seen that the intermediate products would be so unstable that they would form molecular gas immediately. This is equivalent to saying that the ion goes directly to molecular gas, more or less reversibly. This would occur at the surface of the electrode. It is evident, therefore, that too great an increase of current density may tend to lower the concentration of active material by reason of having increased the speed of decomposition. In this case it is conceivable that the atoms lose their charge in close proximity to each other, and at the temperature used they combine at once, forming molecules. In fact Langmuir assumes that the formation and condensation of active gases takes place by the dissolved gas (in platinum or tungsten), which is in the atomic form, being driven out, traversing to the glass wall, which is cooled, without striking another atom. There is little doubt, therefore, that if these atoms come together they would react immediately. Furthermore at the enormous current densities used, there is little doubt but that the atoms are formed in close enough proximity to come together. Thus the reaction of decomposition would be hastened and therefore the overvoltage lowered.

The case of overvoltage of zinc at a zinc electrode is different in that it steadfastly increased, although the increase is slight above 30 amperes per square decimeter. The reaction is different here, in that zinc atom goes to a polymerized complex consisting of half dozen or more atoms. It is evident, that the polymerization of atoms to form a molecule of two atoms in the same state of aggregation may easily become instantaneous, but the polymerization to a molecule of half dozen or more atoms, going first to the complex representing the liquid, then the solid, and finally crystallizing, could not be instantaneous. Thus the effect is different with metals than with gases.

Besides the general effect that metals which show slight catalytic effect on the reaction causing irreversibility, show high overvoltage, the hardness of a specific metal may influence this phenomenon. A hard copper electrode[1] gives a higher overvoltage than one of soft copper. On the other hand, higher values are obtained with soft iron than hard iron. Electrolytically deposited copper gives maximum values while electrolytically deposited iron and nickel give minimum values. It should be noted that a low current density (0.1 ampere per square decimeter) was used. From the foregoing discussion the explanation is probably this. The electrolytic metal is hard, therefore we have to consider only the cases that hard copper and soft iron and nickel give maximum values of overvoltage. Nickel and iron are metals which take up hydrogen but do not readily catalyze the reaction $H_1 \longrightarrow H_2$. Copper neither takes up hydrogen nor catalyzes the reaction. Soft iron and nickel would, therefore, take up more active hydrogen but the reaction of formation of molecules would not be faster than with hard metal. Thus the overvoltage would be increased by an amount depending on how much the concentration of active hydrogen is raised in the metal. In the case of copper, since practically no hydrogen is taken up, the change in the hardness does not effect the concentration of active hydrogen as in the other case. Hardening the metal

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[1] Pring and Curzon: Loc. cit.

serves only to confine the action to the surface and may be considered equivalent to an increase in current density.

The overvoltage probably always increases with time to a maximum and then remains constant or falls off slightly. The following values[1] illustrate this:

TABLE IV—OVERVOLTAGE WITH HYDROGEN AT PLATINUM

After minutes	At milliamperes per square centimeter	
	300	400
1	0.076	0.060
5	0.080	0.068
15	0.088	0.092
30	0.100	0.104
hours		
1	0.112	0.120
6	0.173	0.236
12	0.471	0.200
24	0.511	0.120
5 min. off	0.08	—
10 min. on	0.122	—

These effects must be explained by assuming that the maximum concentration of active products, or saturation is not reached for a definite time. The addition of colloids tends to minimize time effects. The addition of colloids tends to raise the overvoltage of gases. This may be due to an increased adsorption of active gas, and a consequent increase in the stability.

Metal overvoltage is practically not affected by colloids, it being slightly raised in one case and lowered in another. From what has been said, this reaction is not affected by changes in conditions as much as the reactions in the formation of gases. This is particularly noticeable in that accurate and consistent results[1] are easily obtained here, while variation of 5 millivolts with hydrogen overvoltage at platinum and lead cathodes and of from 5–500 millivolts at mercury are encountered.

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[1] Newbery: Loc. cit.

The effect of change of pressure on overvoltage has been studied,[1] and should be mentioned here. It was found that an increase of 100 atmospheres on the hydrogen gas pressure did not appreciably change the hydrogen overvoltage. This follows directly from the theory outlined above. There is practically no H_1, active hydrogen, in the gas above a solution and electrode during electrolysis. At least, we have found it impossible to obtain reduction of zinc oxide by placing it very close to the cathode during electrolysis. An increase of the gaseous hydrogen (H_2) pressure would not increase the pressure of H_1 as such. A change of pressure can only change the solubility of H_2 in the electrode. When, however, hydrogen dissolves in a metal, it is generally present in the atomic state, which means that when the concentration of H_2 in the electrode is increased, there is an equivalent increase in the H_1 concentration. Any change of pressure, therefore, changing the concentration of H_2 tending to change the reaction $H_1 \longrightarrow H_2$ must be accompanied by an equivalent change in the concentration of H_1 in the same direction tending to hold the reaction velocity constant. Therefore, very slight effects on overvoltage of gases should be noted by changing the gaseous pressure.

Another important property of gases newly formed by electrolysis, is their ionization.[2] It has been shown that the charge carried by the gas may vary with the conditions, and also that the quantity of ionization[1] varies inversely with the overvoltage of the gas. For instance the metals arrange themselves in the order of decreasing ionization of hydrogen gas, thus:

$$\mathrm{Pt} - \mathrm{Cu} - \mathrm{Pb} - \mathrm{Hg},$$

which is the order of increasing overvoltage. In the case of hydrogen which has been studied, the ions[3] possible are

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[1] Newbery: Loc. cit.

[2] Townsend: Proc. Camb. Phil. Soc., 5, 9 (1897); Phil. Mag., (5) 45, 125 (1898).

[3] Townsend: Phil. Mag., (6) 7, 276 (1904); Proc. Roy. Soc., 80A, 207 (1908); 81A, 464 (1908); Kleeman: Proc. Camb. Phil. Soc., 16, Pt. 4, 286 (1911); Pt. 7, 621 (1912).

$\overset{-}{H_1}$, $\overset{+}{H_1}$ and $\overset{+}{H_2}$. The latter ion is the ordinary gaseous ion, and is probably formed from gaseous hydrogen by the loss of an electron. At atmospheric pressures, the quantity of the ionized material relative to the unionized is very small indeed.[1] Furthermore, it is not difficult to ionize a gas. Ionization is caused by escaping steam,[2] when a cloud of dust is raised[3] and near waterfalls. Ionization may be produced by collisions[4] of other ions and under such conditions the voltage required for ionization of hydrogen is only about eight volts. It is beyond the scope of this paper to show the mechanism of the reaction of ionization of gases during electrolysis. One or two conclusions may be pointed out, however, which may throw some light on the subject. It has already been noted that as the overvoltage becomes low, the sphere of the reaction moves to the surface of the electrode, that is, the reaction $H_1 \longrightarrow H_2$ is instantaneous. Now since ionization means the setting free of charged particles of material, and since these charged particles exist as dissolved ions, that is, in the solution up to the metallic surface of the electrode, it necessarily follows that as the reaction of formation of gas approaches the surface, there exists greater possibility of contaminating the free H_2, for instance, with charged products. Thus the ionization should increase as the reaction approaches the surface of the electrode. In other words, the ionization should increase with decreasing overvoltage, as is actually found.

One suggestion as to the mechanism of the reaction might be made. If conflicting conditions are absent, only positively charged hydrogen is obtained at the cathode. In other words only under such conditions as the removal of positive hydrogen, is the gas charged negatively. How is the positively charged hydrogen freed, if we neglect temperature and mechanical

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[1] Kleeman: Loc. cit., p. 286.

[2] Rudge: Proc. Camb. Phil. Soc., 18, 127 (1915).

[3] Rudge: Proc. Roy. Soc., 90A, 256 (1914).

[4] Pawlow: Ibid., 405 (1914).

effects? At the surface, the concentration of reacting material must be high. It is possible that the gas (H_2) carries mechanically with it a small quantity of the ions in solution, just as in distillation liquids may carry small quantities of liquids or solids over even though the former be in the vapor state. The quantity need not be weighable, and the possibility of contamination is greater since these substances are probably in the same state of aggregation. In this way the gas might become charged positively by means of $\overset{+}{H}_1$ which is the same as the dissolved ion. The gas, however, is most often charged by means of $\overset{+}{H}_2$, since this is the ordinary gaseous ion. This may be obtained by the reaction of one atom of active hydrogen with one positive ion from the solution, thus:

$$H_1 + \overset{+}{H} \longrightarrow \overset{+}{H}_2$$

This reaction would increase as the sphere of the general reaction approached the surface bounding the heterogeneous system. It would therefore vary inversely with the overvoltage. From this viewpoint, therefore, it follows that ionization of the newly formed gases should vary inversely with the overvoltage of that gas.

From what has been said above, it may be concluded, that:

1. Any chemical reaction, consisting of more than one step, in generating electricity cannot be strictly reversible, but requires more electrical energy to reform the substances than is given by the reverse reaction.

2. This irreversibility gives rise to over or excess voltage, since the quantity factor is constant.

3. A general definition of overvoltage has been given.

4. A general and more elaborate theory of overvoltage has been developed.

5. This theory is that the excess of the back electromotive force of the system during electrolysis over the reversible electromotive force of the system consisting of the final products, is due to the accumulation *during such electrolysis, of*

instable intermediate product; above the equilibrium concentration.

6. These products are unquestionably active hydrogen, H_1, active oxygen, O_1, and etc., in case of gases, and M_1, atomic metal analogous to vaporized metal in the case of metal overvoltages.

7. These products have been shown to be more reactive than the final products, and are sufficiently active to explain overvoltages found experimentally.

8. Active hydrogen has been shown capable of reducing cadmium from cadmium sulphate solutions, and reducing zinc from zinc oxide.

9. The theory put forward satisfactorily explains the known facts of overvoltage, a condition not satisfactorily met by previous theories.

Ithaca, N. Y.

THE TAUTOMERISM OF THE AMIDES

BY H. A. LUBS AND S. F. ACREE

[Nineteenth[1] Communication on Tautomerism]

Theoretical

The constitutional formula of amides in general is usually written in the form $RC(:O)NH_2$. Evidence has been obtained, however, which seems to indicate that an amide may also have the constitution $RC(:NH)OH$. Tafel and Enoch[2] found that when the silver salt of benzamide was treated with ethyl iodide, and the reaction allowed to take place at room temperature, a benzimidoethyl ester was formed instead of the expected benzethylamide. Wheeler and Johnson[3] found that when benzimidoethyl ester was heated with ethyl iodide in a sealed tube at 100°, the imidoester was rearranged into ethylbenzamid. They concluded that the amides are not tautomeric, but that the above mentioned isomeric products were formed by a rearrangement of one form.

Matsui[4] prepared both aliphatic and aromatic imidoesters by the action of dimethyl sulphate on various amides at temperatures below 100°. He believed that the formation of the imidoester took place by direct alkylation of the enolic form and not by the addition of the dimethyl sulphate to the ketonic form, with subsequent rearrangement.

Stieglitz and Ransom[5] prepared chlorimidomethyl benzoate, $C_6H_5.C(NCl).OCH_3$, by the action of diazomethane, CH_2N_2, on benzoylchloramide, $C_6H_5.CO.NHCl$.

The above evidence is not sufficient to enable one to decide

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[1] This work was presented in June, 1914, by H. A. Lubs as a partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University. We are indebted to the Carnegie Institution of Washington for aid in this work.

[2] Ber. deutsch. chem. Ges., 23, 103 (1890).

[3] Am. Chem. Jour., 21, 185 (1899).

[4] Mem. Coll. Sci. Eng. Kyoto, 2, 397-400, 37-45.

[5] Ber. deutsch. chem. Ges., 34, 1615 (1901).

whether amides in general are tautomeric or whether they exist in only one form. In the cases of alkylation reactions discussed above, the investigators did not work quantitatively as we did in studying the urazoles, hence they easily could have overlooked the presence of one compound if formed in small amount.

We have begun a quantitative study of amides and thioamides along the lines developed for the urazoles,[1] in order to determine whether they are really tautomeric compounds or whether only one compound is formed upon alkylation and this then rearranges into the isomeric alkyl derivative. Since an isomer of glycolamide has already been made by Steiner,[2] Plinke,[3] and Eschweiler,[4] we have selected this as the first amide to investigate. Glycolamide, $CH_2OHC(:O)NH_2$, melts at 120° and its isomer, glycolimidohydrin, $CH_2OHC(:NH)OH$, melts at 160°. The methods described for making the latter compound were found to be very unsatisfactory, as the yield is very poor. Work is now in progress to devise a method of obtaining this compound in larger yield.

Preparation of Compounds

Glycollic acid nitrile: This compound was prepared by mixing equivalent amounts of 90 per cent hydrocyanic acid and 35 percent formaldehyde and allowing the reaction mixture to stand for several days. It was found that the addition of less than $^1/_2$ cc of aqueous ammonia catalyzed the reaction to such an extent that vigorous ebullition took place. The greater part of the water was removed by distillation *in vacuo* at 30 to 40 mm pressure. The nitrile remaining in the flask was dissolved in ether and dried with anhydrous copper sulphate. The ether was then filtered off, evaporated and the nitrile fractionated *in vacuo*. The yield varied from 70–80 percent.

Dry glycollic acid nitrile can be distilled at 760 mm pres-

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[1] For references to the earlier articles see Esslinger and Acree: Jour. Am. Chem. Soc., 37, 185 (1915).

[2] Diss. Hannover, 1896.

[3] Diss. Hannover, 1898.

[4] Ber. deutsch. chem. Ges., 30, 998–1003 (1897).

sure with only slight decomposition. It boils at 103° at 16 mm pressure. When heated *in vacuo* with a small amount of water at a temperature of 60–80° it decomposed suddenly with evolution of heat and changed over into a black, tarry mass. When the nitrile is heated with larger quantities of water, the greater part of the water can be distilled off *in vacuo* without the nitrile undergoing any appreciable decomposition.

Glycolimidoester hydrochloride: This substance was prepared by the method of Pinner[1] from glycollic acid nitrile. The yield of this product is practically quantitative.

Glycolimidohydrin: Steiner obtained this compound by adding the imidoester hydrochloride mixed with ether to a 33 per cent solution of potassium carbonate in water. The ethereal layer was pipetted off and the solution extracted further with ether. The ethereal extract was then heated with water. The residue remaining after evaporation of the solvents was recrystallized several times from absolute alcohol. We found that this method yielded only a few tenths of a gram of the imidohydrin from 20 grams of the imidoester hydrochloride. Plinke's method, though unsatisfactory, was found to be much better. He neutralized the imidoester hydrochloride by adding it in small portions to a suspension of freshly precipitated, alkali-free, silver oxide in cold water. At the same time the free imidoester is saponified to the imidohydrin. The solution is filtered, treated with hydrogen sulphide, and again filtered. It is then evaporated to dryness and the residue recrystallized as before. By this method about 0.5 g. of the imidohydrin was obtained from 10 grams of the imidoester hydrochloride. The reason why the yield is poor is because the imidoester hydrochloride is rather unstable and is readily decomposed by water. The imidohydrin melts at 160°.

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[1] Pinner: "Die Imidoather und Ihre Derivate," 2.

ACTIVITY AND CONCENTRATION, TRANSPORT NUMBERS, AND BOUNDARY POTENTIAL[1]

BY ALFRED L. FERGUSON

Introduction

In this investigation of the relation between activity and concentration, a new form of cell was used which permits of two new methods for measuring transport numbers and a direct method for measuring boundary electromotive force.

There are various types of concentration cells, but the type which has excited the most interest and stimulated the greatest amount of experimental and theoretical investigation is that one in which the electrodes are of the same material, but dip into solutions of different concentrations of the same electrolyte. An extensive investigation of such cells was carried out by Hans Jahn. His primary object was to test the existing formulas and theories of solutions when applied to dilute and moderately concentrated solutions of strong electrolytes. From his work Jahn felt justified in concluding: (1) that conductivity measurements do not give satisfactory values for the degree of dissociation; and (2) that the mobility of the ions is a function of the concentration increasing with increasing concentration. These are remarkable conclusions and constitute a blow aimed directly at the formula $\alpha = \mu_v/\mu_\infty$ of Arrhenius for calculating the degree of dissociation. Naturally they provoked much discussion and criticism. The principal participants in this discussion were H. Jahn,[2] Arrhenius,[3] Nernst,[4] Lehfeldt,[5] Goebel,[6] Sand,[7] Planck,[8] and Kruger.[9]

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[1] Contribution from the Chemical Laboratory of the University of Michigan.

[2] Zeit. phys. Chem., 35, 1 (1900); 36, 453; 37, 490; 38, 125 (1901); 41, 257 (1907).

[3] Ibid., 36, 28; 37, 315 (1901).

[4] Ibid., 36, 596; 38, 487 (1901).

[5] Ibid., 35, 257 (1900).

[6] Ibid., 42, 54 (1902).

[7] Ibid., 36, 499 (1901).

[8] Ibid., 41, 212 (1902).

[9] Ibid., 36, 86 (1901).

As a result of this discussion, Jahn was forced to admit several mistakes in his reasoning, but he maintained to the end that the above stated conclusions were justifiable. For a while, however, his work was rather discredited, but within the past fifteen, and particularly within the last five years, results have been obtained supporting his conclusions: Such for instance, as the investigation of F. Flugel[1] on the freezing point lowering and conductivity of very dilute solutions. The study of concentration cells with thalium electrodes by Lewis and Von Ende.[2] The investigation, by Lewis and Edgar,[3] of the equilibrium between nitric acid, nitrous acid, and nitric oxide. The influence of one salt on the solubility of another as worked out by Bray.[4] The work of Washburn and MacInnes[5] on the freezing point lowering and conductivity of cesium nitrate. And an earlier investigation by the author in conjunction with R. C. Tolman[6] on the free energy of dilution of hydrochloric acid.

In this earlier investigation it was concluded that the ratio of concentrations of ions was in every instance greater than the ratio of their activities, while the concentration ratios for the undissociated acid were in every case less than the activity ratios. The variation was found to be much greater for the undissociated acid than for the ions. In all these calculations one concentration was tenth normal and the other was something less. A form of cell was used that eliminated transport numbers.

Theoretical

The application of thermodynamic theory to physicochemical measurements is rapidly increasing in importance and nowhere is it more important than in connection with such cells as form the subject of this investigation.

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[1] Zeit. phys. Chem., 79, 577 (1912).

[2] Jour. Am. Chem. Soc., 32, 737 (1910).

[3] Ibid., 33, 292 (1911).

[4] Ibid., 33, 1673 (1911).

[5] Ibid., 33, 1686 (1911).

[6] Ibid., 34, 232 (1912).

The work which a reversible cell is capable of furnishing must equal its electromotive force times the quantity of electricity passing through the cell. That is, $w = EF$ per equivalent, where F equals one Faraday and E equals electromotive force.

Suppose we consider a hydrochloric acid concentration cell with calomel electrodes and the acid on the two sides having the concentrations C_1 and C_2. When one equivalent of electricity passes through the cell, the following changes take place: On the concentrated side, one equivalent of Cl ion will be removed to combine with the equivalent of Ag ion formed; N_a equivalents of Cl ion will migrate in from the dilute side, where N_a represents the transport number for the Cl ion. On the dilute side one equivalent of Cl ion will form; N_a equivalent of Cl ion will migrate out to the concentrated side, and $1 - N_a$ equivalents of H ion will migrate in from the concentrated side. The net result is then the disappearance of N_a equivalents of HCl from the concentrated side and the appearance of N_a equivalents on the dilute side, or, in other words, the transfer of N_a equivalents of HCl from one concentration to another. The electromotive force of such a cell multiplied by one Faraday gives the free energy of dilution of N_a mols of HCl, so the free energy per mol is $\frac{EF}{N_a}$. This is the type of cell used by Jahn in his measurements of free energy. The objections to this type of cell have been pointed out in an earlier paper.[1]

Let us now consider the conception developed by Lewis[2], which he calls activity. This quantity is defined by the following conditions:

1. "The activity of a molecular species is the same in two phases when these phases are in equilibrium as regards the distribution of that species."

2. "The activity of a gas approaches the gas concentration as a limiting value if the gas is indefinitely rarefied."

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[1] Loc. cit.

[2] Proc. Am. Acad., 43, 257 (1907).

In an earlier paper[1] he developed another quantity which he called "escaping tendency."

In yet another[2] he uses the same conception but calls it, for brevity, "fugacity." The quantity fugacity has the dimensions of pressure while activity has the dimensions of concentration, and the two are connected by the formula $a = \frac{\psi}{RT}$, where a represents activity, ψ fugacity, R the gas constant and T the absolute temperature.

Let us apply this activity conception to a hydrochloric acid concentration cell. If the activities of undissociated HCl in the two solutions be represented by a'_{HCl} and a''_{HCl} and the activities of the ions by a'^{+}_{H}, a''^{+}_{H}, a'^{-}_{Cl}, a''^{-}_{Cl} then by substituting in the equation for free energy

$$F = EF = RT\,ln\,\frac{a_2}{a_1}$$

we have for the free energy change, accompanying the transfer of one mol of HCl from one solution to the other

$$F = EF = RT\,ln\,\frac{a''_{HCl}}{a'_{HCl}} = RT\,ln\,\frac{a''^{+}_{H} \times a''^{-}_{Cl}}{a'^{+}_{H} \times a'^{-}_{Cl}}.$$

We may assume also that $a'^{+}_{H} = a'^{-}_{Cl}$ and that $a''^{+}_{H} = a''^{-}_{Cl}$, then

$$EF = 2RT\,ln\,\frac{a''^{+}_{H}}{a'^{+}_{H}} = 2RT\,ln\,\frac{a''^{-}_{Cl}}{a'^{-}_{Cl}} = RT\,ln\,\frac{a''_{HCl}}{a'_{HCl}}. \quad (1)$$

This equation applies to concentration cells without boundary potential.

For concentration cells having boundary potential, and reversible with respect to the anion, we have the well known formula,

$$E_1 = 2\,\frac{N_c RT}{F}\,ln\,\frac{a''^{+}_{H}}{a'^{+}_{H}}. \quad (2)$$

If the cell is reversible with respect to the cation the formula becomes

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[1] Proc. Am. Acad., 36, 145 (1900).

[2] Ibid., 37, 49 (1901).

$$E_2 = 2\frac{N_aRT}{F} \ln \frac{a''_{\overline{Cl}}}{a'_{\overline{Cl}}}. \tag{3}$$

A combination of (1) and (2) gives $N_c = \frac{E_1}{E}$.

A combination of (1) and (3) gives $N_a = \frac{E_2}{E}$.

Since $N_c + N_a = 1$, we have a very good check on our work, as both of these can be determined. Also, since $N_c + N_a = \frac{E_1 + E_2}{E} = 1$, it is evident that $E_1 + E_2 = E$.

A consideration of these equations shows that all that is necessary, then, to measure the transference number of the hydrogen ion is to measure the electromotive force of a concentration cell with transference and without using hydrogen electrodes. The transference number of the chloride ion in the same solution could be determined in a similar way by using calomel electrodes.

It is a well known fact that the surface of contact between two solutions is a source of potential difference. This potential difference between solutions has been one of the greatest stumbling blocks in the way of potential measurements of concentration cells. Those who have made such measurements have attempted to avoid it in one way or another or dismissed it entirely with the statement that it was too small to consider.

The first investigator to give a reasonable explanation for this liquid potential was Nernst.[1] He based his explanation on the unequal velocities of migration of the ions. Suppose, for example, a concentrated and a dilute solution of hydrochloric acid are in contact. The hydrogen ions and the chloride ions of the concentrated solutions diffuse into the dilute side. But the hydrogen ions travel with a much greater velocity than the chloride ions and, since they carry positive charges and the chloride ions negative charges, the dilute solution becomes positive with reference to the concentrated. This separation cannot take place to any appreciable extent, however, because of the attraction between these electrostatic

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[1] Zeit. phys. Chem., 4, 129 (1889).

charges. The result of this attraction is to increase the velocity of the chloride ions and lessen the velocity of the hydrogen ions till eventually both travel with the same velocity, with the hydrogen in the lead; thus an electrical double layer is formed with its accompanying difference in potential. Nernst not only gave this explanation for the phenomena but he also derived a formula for calculating the values of such potential differences. With activity substituted for concentration the formula derived by him takes the form

$$E = \frac{(1 - 2N_a)RT}{F} \ln \frac{a_1}{a_2}.$$

A consideration of the HCl concentration cell, reversible with respect to the chloride ion, shows that the boundary potential acts in the same direction as the electrode potentials, while in the HCl concentration cell, reversible with respect to the hydrogen ion, the boundary potential is opposed to the electrode potentials. Thus it is evident that this boundary potential is equal to one-half the difference between the electromotive forces of such concentration cells, and, therefore, the measurement of contact potential between solutions differing only in concentration of the same electrolyte resolves itself simply into the simultaneous measurement of the electromotive force between electrodes which furnish the positive ions in the solution and the electromotive force between electrodes which furnish the negative ions. Or, in the case of hydrochloric acid, the measurement of the electromotive force of the hydrogen concentration cell and at the same time the measurement of the electromotive force of the calomel concentration cell.

The formula for the electromotive force of a concentration cell without boundary potential shows that the only variables are the activity ratio and the electromotive force. If one of these is measured the other may be calculated. The concentration ratio can be calculated from conductivity measurements. The expression for the ratio of ion concentrations is $\frac{c''^{+}_{H}}{c'^{+}_{H}} = \frac{\alpha'' n''}{\alpha' n'}$, where α'' and α' are the degrees of dissociation at normalities n'' and n'. The ratio of undissociated acid is $\frac{c''_{\mathrm{HCl}}}{c'_{\mathrm{HCl}}} = \frac{n''(1-\alpha'')}{n'(1-\alpha')}$.

As has been stated, the conclusion was drawn in an earlier paper that the ratios of ion concentrations calculated from conductivity measurements were in every instance greater than the measured ratios of activities, while the ratios for the undissociated acid were in every case less than the activity ratios. Many have realized that this great variation between observed and calculated values should be more thoroughly investigated. These discrepancies between the activity ratios and concentration ratios for both the ions and un-ionized acid can be accounted for in either of two ways. It may be that conductivity measurements give the true value for the degree of dissociation, in which case activity and concentration are not proportional. Or, it may be that activity and concentration are proportional, in which case conductivity measurements can no longer be considered a true measure for ion concentration. The fact that activity and concentration have been shown to be proportional for all ordinary solutions of nonelectrolytes and even for weak electrolytes makes the second of the above alternatives the more probable. In view of this, a careful investigation of the basis for Arrhenius' formula, $\alpha = \frac{\mu_v}{\mu_\infty}$, is likely to reveal something of interest.

The conductivity of a liquid is the current density under unit potential gradient and may be represented by

$$k = F\alpha C(U_a + U_c),$$

where F represents one Faraday, α the degree of dissociation, C the total concentration in gram equivalents per cubic centimeter, U_a the mobility of the anion and U_c the mobility of the cation.

If this specific conductivity is multiplied by the volume V containing one equivalent, it gives the equivalent conductivity which may then be represented by

$$\mu = F\alpha CV(U_a + U_c) = F\alpha(U_a + U_c).$$

As the dilution increases, it is an observed experimental fact that α increases up to a certain limiting value characteristic for each electrolyte. According to the dissociation theory, the explanation for this is that the dissociation becomes greater the greater the dilution up to a certain limit for each electrolyte where $\alpha = 1$. The formula for the equivalent conductivity at this point of complete dissociation would then become $\mu = F(U_a + U_c)$. By a combination of this formula with the one for the equivalent conductivity at any dilution, V, there is obtained an expression

$$\frac{\mu_v}{\mu_\infty} = \frac{F\alpha(U_c + U_a)}{F(U_c + U_a)} = \frac{\alpha(U_c + U_a)}{(U_c + U_a)}.$$

In the numerator of this fraction, U_a and U_c represent the mobilities of cation and anion at the dilution V, while in the denominator the same terms represent the mobilities at infinite dilution. It is evident then, in order that the formula of Arrhenius shall be true, that the mobilities of the ions must be independent of the concentration. It is this assumption that introduces the greatest doubt into this method for calculating ion concentration.

It was with the object of determining whether the ions change their mobility with concentration, that the author devised the method used in this work. This method consists in a combination of electromotive force measurements of concentration cells with contact potential, and without contact potential.

Apparatus and Materials

The Cells.—A variety of cells was tried out before an entirely suitable one was found. The nature of the problem made it desirable to be able to take series of measurements on four different combinations from the same set-up. These measurements were as follows: (1) The electromotive force between a hydrogen and calomel electrode in HCl of concentration C_1. (2) A similar measurement but with HCl of concentration C_2. (3) The electromotive force between the calomel electrode in concentration C_1 and the one in C_2. (4) A similar measurement for the hydrogen electrodes. From (1) could be calculated the free energy of formation of HCl from hydrogen and calomel in concentration C_1. From (2) a similar calculation for the case where the concentration is C_2. From the difference between (1) and (2) could be obtained the free energy of dilution of HCl from one concentration to the other. The difference between (1) and (2) would give also the E of Equation 1. The measurements in (3) would give the electromotive force of the concentration cell having boundary potential with calomel electrodes, or the value of E_1 in Equation 2. Similarly (4) would give E_2 in Equation 3.

The above data would make it possible to calculate the ratios $\frac{a''^{-}_{Cl}}{a'^{-}_{Cl}}$, $\frac{a''^{+}_{H}}{a'^{+}_{H}}$ and $\frac{a''_{HCl}}{a'_{HCl}}$; also the transference numbers for both—the hydrogen and chloride ions. Several other things had to be considered in the construction of these cells in order to be sure that the above electromotive force values represented accurately what they were supposed to. First of all, they should remain constant a reasonable length of time. This necessitated extreme caution to prevent diffusion between the solutions of different concentrations. As a result of an extensive study of the calomel electrodes, it was decided they must be in separate chambers from the hydrogen electrodes. Slight unavoidable movements of the connecting tube when this passed through the calomel to the mercury, as is generally the case, agitated the calomel and mercury in D (Fig. 1) and caused a change in the value of the electrode. To avoid this source of error it was thought advisable to make contact directly with the mercury. With these various requirements in mind a set-up of the type shown in Fig. 1 was finally used. Compartment A contains a calomel electrode in acid of concentration C_2; B contains a hydrogen electrode in acid of the same concentration; C contains a calomel electrode in acid of concentration C_1, and D contains a hydrogen electrode in acid of this same concentration. The various compartments are connected through the three-way stopcocks *a*, *b*, *c* and *d*. The rubber connections between B and D;

and A and C contain filter paper to reduce the diffusion; also the holes of the three-way stopcocks in *b* and *d* contain filter paper. The hydrogen inlet tubes are at *e* and *f*, and the outlet tubes at *g* and *h*. In each hydrogen compartment are two electrodes *i* and *i'*, and *j* and *j'*.

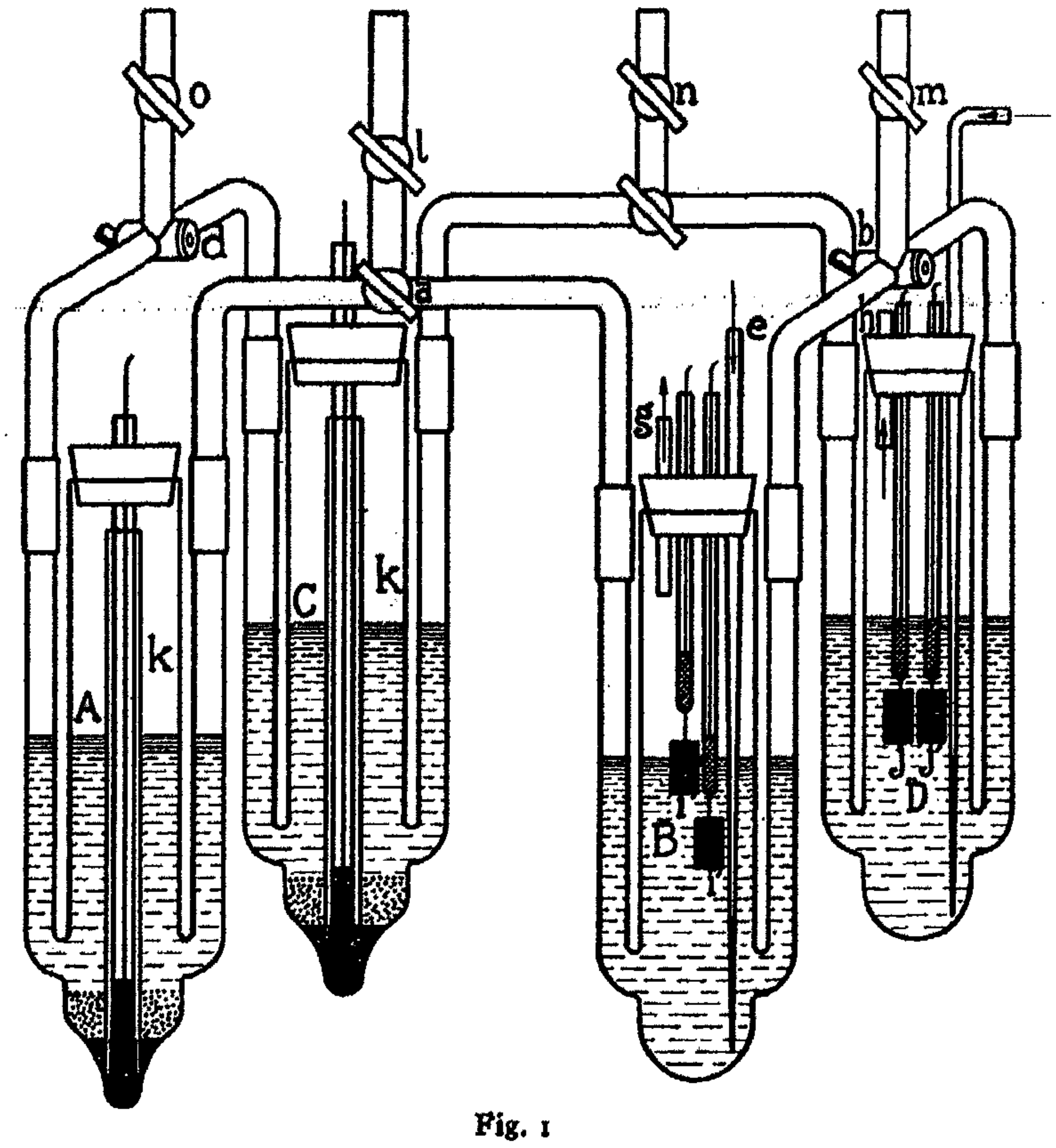

Fig. 1

The Hydrogen Electrodes.—An extended study of the hydrogen electrodes was made to settle the following points: the size and shape most suitable for our cells, ease of construction, effect of varying amounts of platinum black, the constancy when changed from a solution of one concentration to a solution of another concentration, reproducibility, and effect of exposure to air for several days. This study showed that the size and shape of the electrodes has no influence on their value. Those finally used in this work were made of platinum foil about one and one-half centimeters by two centimeters. As long as the coating had a black velvety appearance the electrodes remained constant; but after continued use they turned gray, became less sensitive, and fluctuated in value. The same electrodes were used several times before replatinizing. It was found inadvisable to have too much platinum black. As to constancy, they proved to be perfectly satisfactory. Electrodes were used in solutions of different concentrations, where they remained for several days, in some instances, and when they were returned to the stock solution they were found to have suffered no change. The degree of reproducibility is shown by the fact that when twelve of these electrodes were made and placed in a stock solution of very dilute acid and eleven were compared with the remaining one, eleven were exactly at the same potential and the twelfth showed a variation of only 0.01 mv. Over a period of eight days the greatest variation was 0.02 mv. Some of these electrodes were exposed to the air for several days without any permanent effect. An accident which happened to one of them shows they will stand much abuse. This electrode became unevenly covered with paraffin, and was left on a shelf for several months. To remove the paraffin the electrode was soaked in benzole, and to remove any other organic matter it was boiled in nitric acid and then several times in water. Again it was put through the platinizing and washing process and returned to the stock solution. A comparison showed it to be at exactly the same potential with the standard. This study shows that these hydrogen electrodes would make a better standard than the calomel electrodes. Nernst[1] was the first one to recognize the advantages of the hydrogen electrode and advocated its use as a standard in preference to the calomel electrode.

The Calomel Electrodes.—An investigation of the calomel electrodes, even more extensive than with the hydrogen elec-

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[1] Zeit. Elektrochemie, 7, 253 (1900).

trodes, was necessary because of the gradual and often rapid changes which took place in them.

They were all made from the same stock of Baker and Adamson analyzed calomel (Serial no. 3772) and twice distilled mercury. It was found better not to use mercury in making the paste. The calomel was mixed in a small beaker with a little of the solution to be used, until it was creamy, and then was washed three times by decantation with the same solution. A layer of calomel of considerable depth was found advisable. Connection with the electrode was made through the side arm (*k*), Fig. 1.

The first cells used had the calomel and hydrogen in the same compartment. Two, and often four, of these were made up at the same time. In a few minutes they would come together within a few hundredths of a millivolt. Soon after the hydrogen started to flow through the cell, the calomel electrodes began slowly to change. Some of the solutions, after there had been considerable change in the values of the cells, were titrated against barium hydroxide, and in every case increase in strength of acid was observed. The reason for this change in concentration has not yet been determined. This increase was roughly (not exactly) proportional to the change which had taken place in the electromotive force of the cell. Solutions taken from cells that remained constant gave the same analysis as the original solution. It was observed, moreover, that in the cells which had changed, the surface of the calomel appeared darker. In other cases, when freshly platinized electrodes were used, a few small specks of platinum black became loosened from the electrode by the action of the bubbles of hydrogen. In these cases the rate of change of electromotive force was greater. To prevent these particles of platinum black from reaching the calomel, the electrodes were covered with a filter paper bag, but this did not prove satisfactory. These facts offered an explanation for the changes that had been observed. There appeared to be close connection between the change in the electromotive force and the darkening of the calomel. Often the surface became nearly black; in such cases, a large increase in concentration of acid was found. To determine whether simply the passage of hydrogen through the cell would produce a change in concentration, a sample of calomel mercury paste was placed in each of two tubes and covered with $N/60$ acid. Through one of these, hydrogen was passed for two days while the other was left undisturbed. No change in color of the calomel was observed, and no appreciable change in concentration. These results are not sufficient to establish any conclusion, but they are enough to arouse the suspicion that the changes observed in the calomel electrodes are due to a change in concentration of the acid. This in turn is in some way connected with the combined action of hydrogen, platinum black and calomel. It might be stated, as a possibility, that the hydrogen, aided by the catalytic action of platinum black, decomposes the calomel with the formation of more HCl and free mercury. Much more work would be required before any definite statement could be made, but no difficulties were encountered when the form of cell in Fig. 1 was used.

The Thermostat.—In all earlier work the ordinary form thermostat heated by a gas flame, the size of which was regulated by the rising and lowering of a column of mercury, was used. This did not prove satisfactory. The variation in gas pressure, and the corroding of the mercury surface made close attention necessary and decreased the accuracy of regulation. To avoid these difficulties an electrically heated and regulated thermostat was constructed. In this new thermostat the regulation was so close that no change of temperature could be detected by a Beckman thermometer over a period of several days.

The Electrical Apparatus.—The electromotive forces were measured with an Otto Wolff 15,000 ohm potentiometer and suitable galvanometer. A certified Weston cell was used as a standard and was kept in the same thermostat in which the measurements were carried out.

The Hydrochloric Acid.—An approximately fifth-normal stock solution of hydrochloric acid (Baker & Adamson's analyzed hydrochloric acid C. P.) was prepared by dilution with conductivity water and its concentration determined by precipitation of AgCl. Five analyses showed per 1000 grams solution, 7.259, 7.266, 7.262, 7.263 grams of chlorine. The solutions used for measurement were $N/5$, $N/10$, $N/60$, $N/90$, $N/120$, $N/180$, and $N/300$, made from a weighed quantity of the stock solution by dilution at 18°, using flasks carefully calibrated with standardized weights.

The Hydrogen Generator.—The hydrogen used was generated electrolytically from a strong sodium hydroxide solution in a generator of the type described by Bodenstein.[1] The electrodes were of nickel wire.

In order to remove possible traces of oxygen, the gas was passed, before use, through a tube containing a platinum wire heated to incandescence by an electric current.[2] It was then passed through a wash bottle filled with distilled water, then bubbled from a fine capillary through acid of the same concentration and temperature as that in the cell, and finally allowed to bubble from a fine capillary through the solution surrounding the platinized electrodes and escape through a long tube into the air.

Method of Procedure and Experimental Results

In all of the measurements $N/30$ HCl was taken as the standard for comparison and they were all made at 18° C.[3] The cells constructed as described were, in most cases, set up at night, and by the next night the readings had become constant. Readings were taken at varying intervals over a period of several days.

The following uniform method was adopted: The stopcock *d*, Fig. 1, in the tube connecting the calomel electrode in concentration C_x with the one in C_{30} was opened, also the similar stopcock *b* between the hydrogen electrodes. After

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[1] Zeit. Elektrochemie, 11, 373 (1905).

[2] This precaution was really not necessary as no change in electromotive force could be detected when the wire was not heated.

[3] The bath temperature remained so constant that it was unnecessary to record it in the tables.

about five minutes the potentials were measured and the stopcocks closed. By producing a slight suction on the upward directed tube of the three-way stopcock *a* connecting the hydrogen chamber and calomel chamber of the *N*/30 solution, the liquid in the downward directed branches was drawn up till contact was made within the stopcock *a*; the stopcock *l* in the upward tube was then closed. After the reading was taken *l* was opened sufficiently to permit a separation of the liquid in *a*. The cell was left in this condition till the next reading. A similar procedure was then followed for the cell containing C_x acid.

The experimental data obtained in this work are included in eighteen tables of which Table I in this article is a sample. In column E_{30} is given the electromotive force between the hydrogen electrode and calomel electrode in *N*/30 HCl. Column E_{60}, E_{90}, —, —, etc., in the various tables contains the electromotive force measurements between the hydrogen and calomel electrodes in concentrations *N*/60, *N*/90, —, —, etc. Under E_2 are given the potentials between a hydrogen electrode in *N*/30 HCl and the hydrogen electrode in the other concentration being investigated; and under E_1 are given corresponding values for the calomel electrodes.

As was stated in the discussion above, $E_x - E_{30}$ should equal $E_1 + E_2$. The remarkable agreement found is shown by a comparison of the last two columns.

The slight variations observed between successive readings can be accounted for largely by changes in barometric pressure.[1] The effect of these changes is practically the same in acid of all concentrations, and as we are concerned with differences only, it is not necessary to make corrections for them.

A large number of preliminary experiments were performed before all of the disturbing elements were discovered and eliminated. After the proper conditions were secured, however, no further difficulties were experienced, and the eighteen tables contain all of the measurements that were taken.

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[1] Since there is considerable lag in the effect produced by pressure changes, the changes in electromotive force measurements do not correspond to these unless the changes in pressure were gradual.

TABLE I

No.	Date	Time	Bar.	E_{30}	E_{60}	E_2	E_1	$E_{60} - E_{30}$	$E_2 + E_1$
1	April 22	11 P.M.	—	0.45110	0.48575	—	—	0.03465	—
2	23	8.00 A.M.	744.2	082	432	—	—	350	—
3		1.00 P.M.	—	85	50	—	—	65	—
4		4.00 P.M.	—	98	56	—	—	58	—
5		5.00 P.M.	—	83	40	—	—	57	—
6		6.00 P.M.	—	78	40	—	—	62	—
7	24	12.00 M.	739.1	59	18	—	—	59	—
8		2.00 P.M.	—	61	16	—	—	55	—
9		7.25 P.M.	—	51	05	0.00575	0.02787	54	0.03362
10		8.30 P.M.	—	53	11	69	88	58	57
11	26	10.00 A.M.	735.3	45	395	83	64	50	47
12		11.00 A.M.	—	41	86	77	66	45	43
13		4.00 P.M.	—	49	94	78	64	45	42
14		7.00 P.M.	—	46	96	78	65	50	43
15	27	9.00 A.M.	737.0	57	403	70	77	46	47
			Av.,	0.45062	0.48420	0.00574	0.02776	0.03354	0.03350

Remarks: Cell was set up April 22, 10.00 P.M.

Discussion of Results

To facilitate the study of the results a summary of the values for E, E_1 and E_2 is presented in Tables II, III and IV.

TABLE II—SUMMARY OF VALUES FOR E

Conc. Diff.	Calculated		Measured		
	New formula	Old formula	By diff.	By sum.	Average
n/30 — *n*/5	0.08530	0.08702	0.08567	0.08558	0.08562
n/60 — *n*/30	0.03361	0.03414	0.03350	0.03347	0.03349
n/90 — *n*/30	0.05365	0.05423	0.05334	0.05333	0.05334
n/120 — *n*/30	0.06744	0.06828	0.06711	0.06705	0.06708
n/150 — *n*/30	0.07879	0.07955	0.07847	0.07847	0.07847
n/180 — *n*/30	0.08778	0.08858	0.08784	0.08772	0.08778
n/300 — *n*/30	0.11305	0.11400	0.11361	0.11361	0.11361

In Table II under the head "Old formula" are given the values calculated from the regular formula for concentration cells without boundary potential, namely $E = \frac{2RT}{F} \ln \frac{c_1}{c_2}$. In Tables III and IV in the columns headed "Old formula, $N_c = 826$," are given the values calculated from the formulas for concentration cells with boundary potential, namely, $E_2 = \frac{2RTN_a}{F} \ln \frac{c_1}{c_2}$ and $E_1 = \frac{2RTN_c}{F} \ln \frac{c_1}{c_2}$. In these calculations R was taken equal to 8.3160 joules, T equal to 291.09°, and F equal to 96490. The conductivity data given by Goodwin and Haskell[1] for HCl was plotted and, in the calculation of the degree of dissociation at the various concentrations used by the writer, the conductivity values were taken from this curve. The value for infinite dilution was taken equal to 380.

A comparison of the measured values with the calculated in these three tables shows fairly close agreement; in fact agreements much less close than these have been considered very satisfactory and used as a confirmation of the accuracy of the formulas. A careful inspection of these tables, however,

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[1] Phys. Rev., 19, 386 (1904).

shows that the calculated values are in every instance greater than the measured and this was found to be the case, not only for these results, but also for similar measurements made by others.

TABLE III—SUMMARY OF VALUES FOR E_1

Conc. Diff.	Measured	Calculated			
		Old formula		New formula	
		$N_c = 832$	$N_c = 826$	$N_c = 832$	$N_c = 826$
n/30 — *n*/5	0.01397	0.01463	0.01512	0.01433	0.01484
n/60 — *n*/30	0.00571	0.00580	0.00594	0.00571	0.00585
n/90 — *n*/30	0.00888	0.00910	0.00943	0.00901	0.00933
n/120 — *n*/30	0.01130	0.01147	0.01187	0.01133	0.01173
n/150 — *n*/30	0.01315	0.01337	0.01384	0.01324	0.01371
n/180 — *n*/30	0.01475	0.01488	0.01541	0.01474	0.01527
n/300 — *n*/30	0.01898	0.01916	0.01984	0.01899	0.01967

TABLE IV—SUMMARY OF VALUES FOR E_2

Conc. Diff.	Measured	Calculated			
		New formula		Old formula	
		$N_c = 832$	$N_c = 826$	$N_c = 832$	$N_c = 826$
n/30 — *n*/5	0.07163	0.07140	0.07046	0.07282	0.07188
n/60 — *n*/30	0.02773	0.02789	0.02776	0.02833	0.02820
n/90 — *n*/30	0.04446	0.04463	0.04431	0.04511	0.04479
n/120 — *n*/30	0.05573	0.05611	0.05570	0.05681	0.05640
n/150 — *n*/30	0.06535	0.06555	0.06508	0.06618	0.06571
n/180 — *n*/30	0.07299	0.07304	0.07251	0.07370	0.07317
n/300 — *n*/30	0.09488	0.09406	0.09338	0.09484	0.09416

By substituting the measured values in the formula for the electromotive force of concentration cells without boundary potential, the activity ratios for the various concentration differences were calculated. These are presented in Table V, together with the concentration ratios for the same concentration differences calculated from conductivity measurements.

TABLE V—ACTIVITY AND CONCENTRATION RATIOS

Conc. Diff.	$\frac{a_{1H}}{a_{2H}}$	$\frac{c_{1H}}{c_{2H}}$	$\frac{a_{1HCl}}{a_{2HCl}}$	$\frac{c_{1HCl}}{c_{2HCl}}$
$n/5$ — $n/30$	5.507	5.664	30.311	12.881
$n/60$ — $n/30$	1.949	1.974	3.799	2.723
$n/90$ — $n/30$	2.895	2.946	8.375	4.784
$n/120$ — $n/30$	3.806	3.893	14.455	7.080
$n/150$ — $n/30$	4.776	4.880	22.793	10.570
$n/180$ — $n/30$	5.750	5.842	33.037	13.443
$n/300$ — $n/30$	9.621	9.687	92.449	29.500

This table again brings out the fact that the activity ratios for the ions are in every case less than the corresponding concentration ratios; but for the undissociated part of the acid the activity ratios are much greater than the concentration ratios, and as the dilution becomes greater the activity increases more rapidly than the concentration.

In view of the fact that for all non-electrolytes and even for weak electrolytes, the activity has been shown by others to be proportional to the concentration, the nature of these results is quite remarkable. They confirm the statement made in the consideration of the preliminary experiments, that either conductivity measurements do not give true values for the degree of dissociation or, else the concentration of the ions as well as the undissociated part of the acid is not proportional to the activity in the case of hydrochloric acid.

It will be remembered that Jahn, in his measurements with concentration cells having boundary potential, found his observed values to be less than those calculated from the Nernst equation. Table II shows the same relation for measurements with concentration cells without boundary potential. To explain these discrepancies between his observed and calculated values, Jahn suggested that conductivity is not an accurate method for determining the degree of dissociation. He doubted the validity of the assumption that the transport numbers do not change with concentration, and this assumption must be made when the degree of dissociation is calculated from conductivity data. It will be remembered that the investigation of the relation between transport numbers and concentration is one of the primary objects of this paper.

As was pointed out earlier in the discussion the measurements in this work give two new and distinct methods for calculating transport numbers. One is by the formula $N_c = \frac{E_1}{E}$ or $N_a = \frac{E_2}{E}$, (one serves as a check on the other) and the other by the formula for boundary potential $E = (1 - 2N_c)\frac{RT}{F} ln \frac{c_1}{c_2}$. In the first method nothing is involved but the measurements of E_2, E_1 and E which can be made with a very high degree of accuracy. The second method, however, involves a formula which is possibly questionable, particularly the ratio $\frac{c_1}{c_2}$.

The results obtained by the application of these two formulas are presented in Table VI.

TABLE VI—SUMMARY OF TRANSPORT NUMBER N_c

Conc. Diff.	$\frac{E_1}{E}$	$1 - \frac{E_2}{E}$	Average	From boundary E. M. F.	
				Using $\frac{c_1}{c_2}$	Using $\frac{a_1}{a_2}$
n/30 — *n*/5	0.836	0.8377	0.837	0.831	0.837
n/60 — *n*/30	0.828	0.830	0.829	0.822	0.829
n/90 — *n*/30	0.833	0.833	0.833	0.827	0.833
n/120 — *n*/30	0.830	0.831	0.830	0.825	0.831
n/150 — *n*/30	0.833	0.832	0.832	0.830	0.835
n/180 — *n*/30	0.831	0.8315	0.831	0.829	0.831
n/300 — *n*/30	0.835	0.833	0.834	0.832	0.833

Final av., 0.832

It should be noted that E_2 and E_1 give practically identical values for N_c but these do not agree with the values calculated from the formula for boundary potential. According to the first method N_c remains constant at dilutions greater than *n*/90 and increases slightly between *n*/30 and *n*/5.

In Table VI, under the head $\frac{a_1}{a_2}$, are given the values for N_c calculated from boundary potentials by substituting the activity ratios from Table V in place of concentration ratios. This gives results nearly identical with those given by the other method. One of the most important features of these results is the argument they add to the view that the formula for calculating boundary potential is reliable and that the formula for calculating ionic concentration is unreliable.

To facilitate a comparison of the results of the various investigators who have measured the transport numbers of HCl the data obtained by them is presented in Table VII.

All of the recent investigators except one have used the Hittorf method, with variations to eliminate as far as possible the various sources of error. The wide variation between the different results of each investigator as well as the lack of agreement between the values of different investigators, shows that the method is not very reliable. Washburn[1] has expressed the belief that during such experiments water is transported, due to the hydration of the ions, from one electrode chamber to the other when the solutions are fairly concentrated. Buchböck also came to the same conclusion. Their evidence appears to be strong. If water is so transported then it is evident that transference numbers cannot be accurately determined by this method.

The moving boundary method for measuring transference numbers is not open to the same criticism, but so few measurements have been made on hydrochloric acid by it that scarcely anything can be said.

The two methods used in this present investigation appear to be entirely free from all the sources of error attending the Hittorf method. Their limitations have been discussed but they appear to give more consistent and reproducible values than have been obtained before.

In Table VIII is presented a summary of the measured values for boundary potential together with the calculated values when N_c is given the commonly accepted value 0.826 and also when N_c is given the value 0.832 found in this investi-

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[1] Jour. Am. Chem. Soc., 31, 322 (1909).

TABLE VII—COMPARISON OF VALUES FOR N_c

Volume in L. containing one equivalent	Hopfgartner 1898	Bein 1898	Jahn and Bogden 1901	Noyes and Sammet 1902	Buchböck 1906	Jahn and Joachim 1907	Noyes and Kato 1908	Riesenfeld and Reinhold 1908	Denison and Steele 1908	Drucker and Kranjavi 1908	Ferguson	
											from E_2 E	from boundary E. M. F.
0.4	—	—	—	—	824	—	—	—	—	—	—	—
1	—	—	—	—	842	—	—	845	—	—	—	—
1.1	841	—	—	—	—	—	—	—	—	—	—	—
1.25	843	—	—	—	—	—	—	—	—	—	—	—
2	833	—	—	—	—	—	—	845	—	—	—	—
5	836	—	—	—	—	—	—	—	—	—	837	837
5 to	20	829	—	—	—	—	—	—	—	—	—	—
10	833	825	—	—	—	—	—	839	835	—	—	—
20	—	—	—	836	—	—	—	—	—	—	—	—
30	—	—	823	—	—	835	—	—	—	830.6	—	—
50	—	—	828	—	—	—	—	—	835	—	—	—
60	—	—	—	834	—	833	—	—	—	—	829	829
70	—	—	823	—	—	—	—	—	—	—	—	—
80	—	—	827	—	—	—	—	—	—	—	—	—
90	—	—	—	—	—	832	—	—	—	—	833	833
103	—	—	828	—	—	—	—	—	—	—	—	—
110	—	—	825	—	—	—	—	—	—	—	—	—
120	—	—	—	—	—	834	—	—	—	—	830.5	831
150	—	—	—	—	—	833	—	—	—	—	833	835
180	—	—	—	834	—	—	—	—	—	—	829	831
300	—	—	—	—	—	—	—	—	—	—	832	833
500	—	—	—	—	—	—	831	—	—	—	—	—

gation. The table shows much better agreement between the measured values and those calculated with $N_c = 0.826$ than with $N_c = 0.832$. This is really a false agreement as can easily be shown. In the discussion of transference numbers it was pointed out that the values in Table VI, in the column headed $\frac{a_1}{a_2}$, were obtained by substituting in the formula activity ratios in the place of concentration ratios. This gave values which are in very close agreement with those determined from the ratio $\frac{E_2}{E}$. It is evident then that the error introduced by using $N_c = 0.826$ is approximately counterbalanced by the error introduced by using concentration ratios in the place of activity ratios, and thus causes a false agreement between measured and calculated values.

In Table VIII, in the column headed, $N_c = 0.832$ and $\frac{a_1}{a_2}$, are given the calculated values when, for N_c, the values measured from the ratio $\frac{E_1}{E}$ are used and for $\frac{a_1}{a_2}$ are used the measured activity ratios. The remarkable agreement between these calculated and measured values speaks for itself. There can remain little doubt concerning the exactness of the formula; but the grave necessity for accurate transference values and activity ratios is also made evident.

TABLE VIII—SUMMARY OF BOUNDARY E. M. F.

Conc. Diff.	Calculated			Measured
	$N_c = 0.826$ and $\frac{c_1}{c_2}$	$N_c = 0.832$ and $\frac{c_1}{c_2}$	$N_c = 0.832$ and $\frac{a_1}{a_2}$	
$n/30 - n/5$	0.02837	0.02930[1]	0.02893[1]	0.02883
$n/60 - n/30$	0.01113	0.01126	0.01112	0.01100
$n/90 - n/30$	0.01767	0.01800	0.01771	0.01771
$n/120 - n/30$	0.02226	0.02267	0.02226	0.02221
$n/150 - n/30$	0.02593	0.02641	0.02605	0.02610
$n/180 - n/30$	0.02887	0.02941	0.02914	0.02912
$n/300 - n/30$	0.03715	0.03783	0.03777	0.03785

[1] In calculating this value N_c was taken equal to 0.837.

In the discussion of Tables II, III and IV it was pointed out that the calculated values for electromotive forces were invariably greater than the measured; and that the same is true of all similar measurements made by others. The most probable explanation for this is some constant source of error in the formula. One such source has been pointed out, namely, the formula calls for an activity ratio, but in place of this a concentration ratio, calculated from conductivity measurements, had to be substituted. After a careful study of the most probable changes within the cell, it appears to the writer that the formula does not exactly fit the case. The following discussion is an effort to make this point evident and to suggest an improvement.

The formula as it is commonly used has the form

$$W = EF = 2RT\, ln \frac{c_1}{c_2}.$$

This equation is supposed to represent the work required to transfer one electrochemical equivalent of electricity from one electrode to the other. If this is carried out in a double cell so that there can be no change at the boundary, it would result in the disappearance of one mol of HCl from the more concentrated side and the appearance of one mol in the dilute. The work involved then is that required to transfer a mol of HCl from one side to the other. In case of complete ionization this would mean the transfer of one equivalent of hydrogen ion and one equivalent of chloride ion, and would be represented by the expression $2RT\, ln \frac{c_1}{c_2}$. This is the same as the third member in the above equation. Under the conditions of complete dissociation then this equation is entirely applicable, but in no actual experiment is this the case. What would really take place if a faraday of electricity were passed through such a cell would be, (1) the transfer of an amount of chloride ion equal to the dissociation of the acid, (2) the transfer of an amount of hydrogen ion equal to the dissociation of the acid, (3) the transfer of an amount of undissociated acid equal to the undissociated part.

The work in (1) equals the work in (2) and may be represented by

$$W_1 = \alpha RT \, ln \frac{c_1}{c_2}.$$

The work in (3) may be represented by

$$W_2 = (1 - \alpha) \, RT \, ln \frac{c_1}{c_2}.$$

Now

$$c_{2_{\mathrm{H}}} = c_2\alpha'' = c_{2_{\overline{\mathrm{Cl}}}}$$

and

$$c_{1_{\mathrm{H}}} = c_1\alpha' = c_{1_{\overline{\mathrm{Cl}}}}$$

and

$$c_{2_{\mathrm{HCl}}} = c_2(1 - \alpha'')$$

and

$$c_{1_{\mathrm{HCl}}} = c_1(1 - \alpha').$$

Combining and substituting,

$$W = 2\alpha RT \, ln \frac{c_2\alpha''}{c_1\alpha'} + (1 - \alpha) \, RT \, ln \frac{c_2(1 - \alpha'')}{c_1(1 - \alpha')}.$$

This formula is not absolutely exact because of the uncertainty in α. The assumption is made that the dissociation is the same in both sides, but this evidently is not true; so the most likely value to use for α is $\frac{\alpha'' + \alpha'}{2}$.

The values for E, E_1 and E_2 have been recalculated according to this new formula and are recorded in Tables II, III and IV under the heading "New formula."

In Table IX are presented the differences ($\times 10^5$) between the measured and the calculated values by use of the old formula in one case and the new formula in the other.

It is evident from these differences that the new formula is an improvement.

TABLE IX—SUMMARY OF DIFFERENCES BETWEEN MEASURED AND CALCULATED VALUES

	E		E_1				E_2			
Conc. Diff.	New — meas.	Old — meas.	New — meas.	Old — meas.	New — meas.	Old — meas.	New — meas.	Old — meas.	New — meas.	Old — meas.
			$N_c = 0.832$		$N_c = 0.826$		$N_c = 0.832$		$N_c = 0.826$	
n/30 — *n*/5	—32	140	+7	23	87	115	—23	119	—117	25
n/60 — *n*/30	12	65	00	9	14	23	16	60	+ 3	47
n/90 — *n*/30	31	89	13	22	45	55	17	65	— 15	33
n/120 — *n*/30	36	120	3	17	43	57	38	108	— 3	67
n/150 — *n*/30	32	108	9	22	56	69	20	83	— 27	26
n/180 — *n*/30	00	80	—1	13	53	67	5	71	— 48	18
n/300 — *n*/30	—56	39	+1	18	69	86	—82	—2	—150	—72

Conclusion

From all this it is concluded: (1) that the transport numbers for hydrochloric acid remain constant for dilutions greater than *n*/30, and thus conductivity measurements give an accurate method for determining ion concentrations in dilutions greater than *n*/30, so far as any change in the velocity of the ions is concerned; (2) that the concentration is not proportional to activity; (3) that the Nernst equation cannot be applied to an actual concentration cell without some changes; (4) that the formula for calculating boundary electromotive force gives accurate results if the true transport numbers are used and if activity is substituted in the place of concentration.[1]

The writer wishes to express his earnest appreciation for the kind advice and helpful assistance rendered by Professor R. C. Tolman, under whose direction some preliminary work was carried out, without which the present investigation would not have been possible.

It is with sincere gratitude that acknowledgment is here made to Professor S. L. Bigelow for the interest he has taken in this work and for his most valuable criticisms.

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[1] Since the completion of this investigation, an article by Duncan A. MacInnes and Karr Parker (Jour. Am. Chem. Soc., 37, 1445 (1915)) on the KCl concentration cell has appeared in the literature. The KCl concentration cell is dealt with in much the same way as the present work deals with the HCl concentration cell. The values obtained for the transport numbers show practically no variation with concentrations between 0.5 and 0.005 *n*. It may be said, in general, that the conclusions arrived at in this investigation of HCl solutions agree remarkably well with those stated by MacInnes and Parker for KCl solutions.

ON THE REACTION OF BOTH THE IONS AND MOLECULES OF ACIDS, BASES AND SALTS[1]

BY W. A. TAYLOR AND S. F. ACREE

I. On the Reaction of Sodium Ethylate and Methyl Iodide in Absolute Ethyl Alcohol at 0°

Until comparatively recently chemical transformations were thought by most chemists to be purely ionic. This was a natural consequence of the development of the theory of electrolytic dissociation by Arrhenius, especially since the earlier work on the hydrolysis of sugars, esters and amides by acids and the saponifications of esters by bases showed that these reactions are, in dilute solutions, nearly proportional to the concentration of the ions of the catalyzers. The natural conclusion was drawn that the reactions are brought about simply by the ions present. Notable among the opponents of this theory were Kahlenberg, Michael and Armstrong. Kahlenberg's work[2] was especially important as, besides other cases, he studied a number of very rapid reactions in nonaqueous solvents in which no appreciable ionization could be detected. As a result of this he came to the conclusion that the purely ionic theory of all chemical reactions was not established beyond question.

The work of Brunel[3] and Acree in 1905-6, of Johnson[4] and Acree in 1907 and the later work of Shadinger, Nirdlinger, Rogers, Chandler, Marshall, Robertson, Harrison, Shrader and Brown, brought out an entirely new principle in catalysis, namely, that acceleration may take place through the action of the nonionized acids, bases, and salts, as well as through the ions. In the case of the rearrangement of acetylchloraminobenzene, Johnson and Acree found that the reaction took place almost entirely through the nonionized salt according to the equation

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] Jour. Phys. Chem., 5, 339 (1901); 6, 1 (1902) and other articles.

[3] Am. Chem. Jour., 43, 505 (1910).

[4] Ibid., 38, 259, 260 (1907).

$$CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows CH_3CONHCl_2C_6H_5 \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H} + \overset{-}{Cl}.$$

This theory has now been adopted generally to explain the "deviations" from the ionic reaction, and in the case of the hydrolysis of cane sugar by hydrochloric acid, Worley[1] has shown that the molecular reaction is so great that its velocity is about twelve times that of the ionic reaction, as is shown in the following table:

Molecular proportions $H_2O:HCl$	Molecular hydrolytic activity of acid	Degree of "ionization" μ_v/μ_∞
30	385	0.725
40	323	0.778
50	290	0.813
60	269	0.837
80	243	0.859
100	229	0.871
2000	201	0.901

Dilutions (mols H_2O)	K_i	K_m
30:60	100	1136
30:80	94	1154
30:100	91	1160
30:200	98	1143
40:80	104	1092
40:100	99	1110
40:200	103	1095
50:80	99	1121
50:100	92	1145
50:200	101	1112
60:100	77	1154
60:200	96	1159
80:100	79	1245
80:200	102	1102
100:200	109	1042
	Mean, 96	1138

The work which was taken up in this laboratory to prove this theory quantitatively was chiefly the reactions of ethylates

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[1] Phil. Mag., (6) 27, 459 (1914).

and phenolates with alkyl halides. These substances were chosen because here we have a nonelectrolyte reacting with a univalent electrolyte whose ionization varies over a wide range. Then, too, in these cases, we are not hindered by troublesome side reactions, and the transformations are also easily controlled and easily and accurately determined.

In the present piece of work we took up the study of the reaction of sodium ethylate with methyl iodide at 0°, repeating the work of Miss B. M. Brown, to see if the same constants could be obtained by two independent workers.

If both the ethylate ions and the nonionized ethylate react we should have two reactions going on side by side, the velocity of one of which is proportional to the concentration of the ionized ethylate and the other proportional to the concentration of the nonionized ethylate, according to the equations

Ionic: $C_2H_5I + C_2\overset{-}{H_5}O + \overset{+}{Me} \longrightarrow (C_2H_5)_2O + \overset{+}{Me} + \overset{-}{I}.$

Molecular: $C_2H_5I + C_2H_5OMe \longrightarrow (C_2H_5)_2O + \overset{+}{Me} + \overset{-}{I}.$

If we represent by K_i the velocity constant for the ionic reaction by K_m the velocity constant for the molecular reaction, and by K_N the total velocity constant, in solutions having unit concentrations, by x the change in concentration of the ethylate in time t, by C_{ethylate} the initial concentration of the ethylate in gram mols per liter, by $C_{\text{alkyl halide}}$ the initial concentration of alkyl halide in gram mols per liter, we have the equation

$$dx/dt = K_i\alpha(C_{\text{ethylate}} - x)(C_{\text{alkyl halide}} - x) + K_m(1 - \alpha)\,(C_{\text{ethylate}} - x)(C_{\text{alkyl halide}} - x).$$

If we represent C_{ethylate} by A and $C_{\text{alkyl halide}}$ by B, we obtain on integrating the above equation

$$K_N = K_i\alpha + K_m(1 - \alpha) = \frac{1}{At}\cdot\frac{x}{A - x} \text{ when } A = B$$

$$\text{and } K_N = K_i\alpha + K_m(1 - \alpha) = \frac{1}{(B - A)t}\, ln \frac{A(B - x)}{B(A - x)}$$

when $A >$ or $< B$.

We know the values of A, B and t and can find x by titration. By substituting these values in the equation above we therefore obtain the values for K_N.

By measuring the reaction velocities K_N over a wide range of concentrations we obtain a series of simultaneous equations with different values of K_N, α and $1 - \alpha$, as follows:

$$K_N = K_i\alpha + K_m(1 - \alpha)$$
$$K'_N = K_i\alpha' + K_m(1 - \alpha'), \text{ etc.}$$

By solving these equations for K_i and K_m we obtain the following values:

$$K_i = \frac{K'_N(1 - \alpha) - K_N(1 - \alpha')}{\alpha' - \alpha}$$
$$\text{and } K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha}.$$

Johnson and Acree[1] and Robertson and Acree[2] have given a full discussion of the derivation and application of these equations.

We find that by the use of these equations we obtain constant values for K_i and K_m for any given reaction. Furthermore, if this theory is correct, not only should we obtain constants for K_i and K_m for any given reaction, but K_i should be a constant for the reaction of a given alkyl halide with any ethylate; that is, the ionic velocity should be the same whether the ethylate ions come from sodium, potassium or lithium ethylates. On the other hand K_m may or may not be the same for different reactions. In fact we would expect the molecular velocities to be different in each case. The same, of course, would hold true with the phenolates as with all other analogous substances. That these relations do hold true is shown by the following tables of the values for K_i and K_m for given alkyl halides with different ethylates, phenolates, etc.:

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[1] Am. Chem. Jour., 37, 410; 38, 258 (1907); 48, 352 (1912).
[2] Ibid., 49, 474 (1913).

Temperature 0°

Reagents	K_i	K_m
Sodium ethylate and methyl iodide	0.004861	0.003033
Sodium ethylate and methyl iodide	0.004960	0.002940
Potassium ethylate and methyl iodide	0.005252	0.003369
Lithium ethylate and methyl iodide	0.005204	0.001974

Temperature 25°

Sodium ethylate and ethyl bromide	0.00576	0.00233
Sodium ethylate and ethyl bromide	0.00543	0.00237
Potassium ethylate and ethyl bromide	0.00539	0.00296
Lithium ethylate and ethyl bromide	0.00574	0.00157
Sodium ethylate and ethyl iodide	0.0120	0.00427
Sodium ethylate and ethyl iodide	0.0122	0.00402
Potassium ethylate and ethyl iodide	0.0122	0.00457
Lithium ethylate and ethyl iodide	0.0122	0.00304
Sodium ethylate and methyl iodide	0.127	0.0594
Sodium ethylate and methyl iodide	0.129	0.0581
Potassium ethylate and methyl iodide	0.126	0.0687
Lithium ethylate and methyl iodide	0.137	0.0387
Sodium phenolate and methyl iodide	0.0282	0.00477
Potassium phenolate and methyl iodide	0.0283	0.00370
Lithium phenolate and methyl iodide	0.0287	0.00393
Sodium phenolate and ethyl iodide	0.00551	0.000987
Potassium phenolate and ethyl iodide	0.00518	0.001011
Lithium phenolate and ethyl iodide	0.00534	0.000910
Sodium thiourazole and ethyl iodide	0.435	0.170
Sodium thiourazole and ethyl iodide	0.463	0.158
Acetimidoethylester catalyzed by sodium ethylate	0.344	0.228
Benzimidoethylester catalyzed by sodium ethylate	0.1172	0.0976
p-Brombenzonitrile and sodium ethylate	0.160	0.161
p-Brombenzonitrile and potassium ethylate	0.163	0.144
p-Brombenzonitrile and lithium ethylate	0.159	0.093

Temperature 35°

Sodium phenolate and methyl iodide	0.0909	0.01310
Potassium phenolate and methyl iodide	0.1036	0.00983
Sodium phenolate and ethyl iodide	0.0183	0.00323
Potassium phenolate and ethyl iodide	0.0197	0.00270
Lithium phenolate and ethyl iodide	0.0174	0.00319

REINTERPRETATION OF THE WORK OF OTHERS

Work of Tubandt

Inversion of methone by sodium ethylate	0.41 at 20° 0.93 at 30°	0.41 at 20° 0.93 at 30°

Work of J. Stieglitz

Saponification of benzimidonium ethyl ester chloride at 25°	162.0[1]	50.3[1]
Saponification of benzimidonium ethyl ester bromide at 25°	163.8[1]	46.5[1]
Saponification of benzimidonium ethyl ester nitrate at 25°	163.2[1]	48.2[1]

Work of Bredig and Stern

Change of benzaldehyde into benzoin by potassium cyanide	0.089	0.089

Work of Hecht, Conrad and Brückner

Sodium ethylate and methyl iodide at 0°	0.005799	0.002649
Sodium ethylate and methyl iodide at 12°	0.02896	0.01028
Sodium ethylate and methyl iodide at 18°	0.06305	0.02003
Sodium ethylate and methyl iodide at 24°	0.12877	0.04354
Sodium ethylate and methyl iodide at 36°	0.5606	0.1892
Sodium ethylate and ethyl iodide at 24°	0.0121	0.00294
Sodium ethylate and ethyl iodide at 36°	0.05282	0.01295
Sodium ethylate and propyl iodide at 36°	0.01025	0.001912
Sodium ethylate and cetyl iodide at 36°	0.01464	0.002541
Sodium ethylate and octyl iodide at 36°	0.01426	0.002407

Work of Bruyn, Lulofs and Steger

Sodium methylate and 1,2,4-dinitrochlorbenzene in absolute methyl alcohol at 15°	1.299	0.724
Sodium methylate and 1,2,4-dinitrochlorbenzene in 90.3 percent methyl alcohol at 15°	1.376	0.759
Sodium ethylate and 1,2,4-dinitrobrombenzene in absolute ethyl alcohol at 15°	2.838	0.823
Sodium ethylate and 1,2,4-dinitrochlorbenzene in absolute ethyl alcohol at 15°	4.473	1.195
Sodium methylate and *o*-dinitrobenzene in absolute methyl alcohol at 45°	0.1458	0.1278
Sodium ethylate and *o*-dinitrobenzene in absolute ethyl alcohol at 45°	0.229	0.230

Work of Segaller

Sodium phenolate and propyl iodide at 42.5°	0.0128	0.000753

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[1] These values are given in terms of Stieglitz's constants.

Work of Ostwald		
The inversion of cane sugar		
by hydrochloric acid at 25°	31.2	83.8
by hydrobromic acid at 25°	31.4	93.4
by nitric acid at 25°	31.4	73.1
Work of Koelichen		
The inversion of diacetone alcohol		
by sodium hydroxide	0.2315	0.2315
by barium hydroxide	0.232	0.150

Salt Catalysis

It has been noted that the constants drop off slightly toward the end of the reaction in some cases but increase in others. Several theories have been proposed to explain this phenomenon, among which are a "salt effect," that is, (1) the catalytic effect of the salt formed in the reaction or of the ethylate ions or molecules themselves, and (2) the formation of olefines from the alkyl halides.

Arrhenius[1] and later Euler[2] and Stieglitz[3] thought that the "salt effect" was due to the change in activity or ionization of the water by the action of the salt. Acree[4] has shown that this explanation is untenable because in some cases it would call for a change in the ionization of water many times greater than could probably be caused in this way and also because the same salts in the same concentration sometimes exert a positive and sometimes a negative effect, and hence would have to increase the ionization of water in some cases and decrease it in others, an evident *reductio ad absurdum*. It has also been shown by Acree that in many cases the salt effect is entirely normal, that is, corresponding to the change in ionization of the reacting substances by the salt formed. In other cases an "abnormal salt effect" was observed, that is, a "salt effect" which was either too large or too small to correspond to the change in ionization of the reacting substances by the salt formed. Acree also showed that Stieglitz's own work proves

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[1] Zeit. phys. Chem., 1, 110 (1887); 4, 226 (1889); 31, 197 (1899).

[2] Ibid., 32, 348 (1900).

[3] Am. Chem. Jour., 39, 29, 166, 402, 437, 586, 719 (1908); 32, 221 (1904).

[4] Ibid., 41, 475 (1909).

that the temperature coefficient of the hydrolysis of imidoester salts is normal, whereas, on account of the increase in K_m with rise in temperature, the velocities at 18° and 25° would have to be 5 and 9 times, respectively, as large as those observed if the water caused hydrolysis through its ions alone. One side reaction, which may in part explain this decrease in reaction velocity, is the formation of olefines from the alkyl halide. This possibility was pointed out by Shadinger, Marshall, and especially by Robertson.

To check the accuracy of the values for "K_N found" they were compared with the values of "K_N calculated." The latter are found by substituting the proper values of K_i, K_m, α and $1 - \alpha$, for the different concentrations of the ethylates in the equation

$$K_N = K_i\alpha + K_m(1 - \alpha).$$

From these two values, the calculated and found, the percent error is calculated by using the calculated value of K_N as the standard.

The percent of reaction due to the ions and to the molecules is found by dividing the values of K_i, α and $K_m(1 - \alpha)$, respectively, by the calculated values of K_N for the different concentrations of ethylate.

EXPERIMENTAL

Preparation of Absolute Ethyl Alcohol

The use of the purest alcohol obtainable was necessitated, since it has been shown by several workers[1] in this laboratory and also by Goldschmidt,[2] Lapworth,[3] Bredig and Fraenkel,[4] Kailan,[5] Gyr,[6] and others that reaction velocities are in many cases markedly affected by the presence of small quantities of

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[1] Ber. deutsch. chem. Ges., 41, 3227, 3228 (1908); Am. Chem. Jour., 41, 457, 483 (1909); Ibid., 39, 711 (1906); Zeit. phys. Chem., 60, 728 (1907).

[2] Ber. deutsch. chem. Ges., 39, 711 (1906); Zeit. phys. Chem., 60, 728 (1907).

[3] Jour. Chem. Soc., 93, 2163, 2187 (1908); Proc. Chem. Soc., 24, 101, 152.

[4] Biochem. Zeit., 6, 308; Zeit. phys. Chem., 60, 202 (1907).

[5] Ber. deutsch. chem. Ges., 39, 1055 (1906); Sitzungsber. Akad. Wiss., Wien, 116, II, 155.

[6] Ber. deutsch. chem. Ges., 41, 4322 (1908).

water. The method which has given best results is to boil up the alcohol with pure lime (400 grams of oxide to the liter) for several days, distill off the alcohol and then repeat the operation, using less oxide the second time. By this method it is easily possible to obtain alcohol containing less than 0.04 percent of water.

Preparation of Standard Hydrochloric Acid

The hydrochloric acid used in the titrations was made by the method of Hulett and Bonner,[1] by distilling a 20 percent solution of the acid and thus obtaining a solution of known concentration. This was collected in paraffin bottles which had been thoroughly soaked out and which were kept sealed after the distillation was finished. The acid was made up to the desired strength by weighing out the proper amounts of the constant boiling mixture and of water, and the concentration was checked by silver chloride determinations. The twenty liter bottle in which the acid was kept had been soaked out for several months with dilute acid.

Preparation of the Sodium Ethylate Solution

Sodium ethylate was prepared by dissolving pure sodium in absolute alcohol. As the sodium crust was cut off under kerosene the oil was first roughly removed by wiping the sodium with filter paper. To remove the last traces it was dipped into absolute alcohol before adding it to the alcohol used in making up the ethylate solution. The solution was standardized by drawing off measured quantities of the ethylate by means of a specially constructed pipette, to be described later, pouring it into water and titrating the sodium hydroxide formed against the standard acid. The flask containing the ethylate was placed in the 0° bath and alcohol was added to bring the mixture to the proper concentration. The ethylate solution was made up fresh each day, as it turns dark on standing. Shrader has found that this change in color does not materially affect the reaction velocity but that it interferes greatly in determining the end point in titrations.

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[1] Jour. Am. Chem. Soc., 31, 390 (1909).

Preparation of the Alkyl Halide Solution

The alkyl halide solutions were made up by weighing the required amount of the alkyl halide into alcohol in a glass stoppered measuring flask and diluting to the mark with alcohol. Miss B. M. Brown found that 0.3 percent excess methyl iodide must be added to make up for the loss of the alkyl halide by vaporization.

The Bath

The bath used for this work at 0° was made of copper and lined with tin. It was protected on all sides by pads of lamb's wool and felt. It was kept filled with finely crushed ice and water and was agitated by a specially arranged stirrer. The temperature was found to remain constant to within a few thousandths of a degree.

Machine Pipette

Hecht, Conrad and Brückner, in carrying out their work on reaction velocities, mixed the solutions of ethylates and alkyl halides in one large flask and withdrew portions at definite time intervals for titration. By this method there is a great possibility for loss of alkyl halide on opening the flask, especially at higher temperatures. Therefore, in the work in this laboratory, small flasks of 20 cc or 40 cc capacity were used to contain the individual reaction mixtures.

For transferring the ethylate solution from the large flask in which the solution was made up to the small reaction flasks an ordinary pipette, surrounded by a jacket, which was filled with crushed ice and water, was used. The jacket was refilled once or twice while the solution was being transferred to the different flasks.

On account of the great volatility of methyl iodide, solutions of this substance cannot be transferred to the reaction flasks by means of the pipette described above, as much would be lost in the operation. To obviate this loss a machine which has been fully described by Robertson was used for measureing out the alkyl halide solution into the small flasks already containing the ethylate. A stream of water from the bath was kept running through the machine in order to keep the temperature of the solution at 0°. Even then a small amount of alkyl halide was lost, but, as mentioned above, this was offset by adding 0.3 percent excess of methyl iodide when making up the solution. The small flasks were removed from the bath after definite time periods, the contents were poured into about 200 cc of cold water, and the sodium hydroxide formed from the remaining ethylate was titrated with the standard hydrochloric acid in order to determine the values of x. In these titrations 0.5 N acid was used with methyl orange as the indicator.

On the Reactions of Sodium Ethylate and Methyl Iodide at 0°

TABLE I

0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 0°

A = 10.00

t	x	K_V
150	2.070	0.001740
180	2.354	0.001709
210	2.647	0.001714
240	2.903	0.001704

Average, 0.001717
K_N = 0.003434

TABLE II

0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 0°

A = 10.00

t	x	K_V
150	2.038	0.001706
180	2.323	0.001680
240	2.916	0.001715
264	3.110	0.001708
290	3.314	0.001694

Average, 0.001701
K_N = 0.003402

TABLE III

0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°

A = 10.00

t	x	K_V
60	0.515	0.000905
120	0.967	0.000901
210	1.606	0.000911
270	1.980	0.000914
309	2.158	0.000891
397	2.700	0.000901

Average, 0.000904
K_N = 0.003616

TABLE IV

0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°

A = 10.00

t	x	K_V
60	0.516	0.000906
120	0.976	0.000901
210	1.610	0.000913
270	1.972	0.000909
357	2.460	0.000913
384	2.592	0.000911

Average, 0.000909
K_N = 0.003636

TABLE V

0.25 *N* Sodium Ethylate and 0.25 *N* Methyl Iodide at 0°

A = 10.00

t	*x*	K_V
118	0.958	0.000898
180	1.418	0.000918
240	1.788	0.000906
1277	5.287	0.000899

Average, 0.000905
K_N = 0.003620

TABLE VI

0.25 *N* Sodium Ethylate and 0.25 *N* Methyl Iodide at 0°

A = 10.00

t	*x*	K_V
60	0.522	0.000918
120	0.982	0.000908
180	1.379	0.000899
240	1.772	0.000894
300	2.139	0.000903
360	2.448	0.000900

Average, 0.000902
K_N = 0.003608

TABLE VII

0.125 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide at 0°

A = 10.00

t	*x*	K_V
90	0.420	0.000487
150	0.652	0.000465
210	0.912	0.000478
330	1.344	0.000470
390	1.568	0.000476

Average, 0.000475
K_N = 0.003800

TABLE VIII

0.125 *N* Sodium Ethylate and 0.125 *N* Methyl Iodide at 0°

A = 10.00

t	*x*	K_V
90	0.426	0.000494
150	0.670	0.000479
270	1.145	0.000479
330	1.352	0.000473
390	1.568	0.000476

Average, 0.000480
K_N = 0.003840

Summary of Sodium Ethylate and Methyl Iodide at 0°

TABLE IX—K_N FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	K_N	K_N average
2	0.003434	
	0.003402	0.003418
4	0.003616	
	0.003636	
	0.003620	
	0.003608	0.003620
8	0.003800	
	0.003840	0.003820

TABLE X—THE IONIZATION OF SODIUM ETHYLATE AT 0°[1]

V	α	$1 - \alpha$
1	0.136	0.864
2	0.237	0.763
4	0.335	0.665
8	0.435	0.565
16	0.531	0.469
32	0.633	0.367

TABLE XI—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	K_i	K_m
V = 2:V = 4	0.00499	0.00293
V = 2:V = 8	0.00496	0.00294
V = 4:V = 8	0.00495	0.00295
	Av., 0.00496	0.00294

TABLE XII—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	K_N found	K_N calculated	Error in percent
2	0.003418	0.003419	—0.03
4	0.003620	0.003616	+0.11
8	0.003820	0.003818	+0.05

TABLE XIII—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
2	34.38	65.62
4	45.95	54.05
8	56.51	43.49

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[1] Robertson and Acree: Diss., J. H. U., 1910; Am. Chem. Jour., 49, 474 (1913); Jour. Phys. Chem., 19, 406 (1915).

II. Reinterpretation of the Work of Hecht, Conrad and Brückner on the Reaction of Alkyl Halides with Sodium Ethylate at Different Temperatures

As was mentioned above, some of the earliest work on the velocities of the reactions of alkyl halides with ethylates was done by Hecht, Conrad and Brückner,[1] but they did not interpret their results according to the ionic theory, as they considered these substances nonelectrolytes (nichtleitende Körper). Since we have shown by actual conductivity measurements that the ethylates are electrolytes, it was interesting to take their data and interpret[2] it on the basis of the reaction of both the ions and nonionized molecules of the sodium and potassium ethylates.

To test this theory we used our conductivity measurements at 0°, 25°, and 35° and calculated the ionization of the ethylate at the temperatures employed by Hecht, Conrad and Brückner. We then substituted these values for α and those found for K_N by Hecht, Conrad and Brückner in the equations

$$(1)\ K_i = \frac{K'_N(1-\alpha) - K_N(1-\alpha')}{\alpha' - \alpha} \text{ and } (2)\ K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha}$$

and learned that we obtain constants for K_i and K_m which may be considered to check very well with the values found in this laboratory for the same reaction, if we remember the fact that this earlier work had so many sources of error which have since been eradicated.

From their data on the reaction of sodium ethylate and methyl iodide at 0° we obtain $K_i = 0.005799$ and $K_m = 0.002649$, while, for the same reaction, the values found in this laboratory by Miss Brown[3] are $K_i = 0.004861$ and $K_m = 0.003033$ and the authors have found the values $K_i = 0.004960$ and $K_m = 0.002940$. From their data on the reaction of sodium ethylate and methyl iodide at 24° we obtain $K_i = 0.129$ and $K_m = 0.0435$, while for the same reaction at 25° the values found in this laboratory by Miss Brown are

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[1] Zeit. phys. Chem., **5**, 289 (1890).

[2] Jour. Chem. Soc., **105**, 2582 (1914).

[3] Diss. J. H. U., 1913.

$K_i = 0.129$ and $K_m = 0.0581$ and by Robertson $K_i = 0.127$ and $K_m = 0.0594$. From their data on the reaction of sodium ethylate and ethyl iodide at 24° we obtain $K_i = 0.0121$ and $K_m = 0.00294$, while the same reaction at 25°, the values found in this laboratory by Marshall,[1] are $K_i = 0.0120$ and $K_m = 0.00427$, and by Shrader[2] $K_i = 0.0122$ and $K_m = 0.00402$.

It is therefore seen that their work, which was not done from the standpoint of ionic reaction, can be explained very satisfactorily indeed by the theory that both the ions and molecules react side by side.

Hecht, Conrad and Brückner worked out their values for K_N, the reaction velocity, by the use of a purely empirical formula

$$(3)\qquad \begin{aligned} K'_N &= K_N + a \log (V'/V) \\ K''_N &= K_N + a \log (V''/V) \\ K'''_N &= K_N + a \log (V'''/V) \end{aligned}$$

in which K'_N and K_N are the reaction velocities at any dilutions, "a" is an empirical constant, obtained by solving these simultaneous equations, and V'/V is the ratio of the volumes of the two solutions; that is, if we are comparing two solutions, say $V = 10$ and $V = 2$, the V'/V used in the formula above would be the ratio of 10 to 2, which is 5.

As this formula is purely empirical we attempted to find the value of the Hecht, Conrad and Brückner factor "a" in terms of Acree's formula to see if we could find what this term "a" really means; for although their formula is empirical, it seems to hold in practice and it should be possible to give it some rational physical basis.

Representing by K'_N and K_N the reaction velocities of two substances at different dilutions we have by Acree's formula:

$$(4)\qquad K_N = K_i\alpha + K_m(1 - \alpha)$$

$$(5)\qquad \text{and } K'_N = K_i\alpha' + K_m(1 - \alpha')$$

Subtracting we have,

$$(6)\qquad \begin{aligned} K'_N - K_N &= K_i(\alpha' - \alpha) - K_m(\alpha' - \alpha) \\ &= (K_i - K_m)(\alpha' - \alpha). \end{aligned}$$

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[1] Jour. Phys. Chem., 19, 589 (1915).

[2] Diss. J. H. U., 1913.

According to Hecht, Conrad and Brückner,

$$K'_N = K_N + a \log (V'/V)$$
$$\text{or } K'_N - K_N = a \log (V'/V)$$

Equating these two values for $K'_N - K_N$ we get,

$$a \log V'/V = (K_i - K_m)(\alpha' - \alpha) \tag{7}$$

$$\text{and hence, } a = \frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)}. \tag{8}$$

We then tested this equation (8) to see if we obtain a constant for "*a*" by substituting the proper values for K_i, K_m, α, α' and V'/V. The tables on pages 372, 375, and elsewhere show that the values for "*a*" are really quite constant; since $K_i - K_m$ is also a constant we see that in the work of Hecht, Conrad and Brückner and in the cases studied by us *the difference in ionization of two given solutions seems to be proportional to the logarithm of the ratio of their volumes.* This empirical relation seems to hold over a limited range, especially in the more concentrated solutions, both with those electrolytes which obey the Ostwald dilution law and those which do not. That it cannot hold over all ranges follows at once from the fact that

$$\frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)},$$

or "*a*," becomes gradually smaller and approaches zero for those solutions which are nearly completely ionized. We consider this to be a very important empirical relationship, which we shall develop for all of the cases where the reaction velocities and conductivities are available, whether the substances be organic or inorganic acids, bases and salts.

We then used Formula 3 for obtaining the calculated or theoretical values for K'_N, K''_N, K'''_N, etc., by taking any given value as K_N and using the average of the values of "*a*" found above. For uniformity we have called all these values of K'_N, K''_N, K'''_N, etc., simply "(1) K_N calculated" in the tables. It will be seen from the tables given on pages 372, 375 and elsewhere, that these values for K_N calculated are very close to those found experimentally. From the "K_N

found" and the "(1) K_N calculated," as explained above, the per cent error was determined, 0.00 error showing the value used as K_N in Equation 3.

Under the heading "(2) K_N calculated" we give the values of "K_N calculated" for any given value of "V" by the use of the summation of the equations under (3). The sum assumes the form

$$K'_N + K''_N + K'''_N + K^a_N = nK_N + a \log \left\{ \frac{V'V''V'''V^a}{V^n} \right\}$$

in which n is the number of different concentrations studied and K_N is the reaction velocity, $V \times K_V$, calculated for any particular value of V. Under "(2) Error in per cent" is given the deviation of the "K_N found" from the "(2) K_N calculated."

It is clearly recognized that all the values given in the tables below are not accurate beyond the second or third significant figure, even though four are sometimes given.

To test further the relations between the formula used by Hecht, Conrad and Brückner and that used by us, we used some of the work which was done in this laboratory, in which we have eliminated all sources of error as completely as possible, and obtained the values of "a" from Equation 8, and of "K_N calculated" from Equation 3. In our work on sodium ethylate and methyl iodide at 0° the values for "a" and for "K_N calculated," obtained from Equations 8 and 3, are given in the following tables:

TABLE XIV—"a" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

	"a"
V = 2:V = 4	0.000658
V = 2:V = 6	0.000664
V = 4:V = 8	0.000671
	Average, 0.000664

TABLE XV—K_N FOUND, "K_N CALCULATED," OBTAINED BY USING "a" IN THE EQUATION $K'_N = K_N + "a" \log (V'/V)$ AND ERROR IN PERCENT

V	K_N found	K_N calculated	Error in percent
2	0.003418	0.003418	0.00
4	0.003620	0.003618	+0.06
8	0.003820	0.003818	+0.05

In the work of Shrader on sodium ethylate and ethyl iodide at 25° we find again this close agreement. The average value found for "a" is 0.002297. We give in the following table the values for K_N calculated, the values for K_N found experimentally and the error in percent:

V	K_N found	K_N calculated	Error in percent
1	0.00521	0.00521	0.0
2	0.00595	0.00590	+0.8
4	0.00657	0.00659	—0.3
8	0.00723	0.00728	—0.7
16	0.00800	0.00797	+0.4
32	0.00865	0.00866	—0.1

It is seen that the values for "a" are very constant and that the agreement between the values for K_N found and those calculated is excellent. These are only two of many cases which have been recalculated and in all we find this same excellent agreement.

We therefore find that the empirical formula

$$K'_N = K_N + a \log (V'/V)$$

used so successfully by Hecht, Conrad and Brückner can be transformed into our equations, which have as a rational basis the idea that both the anions and the molecules of the ethylates react with the alkyl halides. This is a beautiful example to illustrate the fact that all valid empirical formulas can be put on a rational basis by the proper study of the questions involved.

On the Reactions of Sodium Ethylate and Methyl Iodide at 0°

TABLE I—K_N FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

Conc. $NaOC_2H_5$ V	K_N found
1	0.002958
2	0.003426
10	0.003996
20	0.004348

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 0°

V	α	$1 - \alpha$
1	0.1362	0.8638
2	0.2372	0.7628
10	0.4587	0.5413
20	0.5766	0.4234

TABLE III—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

	K_i	K_m
V = 1:V = 2	0.006942	0.002324
V = 1:V = 10	0.005738	0.002518
V = 1:V = 20	0.005616	0.002528
V = 2:V = 10	0.005388	0.003120
V = 2:V = 20	0.005498	0.002780
V = 10:V = 20	0.005612	0.002626
	Av., 0.005799	0.002649

TABLE IV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	K_N found	K_N calculated	Error in percent
1	0.002958	0.003078	−4.05
2	0.003426	0.003395	+0.91
10	0.003996	0.004099	−2.57
20	0.004348	0.004465	−2.69

Table V—Percent of Reaction Due to Ions and to Molecules

V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	25.66	74.34
2	40.51	59.49
10	64.89	35.11
20	74.88	25.12

Table VI—"*a*" Found for Sodium Ethylate and Methyl Iodide at 0°

	"*a*"
V = 1:V = 2	0.001057
V = 1:V = 10	0.001016
V = 1:V = 20	0.001066
V = 2:V = 10	0.000998
V = 2:V = 20	0.001069
V = 10:V = 20	0.001233
	Average, 0.001073

Table VII—K_N Found, K_N Calculated by Using "*a*" in the Equation $K'_N = K_N + $ "*a*" Log (V′/V) and Error in Per Cent

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
1	0.002958	0.002958	0.00	0.002981	−0.77
2	0.003426	0.003281	+4.42	0.003306	+3.63
10	0.003996	0.004031	−0.86	0.004379	−8.73
20	0.004346	0.004354	−0.15	0.004593	−5.38

On the Reactions of Sodium Ethylate and Methyl Iodide at 12°

Table I—K_N Found for Sodium Ethylate and Methyl Iodide at 12°

Conc. $NaOC_2H_5$ V	K_N found
2	0.01496
20	0.02014

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 12°

V	α	$1-\alpha$
2	0.2360	0.7640
20	0.5275	0.4725

TABLE III—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 12°

	K_i	K_m
V = 2:V = 20	0.02896	0.01028

TABLE IV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 12°

V	K_N found	K_N calculated	Error in percent
2	0.01469	0.01468	+0.07
20	0.02014	0.02012	+0.10

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1-\alpha)K_m$
2	46.55	53.45
20	75.92	24.08

TABLE VI—"*a*" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 12°

	"*a*"
V = 2:V = 20	0.005445

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "*a*" IN THE EQUATION $K'_N = K_N +$ "*a*" LOG (V′/V) AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in per-cent	(2) K_N calculated	Error in per-cent
2	0.01469	0.01469	0.00	0.01469	+0.00
20	0.02014	0.02013	+0.05	0.02013	+0.05

On the Reactions of Sodium Ethylate and Methyl Iodide at 18°

Table I—K_N Found for Sodium Ethylate and Methyl Iodide at 18°

Conc. $NaOC_2H_5$ V	K_N found
2	0.03020
10	0.03844
20	0.04642

Table II—The Ionization of Sodium Ethylate at 18°

V	α	$1 - \alpha$
2	0.2382	0.7618
10	0.4190	0.5810
20	0.6190	0.3810

Table III—K_i and K_m Found for Sodium Ethylate and Methyl Iodide at 18°

	K_i	K_m
V = 2 : V = 10	0.06490	0.01934
V = 2 : V = 40	0.06264	0.02004
V = 10 : V = 40	0.06162	0.02072
	Av., 0.06305	0.02003

Table IV—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 18°

V	K_N found	K_N calculated	Error in percent
2	0.03020	0.03026	−0.19
10	0.03844	0.03804	+1.04
40	0.04642	0.04645	−0.06

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
2	49.63	50.37
10	69.44	30.56
40	84.04	15.98

TABLE VI—"*a*" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 18°

	"*a*"
V = 2:V = 10	0.01113
V = 2:V = 40	0.01259
V = 10:V = 40	0.01429
	Average, 0.01267

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "*a*" IN THE EQUATION $K'_N = K_N +$ "*a*" LOG (V′/V) AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
2	0.03020	0.02993	+0.9	0.02991	+ 0.97
10	0.03844	0.03879	−0.9	0.04639	−17.1
40	0.04642	0.04642	0.00	0.04721	− 1.67

On the Reaction of Sodium Ethylate and Methyl Iodide at 24°

TABLE I—K_N FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 24°

Conc. $NaOC_2H_5$ V	K_N	Conc. $NaOC_2H_5$ V	K_N
1	0.05512	20	0.08696
2	0.06276	40	0.09448
5	0.07182	80	0.10226
10	0.07950	—	—

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 24°

V	α	$(1 - \alpha)$
1	0.1470	0.8530
2	0.2346	0.7654
5	0.3335	0.6665
10	0.4170	0.5830
20	0.5075	0.4925
40	0.6040	0.3960
80	0.7030	0.2970

TABLE III—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 24°

	K_i	K_m
V = 1:V = 2	0.1294	0.04230
V = 1:V = 5	0.1215	0.04194
V = 1:V = 10	0.1312	0.04184
V = 1:V = 20	0.1304	0.04212
V = 1:V = 40	0.1284	0.04244
V = 1:V = 80	0.1274	0.04264
V = 2:V = 5	0.1328	0.04126
V = 2:V = 10	0.1330	0.04122
V = 2:V = 20	0.1306	0.04194
V = 2:V = 40	0.1281	0.04260
V = 2:V = 80	0.1273	0.04296
V = 5:V = 10	0.1331	0.04114
V = 5:V = 20	0.1297	0.04280
V = 5:V = 40	0.1276	0.04386
V = 5:V = 80	0.1276	0.04434
V = 10:V = 20	0.1275	0.04510
V = 10:V = 40	0.1262	0.04608
V = 10:V = 80	0.1258	0.04630
V = 20:V = 40	0.1253	0.04740
V = 20:V = 80	0.1255	0.04726
V = 40:V = 80	0.1256	0.04700
	Av., 0.12877	0.04354

Table IV—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 24°

V	K_N found	K_N calculated	Error in percent
1	0.05512	0.05605	—1.68
2	0.06276	0.06352	—1.21
5	0.07182	0.07194	—0.16
10	0.07950	0.07905	+0.57
20	0.08696	0.08676	+0.23
40	0.09448	0.09498	—0.52
80	0.10226	0.10340	—1.17

Table V—Percent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	33.75	66.25
2	47.53	52.47
5	59.66	40.34
10	67.89	32.11
20	75.28	24.72
40	81.84	18.16
80	87.51	12.49

Table VI—"*a*" Found for Sodium Ethylate and Methylate Iodide at 24°

	"*a*"		"*a*"
V = 1 : V = 2	0.02478	V = 5 : V = 10	0.02362
V = 1 : V = 5	0.02272	V = 5 : V = 20	0.02461
V = 1 : V = 10	0.02299	V = 5 : V = 40	0.02551
V = 1 : V = 20	0.02359	V = 5 : V = 80	0.02613
V = 1 : V = 40	0.02429	V = 10 : V = 20	0.02560
V = 1 : V = 80	0.02488	V = 10 : V = 40	0.02645
V = 2 : V = 5	0.02116	V = 10 : V = 80	0.02697
V = 2 : V = 10	0.02222	V = 20 : V = 40	0.02730
V = 2 : V = 20	0.02324	V = 20 : V = 80	0.02765
V = 2 : V = 40	0.02416	V = 40 : V = 80	0.02801
V = 2 : V = 80	0.02489		
		Average,	0.02480

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "a" IN THE EQUATION $K'_N = K_N + $ "a" LOG (V′/V) AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
1	0.05512	0.05470	+0.77	0.05486	+0.47
2	0.06276	0.06216	+0.96	0.06233	+0.69
5	0.07182	0.07202	—0.28	0.07220	—0.52
10	0.07950	0.07949	0.00	0.08538	—6.89
20	0.08696	0.08696	0.00	0.09208	—5.56
40	0.09448	0.09442	+0.44	0.09879	—4.36
80	0.10220	0.10189	+0.30	0.10549	—3.12

On the Reaction of Sodium Ethylate and Methyl Iodide at 36°

TABLE I—K_N FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 36°

Conc. $NaOC_2H_5$ V	K_N found	Conc. $NaOC_2H_5$ V	K_N found
1	0.2344	20	0.3730
2	0.2663	40	0.4050
4	0.2984	80	0.4370
5	0.3088	160	0.4692
10	0.3408	1000	0.5540

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3036	0.6964
5	0.3218	0.6782
10	0.3972	0.6028
20	0.4829	0.5171
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134
1000	0.9900	0.0100

TABLE III—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 36°

	K_i	K_m
V = 1:V = 2	0.5818	0.1710
V = 1:V = 4	0.5970	0.1656
V = 1:V = 5	0.6100	0.1659
V = 1:V = 10	0.5568	0.1668
V = 1:V = 20	0.5916	0.1693
V = 1:V = 40	0.5730	0.1725
V = 1:V = 80	0.5324	0.1754
V = 1:V = 160	0.5484	0.1771
V = 1:V = 1000	0.5602	0.1754
V = 2:V = 4	0.5968	0.1625
V = 2:V = 5	0.5626	0.1565
V = 2:V = 10	0.6126	0.1616
V = 2:V = 20	0.6068	0.1677
V = 2:V = 40	0.5724	0.1740
V = 2:V = 80	0.5562	0.1787
V = 2:V = 160	0.5620	0.1815
V = 2:V = 1000	0.5576	0.1775
V = 4:V = 5	0.6700	0.1247
V = 4:V = 10	0.6138	0.1609
V = 4:V = 20	0.5572	0.1722
V = 4:V = 40	0.5742	0.1813
V = 4:V = 80	0.5518	0.1878
V = 4:V = 160	0.5446	0.1911
V = 4:V = 1000	0.5574	0.1853
V = 5:V = 10	0.5968	0.1963
V = 5:V = 20	0.5754	0.1806
V = 5:V = 40	0.5614	0.1501
V = 5:V = 80	0.5486	0.1950
V = 5:V = 160	0.5434	0.1978
V = 5:V = 1000	0.5580	0.1907
V = 10:V = 20	0.5666	0.1916
V = 10:V = 40	0.5514	0.2014
V = 10:V = 80	0.5428	0.2076
V = 10:V = 160	0.5392	0.2098
V = 10:V = 1000	0.5576	0.1980
V = 20:V = 40	0.5432	0.2142
V = 20:V = 80	0.5376	0.2196
V = 20:V = 160	0.5302	0.2200
V = 20:V = 1000	0.5574	0.2248
V = 40:V = 80	0.5342	0.2267
V = 40:V = 160	0.5356	0.2247
V = 40:V = 1000	0.5578	0.2491
V = 80:V = 160	0.5362	0.2414
V = 80:V = 1000	0.5586	0.2234
V = 160:V = 1000	0.5584	0.1676
Average,	0.5606	0.1892

TABLE IV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 36°

V	K_N found	K_N calculated	Error in percent
1	0.2344	0.2464	—4.8
2	0.2664	0.2732	—2.4
4	0.2984	0.3020	—1.1
5	0.3088	0.3087	0.0
10	0.3408	0.3366	+1.2
20	0.3730	0.3686	+1.1
40	0.4050	0.4046	+0.1
80	0.4370	0.4434	—1.4
160	0.4692	0.4814	—2.5
1000	0.5540	0.5568	—0.5

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	35.11	64.89
2	47.64	52.36
4	56.36	43.64
5	58.42	41.58
10	60.20	39.80
20	73.48	26.51
40	80.41	19.59
80	87.00	13.00
160	91.22	8.78
1000	99.06	0.94

TABLE VI—"*a*" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 36°

	"*a*"		"*a*"
V = 1:V = 2	0.1064	V = 5:V = 10	0.1001
V = 1:V = 4	0.1070	V = 5:V = 20	0.1054
V = 1:V = 5	0.1066	V = 5:V = 40	0.1176
V = 1:V = 10	0.0948	V = 5:V = 80	0.1068
V = 1:V = 20	0.1064	V = 5:V = 160	0.1068
V = 1:V = 40	0.1065	V = 5:V = 1000	0.1065
V = 1:V = 80	0.0993	V = 10:V = 20	0.1065
V = 1:V = 160	0.1066	V = 10:V = 40	0.1064
V = 1:V = 1000	0.1070	V = 10:V = 80	0.1066
V = 2:V = 4	0.1029	V = 10:V = 160	0.1064
V = 2:V = 5	0.0914	V = 10:V = 1000	0.1064
V = 2:V = 10	0.1064	V = 20:V = 40	0.1063
V = 2:V = 20	0.1102	V = 20:V = 80	0.1062
V = 2:V = 40	0.1064	V = 20:V = 160	0.1042
V = 2:V = 80	0.1065	V = 20:V = 1000	0.0991
V = 2:V = 160	0.1107	V = 40:V = 80	0.1064
V = 2:V = 1000	0.1068	V = 40:V = 160	0.1066
V = 4:V = 5	0.1025	V = 40:V = 1000	0.0905
V = 4:V = 10	0.1064	V = 80:V = 160	0.1003
V = 4:V = 20	0.0986	V = 80:V = 1000	0.0959
V = 4:V = 40	0.1084	V = 160:V = 1000	0.0997
V = 4:V = 80	0.1063		
V = 4:V = 160	0.1064		Average, 0.1046
V = 4:V = 1000	0.1064		

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "*a*" IN THE EQUATION $K'_N = K_N + $ "*a*" LOG (V′/V) AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
1	0.2344	0.2357	—0.56	0.2368	—1.01
2	0.2664	0.2672	—0.30	0.2683	—0.71
4	0.2984	0.2987	—0.11	0.2998	—0.46
5	0.3088	0.3088	0.00	0.3099	—0.35
10	0.3408	0.3403	+0.14	0.3414	—0.17
20	0.3730	0.3718	+0.32	0.3854	—3.22
40	0.4050	0.4033	+0.42	0.4167	—2.81
80	0.4370	0.4347	+0.52	0.4480	—2.45
160	0.4692	0.4662	+0.64	0.4793	—2.11
1000	0.5540	0.5495	+0.81	0.5634	—1.67

On the Reaction of Sodium Ethylate and Methyl Iodide at 24°

Table I—K_N Found for Sodium Ethylate and Ethyl Iodide at 24°

Conc. $NaOC_2H_5$ V	K_N	Conc. $NaOC_2H_5$ V	K_N
1	0.004326	10	0.006842
2	0.004946	20	0.007624
5	0.006105		

Table II—The Ionization of Sodium Ethylate at 24°

V	α	$1-\alpha$
1	0.148	0.852
2	0.235	0.765
5	0.336	0.864
10	0.422	0.578
20	0.512	0.488

Table III—K_i and K_m Found for Sodium Ethylate and Ethyl Iodide at 24°

	K_i	K_m
V = 1:V = 2	0.0104	0.00328
V = 1:V = 5	0.0124	0.00293
V = 1:V = 10	0.0121	0.00297
V = 1:V = 20	0.0120	0.00299
V = 2:V = 5	0.0137	0.00226
V = 2:V = 10	0.0127	0.00258
V = 2:V = 20	0.0123	0.00269
V = 5:V = 10	0.0117	0.00326
V = 5:V = 20	0.0118	0.00323
V = 10:V = 20	0.0118	0.00318
Average,	0.0121	0.00294

TABLE IV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 24°

V	K_N found	K_N calculated	Error in percent
1	0.004326	0.004294	+0.7
2	0.004946	0.005090	—2.8
5	0.006105	0.006014	+1.2
10	0.006842	0.006801	+0.6
20	0.007624	0.007625	0.0

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	41.70	58.30
2	55.86	44.14
5	67.60	32.40
10	75.08	24.92
20	81.25	18.75

TABLE VI—"*a*" FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 24°

	"*a*"
V = 1:V = 2	0.002647
V = 1:V = 5	0.002464
V = 1:V = 10	0.002510
V = 1:V = 20	0.002563
V = 2:V = 5	0.002325
V = 2:V = 10	0.002451
V = 2:V = 20	0.002537
V = 5:V = 10	0.002616
V = 5:V = 20	0.002678
V = 10:V = 20	0.002738
Average,	0.002553

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "a" IN THE EQUATION $K'_N = K_N + $ "a" LOG (V'/V) AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
1	0.004326	0.004302	+0.5	0.004437	—2.50
2	0.004946	0.005071	—2.4	0.005206	—4.99
5	0.006105	0.006110	0.0	0.006534	—6.56
10	0.006842	0.006855	—0.2	0.007143	—4.21
20	0.007624	0.007624	0.0	0.008417	—9.42

On the Reaction of Sodium Ethylate and Methyl Iodide at 36°

TABLE I—K_N FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 36°

Conc. $NaOC_2H_5$	K_N found	Conc. $NaOC_2H_5$	K_N found
1	0.01817	20	0.03234
2	0.02148	40	0.03594
4	0.02486	80	0.03926
5	0.02586	160	0.04258
10	0.02918	1000	0.05126

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3036	0.6964
5	0.3218	0.6782
10	0.3972	0.6028
20	0.4829	0.5171
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134
1000	0.9900	0.0100

TABLE III—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 36°

	K_i	K_m
V = 1:V = 2	0.05408	0.01162
V = 1:V = 4	0.05604	0.01126
V = 1:V = 5	0.05698	0.01109
V = 1:V = 10	0.05648	0.01118
V = 1:V = 20	0.05462	0.01152
V = 1:V = 40	0.05346	0.01173
V = 1:V = 80	0.05182	0.01203
V = 1:V = 160	0.05080	0.01221
V = 1:V = 1000	0.05164	0.01202
V = 2:V = 4	0.05782	0.01048
V = 2:V = 5	0.05900	0.01013
V = 2:V = 10	0.05730	0.01064
V = 2:V = 20	0.05474	0.01142
V = 2:V = 40	0.05338	0.01183
V = 2:V = 80	0.05168	0.01234
V = 2:V = 160	0.05070	0.01264
V = 2:V = 1000	0.05164	0.01235
V = 4:V = 5	0.06312	0.00818
V = 4:V = 10	0.05700	0.01084
V = 4:V = 20	0.05390	0.01219
V = 4:V = 40	0.05276	0.01273
V = 4:V = 80	0.05120	0.01337
V = 4:V = 160	0.05040	0.01372
V = 4:V = 1000	0.05164	0.01318
V = 5:V = 10	0.05572	0.01169
V = 5:V = 20	0.05312	0.01291
V = 5:V = 40	0.05230	0.01330
V = 5:V = 80	0.05092	0.01396
V = 5:V = 160	0.05024	0.01428
V = 5:V = 1000	0.05162	0.01362
V = 10:V = 20	0.05140	0.01453
V = 10:V = 40	0.05144	0.01449
V = 10:V = 80	0.05034	0.01522
V = 10:V = 160	0.04992	0.01551
V = 10:V = 1000	0.05162	0.01438
V = 20:V = 40	0.05148	0.01445
V = 20:V = 80	0.05010	0.01573
V = 20:V = 160	0.04976	0.01605
V = 20:V = 1000	0.05162	0.01432
V = 40:V = 80	0.04932	0.01744
V = 40:V = 160	0.04956	0.01732
V = 40:V = 1000	0.05162	0.01426
V = 80:V = 160	0.04948	0.01707
V = 80:V = 1000	0.05164	0.01241
V = 160:V = 1000	0.05168	0.00901
Average,	0.05282	0.01295

TABLE IV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 36°

V	K_N found	K_N calculated	Error in percent
1	0.01817	0.01910	—5.11
2	0.02148	0.02220	—3.34
4	0.02486	0.02505	—0.76
5	0.02586	0.02577	+0.35
10	0.02918	0.02878	+1.38
20	0.03234	0.03220	+0.13
40	0.03594	0.03607	—0.36
80	0.03926	0.04022	—2.44
160	0.04258	0.04431	—4.06
1000	0.05126	0.05358	—4.52

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to K_i	Percent of reaction due to $(1 - \alpha)K_m$
1	42.67	57.33
2	55.24	44.76
4	64.01	35.99
5	65.95	34.05
10	72.89	27.11
20	78.59	21.41
40	84.94	15.06
80	89.85	10.15
160	93.76	6.24
1000	97.59	2.41

Table VI—"*a*" Found for Sodium Ethylate and Ethyl Iodide at 36°

	"*a*"		"*a*"
V = 1:V = 2	0.01100	V = 5:V = 10	0.01101
V = 1:V = 4	0.01111	V = 5:V = 20	0.01074
V = 1:V = 5	0.01101	V = 5:V = 40	0.01115
V = 1:V = 10	0.01101	V = 5:V = 80	0.01116
V = 1:V = 20	0.01086	V = 5:V = 160	0.01111
V = 1:V = 40	0.01110	V = 5:V = 1000	0.01102
V = 1:V = 80	0.01106	V = 10:V = 20	0.01047
V = 1:V = 160	0.01079	V = 10:V = 40	0.01123
V = 1:V = 1000	0.01101	V = 10:V = 80	0.01117
V = 2:V = 4	0.01122	V = 10:V = 160	0.01111
V = 2:V = 5	0.01100	V = 10:V = 1000	0.01102
V = 2:V = 10	0.01101	V = 20:V = 40	0.01196
V = 2:V = 20	0.01087	V = 20:V = 80	0.01148
V = 2:V = 40	0.01109	V = 20:V = 160	0.01133
V = 2:V = 80	0.01109	V = 20:V = 1000	0.01112
V = 2:V = 160	0.01108	V = 40:V = 80	0.01103
V = 2:V = 1000	0.01104	V = 40:V = 160	0.01106
V = 4:V = 5	0.01033	V = 40:V = 1000	0.01095
V = 4:V = 10	0.01085	V = 80:V = 160	0.01102
V = 4:V = 20	0.01068	V = 80:V = 1000	0.01122
V = 4:V = 40	0.01105	V = 160:V = 1000	0.01088
V = 4:V = 80	0.01105		
V = 4:V = 160	0.01104	Average,	0.01103
V = 4:V = 1000	0.01100		

Table VII—K_N Found, K_N Calculated by Using "*a*" in the Equation $K'_N = K_N +$ "*a*" Log (V′/V) and Error in Percent

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
1	0.01817	0.01799	+1.00	0.01818	—0.05
2	0.02148	0.02131	+0.79	0.02150	—0.10
4	0.02486	0.02463	+0.93	0.02489	—0.12
5	0.02586	0.02570	+0.62	0.02589	—0.12
10	0.02918	0.02902	+0.55	0.02921	—0.10
20	0.03234	0.03234	0.00	0.03386	—4.49
40	0.03594	0.03566	+0.78	0.03716	—3.25
80	0.03926	0.03898	+0.71	0.04046	—2.96
160	0.04258	0.04230	+0.66	0.04375	—2.69
1000	0.05126	0.05109	+0.33	0.05262	—2.58

On the Reaction of Sodium Ethylate and Propyl Iodide at 36°

TABLE I—K_N FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE AT 36°

Conc. $NaOC_2H_5$ V	K_N	Conc. $NaOC_2H_5$ V	K_N
1	0.002977	40	0.006717
2	0.003670*	80	0.007420
4	0.004383*	160	0.008123
10	0.005312*		

*Only experimental values found were V = 2 0.003696
V = 4 0.004350
V = 10 0.005330

+Values given for K_N above were calculated by the formula of Hecht, Conrad and Brückner.

TABLE II—THE IONIZATION OF SODIUM EYHYLATE AT 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3033	0.6967
10	0.3972	0.6028
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134

TABLE III—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE AT 36°

	K_i	K_m
V = 1:V = 2	0.01050	0.001604
V = 1:V = 4	0.01096	0.001521
V = 1:V = 10	0.01111	0.001494
V = 1:V = 40	0.01040	0.001621
V = 1:V = 80	0.01007	0.001683
V = 1:V = 160	0.00986	0.001721
V = 2:V = 4	0.01137	0.001341
V = 2:V = 10	0.01131	0.001359
V = 2:V = 40	0.01039	0.001637
V = 2:V = 80	0.01004	0.001743
V = 2:V = 160	0.00984	0.001803
V = 4:V = 10	0.01127	0.001382
V = 4:V = 40	0.01025	0.001826
V = 4:V = 80	0.00994	0.001964
V = 4:V = 160	0.00997	0.002036
V = 10:V = 40	0.00994	0.002261
V = 10:V = 80	0.00974	0.002394
V = 10:V = 160	0.00966	0.002445
V = 40:V = 80	0.00955	0.002799
V = 40:V = 160	0.00957	0.002767
V = 80:V = 160	0.00959	0.002723
Average,	0.01025	0.001912

TABLE IV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE AT 36°

V	K_N found	K_N calculated	Error in percent
1	0.002977	0.003205	−7.1
2	0.003670	0.003948	−7.1
4	0.004383	0.004455	−1.6
10	0.005312	0.005243	+1.3
40	0.006717	0.006777	−0.9
80	0.007420	0.007650	−3.0
160	0.008123	0.008509	−4.5

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	49.59	50.51
2	60.58	39.42
4	70.12	29.88
10	78.03	21.97
40	88.16	11.84
80	92.12	7.88
160	95.22	4.78

TABLE VI—"*a*" FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE AT 36°

	"*a*"		"*a*"
V = 1:V = 2	0.002154	V = 4:V = 10	0.001965
V = 1:V = 4	0.002063	V = 4:V = 40	0.002308
V = 1:V = 10	0.002025	V = 4:V = 80	0.002441
V = 1:V = 40	0.002216	V = 4:V = 160	0.001947
V = 1:V = 80	0.002321	V = 10:V = 40	0.001946
V = 1:V = 160	0.002392	V = 10:V = 80	0.001946
V = 2:V = 4	0.001969	V = 10:V = 160	0.001946
V = 2:V = 10	0.001968	V = 40:V = 80	0.002883*
V = 2:V = 40	0.002229	V = 40:V = 160	0.002859*
V = 2:V = 80	0.002352	V = 80:V = 160	0.002836*
V = 2:V = 160	0.002428		
		Average,	0.002247

* Omitting marked values 0.002145.

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "*a*" IN THE EQUATION $K'_N = K_N + \text{"}a\text{"} \log (V'/V)$ AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
1	0.002977	0.003167	−5.9	0.003071	−3.06
2	0.003670	0.003823	−4.0	0.003747	−2.05
4	0.004383	0.004458	−1.6	0.004424	−0.92
10	0.005312	0.005312	0.0	0.005318	−0.10
40	0.006717	0.006603	+1.7	0.006926	−3.02
80	0.007420	0.007249	+2.3	0.007534	−1.51
160	0.008123	0.007894	+2.9	0.008142	−0.23

On the Reaction of Sodium Ethylate and Cetyl Iodide at 36°

Table I—K_N Found for Sodium Ethylate and Cetyl Iodide at 36°

Conc. $NaOC_2H_5$ V	K_N found	Conc. $NaOC_2H_5$ V	K_N found
1	0.004220	80	0.010510
4	0.006212	1000	0.014140
10	0.007530		

Table II—The Ionization of Sodium Ethylate at 36°

V	α	$1-\alpha$
1	0.1543	0.8457
4	0.3036	0.6964
10	0.3972	0.6028
80	0.6842	0.3158
1000	0.9900	0.0100

Table III—K_i and K_m Found for Sodium Ethylate and Cetyl Iodide at 36°

	K_i	K_m
V = 1:V = 4	0.01550	0.002160
V = 1:V = 10	0.01574	0.002116
V = 1:V = 80	0.01427	0.002386
V = 1:V = 1000	0.01426	0.002386
V = 4:V = 10	0.01601	0.001936
V = 4:V = 80	0.01412	0.002776
V = 4:V = 1000	0.01426	0.002770
V = 10:V = 80	0.01380	0.003394
V = 10:V = 1000	0.01425	0.003094
V = 80:V = 1000	0.01426	0.002396
Average,	0.01464	0.002541

Table IV—K_N Calculated and Found for Sodium Ethylate and Cetyl Iodide at 36°

V	K_N found	K_N calculated	Error in percent
1	0.004220	0.004406	−4.40
4	0.006212	0.006213	−0.01
10	0.007530	0.007346	+3.30
80	0.010510	0.010810	−2.85
1000	0.014140	0.014740	−4.24

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	51.26	48.74
4	71.53	28.47
10	79.15	20.86
80	92.66	7.34
1000	98.32	1.68

TABLE VI—"*a*" FOUND FOR SODIUM ETHYLATE AND CETYL IODIDE AT 36°

	"*a*"
V = 1:V = 4	0.003308
V = 1:V = 10	0.003309
V = 1:V = 80	0.003303
V = 1:V = 1000	0.003300
V = 4:V = 10	0.003306
V = 4:V = 80	0.003311
V = 4:V = 1000	0.003286
V = 10:V = 80	0.003310
V = 10:V = 1000	0.003303
V = 80:V = 1000	0.003392
Average,	0.003313

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "*a*" IN THE EQUATION $K'_N = K_N +$ "*a*" LOG (V′/V) AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
4	0.006212	0.006217	—0.09	0.006205	+ 0.10
10	0.007530	0.007532	—0.03	0.007523	+ 0.10
80	0.010510	0.010524	—0.14	0.011994	—12.37
1000	0.014140	0.014154	—0.10	0.014986	— 5.64

On the Reaction of Sodium Ethylate and Octyl Iodide at 36°

TABLE I—K_N FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

Conc. $NaOC_2H_5$ V	K_N found	Conc. $NaOC_2H_5$ V	K_N found
1	0.003994	80	0.010190
4	0.006018	1000	0.013700
10	0.007294		

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
4	0.3036	0.6964
10	0.3972	0.6028
80	0.6842	0.3158
1000	0.9900	0.0100

TABLE III—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

	K_i	K_m
V = 1:V = 4	0.01545	0.001902
V = 1:V = 10	0.01548	0.001997
V = 1:V = 80	0.01388	0.002188
V = 1:V = 1000	0.01382	0.002200
V = 4:V = 10	0.01551	0.001879
V = 4:V = 80	0.01365	0.002690
V = 4:V = 1000	0.01381	0.002616
V = 10:V = 80	0.01337	0.003286
V = 10:V = 1000	0.01381	0.002996
V = 80:V = 1000	0.01382	0.002322
Average,	0.01426	0.002407

TABLE IV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

V	K_N found	K_N calculated	Error in percent
1	0.003994	0.004235	—6.03
4	0.006018	0.006005	+0.22
10	0.007294	0.007114	+2.49
80	0.010190	0.010510	—3.14
1000	0.013700	0.014140	—3.21

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	51.95	48.05
4	72.09	27.91
10	79.61	20.39
80	92.83	7.17
1000	99.84	0.16

TABLE VI—"*a*" FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

	"*a*"
V = 1:V = 4	0.003360
V = 1:V = 10	0.003276
V = 1:V = 80	0.003250
V = 1:V = 1000	0.003230
V = 4:V = 10	0.003203
V = 4:V = 80	0.003200
V = 4:V = 1000	0.003200
V = 10:V = 80	0.003205
V = 10:V = 1000	0.003200
V = 80:V = 1000	0.003289
Average,	0.003241

TABLE VII—K_N FOUND, K_N CALCULATED BY USING "*a*" IN THE EQUATION $K'_N = K_N + $ "*a*" LOG (V'/V) AND ERROR IN PERCENT

V	K_N found	(1) K_N calculated	Error in percent	(2) K_N calculated	Error in percent
4	0.006018	0.005945	+1.22	0.005981	+ 0.62
10	0.007294	0.007271	+0.39	0.007271	+ 0.32
80	0.010190	0.010212	−0.32	0.011644	−12.55
1000	0.013700	0.013757	−0.42	0.014571	− 5.98

Conclusions

1. The fact that chemical reactions may be accelerated through the action of the nonionized acids, bases and salts, as well as through the ions, is further proved by our work on sodium ethylate and methyl iodide at 0°.

2. The values found for K_i and K_m for the above reaction were: $K_i = 0.004960$ and $K_m = 0.002940$, while the values found by Miss B. M. Brown for the same reaction were $K_i = 0.004861$ and $K_m = 0.003033$. It will be seen that the two sets of values check very closely.

3. By a reinterpretation of the work of Hecht, Conrad and Brückner, from the standpoint that both ions and molecules react, it was found that we obtain constants for K_i and K_m which may be considered to check very well with the values

found in this laboratory for the same reaction, if we remember the fact that this earlier work had so many sources of error which have since been eradicated.

4. Hecht, Conrad and Brückner worked out their values for K_N, the reaction velocity, by the use of a purely empirical formula

$$K'_N = K_N + a \log (V'/V)$$
$$K''_N = K_N + a \log (V''/V) \text{ etc.,}$$

in which K'_N and K_N are the reaction velocities at any dilutions, "*a*" is an empirical constant, obtained by solving these simultaneous equations, and V and V′ are the volumes containing unit masses of the solutes. In terms of Acree's equation

$$\text{“}a\text{”} = \frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)}.$$

By substituting the values for K_i, K_m, α', α, V' and V in the above equation it was found that the values for "*a*" are quite constant; since $K_i - K_m$ is also a constant, we see that *the difference in ionization of two given solutions seems to be proportional to the logarithm of the ratio of their volumes.* This empirical relationship holds over a limited range, especially in the more concentrated solutions. That it cannot hold for more dilute solutions follows from the fact that

$$\frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)}$$

or "*a*" becomes gradually smaller and approaches zero for those solutions which are nearly completely ionized.

5. It is seen that the empirical formula $K'_N = K_N + a \log (V'/V)$ used by Hecht, Conrad and Brückner can be transformed into our equations, which have as a rational basis the idea that both the anions and molecules of the ethylate react with the alkyl halides.

OVER-VOLTAGE AND MONATOMIC HYDROGEN

BY WILDER D. BANCROFT

When an attack along any given line has failed for many years to yield any appreciable progress, it is always a good plan to see whether a radically different formulation of the problem may not help matters considerably. For more than fifteen years we have been trying to explain over-voltage on the assumption that the electrolytic decomposition of water is essentially a reversible one. This made it necessary to account for the abnormally large voltages observed at mercury cathodes and platinum anodes for instance. The total result is anything but gratifying from a theoretical stand-point. It is, therefore, desirable to see whether we can make more progress by starting with the assumption that the electrolytic decomposition of water is essentially an irreversible process, an intermediate product being obtained at the cathode which is a stronger reducing agent than hydrogen and which gives rise to hydrogen relatively slowly, while an intermediate product is obtained at the anode which is a stronger oxidizing agent than oxygen and which gives rise to oxygen relatively slowly. We can make the requirements more definite. The intermediate cathode product must be a stronger reducing agent than cadmium, because cadmium can be precipitated electrolytically from a distinctly acid solution. The intermediate anode product must be a stronger oxidizing agent than ozone, hydrogen peroxide, persulphuric acid, or lead peroxide, because these substances may be formed electrolytically at the anode before oxygen is set free. The potentials of intermediate products having these properties are evidently sufficient to account for the over-voltages and the problem is, therefore, to account for the values which we have hitherto called the normal ones. This is easily done, because the observed potentials will coincide with the values for the reversible evolution of hydrogen and oxygen, if specific electrodes catalyze the reaction to such an extent that the concentrations of the intermediate products do not rise above equilibrium values.

This line of attack has been developed by Bennett.[1] The intermediate products are not necessarily compounds of the electrodes, because water is decomposed by radium emanation or by ultra-violet light,[2] the reaction products being hydrogen, and hydrogen peroxide with varying amounts of oxygen depending on the conditions of the experiment. Since hydrogen gas does not reduce oxygen gas to hydrogen peroxide, an active form of hydrogen must have been set free even though no electrodes were present. Any hydrides or oxides which may be formed during electrolysis with metal electrodes are, therefore, substances having lower potentials than the intermediate products and these latter must be special modifications of hydrogen and of oxygen.

Bennett shows that Langmuir's electrically neutral monatomic hydrogen has all the properties which we need to ascribe at present to the intermediate cathode product and he, therefore, concludes that this substance is electrically neutral monatomic hydrogen while the corresponding anode product is probably electrically neutral monatomic oxygen. When the reaction $2H \longrightarrow H_2$ takes place relatively slowly, we get high over-voltage. When the reaction takes place relatively slowly, we get low over-voltage. This point of view is not new; but it is timely. Ostwald[3] referred to it as a possible hydrothesis and so did E. Müller.[4] It was brought forward seriously by Tafel[5] and was urged again by Lewis and Jackson[6] and by Brunner.[7] These men advanced the theory only to meet special cases and it seems not to have been accepted by anybody else. Bennett has emphasized the irreversibility and has generalized the application. The work

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[1] Jour. Phys. Chem., 20, 296 (1916).

[2] Soddy: "The Chemistry of Radio-Elements," 14 (1915).

[3] Zeit. Elektrochemie, 6, 40 (1889).

[4] Zeit. anorg. Chem., 26, 11 (1901).

[5] Zeit. phys. Chem., 34, 200 (1900); 50, 641, 713 (1905).

[6] Proc. Am. Acad., 41, 399; Zeit. phys. Chem., 56, 207 (1906).

[7] Zeit. phys. Chem., 56, 331 (1906).

of Langmuir gives an independent experimental confirmation which was lacking when Tafel and when Lewis and Jackson wrote.

The test of such a theory is its usefulness in accounting for other phenomena. The rapid breaking down of sodium amalgam when certain impurities such as iron, cobalt, or nickel are present[1] is due unquestionably to the decrease in the over-voltage, or, in other words, to the increased rate of formation of ordinary hydrogen from monatomic hydrogen.[2] It is for this reason that sodium amalgam must be made in porcelain vessels and not in iron pots or enamelled ware.[3] It is interesting to note that Aschan[4] attributes the slight reducing power of certain sodium amalgams to the fact that hydrogen is given off in the molecular form and is, therefore, inactive. It has taken us a long time to get back to the view that nascent hydrogen is monatomic hydrogen; but we are there at last. Bamberger[5] accounted for the enormous variations in the reducing power of different samples of zinc dust by saying that some give molecular and, therefore, inactive hydrogen. Nowadays we say that, owing to the increased catalysis of the reaction, $2H \longrightarrow H_2$, the concentration of active hydrogen is less in certain cases than in others. The essential difference between the two points of view is that we know that the zinc dust was contaminated in one case by a metal having a lower over-voltage for hydrogen[6] so that we are not reducing at a zinc cathode, while Bamberger did not bother about the intermediate steps.

It is not solely the organic chemists who have to change their formulation. Peters[7] showed that platinum accelerated the evolution of hydrogen from a chromous chloride solution and Jablczynski[8] showed that mercury had no such

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[1] Walker and Paterson: Trans. Am. Electrochem. Soc., 3, 185 (1903).

[2] Cf. Lewis and Jackson: Proc. Am. Acad., 41, 403 (1906).

[3] Baeyer: Ber. deutsch. chem. Ges., 25, 1255 (1892).

[4] Ber. deutsch. chem. Ges., 24, 1865 (1891).

[5] Ibid., 27, 1548 (1894).

[6] Frederiksen: Jour. Phys. Chem., 19, 696 (1915).

[7] Zeit. phys. Chem., 26, 217 (1898).

[8] Ibid., 64, 750 (1908).

action. It was considered that platinum catalyzed the reaction and that mercury did not. To-day we say that hydrogen is set free at the platinum because of the low over-voltage for hydrogen and is not set free at the mercury because of the high over-voltage. The advantage of the latter point of view is that it shows the desirability of trying other metals with chromous chloride solution so as to find out at what degree of over-voltage the hydrogen ceases to be evolved rapidly.

It seems probable that an explanation can now be suggested for the remarkable results obtained by Fernekes[1] on the action of sodium amalgam on solutions. Fernekes found that alcohol and many other organic substances increased the rate of reaction between sodium amalgam and water. He accounts for the phenomenon by assuming the intermediate formation of hypothetical compounds between solvent and solute which are extremely instable towards sodium amalgam and, therefore, react very rapidly with it. While this explanation may be right, it has not proved helpful and is, therefore, useless, at any rate for the present. It seems probable that certain organic substances lower the over-voltage at mercury and consequently make the sodium amalgam instable. This hypothesis is susceptible of proof by direct experiment. While there are no measurements as yet made under conditions strictly comparable to those in Fernekes' experiments, Carrara[2] has shown that the over-voltages are quite different in methyl alcohol and in ethyl alcohol from what they are in water. I have often wondered whether the reason that nobody has ever prepared electrolytically a sodium alloy using a cathode of fused Wood's alloy, might not be because the over-voltage is not sufficient in this case.

While a high hydrogen over-voltage and high reducing power generally run parallel, it does not necessarily follow that all reductions will take place more readily at the cathode showing the higher over-voltage. Other factors may come in, as in the case of nitrates and nitrites. If the over-voltage

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[1] Jour. Phys. Chem., 7, 611 (1903).

[2] Zeit. phys. Chem., 69, 75 (1909).

were the only factor, it would not be possible for nitrates to be reduced more readily than nitrites at one cathode and less readily at another. This is the case, however.[1] At cathodes of zinc, iron, lead, platinum, and gold, nitrite is reduced more readily than nitrate. At cathodes of spongy copper or spongy silver, nitrate is the more readily reduced. Boehringer and Sons[2] claim that with hot solutions and a mercury cathode sodium nitrate is reduced much more readily than sodium nitrite. Caffeine is reduced more readily at a mercury cathode than at a lead one,[3] while the reverse is true with succinimide. Müller[4] has called attention to a number of apparently abnormal cases and Chilesotti[5] has pointed out the peculiar behavior of molybdic acid at different cathodes. There are three distinct factors which may mask the relation between over-voltage and reducing (or oxidizing) power. One of the substances to be reduced may be adsorbed much more than the other, so that the effective concentration at the surface of the electrode may be very much higher than the mean concentration in the solution. The electrode may catalyze other reaction besides the one, $2H \longrightarrow H_2$. This possibility was foreseen by Ostwald[6] a dozen years ago. A third possibility was pointed out to me by Mr. Bennett, that particular substances may catalyze the reaction, $2H \longrightarrow H_2$, so that the over-voltage at a given cathode may vary with the nature of the apparently inert substances in the solution. We know that this happens when the solvent changes[7] to methyl alcohol or ethyl alcohol and we know that it happens when we add something which "poisons" the electrode.[8] In this paper it is not necessary to consider these points in detail. I merely

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[1] Müller: Zeit. anorg. Chem., 26, 1 (1901); Zeit. Elektrochemie, 9, 955 (1903); 11, 509 (1905).

[2] Zeit. Elektrochemie, 12, 745 (1906).

[3] Tafel and Neumann: Zeit. phys. Chem., 50, 713 (1915).

[4] Zeit. Elektrochemie, 13, 681 (1907); 14, 429 (1908).

[5] Ibid., 12, 146, 173, 197 (1906).

[6] Trans. Am. Electrochem. Soc., 6 II, 187 (1904).

[7] Carrara: Zeit. phys. Chem., 69, 75 (1909).

[8] Cf. Reichinstein: Zeit. Elektrochemie, 16, 927 (1910).

wish to emphasize that the theory of over-voltage, as expounded by Bennett, does not require that high over-voltage and high reducing (or oxidizing) power necessarily go together, though this is usually the case.

In this paper it has been shown that the theory of the irreversible electrolytic decomposition of water gives us a very plausible explanation for some of the peculiarities of sodium amalgam, chromous chloride, and zinc dust. The normal relation between high over-voltage and high reducing power or oxidizing power may be obscured or made to disappear entirely in case of special adsorption of the reacting substance by the electrode, in case of a specific catalytic action of the electrode on the reaction, or in case of a catalytic action of the dissolved substance on the reaction, $2H \longrightarrow H_2$, either directly or indirectly by affecting the electrode catalysis. The assumption of monatomic hydrogen as intermediate product at the cathode has proved useful as a working hypothesis. While we now consider nascent hydrogen as consisting in part of electrically neutral monatomic hydrogen, we recognize that the percentage of monatomic hydrogen may vary enormously and that nascent hydrogen from one source is not necessarily equivalent to nascent hydrogen from another source.

Cornell University

DEPOLARIZATION BY ELECTRICAL WAVES

BY WILDER D. BANCROFT

Since we know now that hydrogen over-voltage is due to the concentration of electrically neutral monatomic hydrogen at the cathode rising above the equilibrium value,[1] it is possible to account for a phenomenon which appears to have puzzled people considerably, namely, the effect of electrical waves on over-voltage. Bennewitz[2] electrolyzed sulphuric acid using a very small platinum anode. When this anode was exposed to strong electrical waves, the potential against a hydrogen electrode was found to be 1.28, 1.27, 1.24 volts. Since the theoretical value for the hydrogen-oxygen gas cell is 1.23 volts, this means that the over-voltage at the oxygen electrode has been reduced to the negligible value of 0.01–0.05 volt. Bennewitz offered no explanation for the phenomenon and did not even discuss whether it was general or specific.

I think that we are safe in assuming that the phenomenon is general and not limited to this special case. It is, therefore, necessary to find a general explanation. From experiments on the disruptive discharge in gases, Schuster[3] concluded that there must be a layer of adsorbed gas on the electrodes, having a high inductive capacity and, therefore, offering an increased resistance to the discharge. If this is true, it follows from the theorem of Le Chatelier that an electrical stress will tend to remove the film of adsorbed gas.[4] This conclusion can be used to account for the behavior of fountains, impinging jets, rolling drops, and soap bubbles, when electrified slightly. It is, therefore, a good working hypothesis. If an electrical stress tends to remove a gas from the surface of a solid, electrical waves will tend to remove active oxygen from the surface

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[1] Bennett: Jour. Phys. Chem., 20, 296 (1916).

[2] Zeit. phys. Chem., 72, 223 (1910); cf. Foerster: "Elektrochemie wässeriger Lösungen," 293 (1915).

[3] Phil. Mag., (5) 29, 197 (1890).

[4] Cf. Bancroft: Jour. Phys. Chem., 20, 18 (1916).

of an electrode and will, therefore, cut down the over-voltage, which is what Bennewitz found. We ought to find also that electrical waves cut down the hydrogen over-voltage. This has been shown to be the case by Rothmund.[1] whose paper seems to have been overlooked both by Bennewitz and by Foerster. More recently Archibald and von Wartenberg[2] have found that the anodic over-voltage is cut down when an alternating current is superposed on a direct current. Reitlinger[3] continued the work of von Wartenberg and sums up his results as follows: "Alternating current destroys the over-voltage due to direct current electrolysis, the potential difference between the electrode and the solution being decreased. The lower potential makes possible the isolation of intermediate products which are destroyed at higher potentials. When an alternating current is superposed on a direct current, there is an increase in the yield of the intermediate products and a decrease in the amount of the final products. Thus ozone is formed instead of persulphuric acid when sulphuric acid is electrolyzed. When alcohols are electrolyzed, aldehydes are formed instead of the corresponding acids. In an indirect way this confirms the experiments of Dony-Hénault, for he showed that aldehyde is formed from alcohol when the potential is kept sufficiently low, whereas acetic acid is the chief product when the potential is higher.

"It is only the negative portion of the alternating current which causes the lowering of the potential and makes possible the formation of intermediate products in relatively large amount. This is made clear in the experiments on ozone, for the potential falls and the yield of ozone increases only when the anode becomes cathode intermittently. With high-frequency currents the depolarizing action is less, owing to the great displacement of phase caused by the capacity of the electrodes."

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[1] Drude's Ann., 15, 193 (1904).

[2] Zeit. Elektrochemie, 17, 812 (1911).

[3] Ibid., 20, 261 (1914).

About a year ago, Ghosh[1] published a paper on the effect of superposing an alternating current from an induction coil on a direct current. He found that the cathode effect is slight with a platinum black cathode where the over-voltage is negligible, and is large with a mercury cathode where the over-voltage is high. He showed that the effect was due to the cutting down of the polarization; but he was unable to account for the phenomenon. "The alternating current acts primarily on the surfaces of the electrodes. Of course, it is very difficult to suggest how it facilitates the liberation of the ions at the electrode surfaces, since we have not got very definite views as to the cause of the over-voltage phenomenon. It is not easy to imagine how an alternating current can destroy the supersaturation on the electrode surface, which is generally ascribed to be the cause of the over-voltage. The hypothesis that the alternating current somehow alters the nature of the electrode surface appears to be most reasonable."

As a matter of fact, the one assumption made by Schuster accounts for all these facts as well as for many others. An interesting corollary from the work of Rothmund, Bennewitz, Archibald and von Wartenberg, Reitlinger, and Ghosh is that with a sufficient depolarizing action at the anode lead peroxide should not be formed with lead electrodes in sulphuric acid because the formation of lead peroxide calls for an over-voltage of about half a volt.[2] This seems to have been confirmed experimentally by Ruer,[3] who used a very dilute sulphuric acid (2.5 percent) however, and who seems to have obtained some lead peroxide at times. These experiments should be repeated with a more concentrated acid. With alternating current alone, lead sulphate is formed and no lead peroxide.[4]

Sufficiently strong electrical waves should also prevent the formation of sodium amalgam at a mercury cathode.

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[1] Jour. Am. Chem. Soc., 37, 733 (1915).

[2] Dolezalek: Zeit. Elektrochemie, 5, 537 (1899).

[3] Zeit. phys. Chem., 44, 105 (1903).

[4] Cf. Schluederberg: Jour. Phys. Chem., 12, 623 (1908).

Zinc, cadmium, and nickel should dissolve readily in sulphuric acid under similar conditions. Since lead peroxide is theoretically instable, there is a possibility of causing it to break down into lead oxide and oxygen. This seems not to have happened in Reitlinger's work for he used lead peroxide anodes in some experiments. Until we can make this reaction occur, it is hardly worth while to speculate on the fascinating possibility of making potassium chlorate break up at ordinary temperatures into potassium chloride and oxygen, to say nothing of the more remote possibility of eliminating passive resistances to change in the case of organic compounds.

The experiments of Margules[1] and Ruer[2] on the dissolving of platinum find their explanation in the cutting down of the over-voltage, as was recognized explicitly by Reitlinger.[3] With a direct current we get oxidation to a higher and insoluble stage. With alternating current the over-voltage is decreased and we get little or none of the insoluble compound.

There is one other point of distinct interest with respect to electric waves. The more recent determinations of over-voltage have given lower values than those obtained by Caspari.[4] This may be due to experimental error on Caspari's part. On the other hand many of the recent determinations have been made with an intermittent direct current, the polarized electrode being connected with the potentiometer circuit during the breaks. It is possible that the polarization might have been cut down somewhat by induced currents during the make and break. If this were so, the measurements by this method would be in error. It may be that the error from this source is negligible; but this should be proved and not assumed.

The general results of this paper are that electrical waves must cause depolarization if we admit that electrical stress

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[1] Weid. Ann., 65, 629; 66, 540 (1898).

[2] Zeit. phys. Chem., 44, 81; Zeit. Elektrochemie, 9, 235 (1903); 11, 10, 661 (1905); Haber: Zeit. anorg. Chem., 51, 365 (1906).

[3] Zeit. Elektrochemie, 20, 261 (1914).

[4] Cf. Bennett: Jour. Phys. Chem., 20, 296 (1916).

cuts down the adsorption of a gas by a solid. This assumption is a necessary consequence of Schuster's work on disruptive discharges and has been shown to account for the behavior of fountains, impinging jets, rolling drops, and soap-bubbles, when electrified slightly. It is shown that electrical waves do decrease over-voltage at the cathode and at the anode, and that the assumption accounts for all the facts so far known. It is also pointed out that measurements of decomposition voltage involving the use of an intermittent direct current are subject to an error which is perhaps not negligible.

Cornell University

PROTOPLASMIC EQUILIBRIUM[1]

BY G. H. A. CLOWES

I. ACTION OF ANTAGONISTIC ELECTROLYTES ON EMULSIONS AND LIVING CELLS[2]

Introduction

The purpose of this and succeeding papers is to study the action exerted by a variety of electrolytes, used singly and in combination, on the equilibrium of emulsions, sols, jellies, and other physical systems; and to compare the results with the data already available regarding the influence exerted by the same electrolytes and electrolyte combinations on living cells. It is hoped in this way to explain the antagonistic electrolyte effects which appear to play so great a rôle in cell life, and to throw some light on the physical structure of protoplasm and the mechanism of certain vital processes.

This series of investigations was undertaken as a result of the observation, made by Bancroft while studying emulsion equilibrium, that soaps of Na, used as emulsifying agents for oil and water, promote the formation of emulsions consisting of globules of oil dispersed in water, like cream, while soaps of Ca, used as emulsifying agents, exert the reverse effect, promoting the formation of emulsions consisting of globules of water dispersed in oil, like butter. These diametrically opposite effects exerted by soaps of Ca and Na appeared to the writer to present a striking analogy to the antagonistic action of salts of Ca and Na in such purely physical processes as the formation of a blood clot from blood plasma, or a casein clot from a casein suspension, since both of these processes are promoted by salts of Ca and inhibited or retarded by alkalies, and salts of Na.

In the process of blood coagulation, blood plasma, a sol

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[1] From the Biological-Chemical Laboratory of the State Institute for the Study of Malignant Disease, Buffalo, N. Y.

[2] Read before the general session of the American Chemical Society at Urbana, April 18, 1916.

consisting of fibrinogen and other colloidal particles dispersed in water, is converted into the blood clot, a jelly, which appears to consist of water more or less perfectly dispersed in fibrin. This transformation of a system consisting of a non-aqueous phase dispersed in water into a system consisting of water dispersed in a non-aqueous phase (see Fig. 2) is analogous, to use a crude illustration, to the conversion of a system consisting of islands surrounded by water into the reverse type of system in which lakes are surrounded by land. It appeared desirable to determine whether a similar transformation from one type of emulsion into another could be effected by simply varying the proportions of salts of Ca and Na introduced into an emulsion system. In a preliminary paper published in 1913, the writer was able to demonstrate that an emulsion of oil in water may be converted into an emulsion of water in oil by shaking with salts of Ca; that the transformation in question may be inhibited or a reverse transformation effected by shaking with the requisite proportion of NaOH. It was subsequently demonstrated that NaCl and other salts of Na are capable of functioning as antagonists of $CaCl_2$ in a similar manner, but to a far less marked degree than is NaOH.

To avoid any possibility of confusion or any idea that the antagonism between soaps of Ca and Na, or between salts like $CaCl_2$ and NaCl, is due to antagonism between the cations Ca and Na, the writer wishes to emphasize particularly the fact that these antagonistic effects are attributable, as will be shown later, to a balance between cations on the one hand, and anions on the other, adsorbed on or reacting with soaps or other colloidal constituents of surface films or membranes. It simply happens that, in the case of $CaCl_2$, the cation Ca is far more readily adsorbed than the anion Cl, while, in the case of NaCl, the anion Cl is somewhat more readily adsorbed than the cation Na. Since the effect obtained from each individual salt is a resultant of the relative adsorption of its cations and anions, it is obvious that in a mixture of $CaCl_2$ and NaCl the cations Ca and Na are ranged on one side of the scale and the anion Cl on the other, but, since the relative adsorption of Cl lies between that of Ca and Na, a mixture of $CaCl_2$ and NaCl exerts an effect intermediate between that of $CaCl_2$ or NaCl alone. This effect may readily be visualized by using the analogy of riders placed at different points on the beam of a balance, those on one side being cations and those on the other anions. If Ca is placed at the extreme end, and Na close to the balancing point on one side of the scale, and, on the other side, an equivalent proportion of Cl at a distance from the center less than that of Ca and more than that of Na, it is obvious that by using suitable proportions of Ca and Na with their equivalent Cl an exact balance may be established, but that, when Na is employed with its equivalent of Cl, the weight will be greater on the Cl side of the scale, and when Ca is employed with its equivalent of Cl, the weight will be greater on the Ca side of the scale.

To return to the discussion of the influence exerted by salts of Ca and Na on the diphasic systems considered above: the fact that similar reversals of phase relations are promoted by salts of Ca and inhibited by salts of Na in two such widely differing processes as blood coagulation and emulsion transformation, suggested the existence of some heretofore unappreciated physical principle governing the phase relations of certain heterogeneous systems. The question arose whether the mutually antagonistic or compensatory effects exerted on living cells by salts of Ca and Na in sea-water, the blood of mammals, etc., might not also be attributable to salts of Ca promoting a reversal in one direction, and salts of Na in the opposite direction, in the phase relations of the heterogeneous system which we designate as protoplasm. It should be explained at this point that the protoplasmic material of the living cell consists of two distinct systems, the chromatin or nuclear material which is generally surrounded by the cytoplasmic material. Throughout this paper the term protoplasm will be used to denote cytoplasm, the discussion regarding the physical structure of nuclear and chromatin material being reserved for a subsequent publication.

The obvious course to pursue in order to test the validity of this theory was to determine the ratios in which given salts of Na and Ca exert antagonistic effects on one another in a variety of physical and biological systems. Before proceeding to the presentation of the experimental data regarding the influence exerted by salts of Ca and Na and certain other electrolytes on the equilibrium of emulsions and soaps, which, as we have seen above, play so important a rôle in the establishment of emulsion equilibrium, it is necessary to review briefly certain experiments regarding the influence of electrolytes on living cells in order to afford a convenient basis for comparison of biological and physical experiments.

From the data accumulated on this subject by Jacques Loeb and other biologists, it has long been recognized that mineral salts are individually toxic for the cell when used at sufficient concentration, but that a favorable medium is afforded for the maintenance of cell life when certain salts are used collectively, preferably in those approximately fixed ratios in which they occur in nature. For example, certain marine organisms are instantly killed when transferred from sea-water to a solution of NaCl containing that substance at the concentration at which it occurs in sea-water, but may be protected against the destructive effect of the NaCl by the addition of $CaCl_2$, in a proportion of one or two molecules of the latter to 100 of the former. This ratio of 100 molecules of NaCl to one or two of $CaCl_2$ is peculiarly significant in view of the fact that this is the ratio in which NaCl and $CaCl_2$ tend to occur in nature, in sea-water, in the blood of mammals, etc. Osterhout has demonstrated that wheat grown in an aqueous solution containing 0.12 M NaCl + 0.0012 M $CaCl_2$ developed extensive rootlets and showed other signs of healthy activity, but that, in control experiments in which either a 0.12 M NaCl or a 0.12 M $CaCl_2$ solution was employed, virtually no growth occurred. Similarly zoöspores of vaucheria grew rapidly in a mixture containing 0.01 M NaCl + 0.0001 M $CaCl_2$, or even in pure distilled water, but failed to show any signs of growth in solutions containing 0.01 M NaCl or 0.01 M

$CaCl_2$. Osterhout has recently published an extremely important series of experiments on the influence exerted by various electrolytes on the conductivity of Laminaria tissues. The tissues tested immediately after removal from sea-water appeared to exhibit a practically constant resistance to the passage of an electric current, but, after exposure to a comparable solution of NaCl, a markedly diminished resistance was noted; after exposure to a comparable $CaCl_2$ solution a markedly increased resistance was exhibited, at least for a short period; but no appreciable variation from the normal occurred after exposure of the tissues to properly balanced mixtures containing NaCl and $CaCl_2$ in ratios of 100 molecules of the former to one or two of the latter. Osterhout naturally concluded that NaCl increases and $CaCl_2$ diminishes the permeability of the tissues to the passage of water and water-soluble ions, and that, in those solutions in which no change in conductivity occurs, the destructive effect of NaCl is exactly balanced by the protective effect of $CaCl_2$.

To summarize the above data: since a large variety of marine and other organisms are killed by solutions of NaCl on the one hand, or $CaCl_2$ on the other, but may be kept alive in appropriate mixtures of NaCl and $CaCl_2$, and, under certain circumstances, may even be transferred without injury to distilled water, and since $CaCl_2$ diminishes and NaCl increases the permeability of the protoplasmic system, it may well be concluded that the $CaCl_2$ exerts its destructive effect on protoplasm by causing the formation of a protoplasmic film or membrane too impermeable for the performance of normal vital functions, while NaCl exerts the reverse effect, interfering with the formation of a film or rendering the film already formed too permeable. The maintenance of vital processes may well depend upon the production of a protoplasmic film or membrane capable of exhibiting variations in permeability within comparatively narrow limits, just as the maintenance of function of an engine or machine depends upon an accurately regulated valve system. Osterhout has recently demonstrated that the tissues of marine organisms may be made to undergo repeated variations in permeability within certain limits without apparent injury, by short alternating exposures to solutions of NaCl and $CaCl_2$. It must be concluded, therefore, that the protoplasmic film is a physical system capable of undergoing reversible variations in permeability as a result of exposure to solutions containing varying proportions of salts of Na and Ca.

Can such reversible variations in permeability be realized in the physical systems considered above? It has been noted that a marked analogy appears to exist between the transformation of an emulsion of oil in water into an emulsion of water in oil, of blood plasma into a blood clot, and of a casein suspension into a casein clot. In all three cases, salts of Ca promote and alkalies and salts of Na inhibit the transformation of a system consisting of a non-aqueous phase dispersed in water into the reverse type of system, consisting of water more or less perfectly dispersed in a non-aqueous phase. If the analogy of islands surrounded by water and lakes surrounded by land is considered, it will be obvious that a transformation has been effected from a system which is freely permeable to water, to one which is impermeable if the transformation is complete. Since the transformation in one direction is effected by salts of Ca and in the reverse direction by alkalies and salts of Na, any intermediate degree of permeability might well be obtainable by simply varying the proportions of the salts of Na and Ca introduced into the system. The process of blood coagulation, when carried beyond a certain point, is not reversible, presumably owing to the formation of the solid or semi-solid fibrin phase, but emulsion systems appear to be freely reversible, since a transformation is effected comparatively easily in either direction by increasing or decreasing the ratios of $CaCl_2$ and NaOH introduced into the system. The analogy between the antagonistic effects exerted by salts of Ca and Na on these purely physical systems and on living protoplasm is therefore sufficiently marked to justify further consideration as to whether what is actually known about the physical and chemical structure of protoplasm and the protoplasmic film would conform to the theory that a protoplasmic system, in which water is the continuous phase, is partially transformed by contact with salts of Ca into a protoplasmic film, in which water functions at least to a certain extent as the dispersed phase. The active Brownian movement exhibited when protoplasm is examined by means of the ultra microscope, indicating colloidal particles dispersed in water, and the facility with which water-soluble substances penetrate protoplasm when they have passed the protoplasmic film suggest the possibility that the original protoplasmic structure approximates to a dispersion of proteins, lipoids, fats and other non-aqueous constituents in water. The resistance offered by the protoplasmic film to the passage of salts, sugars, and other simple water-soluble substances, the difference in the proportions of certain electrolytes within and without the cell, the phenomena of osmotic pressure, and resistance to the passage of an electric current all support the view that, at least under certain conditions, water communications through the protoplasmic film are somewhat limited, and suggest the possibility that the protoplasmic film may approximate to the reverse type of system in which water is more or less dispersed in the non-aqueous constituents of protoplasm. The freedom with which anesthetics and other substances readily miscible with or soluble in fats and lipoids penetrate the cell is a further argument in support of the contention that a fatty or lipoid film constitutes, at least under certain conditions, the outer or continuous phase of the protoplasmic membrane. Since proteins present in protoplasm are analogous to the fibrinogen functioning in the production of a blood clot, since the fats are analogous to the oil employed in the emulsion systems, and the lipoids are substances possessed of chemical and physical characteristics in part those of proteins and in part those of fats, it does not appear at all improbable that the physical structure of the protoplasmic film which regulates the intake of foodstuffs and the output of waste products is analogous to that of the reversible di-phasic systems discussed above.

On account of space limitations, no reference has been made to electrolyte antagonisms other than those exhibited by salts of Na and Ca, but it must be remembered that all electrolytes are capable of exhibiting similar antagonistic effects, and appear to be divided roughly into two main antagonistic groups. Substances of the first group, comprising acids and salts of di- and trivalent cations, which possess a more reactive or more readily adsorbed cation, appear to exert their destructive effect by too greatly diminishing the permeability of the protoplasmic membrane, at least for a short period. Substances of the second group, comprising alkalies, salts of monovalent cations, and of di- and trivalent anions, which possess a more reactive or more readily adsorbed anion, appear to exert a destructive effect by too greatly increasing the permeability of the membrane. Balanced solutions appear to be those in which substances of the first and second groups are present in such proportions as to counterbalance one another exactly. There appear to be certain notable exceptions to this general grouping, salts of Mg, for example, being capable of functioning under varying circumstances in one or the other group.

In the following experimental section the action exerted by individual electrolytes on emulsion equilibrium will be determined, and, by comparing the ratios in which they exert a compensatory effect upon one another in these purely physical systems with those in which they exhibit antagonistic effects in biological systems, an attempt will be made to determine to what extent protoplasmic function may be explained on a purely physical basis.

Experimental

It is not proposed to discuss emulsions in general, since reference may be made for information regarding this subject to a series of papers by Bancroft which have recently appeared in THIS JOURNAL. The purpose of this paper is simply to determine the influence exerted by electrolytes on the phase relations of emulsion systems.

When pure oil and water are shaken together no emulsion results. The production of a permanent or even a temporary emulsion appears to depend on the presence in the system of some emulsifying agent like soap, which by concentration at the interface between oil and water forms a film which prevents the particles of the dispersed phase from coalescing. The dispersing or stabilizing influence exerted by the film is probably attributable in part to lowering of the surface tension, reducing the tendency of the dispersed particles to coalesce, in part to an electric charge conferred to the particles by constituents of the film, causing the similarly charged particles to repel one another, and in part to the purely mechanical action of the film keeping the particles apart, just as gelatine, or some other agent capable of forming a film around individual particles, increases the stability of a gold or other metallic sol. Should any doubt exist regarding the formation of films of this type, reference may be made to a subsequent section describing experiments carried out by means of a capillary pipette in which suitable aqueous solutions of soap or NaOH are allowed to flow slowly through olive oil containing oleic acid, in which the films formed at the interface between oil and water are recognizable, particularly if a small amount of $CaCl_2$ is employed as in the case illustrated (Fig. 3).

It is true that when oil and water are shaken together vigorously or otherwise mechanically admixed, in the absence of an emulsifying agent oil and water masses will be continually broken up and reunited in such a manner that at any given moment a certain number of drops of the one phase are surrounded by the other phase, but, in the absence of a dispersing agent capable of keeping the particles apart, the two phases separate immediately under the influence of gravity when mechanical agitation ceases. The emulsifying agent may be said therefore to function in two ways, first, by concentration at the interface between water and oil, lowering the surface tension of the phase in which it is contained and thereby facilitating the mechanical disintegration of the opposing phases, and, second, by forming a film which is adsorbed by and surrounds the particles of the dispersed phase, and thus prevents the latter from subsequent coalescence.

A simple analogy is a dispersion of one army by another, which is complete only when isolated individuals or detachments are taken prisoner or otherwise prevented from reuniting.

Reference has already been made to Bancroft's observation that soaps of the monovalent cations, Na, K, etc., used as emulsifying agents for oil and water, cause the formation of an emulsion consisting of drops of oil dispersed in water, while soaps of Ca, Mg, and other di- and trivalent cations used as emulsifying agents, cause the production of the reverse type of emulsion consisting of drops of water dispersed in oil. Bancroft's ingenious explanation may be briefly summarized as follows:

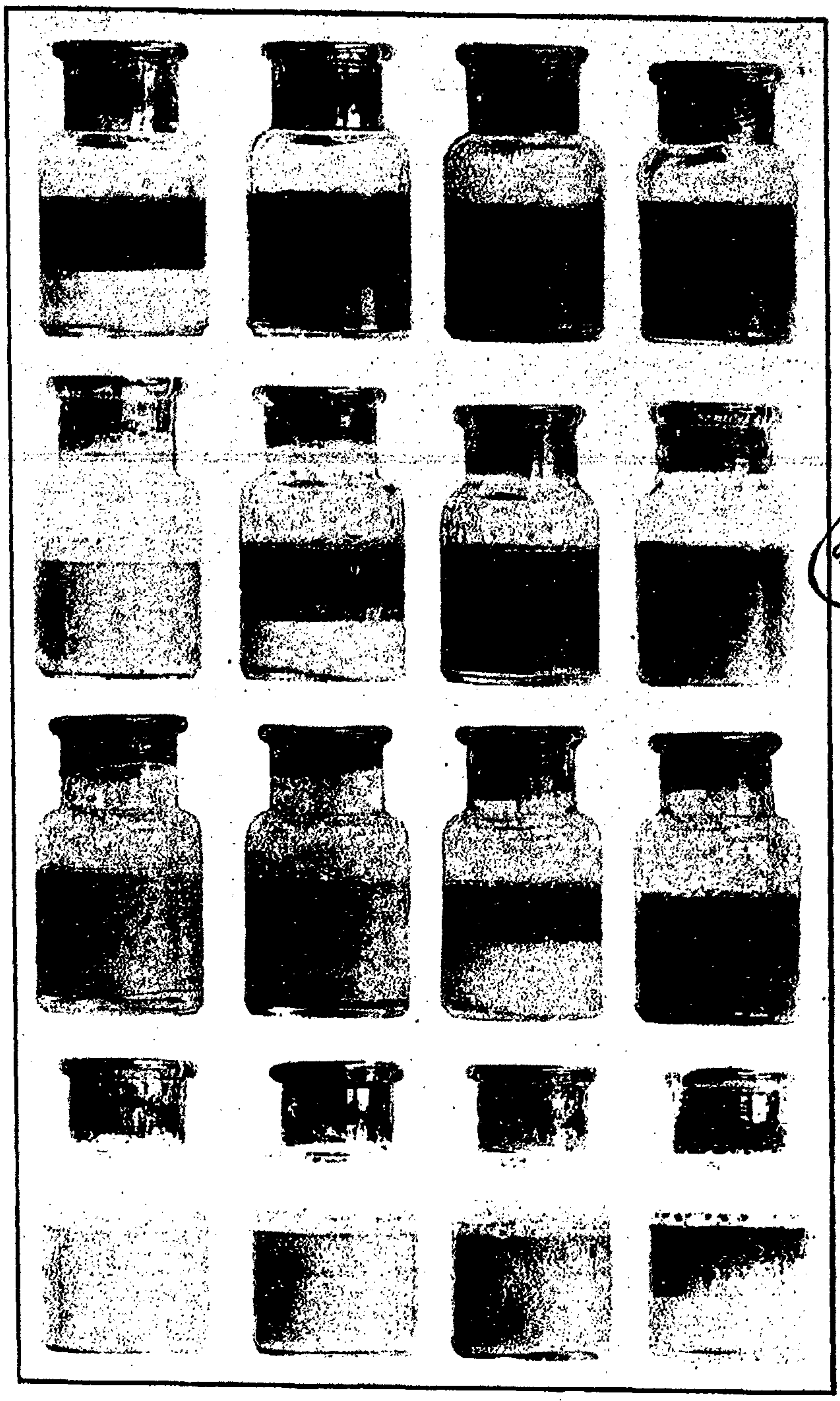
The soaps present in the system tend, as stated above, to concentrate at the interface between water and oil and to form a coherent film. Soaps of monovalent cations, being readily dispersed in water but not in oil, form a film or diaphragm which is wetted more readily by water than by oil, consequently the surface tension is lower on the water than on the oil side. Since the area of the inside face of a film surrounding a sphere is obviously smaller than that of the outside face, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of higher surface tension to a minimum as compared with that of lower surface tension. On the other hand, a film composed of soaps of divalent or trivalent cations, being freely dispersed in oil but not in water, is wetted more readily by the oil than by the water, the surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase (see Fig. 1).

In order fully to appreciate the significance of experiments to be described later, it is necessary to consider the problem somewhat further at this stage, and possibly to anticipate certain theoretical conclusions. When two nations are at war and their armies are concentrated in two lines immediately adjacent to one another but on the opposite sides of the frontier, it does not necessarily follow that the larger nation or the larger army will be victorious. The speed with which troops can be concentrated at a given point, the arms at their disposal, and the supply of ammunition, are all important factors in determining which will ultimately break through and envelop or disperse the other. In the same manner the dispersion of oil by water or water by oil in an emulsion system is apparently independent of the volumes of water and oil employed. It is dependent upon three factors: (1) the amount of a given dispersing agent, analogous to troops, present in the system; (2) upon the facility with which the dispersing agents in question can be mobilized at the dividing surface, analogous to the mobilization of troops on the frontier; and (3) as we shall see later, upon a factor of considerable importance, the ions adsorbed on the particles of the dispersing agent, which may be said to be analogous to arms and ammunition. An emulsifying agent like Na oleate is itself a dispersion of particles of oleic acid by means of adsorbed ions. The extent to which it is dispersed depends to a great extent upon the proportion of anions present in the system capable of being adsorbed on the soap particles thereby increasing the negative charge which the particles already possess, and promoting the dispersion of the particles themselves in water. The more perfect the dispersion of the soap particles in the water phase, the greater will be the effect which they exert in promoting the dispersion of oil in water, and in overcoming the counter-effect of dispersing agents present in oil exerting the reverse effect, just as the more perfect the arms and the larger the supply of ammunition of a military unit the more efficacious will it be as a dispersing agent.

We may now consider the conditions that obtain when the dispersing agents are present in equivalent or balanced proportions in both phases. When two engaged armies are evenly matched, the line may swing backward and forward in the course of the engagement and single individuals or detachments may be destroyed or captured, but at the end of the engagement the contending forces still remain sharply differentiated on opposing sides of the line. In the same manner if the dispersing agents present in the oil and water phases are evenly matched it is obvious that the surface tension will be lowered to the same extent on both sides of the dividing line. On the basis of Bancroft's theory the film will be unable to curve in either direction, consequently neither side will be able to envelop the other, and, when mechanical agitation ceases, the two layers should tend to separate under the influence of gravity, as in the case considered above in which no emulsifying agents were employed. It will be seen from the subsequent experimental data how fully this conclusion may be realized.

Bancroft's observation regarding the influence exerted by soaps of monovalent cations on the one hand, and divalent cations on the other, appeared to the writer, as stated above, to present a possible explanation for the phenomenon of electrolyte antagonisms in biological systems. The first step was obviously to determine the effect exerted by various electrolytes used in varying proportions upon the equilibrium of emulsion systems, and to determine to what extent emulsions of the one type could be converted into emulsions of the other type, and *vice versa*, by the addition of one or the other type of electrolytes. Instead of employing the procedure adopted by Bancroft of preparing soaps of the various monovalent and divalent cations and making dispersions of the soaps in question in water or oil, the writer employed the somewhat simpler procedure of dissolving the salts to be tested in water and employing the solutions in question as the aqueous phases of emulsions. To insure comparable conditions, equal volumes of olive oil and water were employed in all the experiments recorded in this paper, the olive oil containing—unless otherwise stated—sufficient oleic acid to form soap with all the NaOH introduced into the aqueous phase. Emulsification was effected by means of a mechanical shaker supplemented with shaking by hand. In a preliminary communication referred to above

Plate I



it was demonstrated that suitably constituted emulsions of oil dispersed in water could be transformed into the reverse type of emulsions consisting of water dispersed in oil by shaking with a sufficient amount of $CaCl_2$. This transformation could be prevented or the reverse transformation effected, an emulsion of water dispersed in oil being transformed into one of oil dispersed in water, by shaking with a sufficient proportion of NaOH. The results, obtained by shaking together equal volumes of oil and water in which varying proportions of NaOH and $CaCl_2$ were added prior to emulsification, are recorded in Table I, and Plate I represents a photograph of the same series of bottles taken three or four minutes after emulsification. It will be seen that emulsions of oil in water are produced whenever there are more than four molecules of NaOH to one of $CaCl_2$, emulsions of water in oil whenever there are less than four molecules of NaOH to one of $CaCl_2$, while at those points at which the ratio of NaOH to $CaCl_2$ is exactly 4 : 1 neither type of emulsion appears to predominate. The oil phase was colored red with Sudan III consequently the oil appears black in the photograph. If we remember that the same proportions of oil, water, and Sudan III, are present in all the bottles it is obvious from an inspection of the photograph that, by simply varying the proportions of NaOH and $CaCl_2$, three different

TABLE I

Effect of NaOH and $CaCl_2$ on Emulsion Equilibrium

Vol. of M/10 NaOH in cc employed	Vol. of M/10 $CaCl_2$ in cc employed			
	0.25	0.5	0.75	1.0
1	o+	+++	+++	+++
2	ooo	o+	+++	+++
3	ooo	ooo	o+	+++
4	ooo	ooo	ooo	o+

Vol. of H_2O and oil phases always 10 cc each.
ooo indicates oil dispersed in water.
o+ indicates critical point.
+++ indicates water dispersed in oil.

types of systems have been produced; those on the left lower side of the picture, which in certain cases give visible evidence of minute particles of colored oil dispersed in water; those down the central diagonal, in which the colored oil and colorless water layers appear to have separated almost entirely; and those in the right upper corner, which appear black in the picture, thus indicating that water is dispersed in an outer oil phase. A closer inspection of the picture brings out the fact that at the critical point separation is not quite complete in all cases, definite white lines of water being still recognizable in the oil phase, also in certain of the emulsions of oil in water, immediately adjacent to the critical point, a slight tendency toward separation of oil globules is exhibited by the larger size of the particles and their concentration toward the upper surface. As a matter of fact the critical point in this system would have been shifted somewhat to the right, particularly at the lower more concentrated end of the curve, by using larger proportions of oleic acid in the oil and somewhat to the left by using smaller proportions. An explanation for this phenomenon will be given in a subsequent paper.

Since, in the experiment presented, oleic acid is present in sufficient excess in the oil to form soap with all the NaOH introduced into the system and NaOH and $CaCl_2$ are always present at the critical point in ratios of one chemical equivalent of $CaCl_2$ to two of NaOH, it is obvious that this critical point, which is characterized by a tendency of the oil and water layers to separate, is the point at which Na oleate and Ca oleate are present in equivalent proportions. This critical point anticipated previously as a result of theoretical considerations may be explained by reference to Fig. 1, from which it will be seen that while Na oleate promotes a curvature of the film in one direction, and Ca oleate a curvature in the other direction, when these substances are present in balancing proportions, the surface tension being equal on both sides of the film, there will be no tendency to curve in either direction, consequently neither phase can enclose the other, and since oil and water are fluids, they would obviously tend to separate rapidly into two layers under the influence of gravity. Furthermore, we may conclude that chemical equivalents of Na and Ca oleate are the balancing antagonistic ratios in question. Further experiments demonstrated that the oil-water emulsions on the lower left side of the critical point diagonal (Table I and Plate I) could always be converted into water-oil emulsions by the addition of a sufficient proportion of $CaCl_2$, and that the water-oil emulsions on the upper right side of the diagonal could be reconverted into oil-water emulsions by the addition of a sufficient proportion of NaOH, provided, of course, that a sufficient amount of fatty acid was present in the oil phase to permit of the formation of the additional amount of Na oleate required to overcome the effect of the Ca oleate already present. The two types of emulsions may be roughly differentiated from one another by the fact that an emulsion of oil in water resembles milk or cream, flows comparatively readily, and when shaken vigorously against

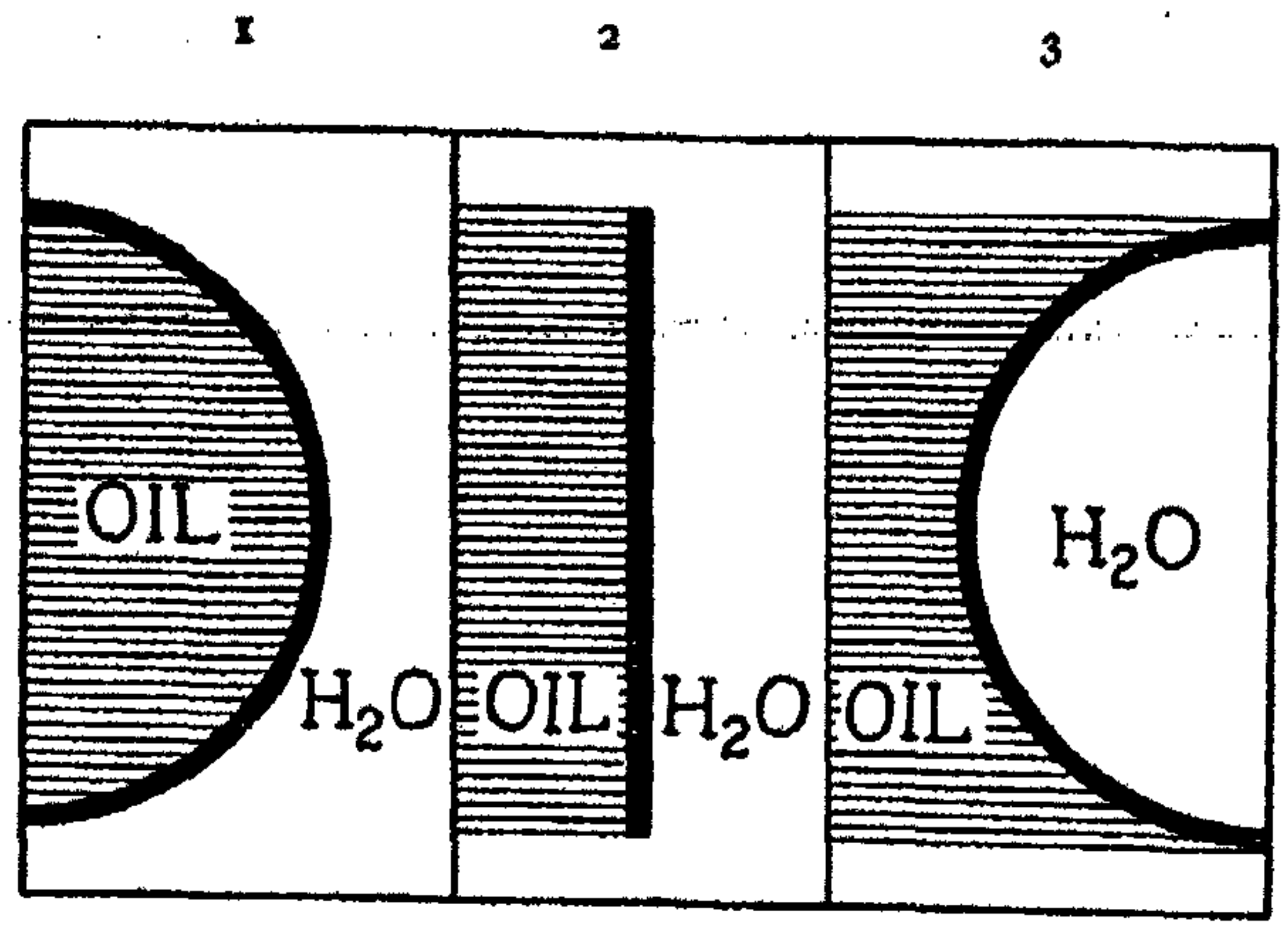


Fig. 1

	1	2	3
Emulsifying agent or film	Na oleate alone or Na oleate in excess of Ca oleate equiv.	Equiv. chem. proportion Na oleate and Ca oleate	Ca oleate alone or Ca oleate in excess of Na oleate equiv.
Emulsion formed	Oil in water	Critical point	Water in oil

the ear gives a metallic sound similar to that given by water, while emulsions of water in oil more closely resemble butter, are more viscous and when shaken vigorously give a sound resembling that given by oil. The addition of Sudan III which stains the oil phase red, or of some aniline dye like methylene blue which stains the water phase blue, facilitates both gross and microscopic examinations. If the transformation of an oil-water emulsion to a water-oil emulsion by means of Ca salts be followed microscopically, it is noted that the oil globules, B dispersed in the water phase A (see Fig. 2), are first distorted, then elongated as the critical point is approached and Brownian movement is very marked. At the critical point extremely active movement of large oil and water masses suggesting that of amoebae is probably due to the existence of two continuous phases, as suggested above. Beyond the critical point the emulsion consists principally

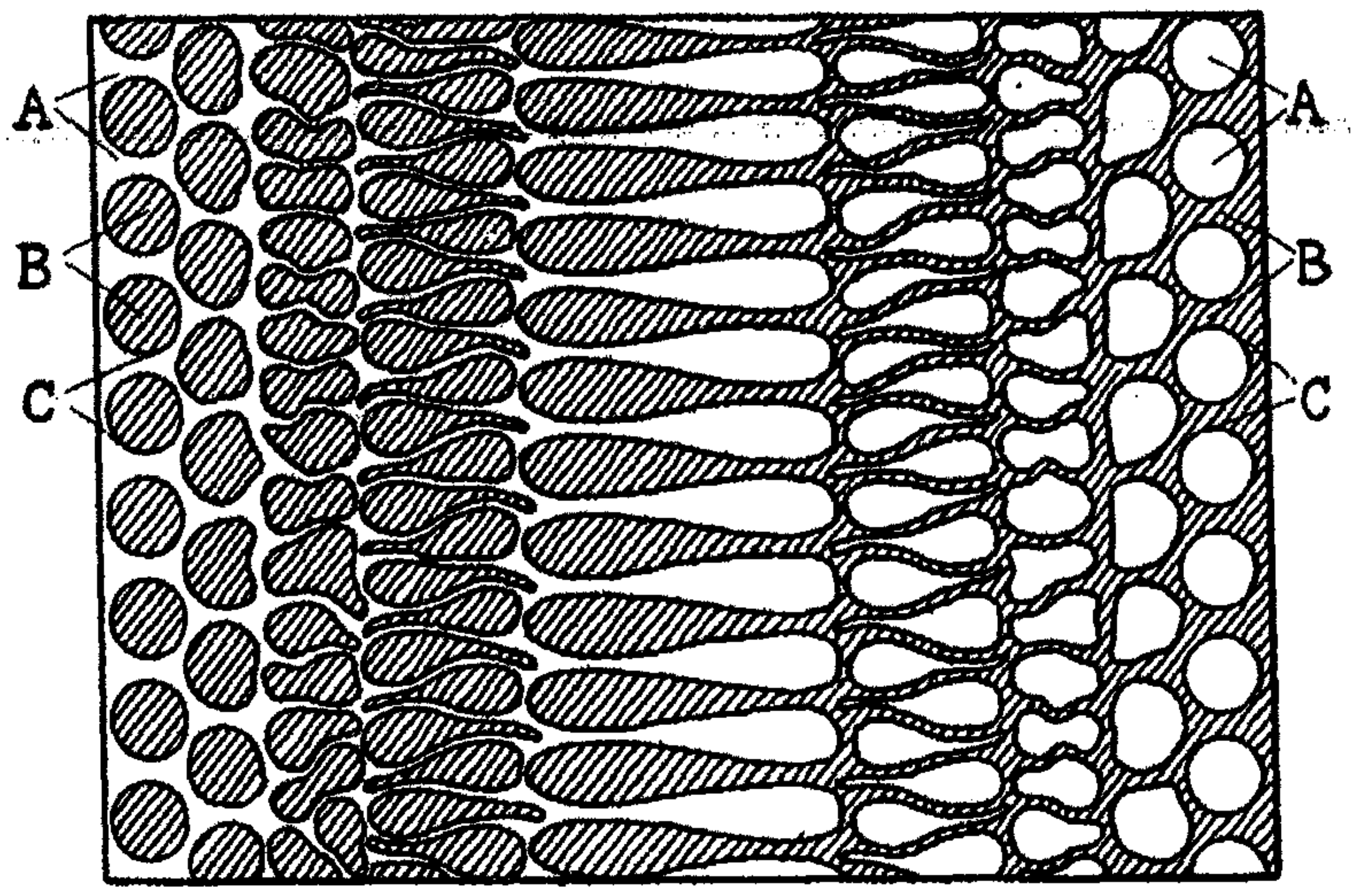


Fig. 2
A = aqueous phase, B = oil or other non-aqueous phase, C = surface film of soap or other dispersing agent. Diagram illustrates transformation of emulsion of oil in water to emulsion of water in oil and *vice versa* under the influence of antagonistic electrolytes

of large drops of water surrounded by oil which are characterized by the fact that they still contain numerous oil globules in rapid Brownian movement, the whole figure resembling a leucocyte under dark ground illumination. The complete conversion of the system into an emulsion of water in oil at the point at which Na oleate is entirely converted into Ca oleate is perhaps most readily recognized by observing the point at which the Brownian movement of these oil particles dispersed in water entirely ceases.

If a slow transformation from one type of system to another is followed by means of the microscope, it is interesting to note that the original continuous phase may occasionally be transformed into the dispersed phase with explosive violence, the minute drops formed assuming an arrangement suggestive of iron filings in a magnetic field or karyokinetic figures in the process of cell division. This arrangement is presumably attributable to electric charges carried by the particles.

Brief reference must now be made to the effects exerted on emulsion systems by substances other than $CaCl_2$ and NaOH. Salts of Mg, Sr, Ba, Fe, Al, etc., exert an effect similar to that of Ca while KOH, LiOH, etc., may be substituted for NaOH. Mg exhibits peculiarities similar to those observed in biological systems. In ordinary systems of the type described above in which oleic acid is present in sufficient proportion to form soap with all the NaOH introduced, Mg like Ca gives a critical point when the proportions of the Na oleate and Mg oleate are equivalent. When NaOH is present in considerable excess and oleic acid in diminished proportion, it may still give a typical emulsion of oil in water at a stage at which Ca, Ba, Sr, etc., give an emulsion of a different type to be discussed in a subsequent publication.

The effect exerted on emulsions by NaCl, KCl, etc., which cannot possibly interact with the film is extremely interesting. Added in small amounts, NaCl undoubtedly promotes the formation of emulsions of oil in water, improving the dispersion of the oil in water and counteracting the effect of $CaCl_2$, in ratios which as far as can be ascertained by the crude measures available are approximately 100 to 150 molecules of NaCl to one of $CaCl_2$. That this is due to an adsorption of Cl ions in excess of Na ions on the soap particles, or to an increased adsorption of OH ions already present in the system, is rendered extremely probable from the fact that emulsions of oil in water, to which enough NaOH has been added to render them strongly pink to phenolphthalein, may subsequently be decolorized by the addition of moderate amounts of NaCl. To test this question the following procedure was adopted. Increasing proportions of NaCl up to a concentration of 0.1 *M* were added to a series of bottles containing equal proportions of oil, water, soap, NaOH and phenolphthalein. The emulsions were titrated rapidly to a common color standard with HCl and it was found that the amount of HCl required exhibited an approximately logarithmic relation to the amount of NaCl added, the maximum amount being required for the control tube to which no NaCl had been added, and the minimum for the tube containing NaCl at a concentration of 0.1 *M*. A similar result was obtained by titrating soap suspensions to which alkali and varying proportions of NaCl had been added, but without the addition of any oil, thus indicating that the phenomenon in question is attributable to an effect exerted on the soap particles themselves. These results were further confirmed by careful ultramicroscopic investigation of comparable emulsion and soap systems containing varying proportions of NaCl. These somewhat crude experiments, full details regarding which will shortly be published, indicate that the addition of NaCl to an emulsion system up to a concentration of 0.1 *M* promotes the adsorption of negative ions on the soap particles and consequently promotes the dispersion of soap in water, thus facilitating the formation of emulsions of oil dispersed in water.

At higher concentrations of NaCl the adsorption of negative ions in excess of positive does not appear to occur to the same extent. The titration curve changes and at 0.35 *M* to 0.4 *M* NaCl the stabilizing soap film of the emulsion is precipitated, the oil and water layers tend to separate just as is the case at the critical point of an emulsion or in the absence of any emulsifying agent. This is significant in view of Jacques Loeb's observation that marine organisms are destroyed by NaCl at concentrations of 0.3 *M* to 0.4 *M* unless protected by the addition of $CaCl_2$.

Experiments with emulsions are necessarily extremely crude, since the mixtures tend to exhibit considerable variations at different points. In order to obtain accurate information regarding the effect exerted by various anions and cations either reacting with or adsorbed on soap films of the type presumed to be present in emulsions, it is necessary to study single films under conditions approximately constant. The procedure finally adopted, which when carefully controlled affords remarkably accurate results, is to permit aqueous solutions containing NaOH or Na oleate, or a mixture of both, to flow from a Traube stalagmometer of the type referred to above through olive oil containing a certain amount of fatty acid (see Figs. 3 and 4). If the stalagmometer is so constructed that it will not permit too rapid a flow, a given volume of the aqueous solution yields a varying number of drops, dependent entirely upon the concentration of alkali or soap which it contains.

Under the conditions of experiment normally employed, a *M*/1000 NaOH passed through oil containing a constant small amount of oleic acid yields a system of 40 to 45 drops. A solution of half this strength would yield 20 to 25 drops, while one of double the strength would yield several hundred drops or would run through the oil without forming drops. $CaCl_2$ and other substances capable of counteracting the effect of NaOH in emulsion systems, are likewise capable of counteracting the effect exerted by NaOH on these drop systems, causing a diminution in the number of drops.

The accompanying Table II, showing the number of drops given by different strengths of NaOH and $Ca(OH)_2$ when allowed to pass through a given olive oil under the same physical conditions, indicates in the first place that Ca exerts a protective or antagonistic effect against OH which is fully twenty times as great as that exerted by Na and furthermore, that, if the upper and lower figures, which are unreliable, are excluded, the central zone shows an approximately logarithmic relation between the concentration of NaOH or $Ca(OH)_2$ and the number of drops produced, from which we are justified in concluding that we are dealing with adsorption phenomena and the formation of surface films.

TABLE II

NaOH	No. of drops	$Ca(OH)_2$	No. of drops
0.0005 *N*	22	0.01 *N*	30
0.0006 *N*	26	0.02 *N*	39
0.0008 *N*	33	0.03 *N*	47
0.001 *N*	39	0.032 *N*	53
0.0012 *N*	50	0.036 *N*	73
0.0014 *N*	79	0.04 *N*	chain
0.0016 *N*	about 120	—	—
0.002 *N*	chain	—	—

Space precludes an exhaustive discussion of these drop systems, but an attempt will be made in the following paragraphs to demonstrate that the drop method affords an accurate means of determining the exact effect exerted by given substances on the colloidal equilibrium of the interfacial films, which, as we have seen above, play so important a rôle in the establishment of emulsion equilibrium. If neutral or acidified water, containing no soap or other agent capable of lowering the surface tension, is allowed to flow through oil, the number of drops produced is small and depends on the relative densities and surface tension relations of oil and water. If, however, soap or some other agent capable of lowering the surface tension is added to the aqueous solution passed through the oil, the number of drops formed is immediately increased, and with each additional increase in the concentration of soap a corresponding increase in the number of drops takes place, until finally no drops are formed, and the aqueous solution flows uninterrupted through the oil. The logarithmic ratios observed above indicate that, just as in the case of emulsions, a surface film or membrane is formed, and that, the greater the dispersion of the film in water, the lower is the relative surface tension on the water as compared with the oil side of the film, the weaker will be the film, the smaller will be the weight of the average drop formed before the break occurs, and, since the volume of the aqueous phase is constant, the larger will be the number of drops. As the number of drops increases, the relative permeability of the system to water may be said to be increasing, just as in the case of an emulsion of water in oil which, under the influence of Na oleate or NaOH, is approaching but has not quite reached the critical point, at which it is transformed into the freely permeable emulsion of oil in water. Finally when the concentration of Na oleate, NaOH, or other dispersing agents in the aqueous phase of the drop system, reaches such a concentration that drops are no longer formed and the water streams straight through the oil, the system may be said to be freely permeable to water, to have passed the critical point, and to correspond with the freely permeable emulsion of oil in water referred to above. If $CaCl_2$ is added to a drop system of the type described, the number of drops is lowered; and by the addition of further proportions of $CaCl_2$, the number of drops is still further diminished in a logarithmic ratio indicating adsorption phenomena. A transformation in this direction is analogous to the conversion of an emulsion of oil in water to an emulsion of water in oil, or the transition from a system relatively more permeable to water to a system relatively less permeable.

To sum up the situation, it may be said that an increase in the number of drops corresponds with a relative increase in the permeability of the system to water, and with the transformation of an emulsion in the direction of oil in water; while a decrease in the number of drops corresponds with a reduction in the relative permeability of the system to water, and the transformation of an emulsion system in the reverse direction towards water in oil. This method has been adopted because we are dealing with a single film, and can consequently obtain far more accurate information regarding the influence exerted on the equilibrium of the system by the addition of extremely small amounts of various electrolytes. In experiments to be described later it will be demonstrated that substances like NaOH and NaCl, the anions of which are more readily adsorbed, increase the number of drops, presumably by still further increasing the dispersion of soap particles in the water phase; while substances like $CaCl_2$, possessing cations more readily adsorbed than anions, exert the reverse effect, lowering the number of drops.

For convenience in designating the effects exerted by different substances on the films produced in these drop systems, and to emphasize the analogy to the effect exerted by the substances in question on the protoplasmic film, the terms "destructive" and "protective" have been employed. Substances like soap, NaOH, NaCl, etc., which increase the dispersion of the film in water and promote the passage of water through the system as indicated by an increase in the number of drops, are termed destructive; those like $CaCl_2$, which exert the reverse effect diminishing the dispersion of the film in water and reducing the permeability of the system to water as indicated by a reduction in the number of drops, are termed protective. The relative effect exerted by a variety of electrolytes may readily be ascertained by adding the substances in question in varying proportions to a given NaOH system and determining the number of drops produced.

Electrolytes are found to be divided roughly into two main groups: (1) salts of the monovalent cations Li, Na, K, etc., alkalies, salts of di- and trivalent anions, etc., which raise the number of drops, indicating a destructive effect upon the film; and (2) salts of the di- and trivalent cations, Ca, Sr, Ba, Fe, Al, etc., which tend to diminish the number of drops thus indicating a protective effect.

The ratios in which individual substances belonging to these two classes exert compensatory effects upon one another may be readily determined by adding to a given system a constant proportion of one substance and varying proportions of the other, and by noting the point at which the antagonistic substances so balance one another that the number of drops coincides with that of the original system. To illustrate this principle, and also to demonstrate the similarity between antagonistic electrolyte effects in physical and biological systems, a single experiment showing the antagonism between NaCl and $CaCl_2$ has been selected from upwards of one hundred similar experiments. Reference to Table III and to the accompanying Figs. 3 and 4 in which an attempt has been made to illustrate the passage of the drops through the oil and thus to visualize more clearly the nature of the effects produced, shows that in experiment 1 a *M*/1000 NaOH gives 44 drops. In experiment 2 the addition of NaCl at a concentration of 0.15 *M* has increased the number of drops to 300. In experiment 3 in which $CaCl_2$ has been added to the system in such proportion as to give a concentration of 0.0015 *M* the number of drops has been reduced to 24, a figure not far in excess of that given by plain water or an acid solution. When, however, NaCl and $CaCl_2$ are employed together at concentrations of 0.15 *M* of the former and 0.0015 *M* of the latter, as in experiment 4, the number of drops corresponds so closely with that given by the original NaOH system as to indicate that the dispersing or destructive effect exerted by NaCl on the film is counteracted by the aggregating or protective effect of $CaCl_2$.

TABLE III

Exper. No.	Concentration of			No. of drops	Mol. ratio NaCl : $CaCl_2$
	NaOH	NaCl	$CaCl_2$		
1	0.001 *M*	—	—	44	—
2	0.001 *M*	0.15 *M*	—	300	—
3	0.001 *M*	—	0.0015 *M*	24	—
4	0.001 *M*	0.15 *M*	0.0015 *M*	44	100 : 1
5	0.001 *M*	0.3 *M*	0.003 *M*	43	100 : 1
6	0.001 *M*	0.45 *M*	0.005 *M*	43	100 : 1.1
7	0.001 *M*	0.6 *M*	0.01 *M*	43	100 : 1.6

At higher concentrations (experiment 7) the proportion of $CaCl_2$ required to antagonize NaCl is increased, as might be anticipated.

It will be seen from these experiments that NaCl and $CaCl_2$ exert a compensatory effect upon one another in ratios ranging from 100 molecules of the former to 1 or 2 of the latter, according to concentration. These ratios correspond very closely with the proportions in which NaCl and $CaCl_2$ tend to occur in nature, in sea-water, the blood of mammals, etc. Furthermore, as stated in the introduction, it has frequently been demonstrated by Jacques Loeb and other biologists that the toxic effect exerted by pure NaCl solutions on marine organisms may be in great measure counteracted or neutralized by adding one or two molecules of $CaCl_2$ for every hundred molecules of NaCl. This ratio of 100 : 1

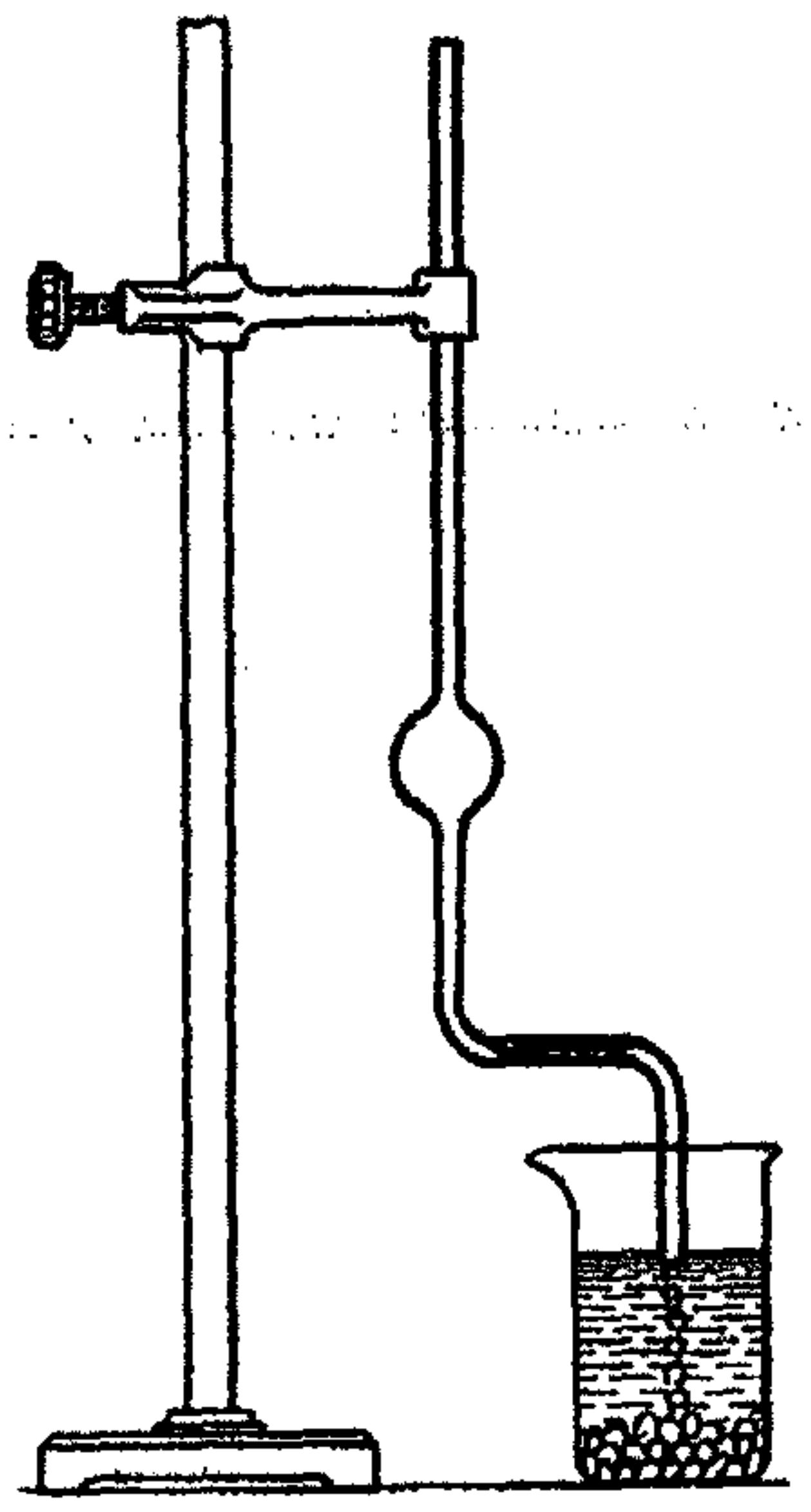


Fig. 3

This diagram is included to illustrate the procedure employed in studying the effect exerted by various antagonistic electrolytes on interfacial soap films. No attempt has been made to draw the capillary pipette to scale. For these and other details regarding the experimental method reference must be made to a subsequent paper or 2 appears, therefore, to be the natural balancing point for both physical and biological systems, but, just as in nature these balancing proportions are liable to vary with changing conditions, so it is found that in these purely physical systems considerable variations may be effected by dilution or concentration or by varying the amount of NaOH introduced into the original system. In experiments which will be presented in a subsequent publication, antagonistic effects have been produced in molecular ratios of NaCl to $CaCl_2$ as high as 400 or 500 : 1 and as low as 10 or 15 : 1. In fact, $CaCl_2$ can exert a direct compensatory effect upon NaOH alone, in ratios varying from chemical equivalents to molecular proportions; and from information kindly supplied by Prof. Osterhout regarding experiments as yet only partially published, it appears probable that similar compensatory ratios in which NaOH is directly antagonized by $CaCl_2$ may be obtained in experiments with marine organisms.

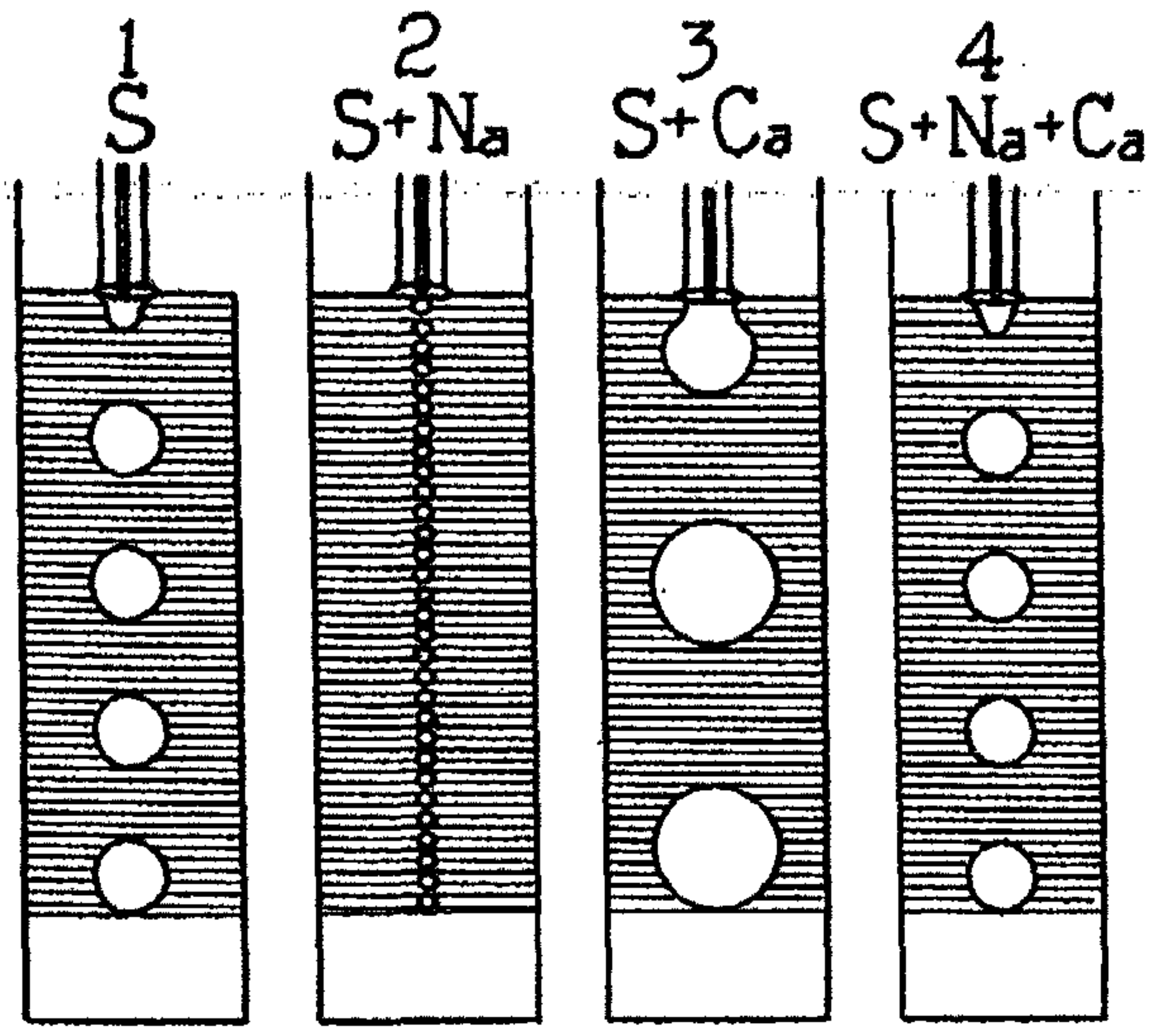


Fig. 4
Illustrating Expts. 1–4 in Table II. In each case the number of drops in the diagram is one-tenth of the number actually obtained

The above experiment with NaCl and $CaCl_2$ serves to illustrate the correspondence between physical and biological antagonisms of those electrolytes commonly occurring in the environment of the cell. Loeb has demonstrated that a large variety of salts not normally present are equally capable of exerting antagonistic effects. For example, $ZnSO_4$ and NaCl, both of which are toxic for fundulus eggs mutually counteract one another when admixed in ratios of one molecule of the former to 50 of the latter at concentrations of $M/400$ $ZnSO_4$ and $M/8$ NaCl. In studying the influence exerted by NaCl and $ZnSO_4$ on drop systems of the type described above, it was found that the protective effect exerted by $M/400$ $ZnSO_4$ was exactly sufficient to counteract the destructive effect of $M/8$ NaCl, thus showing a remarkable coincidence between the physical and biological experiments.

Before concluding this section of the paper, it is necessary to refer briefly to the relative effect exerted by mono-, di-, and trivalent cations and anions.

It has already been demonstrated in a previous section of this paper, that Ca exerts a vastly greater protective effect against OH, than does Na. Fe is found to exert an even greater protective effect than Ca.

In fact, in a previous paper, it was demonstrated, that these protective ratios are approximately logarithmic, and correspond roughly with the precipitating effect exerted by the cations in question on soap dispersed in water, and the fact that similar approximately logarithmic ratios have been observed while studying the effects exerted by these mono-, di-, and trivalent cations on a variety of colloidal and biological systems lends strong support to the theory that we are dealing in all these cases at least to a certain extent with adsorption phenomena. A comparison of the destructive effect exerted by mono-, di-, and trivalent anions on soap films brings out a similar relation, the trivalent anions being more powerful than the divalent, and the divalent than the monovalent. The H and OH ions are, as is usually the case in physical and biological systems, exceptions to this rule, being fully as active or more active than the di- and trivalent ions. The H ion exerts a greater protective effect than other monovalent cations, presumably owing to the fact that acids react directly with soaps, causing decomposition to fatty acids and salts, thus eliminating the surface tension lowering effect and consequently the dispersing power of the removed soap. OH ions, likewise, exert a far greater destructive effect on the film than do monovalent anions, presumably on account of the increased production of soaps by interaction with available fatty acids.

These results and the analogy which they exhibit to antagonistic phenomena in biological systems suggest the possibility that in both cases we are dealing with antagonisms between two main groups of electrolytes: (1) those possessing a relatively more readily adsorbed or reactive cation than anion, and (2) those possessing a relatively more readily adsorbed or reactive anion than cation; and that balanced solutions are those in which the relative proportions of cations and anions reacting with or adsorbed by colloidal constituents of the surface film are such that no change occurs in the charge, in the state of dispersion, and consequently in the permeability of the film. Biologists would immediately raise the objection that certain substances, salts of Mg for example, appear to be capable of functioning under varying conditions in one or the other class, either as a destructive agent like NaCl or as a protective agent like $CaCl_2$. In an attempt to parallel certain experiments of Jacques Loeb regarding the influence exerted by salts of Mg on marine organisms and their eggs, it has been demonstrated that just as in the case of the emulsion systems considered above Mg is capable of functioning under varying conditions in these drop systems either as a destructive agent like NaCl or as a protective agent like $CaCl_2$. If soap is employed as the dispersing agent in making up a drop system, $MgCl_2$ functions like $CaCl_2$, antagonizing NaCl. If, however, NaOH is employed as the dispersing agent, and soap is formed by interaction between the fatty acid in the oil phase and the NaOH, $MgCl_2$ functions in an entirely different manner, exerting a dispersing effect similar to but considerably stronger than that of NaCl, which may be counteracted by $CaCl_2$ in ratios of 1 or 2 of Mg to one of Ca. We can only suggest that this peculiarity is possibly attributable to the absolute insolubility of $Mg(OH)_2$ in water. In one case soap is present in the system prior to the introduction of $MgCl_2$; in the other case $MgCl_2$ has had an opportunity of reacting with NaOH with the formation of colloidal aggregates of $Mg(OH)_2$ prior to the production of soap or contact with colloidal particles of soap or oleic acid. Such variations in behavior, dependent upon the condition of colloidal aggregation, are not uncommon. From what we know of adsorption phenomena and their dependence on the chemical and physical structure of both substrate and adsorbed substance, and if the latter be an ion, on valence and electric charge, it becomes less difficult to understand how Mg may function under certain conditions as an anesthetic or protective agent, and under other conditions as a destructive agent. KCl, like $MgCl_2$, presents differences of the same type, in biological systems functioning normally as a destructive agent like NaCl, it is capable, nevertheless, of exerting under certain circumstances an antagonistic effect upon NaCl. It has been found possible by using drop systems containing a large amount of oleic acid in conjunction with Na oleate to produce similar somewhat feeble antagonistic effects between KCl and NaCl, although normally in a NaOH system KCl functions like NaCl as an antagonist for $CaCl_2$.

A brief reference must be made in passing to a group of non-electrolytes, the organic anesthetics, which appear, from the experiments of Osterhout, Lillie, and others, to exert a protective effect on the protoplasmic film analogous to that exerted by Ca and Mg. The facility with which these substances are dissolved or dispersed in fats and lipoids naturally suggests that they function as protective agents in the same manner as soaps of di- and trivalent cations. Lillie and others who have considered this question have experienced difficulty in bringing the protective effects exerted by anesthetics into line with those exerted by salts of Ca, Mg, etc., presumably because they have assumed that salts of Ca and Mg were absolutely insoluble in oil, having overlooked the fact that the soaps of Mg, Ca, etc., are, like anesthetics, freely dispersed by fats. As would be expected, anesthetics, when used at suitable concentrations, are found to exert a protective effect upon soap films, causing a diminution in the number of drops in physical systems of the type described above. There is, however, a remarkable analogy between the results obtained in these physical systems and those observed by Lillie while studying the destructive effect exerted by NaCl salts on arenicola larvae. Lillie noted that this destructive effect might be counteracted by the use of anesthetics, and that for each anesthetic an optimum concentration obtains, but that at higher concentrations the larvae are destroyed, just as rapidly as in pure salt solutions. He found, for example, an optimum protective effect for propyl alcohol at about $2^1/_2$ percent, for ether at about 1 percent, and for chloroform at about $^1/_2$ percent. Using a specially prepared system containing a mixture of NaOH, Na oleate, $MgCl_2$, etc., full details regarding which will shortly be published, anesthetic curves closely resembling those of Lillie may be obtained. For each anesthetic there appears to be a concentration at which the number of drops is reduced to a minimum; for propyl alcohol $2^1/_2$ percent, for ether 1 percent, for chloroform $^1/_2$ percent on a given system. If the NaOH content of the system is increased its optimum points are likewise increased in a definite ratio to one another. A similar irregular curve may be obtained with salts of Mg, but not as far as has thus far been ascertained with salts of Ca, Sr, etc. This point is extremely significant in view of the well-known capacity of Mg to function as an anesthetic.

In the accompanying Table IV the effect exerted by propyl alcohol on arenicola larvae as determined by Lillie, and on a somewhat complicated drop system, full details regarding which will shortly be published, indicates a close analogy between these physical and biological systems. It may be concluded that anesthetics exert their effect on protoplasm by inhibiting those functions which depend upon an intermittent intercommunication between adjacent aqueous phases.

TABLE IV

C_3H_7OH added	Drop system		Larvae protection (Lillie)
	No. of drops	Membrane protection	
nil	52	—	—
1%	23	++	++
2½%	18	+++	+++
5%	27	++	++
10%	76	—	—

Weak bases, like NH_4OH, exert far less destructive effect on drop films than NaOH, and weak acids, like butyric acid, exert less protective effect than stronger mineral acids. In view of the fact that NH_4OH and NH_4Cl penetrate the cell more readily than NaOH and NaCl, it should be pointed out that this difference is attributable to the fact that NH_4OH and NH_4Cl are soluble or dispersed to a certain extent in constituents of the non-aqueous phase of protoplasm, and consequently pass through the protoplasmic film in much the same way as do anesthetics. The penetration of NaOH and NaCl is attributable to the available OH and Cl ions which, by adsorption on interfacial soap films, promote the dispersion of the non-aqueous phase in the aqueous phase, and so facilitate the passage through the film of substances which depend upon aqueous lines of communication.

In conclusion a single experiment has been selected to show the close relation between the influence exerted by $CaCl_2$ and its antagonist Na citrate on (1) a purely physical drop system; (2) living mice; (3) the blood coagulation process; and (4) the hemolysis of blood corpuscles by complement and amboceptor. Na citrate has been employed instead of NaCl as an antagonist for $CaCl_2$, not because equally good results could not be obtained with NaCl, but because they are more difficult to demonstrate on account of the enormous concentration of NaCl required to antagonize $CaCl_2$ and the consequent disturbance in osmotic pressure resulting from intravenous injection of such highly concentrated solutions. In the experiments recorded in Table III a $M/10$ $CaCl_2$ and its equivalent a $M/15$ Na citrate are mixed in various proportions ranging from 100 percent of $CaCl_2$ solution containing no citrate, to 100 percent of citrate solution containing no Ca, and the effects exerted by each of the solutions on each system noted as follows:

1. Drop system as above. Effect on equilibrium of soap film determined by noting the number of drops produced, the balancing point being that at which the number of drops obtained corresponds with that given by the original system.
2. Toxicity to mice when injected intravenously. The balancing point being that at which the maximum dose may be injected without fatal result.
3. Coagulation of blood plasma. The balancing point being that at which the coagulating effect exerted by Ca is just counterbalanced by the inhibiting effect of citrate.
4. Hemolysis of corpuscles by means of complement and amboceptor. Hemolysis is interfered with at the Ca and citrate end of the scale but the critical point is that point at which Ca and citrate balance one another to such an extent as to exert no disturbing effect upon the hemolytic process.

It will be noted that the point at which the solutions balance one another is approximately the same in all cases. About 30 to 33 percent $CaCl_2$ to 70 to 67 percent citrate. Those mixtures in which the $CaCl_2$ appears to predominate cause a diminution in the number of drops; presumably by increasing the resistance of the soap film; exhibit a remarkable toxicity for mice, presumably by rendering the protoplasmic film too impermeable; produce complete interference with complement hemolysis; and cause blood coagulation, presumably on account of the aggregating effect which they exert upon the dispersed fibrinogen—a problem which will be further discussed in a forthcoming paper on jellies. Those solutions in which citrate appears to predominate, increase the number of drops, presumably by dispersing the soap film and thus diminishing its resistance; are extremely toxic for the mouse, presumably because of the dispersing or weakening effect which they exert upon the protoplasmic film; prevent coagulation, presumably by promoting or maintaining dispersion of the fibrinogen sol; and exert an interfering effect with the process of complement hemolysis. The logarithmic relation between the concentration of $CaCl_2$ and the number of drops observed indicating adsorption phenomena, will be considered in a subsequent publication.

TABLE V

Exper.	Solution containing		1 Drop system	2 Toxicity to mice dose in cc		3 Blood coag.		4 Hemolysis corpuscles
	$M/10$ $CaCl_2$ %	$M/15$ Na citrate %		Non-lethal	Lethal	10 min.	2 hrs.	
1	—	—	51	—	—	—	—	—
2	100	—	39	0.25	0.3	+++	+++	+++
3	75	25	22	0.5	1.0	+++	+++	+++
4	50	50	25	2.5[0.5]	3.0[0.6]	+++	+++	++
5	40	60	34	7.5[1.5]	10.0[2.0]	+++	+++	++
6	34	66	45	7.5[1.5]	10.0[2.0]	+++	+++	—
7	30	70	53	8.0[2.0]	10.0[2.0]	+	++	—
8	25	75	—	5.0[1.0]	7.5[1.5]	—	—	+
9	20	80	94	1.5	2.0	—	—	++
10	—	100	250	0.22	0.25	—	—	+++

(NOTE: the figures in brackets represent a $M/2$ solution injected instead of the $M/10$ solution in those cases in which it would be a physical impossibility to introduce the bulk of fluid involved into the tail vein of a mouse.)

Theoretical Considerations

In the summary of a preliminary communication regarding this work, to which reference has already been made, the writer drew the following conclusions:

"The equilibrium of emulsions and other aqueous-lipoid systems appears to depend upon the relative proportion of positive and negative ions adsorbed by a stabilizing membrane formed between the aqueous and lipoid phases; an excess of negative ions causes the formation of oil-water emulsions and an excess of positive ions has the reverse effect."

"The relative effect exerted by mono-, di-, and trivalent cations in such a system appears to be dependent upon the relative capacity of the ions in question to precipitate lipoids from aqueous suspension and to be in the logarithmic ratios observed by Hardy and others for the precipitation of colloids."

"The destructive effect of negative ions upon lipoid concentration membranes formed between aqueous and lipoid phases may be counteracted either by cations or anesthetics, the concentrations at which these bodies produce their maximum effect corresponding with those observed by Lillie on arenicola larvae."

"The fact that anesthetics and cations exert similar protective effects against negative ions in a series of purely physical systems on the one hand, and biological systems on the other, lends support to the theory that protoplasm may consist of an aqueous-lipoid system in which a delicate film of partially lipoid material represents the continuous or external phase."

"Whether this be the case or not, it is evident that the protoplasmic membrane consists in part of lipoids, and we believe that the adsorption of varying proportions of negative or positive ions, or other substances capable of rendering the membrane more or less soluble in the surrounding aqueous medium, thereby changing the surface tension relation and consequently the state of colloidal equilibrium of certain constituents of the membrane, is probably responsible for effects of the type recorded in this paper."

In the above summary the term "lipoid" was used in a general sense to denote oils, fats, and lipoids. The above conclusions based upon preliminary experiments have now been amply confirmed. From the experimental data presented in this paper it is evident that electrolytes may be divided roughly, as regards their effect on surface films in both physical and biological systems, into two main antagonistic groups. The first comprises those substances like acids and salts of di- and trivalent cations, which possess a more readily adsorbed or reactive cation than anion, and which appear to exert what we may designate as a protective effect on physical and biological membranes, diminishing their dispersion in water and consequently their permeability to water. The second comprises those substances like alkalies, salts of monovalent cations and di- and trivalent anions, which possess a more readily adsorbed or reactive anion than cation, and which appear to exert a destructive effect on both physical and biological membranes by promoting their dispersion in water and thus increasing their permeability to water. Individual substances belonging to the first group appear to antagonize individual substances of the second group in approximately the same ratios in both physical and biological systems. Substances like $MgCl_2$, which exhibit an abnormal behavior in biological systems functioning under varying conditions as protective or destructive agents, appear to exhibit similar abnormalities under like conditions in physical systems. The equilibrium of emulsions depends, as we have seen above, on the relative degree of dispersion of an interfacial film in the aqueous and non-aqueous phases. Substances of the first class, possessing more readily adsorbed cations, diminish the dispersion of the film in water, and thus promote the formation of systems in which water is the dispersed phase with a consequent reduction in the permeability of the system as a whole to water and water-soluble substances. Substances of the second class possessing more readily adsorbed or reactive anions exert the reverse effect promoting the dispersion of the film in water, and consequently the formation of a system in which water is the external or continuous phase, thus leading to an increase in the permeability of the system as a whole to water and water-soluble substances. Presumably in balanced electrolyte solutions the adsorption of cations and anions is equal or compensatory, consequently no change takes place in the relative dispersion of the film in the aqueous and non-aqueous phases and the permeability of the system remains unchanged.

The question arises as to how far the structure of the protoplasmic film, and the variations in permeability which it exhibits under the influence of varying proportions of salts of Ca and Na, is attributable to a more or less complete transformation of phase relations analogous to those discussed in the case of emulsions, sols, and jellies. It was noted in the introduction that the original protoplasmic structure might well consist of a dispersion of proteins, lipoids, fats, etc., in water, and that the protoplasmic film appeared to approximate to a structure of the reverse type in which water was more or less dispersed in an external or continuous fatty or lipoid phase. We know that soaps are present in the protoplasmic system and, since they tend to concentrate at the interface between fatty or lipoid materials and water, it may reasonably be assumed that the particles of fatty or lipoid material present in protoplasm are more or less dispersed in an aqueous medium by means of adsorbed soap films. If we now consider what occurs when naked protoplasm comes in contact with sea-water or other aqueous saline solutions containing salts of Ca, it is obvious that, if salts of Ca are present in sufficient proportion, the equilibrium of the particles of fatty or lipoid material which find themselves immediately on the surface in contact with the sea-water may be disturbed. A system, which consists of fatty or lipoid material dispersed by means of a Na soap film in water, may be converted more or less perfectly by the adsorption of Ca ions on the film into the reverse type of system in which water is dispersed by means of a Ca soap film in an external fatty or lipoid phase. The permeability of such a system to water, the extent to which water channels would be formed from point to point through such a film or membrane, might well depend on the proportions of those electrolytes like $CaCl_2$, on the one hand, which tend to render the system less permeable, and those like NaCl, on the other, which exert the reverse effect.

In order more clearly to visualize the process involved, we may take as an example the conversion of a dispersion of particles of wax in water into a honeycomb-like structure in which the water phase is surrounded by the continuous wax walls of the cells. It will readily be appreciated that any agent capable of corroding or perforating the walls of the honeycomb structure would promote the continuity or intercommunication of a previously dispersed water phase, and would ultimately open up water channels of communication throughout the whole system. Agents capable of exerting the reverse effect, tending to protect the wax walls, would obviously antagonize those agents which corrode or break down the walls with the result that the permeability of such a system would depend ultimately upon the proportions in which the antagonistic agents in question are introduced into the system.

The writer believes that a somewhat similar explanation may be found for the formation of the protoplasmic film, and for the antagonisms between those electrolytes like $CaCl_2$ which possess a more readily adsorbed cation and tend to promote the formation of a less permeable system, and those like NaOH or NaCl which possess a more readily adsorbed anion and tend to exert the reverse effect. It is perfectly possible to conceive of innumerable intermediate systems, analogous to a sponge in water or to the perforated honeycomb structure, possessing more or less constricted water communications, but which may be converted by means of salts of Ca, anesthetics, etc., into systems in which the water communications are completely cut off; and which, by means of NaOH, NaCl, etc., may be converted into systems in which the water communications are too extensive for the maintenance of normal vital function. The proteins present in protoplasm may well be transformed under the influence of Ca into a non-reversible but more or less permeable system analogous to a blood clot in which the protein, being a continuous phase, affords a mesh-like skeleton or framework to the structure and confers a certain measure of rigidity, elasticity, and continuity to the membrane. Fatty or lipoid materials, on the other hand, which produce readily reversiable emulsion systems with water, might, when supported by the protein framework, yield a system sufficiently sensitive to exhibit variations in permeability to water under the influence of varying proportions of antagonistic electrolytes like NaCl and $CaCl_2$. Hofmeister, and other investigators who have studied the dispersing and aggregating effects exerted by a variety of electrolytes on proteins, lipoids, soaps, and other colloids known to be present in the living cell, have failed to demonstrate a satisfactory analogy between physical structures and living protoplasm, presumably because they have looked on one side of the picture only, considering solely the influence exerted by electrolytes on the state of dispersion of colloids in water, and ignoring the all-important fact that colloidal concentration films are formed not between two layers of water, but at the interface between water and some non-aqueous phase, be it protein, lipoid, or fat. Consequently the condition of dispersion of the film in the non-aqueous phase is, as we have seen above, quite as important as its dispersion in water in determining the equilibrium of the system, its capacity for reversal under the influence of varying proportions of antagonistic electrolytes, and its consequent permeability to substances present in the environing aqueous medium. The theory advanced above affords a satisfactory explanation for growth by intussusception which characterizes living structures and differentiates them from crystals and the generality of mechanical structures which grow by accretion. The possible mechanism involved will be readily understood if we consider the break which occurs in the continuity of films of the type described above in considering the drop system. Whenever such a break occurs, substances, derived from the adjacent nonmiscible phases possessing the capacity to form surface films, will tend to concentrate on the surface and thus to reëstablish the conditions of equilibrium as long as the reserve of the necessary materials is available. When the reserve in question is exhausted, it is obvious that protoplasmic equilibrium can no longer be maintained and death must necessarily ensue, just as in the drop systems aqueous solutions containing too great a proportion of alkali run through without the formation of drops.

It has been demonstrated that anesthetics reduce the permeability of both emulsion systems and protoplasm to water. It may well be that a temporary block of those channels through which nervous sensations are transmitted is effected by a temporary interruption of a normal intermittent intercommunication between adjacent aqueous phases, which is analogous to the valve system of an engine or machine.

The relative differences of potential between the interior and exterior of a cell, the negative charge on the surface, and the relatively greater negative charge in the interior, harmonize with the assumption that protoplasm has been transformed into a less permeable protoplasmic membrane by the adsorption of cations, and that the interior constituents of the protoplasm are in a state more nearly approximating to dispersion in water than are those on the surface. It is quite reasonable to suppose that the maintenance of vital processes depends upon the maintenance of a state of equilibrium within comparatively narrow limits of permeability, and that any considerable variation from those limits effected by a too great preponderance of one or the other type of antagonistic electrolytes would cause a disturbance of the system similar to that which results if the valves of an engine or machine are not properly adjusted. It is well known that the efficiency of such a mechanical system may be entirely destroyed by too greatly increasing or too greatly diminishing the size and speed of action of the valves.

The mechanism whereby protoplasm takes in sugars and other water-soluble food stuffs has always presented difficulties, but may possibly be explained by assuming rhythmical and intermittent variations in permeability of the protoplasmic membrane actuated by variations in the concentration of CO_2 and other products of metabolism. From experiments which will shortly be published it will be demonstrated that CO_2 and other products of metabolism exert a profound effect on the equilibrium of soap films, presumably owing to the influence they exert on the OH ion content of the system. It appears by no means inconceivable that metabolic products accumulate at certain points until such concentrations are reached that a disturbance in equilibrium of the system takes place, resulting in a temporarily more perfect communication between the interior water phases and the external aqueous medium, thus promoting a discharge of the metabolic products in question and an intake of water-soluble products from without.

To avoid any misconception, it should be stated that protoplasm, and the protoplasmic film, do not, under normal conditions, present any such sharp differentiations of phase relations as are indicated by our crude illustrations. Protoplasm appears to resemble a system in a state of flux, in which the phases are brought into extremely intimate relation with one another, possibly owing to the presence in the system, in addition to dispersing agents of the type considered above, of substances which are freely miscible with both phases.

The action exerted by acetone, or a mixture of acetone and ether, or alcohol and ether, on an emulsion of oil in water, may serve to indicate the nature of the effect produced by such substances in suitably constituted diphasic, heterogeneous systems.

The writer has noted, that the addition of a large amount of any one of the organic agents in question, promotes the dispersion of oil in water to such an extent, that the dispersed particles can no longer be recognized by means of the microscope but only by means of the ultra microscope.

A smaller amount of the organic agent gives a system in which the dispersion of oil in water is still recognizable by means of the microscope, and systems of this type are found to be extremely sensitive to slight variations in the proporsions of antagonistic electrolytes, and to exhibit a much sharper critical point, than do ordinary emulsions.

These experiments with antagonistic electrolytes offer substantial support to the theory, first advanced by A. B. Macallum, that the similarity in the proportions of certain electrolytes in sea-water, the blood of mammals, etc., is attributable to the fact that living protoplasm has inherited from an original protoplasmic ancestor an adjustment of colloidal equilibrium to those electrolytes which were present in sea-water at the time that protoplasmic material first came into being. Electrolytes appear to play an extremely important role in conditioning the form and structure and in maintaining the equilibrium of the complex colloidal system which we designate as living protoplasm.

It is proposed to publish in the near future a series of papers dealing with various physical and biological phases of the questions which have only been dealt with superficially in this paper.

In conclusion, the writer wishes to express his appreciation of the courtesy exhibited by Prof. Bancroft in informing him prior to publication of his observations regarding the influence exerted by soaps of Ca and Na on the equilibrium of emulsion systems, and also to acknowledge his indebtedness to Mr. F. West for his coöperation in the conduct of the experiments recorded in this communication.

Summary

1. Salts of Ca appear to promote and alkalies and salts of Na to inhibit reversal or transposition of phase relations in widely diversified heterogeneous systems: for example the transformation of an emulsion of oil in water, like cream, into an emulsion of water in oil, like butter; of a protein sol, like blood plasma, into a jelly, like the blood clot; and of protoplasm into the protoplasmic membrane. The proportions in which alkalies and salts of Na exert an antagonistic or inhibiting effect on salts of Ca are found to be approximately the same in these different systems.

2. In all these cases, a system consisting of a non-aqueous phase dispersed in water is converted more or less completely

into a system in which water is dispersed in an external or continuous non-aqueous phase. The transposition of phase relations involved is analogous to the transformation of islands surrounded by water into lakes surrounded by land. The former system is freely permeable to water, while the latter is impermeable, if the reversal of phase relations is complete; but it is possible to conceive of a variety of intermediate systems, possessing any desired degree of permeability, which may be obtained by introducing varying proportions of those agents which promote or inhibit the transformation in question.

3. This appears to afford a possible explanation for the phenomenon of electrolyte antagonism in biological systems, salts of Ca promoting the formation of a protoplasmic membrane too impermeable for the performance of normal vital functions, alkalies and salts of Na exerting the reverse effect, preventing the formation of a membrane or rendering the membrane already formed too permeable, while balanced solutions, like sea-water, the blood of mammals, etc., appear to be those in which antagonistic electrolytes are present in such proportions that the protoplasmic membrane formed possesses that measure of permeability most favorable for cell life.

4. Reserving the problem of jelly formation and the process of blood coagulation for a subsequent communication, the antagonistic effects exerted by electrolytes on emulsion and protoplasmic equilibrium were further investigated with the following results: suitably constituted emulsions of oil dispersed in water may be converted into emulsions of water dispersed in oil by shaking with salts of Ca, Mg, Fe, and other di-, and trivalent cations, and the transformation in question may be prevented or the reverse transformation effected by shaking with a sufficient excess of NaOH or other alkali.

5. When the antagonistic electrolytes in question are present in certain balanced ratios, a critical point occurs at which neither type of emulsion is formed, and the oil and water separate into two layers.

6. Electrolytes appear to be divided roughly into two main antagonistic groups as regards the effect they exert on the equilibrium of emulsions. The first consists of salts of di- and trivalent cations, etc., which possess a more reactive or more readily adsorbed cation and appear to promote the formation of emulsions of water in oil; the second consists of alkalies, salts of monovalent cations and of di- and trivalent anions which possess a more reactive or more readily adsorbed anion and appear to exert the reverse effect promoting the formation of emulsions of oil dispersed in water.

7. Bancroft observed that soaps of Na, used as emulsifying agents for oil and water, promote the formation of emulsions of oil in water, while soaps of Ca used as emulsifying agents exert the reverse effect, promoting the formation of emulsions of water in oil. He concluded that soaps of Na, being readily dispersed in water and not in oil, form a concentration film at the interface between water and oil, the surface tension on the water side of which is lower than on the oil side and consequently the film curves in such a manner as to enclose oil in water. Conversely soaps of Ca, being more readily dispersed in oil than water, produce a film, the surface tension relations of which are such that an emulsion of water in oil is formed.

The grouping of antagonistic electrolytes in emulsion systems appears to correspond with this theory; adsorbed anions increase the dispersion of interfacial soap films in water as compared with oil, and thus promote the formation of emulsions of oil in water, while adsorbed cations increase the dispersion of soap films in oil as compared with water and thus promote the formation of emulsions of water in oil.

8. To obtain accurate data regarding the influence exerted by electrolytes on soap films, the procedure was adopted of allowing aqueous solutions of soap or NaOH, containing the salts to be tested, to flow from a capillary pipette through olive oil, and of counting the number of drops produced. Those electrolytes which possess a readily adsorbed anion appear to cause an increase in the number of drops, thus in-

dicating increased dispersion or destruction of the surface film and an increased permeability of the system to water. Those electrolytes which possess a readily adsorbed cation exert the reverse effect diminishing the number of drops, which indicates diminished dispersion or destruction of the film and diminished permeability of the system to water.

9. The ratio in which given electrolytes exert a compensatory effect on one another, as indicated by the point at which the number of drops corresponds with that of the original system, is almost invariably the same as that at which the electrolytes in question exert antagonistic or compensatory effects on one another in biological systems.

For example, NaCl which increases the number of drops, and $CaCl_2$ which diminishes the number of drops, appear to balance one another in a ratio of 100 molecules of the former to one or two of the latter according to the concentration, these ratios being approximately the same as those in which the salts in question occur in sea-water, the blood of mammals, etc., and in which they have been found to exert antagonistic effects on one another in innumerable experiments carried out by Loeb, Osterhout and other biologists.

10. The relative protective effects exerted by monovalent, divalent, and trivalent cations, and the relative destructive effects exerted by monovalent, divalent, and trivalent anions, as well as the effects exerted by acids and alkalies, are in the ratios commonly encountered in colloidal and biological systems.

11. The ratio between the number of drops obtained and the concentration of soap employed, or of NaOH or any salt added, whether protective or destructive, is invariably logarithmic, suggesting the extreme probability that we are dealing with adsorption phenomena. This conclusion is supported by the observation that the addition of varying proportions of NaCl to an emulsion of oil in water lowers the concentration of OH ions in the aqueous phase in a logarithmic ratio.

12. Salts of Mg, and other substances which exhibit

abnormalities in biological systems exerting under varying conditions a protective or destructive effect on the protoplasmic film, exhibit similar abnormalities under similar conditions in emulsion and drop systems, functioning, according to circumstances, as protective agents like $CaCl_2$ or destructive agents like NaOH or NaCl.

13. Anesthetics exhibit a similar effect, exerting at certain optimum concentrations a protective effect indicated by a diminution in the number of drops. The concentrations at which given anesthetics exert maximum protective effects in suitably constituted drop systems appear to correspond with those at which they exert similar protective effects on living cells.

14. A comparison of the antagonistic effects exerted by $CaCl_2$ and Na citrate on a variety of physical and biological systems including the drop system, the blood coagulation process, living mice, and the hemolysis of blood corpuscles, brought out the fact that the critical point at which these substances exert a compensatory effect on one another is approximately the same in all cases. From further observations, regarding the influence exerted by varying the concentration of the substances in question, it is extremely probable that the effects in question are attributable to a disturbance of equilibrium of colloidal substances resulting from the adsorption of ions, and the balancing points observed above are those at which no disturbance of equilibrium occurs, since the adsorption of anions and cations is equal or compensatory.

15. The above conclusions regarding the influence exerted by antagonistic electrolytes on the permeability of the protoplasmic membrane receive substantial support from the fact that Osterhout, by employing a purely biological procedure, has reached independently the somewhat similar conclusion that electrolytes may be divided into two antagonistic groups, according to whether they can or cannot decrease the permeability of the protoplasmic membrane.

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W. J. V. Osterhout: Science, 41, 255 (1915).

Since the completion of this paper, the writer has learned that as far back as 1904, A. P. Mathews concluded that the stimulating or depressing effects exerted by electrolytes on the nervous system depend upon the relative efficiency of anions and cations.

If in a given salt the anion markedly predominates, the salt stimulates; if the cation predominates, the salt depresses. From this it naturally follows that the antagonism between NaCl and $CaCl_2$ in certain biological systems is not attributable to antagonism between Na and Ca ions, but to an antagonism between the cations on the one hand, and the anions on the other.

In this and previous papers the writer has demonstrated repeatedly that the antagonism between NaCl and $CaCl_2$ in purely physical systems is attributable not to antagonism between Na and Ca, but to antagonism between the cations on the one hand and the anions on the other.

The remarkable parallel between the antagonistic effects exerted by given electrolytes in physical and biological systems together with the simple theoretical considerations outlined above led the writer to challenge the view so widely expressed in biological and physiological literature that one cation antagonizes another cation, that Na antagonizes Ca.

There can be no doubt that, as far as physiological systems are concerned, Mathews was the first to recognize this principle.[1] It should be pointed out incidentally that the correspondence between the data accumulated by Mathews and that presented above lends further support to the view previously expressed, that, whatever the ultimate theoretical interpretation may be, the close correspondence between data accumulated in such widely diversified fields affords substantial evidence of the existence of some heretofore unappreciated fundamental physical principle.

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[1] A. P. Mathews: Am. Jour. Physiology, 11, 455 (1904).

NEW BOOKS

The Molecular Volumes of Liquid Chemical Compounds. *By Gervaise LeBas. 22 × 15 cm; pp. xii + 275. New York: Longmans, Green and Co., 1915. Price: $2.25 net.*—The subject is treated under the headings: the molecular volumes of organic compounds at the melting point; the molecular volumes of the hydrocarbons at the boiling point; the molecular volumes of the halogen compounds; the molecular volumes of organic compounds containing oxygen; the molecular volumes of sulphur compounds; the molecular volumes of nitrogen compounds; the molecular volumes of phosphorus compounds, etc.; summary of the theory of molecular volumes.

In the last chapter, p. 235, the author says in regard to the additive principle: "This feature, which characterizes most physical properties, is very prominent in molecular volumes, although not, as Kopp thought, unqualified. This being so, it is essential that accurate volumes should be found, at least in so far as this can be done with a property in which the influence of the homologous increment is felt even from compound to compound in a series. The numbers determined by Kopp were, for the most part, inaccurate, chiefly because the values for the fundamental atoms, carbon and hydrogen, were altogether wrong."

On page 255 there is an interesting, though perhaps obscure, passage which apparently implies that colored vapors are unknown. "In our view, one circumstance of great significance is that when a vapor condenses it becomes *visible*. Steam, for example, condenses to a transparent but visible liquid water, which, except for conditions of mobility, maintains certain characteristics below the melting point and in the solid state which are noticed in the liquid. The clear limpid water solidifies to the clear glassy ice and this characteristic is maintained down to absolute zero. For that matter an opaque liquid like mercury maintains this characteristic below the melting point, and so far as we know even to absolute zero. In both cases, however, the vapors are transparent [?]. The reason is, that in the vapors, the light passes through the interfaces which separate the molecules, but in liquids when transparent, it passes through a different medium, the dielectric shells of the atoms and possibly of the molecules as a whole, and this condition is maintained down to absolute zero. We believe that the features just noted can only be explained on the assumption of *compact structure* in the sense indicated. It is also to be remarked that the theory of absorption spectra implies that light traverses a medium different to that of the external ether."

Wilder D. Bancroft

Quantitative Laws in Biological Chemistry. *By Svante Arrhenius. 22 × 15 cm; pp. xi + 164. London: G. Bell and Sons, Ltd., 1915. Price: 6 shillings net.*—This book is based on the Tyndall lectures given in the Royal Institution in May, 1914. The subject is treated under the headings: introduction; velocity of reactions; the influence of temperature on the velocity of reactions—reaction of cells; the quantitative laws of digestion and resorption; chemical equilibria; immunization. Arrhenius considers that egg albumin forms a true solution; but he does recognize, pp. 16, 108, that agglutination may be regarded as a kind of coagulation, though he rather spoils this by saying, p. 110, that "the predominant influence which is ascribed by the school of colloidal chemistry to these [adsorption] phenomena seems to be greatly over-estimated." While one must regret that Arrhenius has not availed himself, as much as he might and should have done, of the principles of colloid chemistry, one may rejoice at the firm stand which he takes in opposition to the theoretical views of the Ehrlich school.

The attitude of Arrhenius toward vitalism is perfectly clear, p. 19: "Our special question is if living matter obeys the same fundamental quantitative laws as those which govern the reactions of inanimate matter. In other words, we will look upon the problem of vitalism from a chemical standpoint. We will limit this investigation to such laws as are expressed by formulae, giving the relations between quantities dependent the one on the other. It is chiefly with laws of this kind that we are concerned in exact science."

When ammonia acts upon ethyl acetate in great excess, p. 41, the ammonium acetate, formed by the reaction, forces back the dissociation to such an extent that the rate apparently depends on the square root of the time instead of the first power of the time. Arrhenius was interested in working this out because the results are in accordance with Schütz's rule. It would be interesting to know whether a somewhat similar explanation accounts for Hjelt's results on the saponification of alkyl malonic esters. *Wilder D. Bancroft*

A Handbook of Colloid-chemistry. *By Wolfgang Ostwald. Translated by Martin H. Fischer. 23 × 16 cm; pp. xii + 278. Philadelphia: P. Blakiston's Son and Co., 1915. Price: $3.00 net.*—This book is translated from the third German edition which has been reviewed (17, 562). It is a good thing to have more books on colloid chemistry in English, because there exists a very strong demand. On the other hand it seems a pity, with a rapidly developing subject like colloid chemistry, for anybody to translate a book which is practically five years old and which never was very good at any time. Wolfgang Ostwald has some of the fluency of his father; but Wilhelm Ostwald used words to make clear his ideas, while the son lays himself open to the criticism of substituting words for ideas. It is quite impossible to agree with the translator when he says: "Wolfgang Ostwald's writings represent in colloid chemistry what those of Charles Gerhardt represent in organic, Justus Liebig in agricultural, and Wilhelm Ostwald in physical chemistry."

While the translation has been done fairly well, the reviewer protests against rendering "Dispersionsmittel" as dispersion means instead of dispersing medium or dispersing phase. *Wilder D. Bancroft*

The Metallography and Heat Treatment of Iron and Steel. *By Albert Sauveur. Second edition. 27 × 19 cm; pp. xvi + 486. Cambridge: Sauveur and Boylston, 1916. Price: $6.00 net.*—The first edition of this book has been reviewed (17, 275). "Nearly every chapter has been revised, while some fifty pages of new text has been added and nearly one hundred new illustrations used. With the exception of the last sixty-four pages, the book has been entirely reset."

The division is into chapters and the paging is consecutive. As a book, therefore, the appearance is much better than the first edition.

The phase rule treatment is relegated to the end of the book, as in the first edition, where it is useless. Several errors in the first edition have not been corrected. Page 304—complete reversibility is assumed in heating and cooling steel. This is not true. In discussing the hardening of steel, the author leans to the view that β iron is the most important factor. As a matter of fact α iron may be hardened by cold working. In several places solidification point is found where solidification range should be. The equilibrium diagram given according to Upton, is unfortunately the one published in 1908. Several have been published since then. A dearth of references to the original literature is noted.

The book, however, is an improvement on the first edition.

C. W. Bennett

An Introduction to the Principals of Physical Chemistry. *By Edward W. Washburn. 21 × 15 cm; pp. xxv + 445. New York: McGraw-Hill Book Company, Inc., 1915. Price: $3.50.*—In the preface the author says: "The method of presentation adopted presupposes on the part of the student a collegiate training in general or elementary chemistry and in general physics, and a training in mathematics which includes the elements of differential and integral calculus. The author is aware that in many elementary text-books of Physical Chemistry it is customary to avoid the use of the calculus as far as possible, frequently even with the sacrifice of accuracy and at the risk of conveying erroneous impressions concerning some of the most fundamental relationships; and in those cases where the use of the calculus seems to be unavoidable some authors have felt it incumbent upon themselves to assume a somewhat apologetic attitude and to explain that the student must take on faith 'these few derivations' but that he should not allow this fact to worry him, since with the aid of the accompanying explanations and illustrations he will still be able to understand the relationships and to apply them, even though he is not in a position to appreciate clearly what is involved in their derivation. With this dilettant attitude the writer finds himself entirely out of sympathy, and the literature of chemistry unfortunately abounds in illustrations of the dangers of inculcating such an attitude in the minds of the student. In the following pages the calculus has been freely employed, and while pains have been taken to explain, illustrate and emphasize the significance and physical meaning of the derived relationships, the student who is unfamiliar with the calculus will probably realize that his grasp of the subject must in many particulars be very inadequate and if he hopes to employ the laws and principles of Physical Chemistry in an intelligent and confident manner he is strongly advised to acquire the elements of the calculus before attempting to secure any special training in Physical Chemistry."

The author is tremendously in earnest as is shown by the announcement in the circular of information of the Department of Chemistry of the University of Illinois that the main emphasis of the chief course in physical chemistry is the application of mathematics and physics to chemistry. To this end a major part of the time is spent in the solution of mathematical problems embodying the principles of theoretical chemistry.

The reviewer's sympathy is entirely with the slipshod teachers who crowd as much chemistry as possible into their courses and who cut down the mathematics to the irreducible minimum perhaps even omitting it altogether. It is clear, however, that there are many very worthy people who look at things differently. One of the very good things about the development of physical chemistry in America is that nearly every laboratory has worked out a special brand of its own. In Germany the laboratories of physical chemistry are practically all of one pattern and differ only in the particular problems which are being studied. In this country each one of us has his own point of view which often differs surprisingly from that of anybody else. This diversity of point of view has the disadvantage of keeping people from getting together as much as is desirable; but it has the overwhelming advantage that progress is being made in at least one place and perhaps in more.

It may very well be, therefore, that Mr. Washburn's book is exactly what is needed in some places. The subject matter is surprisingly elementary and the treatment is conspicuously mathematical. Whether an elaborate use of the calculus really connotes great accuracy is a point that each man must decide for himself. The reviewer has always believed that mathematics was a tool and that no amount of mathematics would bring one out right if one's premises were wrong. It is quite certain that nobody would learn the limitations and assumptions involved in the van't Hoff-Raoult equation from anything in Mr. Washburn's book, although these were brought out quite clearly in van't Hoff's original paper. On p. 112 the author gives a thermodynamic proof that the vapor pressures of liquid water and of ice are equal at the freezing point. The difficulty with this is that Wald has pointed out that the two are equal only in case we make the ridiculous assumption that water does not wet ice. The author's proof is invalid anyway because he has forgotten about gravity. From the standpoint of chemistry it is unfortunate to take up reaction velocity before chemical equilibrium, though the other course may appeal to the mathematical mind.

While the reviewer is probably not alone in disliking the author's point of view, it is always well to have these things tried out and the book will unquestionably be serviceable to many people as a reference book.

Wilder D. Bancroft

Catalysis and Its Industrial Applications. *By E. Jobling. 19 × 13 cm; pp. viii + 120. Philadelphia: P. Blakiston's Son and Company, 1916. Price: $1.00.*—The subject matter of this book appeared originally in *The Chemical World.* Owing to the war the articles have not been revised and the subject matter, therefore, appears practically in its original form. The headings of the chapters are: introduction; sulphuric acid manufacture; industrial chlorine, salt-cake and sulphur recovery; fixation of atmospheric nitrogen; surface action; hydrogenation; dehydrogenation and oxidation; dehydration, hydrolysis, etc.

When one considers the limited space at the author's disposal, it is quite surprising how much he has given and how well he has done it. The reviewer confesses to having taken up the book with fear and misgivings. It gives him great pleasure to recommend this book as an admirable one of its type.

Wilder D. Bancroft

An Introduction to the Physics and Chemistry of Colloids. *By Emil Hatschek. Second edition. 19 × 13 cm; pp. ix + 107. Philadelphia: P. Blakiston's Son and Co., 1916. Price: $1.00.*—The first edition was reviewed less than three years ago (17, 711), which speaks well for the popularity of the book. In the preface the author says: "Apart from small corrections the only substantial addition to the text of the first edition consists in an appendix on experimental technique. In view of the unfamiliar nature of so many of the procedures and devices employed in the investigation of colloids, and in the absence of any work devoted to colloidal laboratory practice even the brief directions given may be of assistance to the student."

In the appendix the author discusses the Tyndall effect, the ultra-microscope, cataphoresis, ultra-filtration, and precipitation by salts. He also points out that the adsorption of oxalic acid by charcoal makes a good experiment, because the analysis is easy and the data give a good parabola. *Wilder D. Bancroft*

Handbuch der Mineralchemie. *By C. Doelter. Vol. II, Part IX. 25 × 18 cm; pp. 160. Dresden: Theodor Steinkopff, 1915. Price: 6.50 marks.*—The numbers continue to appear with praiseworthy promptness in spite of the war. The potash feldspars are the important things in this number, nearly one hundred pages being devoted to analysis, to formation by the wet way, and to technical utilization. Next in importance are the beryllium aluminum silicates and the magnesium aluminum silicates. *Wilder D. Bancroft*

The Manufacture of Paint. *By J. Cruickshank Smith. Second revised edition. 22 × 15 cm; pp. xiv + 271. London: Scott, Greenwood and Son, 1915. Price: 10 shillings, six pence, net. (New York: D. Van Nostrand Company. Price: $3.50 net.)*—In the previous review (20, 267) the name of the American agent was not given.

Bibliography: Concentrating Ores by Flotation. *By Jesse Cunningham. 23 × 16 cm; pp. 106. Rolla: University of Missouri, 1916.*—This is a bulletin on ore flotation issued by the School of Mines and Metallurgy. "This list has been prepared primarily for the use of the Mining Experiment Station and students of the School of Mines and Metallurgy engaged in experimentation at the flotation laboratory of this institution, and is based on the collection of material now in the laboratory of the school. It is hoped, however, that the list will serve as a guide, at least in America, to the study of the subject. Emphasis has been placed on no particular feature of the process, the intent being to include all important material coming under the observation of the compiler. Articles containing mere mention of the name of a process or the name of a company using a process are not included." This is a most useful piece of work and the pamphlet will be of great assistance to those interested in flotation.

Wilder D. Bancroft

THE CAUSE AND NATURE OF SOIL ACIDITY WITH SPECIAL REGARD TO COLLOIDS AND ADSORPTION[1]

BY E. TRUOG

Soil acidity is prevalent over the greater portion of the humid region of the United States. For general farming this acid condition of the soil is unfavorable to the highest productivity, and the use of ground limestone and burned lime to neutralize the acidity usually gives profitable returns. The great practical importance of recognizing soil acidity is thus easily understood. Unfortunately the cause and nature of soil acidity are not so easily understood. At present there is perhaps no other subject of soils about which there are so many conflicting ideas, opinions and theories. The conclusions given in this article are the results of a review of a large amount of literature coupled with a considerable amount of laboratory research. No pretense is made at giving a complete reference to the literature as that would require too large an amount of space. However, it is believed that the selection of references and data is impartial and that the different theories are justly dealt with.

Historical

Until quite recently soil acidity has usually been ascribed to the presence of organic acids which arise from the decomposition of organic matter. The term humic acids has been used to designate complex, acid reacting, organic compounds that are obtained from soils by extraction with alkaline solutions.[2] Schreiner and Shorey[3] have found that the material obtained by this extraction consists of a mixture of

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[1] Published with the permission of the Director of the Wis. Expt. Sta.

[2] For detailed references regarding humic acids see the following: Harris: Jour. Phys. Chem., 18, 355 (1914); and Tech. Bull. 19, Mich. Agr. Expt. Sta.; Gully: Inter. Mitt. fur Bodk., 5, 231 (1915); Baumann: Mitt. K. B. Moorkulturanstalt, 3, 52 (1909); and Frear: Bull. 261, Pa. Dept. Agr.

[3] U. S. Dept. Agr., Bur. Soils, Bull. 74, 14 (1910).

several complex organic acids and other substances. The existence of acidity in soils containing considerable organic matter could thus be easily attributed to organic acids. In recent years the prevalence of acidity in soils almost devoid of organic matter has been recognized and since the cause in these cases could hardly be attributed to organic acids two theories have been advanced to explain this acidity, *viz.*, The Adsorption Theory and The Mineral Acid Theory. As indicated in some of the following references several investigators have also attributed the acid reaction of the so-called humic acids to adsorption. The adsorption theory received its great impetus through the work of J. M. Van Bemmelen, who after extensive investigations on adsorption by soils summarized as follows:

"Adsorption[1] compounds are formed according to inconstant molecular ratios of the components. They must be distinguished from chemical compounds, although they may often be rearranged into such compounds. Colloidal substances form such adsorption compounds with water or other liquids and with bases, acids and salts when in contact with solutions of these. The adsorptive capacity of a colloid is dependent upon its molecular state of aggregation and also varies for different adsorbed substances. The adsorptive power decreases as the amount adsorbed by the colloid increases. The relation between the concentration in the colloid and the concentration in the solution at equilibrium is a complex (still unknown) function of these concentrations and the temperature. The adsorbed substances can be displaced by other substances in solution (substituted); *bases are thus displaced in equivalent ratios by other bases of salt solutions.* Colloids can often, through their adsorptive power, cause chemical decomposition of salts.

"The soil contains colloids: colloidal silicates, iron oxide, silicic acid and humus substances, all of which can bring about

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[1] Landw. Vers. Sta., **35**, 136 (1888). See also Ibid., **21**, 135 (1877); **23**, 265 (1878); **37**, 347 (1890); Zeit. anorg. Chem., **23**, 321 (1900); **42**, 265 (1904); **66**, 322 (1910); also "Die Absorption."

the aforesaid reactions. The adsorption phenomena produced when soils are treated with solutions are mostly due to colloidal silicates, whose adsorption capacity for whole salts is extremely small."

The views of Van Bemmelen, as indicated by his later writings, remained practically as given in the summary after 20 years of further study and investigation. The recent development of colloid chemistry has greatly emphasized adsorptive phenomena which in turn have been confused in a way to offer an explanation of soil acidity.

F. K. Cameron,[1] formerly of the U. S. Bureau of Soils, was one of the first to attribute acid reactions of soils to adsorption. He states that the popular belief that most soils are acid is unwarranted, and that this popular fallacy has its origin in the fact that most soils when moistened and pressed against blue litmus paper, redden it. In support of his view he states that various adsorbents such as absorbent cotton (washed in order to be acid free) redden blue litmus paper when the paper is pressed between wads of the moistened cotton. He also states that acid soils undoubtedly do exist, but they are by no means common or widespread, and are to be regarded as exceptional and abnormal.[2]

J. E. Harris[3] after investigating some acid sandy loam soils of Michigan came to the conclusion that the acid reaction is due to selective adsorption and not to the existence of acids in the soils.

E. G. Parker[4] states that soils have the power of adsorbing the cation at a greater rate than the anion. This would account for the acid reaction of soils.

G. Daikuhara[5] after an extensive and excellent investigation of acid soils of Japan states that the acidity is due not

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[1] U. S. Dept. Agr., Bur. Soils, Bull. 30, 60 (1905); also "The Soil Solution," p. 65.

[2] "The Soil Solution," p. 66.

[3] Mich. Agr. Expt. Sta., Tech. Bull. 19; also Jour. Phys. Chem., 18, 355 (1914).

[4] Jour. Ind. Eng. Chem., 6, 831 (1914).

[5] Bull. Imp. Cent. Agr. Expt. Sta., Japan, 2, 1 (1914).

only to humic acids but also to colloidal adsorption compounds of iron and aluminum. On treatment with salt solutions the iron and aluminum are replaced and go into solution as salts which because of hydrolysis give the well-known, marked, acid reaction.

O. Loew,[1] after investigating acid soils of Porto Rico, concluded that the acidity of some is due to an acid clay, which he called argillic acid.

R. Gans,[2] in an extensive and excellent treatment of the HCl soluble silicates of the soil, indicates that acid alumino-silicates arise through weathering and give an acid reaction to the soil.

E. Gully[3] in a recent article on humic acids defends the previous contention of Baumann and Gully[4] that the acid reaction of peat moss and peat soils is due to the colloidal matter of the coverings of the hyalin sphagnum cells.

In reporting on an extensive investigation Tacke and Süchting[5] state that the acidity of humic acids can only be explained on the basis of true acids. The views of Baumann and Gully are vigorously attacked.

C. G. Hopkins[6] states that soil acidity is usually due at least in part to organic acids, but that many soils exist in which the organic matter content is low and the acidity high, in which case acid silicates probably account for most of the acidity.

Wiegner[7] observed that the exchange of bases between soil silicates and neutral salts conforms closely with the law or formula of adsorption and hence concluded it to be a case of adsorption.

In a former publication[8] the writer expressed the opinion that soil acidity is caused by true acids and not adsorption.

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[1] Porto Rico Agr. Expt. Sta., Bull. 13 (1913).

[2] Int. Mitteil f. Bodk., 3, 529 (1913).

[3] Ibid., 5, 232 (1915).

[4] Mitteil. I. K. B. Moorkult., 3, 31 (1910).

[5] Landw. Jahrb., 41, 717 (1911).

[6] "Soil Fertility and Permanent Agriculture," 176.

[7] Jour. f. Landw., 60, 111 (1912).

[8] Science, 42, 505 (1915).

Adsorption[1] as a Cause of Soil Acidity

Definition of Terms.—The terms adsorption and absorption have been used rather loosely and often interchangeably by various writers. This has resulted in considerable confusion and lack of clear thinking.

Adsorption.—The leading investigators regard adsorption as a change in concentration of a substance at the interfacial boundary of two phases, *e. g.*, when a solution of acetic acid in water is shaken with powdered charcoal there results a higher concentration of acid at the interfacial boundaries or surfaces of the particles of charcoal than in other parts of the solution. Various salts and substances in solution are adsorbed in a similar way. As indicated by the definition the adsorption may be negative as well as positive. The amount of adsorption depends upon the nature of the adsorbent, the solute, the solvent and upon the concentration of solute in solvent.[2] Adsorption is usually recognized with finely divided material which, because of its great surface, shows measurable amounts of adsorption. Soil material presents an enormous surface and hence should exhibit an appreciable adsorptive phenomenon. Porous substances like charcoal have a large internal surface which greatly increases adsorption. In the adsorption of common salt and most other substances, the molecules as a whole are adsorbed and may be again removed as such by simple washing. The maximum adsorption has absolutely no relation to chemical equivalence between adsorbent and adsorbed substance and hence adsorption is to be regarded as a physical phenomenon.

Absorption.—The solution of a gas like oxygen in water is a case of absorption. In absorption there takes place a complete intermingling of molecules resulting in a homogeneous mixture of the absorbent and absorbed substance. Here again there is no evidence of chemical equivalence even at

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[1] For detailed references on adsorption by soils see Bull. 52 (1908), Bur. Soils, U. S. Dept. Agr., and Bull. 312 (1907), U. S. Geo. Sur., and Science, 42, 505 (1915).

[2] For details see H. Freundlich: "Kapillarchemie," 153.

maximum absorption between the two substances. Absorption is really identical with solution.

If the particles of an adsorbing medium are made sufficiently small or sufficiently porous as may be the case with gels, then the conditions approach those of absorption, and the nearer this is approached, the more difficult will it be to distinguish between absorption and adsorption. Because of this difficulty, Van Bemmelen[1] used the term absorption to cover both adsorption and absorption. However, the present-day use of the terms by most of the leading investigators will undoubtedly establish the classification in which adsorption refers to surface concentration and absorption to true solution. As will be indicated later, apparently part of Van Bemmelen's difficulty arose from the use of the term absorption compounds for gels which consist of mixtures of two or more chemical compounds.

Selective Adsorption.—The expression selective adsorption is often used in speaking of adsorption by soils and should have reference to the adsorption of certain salts or substances in preference to, or in larger amounts than others. Selective adsorption of the basic or acidic part of salts may conveniently be designated as selective ion adsorption. Selective ion adsorption from the common, simple, stable, neutral salts has never been demonstrated conclusively. The taking up by certain substances from neutral solutions of these common salts, of the anions in preference to the cations or *vice versa,* resulting in an acid or alkaline solution is probably not a case of selective ion adsorption as often stated, but is due to chemical reactions as will be indicated more clearly in what follows. The acid reaction of soils is held by some to be due to this selective ion adsorption.

Cotton as a Selective Ion Adsorbent.—Cameron[2] likens the reddening of blue litmus paper and the removal from salt solutions of cations in excess over anions by acid soils, to

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[1] "Die Absorption," 410.

[2] U. S. Dept. Agr., Bur. Soils, Bull. 30, 60 (1905); also "The Soil Solution," 65.

similar phenomena which he found were exhibited by absorbent cotton. He states that the absorbent cotton was washed with distilled water and hence the phenomena could not be due to acids in the cotton. From this he argues that the so-called soil acidity is usually not due to acids but to selective adsorption. At first sight this explanation appears very attractive and tempting, but a careful study of the composition of the cotton fiber reveals a fallacy.

Each mature cotton fiber represents an elongated single cell, and as such one would expect it to consist of a considerable variety of substances. Schunk[1] found that raw cotton consists, besides cellulose, of 13 percent or more of other ingredients as follows: water, waxes, a fatty acid, coloring matter, a peptic acid and a trace of albuminous matter. O'Neil[2] states that the fatty acid is identical to margaric acid by analysis.

In experimenting with various samples of raw and absorbent cotton[2] the writer found that raw cotton reddens blue litmus and removes the cation from salt solutions to a much greater extent than the absorbent cotton. The acid reaction of the raw cotton is not at all surprising when one recognizes the presence of the true acids, and there is little cause for propounding new theories to explain it. That the acid reaction of the absorbent cotton is also due to true acids may be gleaned from the following: In the preparation of absorbent cotton from raw cotton, the material is first treated with an alkaline solution and then with a dilute acid solution. That an insoluble fatty acid would not be completely removed in this process seems almost certain. The treatment, first, with an alkali changes the fatty acid over to a salt, which even if completely soluble will probably not be entirely removed, especially from the interior of the fibers, by the washing that the cotton is given. The subsequent washing with dilute sulphuric acid removes at least part of the cation from the

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[1] U. S. Dept. Agr., Off. Expt. Sta., Bull. 33, 91.

[2] Samples of raw cotton were kindly furnished by M. S. Baker of Ark. Agr. Expt. Sta., and M. J. Funchess of Ala. Agr. Expt. Sta.

fatty acid salt, leaving the insoluble fatty acid which produces the acid reactions already noted. The precaution of thoroughly washing the absorbent cotton with water to free it of all acids appears quite futile, when it is realized that fatty acids which are insoluble in water probably exist through the whole body of the fibers.

Cameron and Bell[1] describe a further experiment with absorbent cotton which is apparently designed to give strong proof of their theory. The experiment is described as follows:

"Two wads of this same cotton were placed in beakers, one containing a solution of potassium chloride neutral to litmus, and the other containing potassium acetate with a slight but sufficient excess of acetic acid to redden litmus. Within a few minutes the supernatant liquor in the beaker containing potassium chloride had become distinctly acid, as shown by the further addition of litmus, while the supernatant solution in the beaker containing the acetate had become distinctly alkaline to both litmus and phenolphthalein."

Since, according to this experiment, the cation is adsorbed from the potassium chloride and the anion from the potassium acetate, it is apparently argued that the phenomena are due to selective adsorption of ions and not to acids or bases in the cotton.

The writer has repeated experiments similar to those of Cameron and Bell using absorbent cotton from several sources. *In repeated trials the results of these investigators were confirmed when potassium chloride was used but not when potassium acetate was used.* In the latter case the reaction was the same as with potassium chloride only less pronounced, due to the fact that litmus is much less sensitive to acetic acid than to hydrochloric acid. In fact, when two 1 g samples of cotton were each placed in an Erlenmeyer flask, treated with 100 cc of normal potassium chloride and potassium acetate solutions, respectively, the flasks were shaken occasionally over a 24-hour period, and the solutions were filtered and titrated with $N/25$ NaOH using phenolphthalein as indicator; it

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[1] U. S. Dept. Agr., Bur. Soils, Bull. 30, 59 (1905).

was found that the acetate solution had become more acid than the chloride solution.

When the cotton was extracted with pure water for 24 hours there was no indication of acidity in the extract. When neutral alcohol or ether was used in place of water, then the extract became distinctly acid. This is to be expected since fatty acids like margaric acid are considerably more soluble in these than in water, being practically insoluble in the latter. If the cotton is treated with a salt solution there results a reaction between the salt and insoluble fatty acid until equilibrium is established, in which part of the cation is removed from the salt and an equivalent amount of soluble acid is set free.

Charcoal as a Selective Ion Adsorbent.—Charcoal has been used quite frequently by investigators[1] in their efforts to demonstrate selective adsorption of ions from neutral salts. It is important to note that there is reported in some cases selective adsorption of the cation, in others selective adsorption of the anion and in still others the ions are adsorbed equally.

Parker[2] states that when a silver nitrate solution is shaken with animal charcoal, the filtrate therefrom reacts distinctly acid to litmus or methyl orange. As is well known silver nitrate decomposes rapidly when in contact with even small amounts of organic matter, and it is not at all surprising that animal charcoal, which usually contains 5 to 10 percent of impurities, should bring about this decomposition. Animal charcoal contains both acids and bases and is usually purified with an acid, after which it is almost certain to contain an excess of acids over bases which may give rise to acid solutions. This same investigator also reports that when potassium chloride or nitrate solutions are shaken with cane sugar charcoal, the liquid therefrom reacts strongly alkaline to phenolphthalein. To explain these phenomena on the basis of selective adsorption, as Parker does, causes great difficulty in

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[1] For references see U. S. Dept. Agr., Bur. Soils, Bull. 52, 27, 32 (1908). Also Freundlich: "Kapillarchemie," 168.

[2] Jour. Ind. Eng. Chem., 6, 831 (1914).

arriving at a clear understanding. Why animal charcoal should adsorb the basic ion and sugar charcoal the acid ion is certainly difficult to explain on the basis of any selective adsorption theory. The writer found on burning a sample of sugar in a platinum dish that the residue when taken up with water gave a solution alkaline to phenolphthalein. Since lime is used in the purification of sugar, this result is easily explained as due to the presence of small amounts of lime in the sugar. Charcoal produced from such sugar would also contain lime which could easily cause the alkaline reaction noted by Parker.

In order to prove the existence of selective adsorption of ions, it is necessary to use stable, neutral salts and adsorbents which are absolutely neutral and free from substances that may induce or take part in chemical reactions with the salts in question. Of all the experiments reported on the selective adsorption of ions from the common, stable, neutral salts, the writer has been unable to find any in which the selective adsorption reported could not be attributed to chemical reactions with impurities in the adsorbent. The extent of the selective ion adsorption reported is always very small and comparable to what would be expected, if due to reactions with impurities in the absorbent. The use of silk and wool has probably the same objections as cotton and charcoal. Numerous reports on the selective adsorption of the basic or acidic part of various complicated dyes are to be found, but whether or not these are true cases of selective adsorption or are due to chemical reactions matters little as regards the point under discussion. To show by a controlled experiment that soils selectively adsorb the one or the other ion from solutions of the common stable salts like potassium and sodium chloride or nitrate, etc., requires that in the experiment these same salts be actually used, and that the amount of the adsorption be at least approachingly comparable to the phenomena exhibited by soils. The so-called selective adsorption of ions by cotton, charcoal, etc., is only several percent of the phenomenon exhibited by soils, and hence were it granted that cotton, charcoal, etc., actually do selectively adsorb the ions from the common stable salts (the facts point to the opposite), the adherents of the selective adsorption theory, in order to prove their point, would still have to demonstrate why soils should exhibit this property to such a vastly greater extent.

Colloids as Selective Ion Adsorbents.—The term colloid is defined by Bancroft[1] as "a phase sufficiently divided." According to this definition finely powdered charcoal, and in fact any substance sufficiently divided and thus exposing a large surface, is to be regarded as a colloid. There is, however, a wide range in the degree of division in passing from the coarse colloidal suspensions in which the particles are discernable with the naked eye, *e. g.*, suspensions of clay, to the colloidal solutions which appear entirely homogeneous to the naked eye but not to the ultramicroscope, *e. g.*, solutions of glue and hydrosols of arsenious sulphide. The extent of surface of colloidal solutions and of gels therefrom, which have an enormous internal surface, must be much greater than that of colloidal suspensions. The surface exposed by charcoal, cotton, silk and wool is probably roughly comparable to that exposed by suspensions of the coarse and medium clay. Besides the extremely fine particles of clay in soils there are probably also some colloidal solutions and gels. The entire range of colloids as regards size of particles and extent of surface exposed is thus probably represented in soils. The relation of colloidal suspensions to soil acidity is covered by the discussion on the selective adsorption of ions by cotton and charcoal. The bearing of colloidal solutions and gels on soil acidity will now be taken up.

J. E. Harris[2] has published several papers in which the bold contention is strongly made that soil acidity is due to selective adsorption by colloids. Harris[3] states that he has

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[1] Jour. Phys. Chem., 18, 549 (1914).

[2] Ibid., 18, 355 (1914); Mich. Agr. Expt. Sta., Tech. Bull. 19; Science, 40, 491 (1914).

[3] Science, 40, 492 (1914).

thoroughly investigated the acidity of the sandy upland type of soils. The experiments of various investigators on the adsorption of the cation on precipitation of colloidal arsenious sulphide solutions are cited by Harris in support of his views. It will thus be well to consider these experiments first.

Picton and Linder[1] in extensive investigations on colloidal solutions found that, when colloidal solutions of arsenious sulphide were coagulated and precipitated by the addition of barium chloride, a small part of the barium was taken up and held by the precipitate, in such a way that it could not be washed out with water but could be displaced by another base. When colloidal solutions of ferric hydroxide were coagulated with salts a small amount of the acid part of the salt was taken up.[2] In general, acidic colloids like arsenious sulphide take up the cations and basic colloids like ferric hydroxide take up the anions. Since this paper deals with soil acidity the discussion may well be limited to colloids that remove bases and since colloidal solutions of arsenious sulphide have been by far the most completely investigated and are usually cited, the discussion may further be limited to these. The important question may now be asked: Why do colloidal solutions of arsenious sulphide take up cations on being precipitated by salts? The publications of Harris and various other writers would lead one to believe that the prominent investigators of the subject considered it a case of adsorption. A review of the writings of these investigators, however, shows that they considered it due to chemical reactions as indicated by the following:

Picton and Linder[3] state that when a metallic salt is added to an arsenious sulphide solution, an interchange takes place between metal of salt and hydrogen of hydrosulphide. The sulphide is regarded as a hydrosulphide and the reaction is indicated by them as follows:

$$M.As_2S_3 \cdot H_2S + BaCl_2 \rightleftarrows M.As_2S_3 \cdot BaS + 2HCl$$

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[1] Jour. Chem. Soc., 67, 63 (1895).

[2] Ibid., 87, 1906 (1905).

[3] Ibid., 87, 1914 (1905).

They further state that the chemical reaction which ensues as just indicated must be considered as an incidental rather than a controlling factor in the coagulation, since acids, in which case no base can be taken up, will coagulate in the same way as salts. Because of their extensive and apparently very painstaking investigations the views of Picton and Linder just stated must be given considerable weight.

Whitney and Ober[1] found that, when colloidal solutions of arsenious sulphide were precipitated with barium, calcium, strontium and potassium salts, equivalent amounts of the different cations were taken up by the colloid. This is a characteristic feature of chemical reactions which serves to distinguish them from physical phenomena like adsorption. The composition of the precipitated colloid was also found to be independent of both its own concentration in the solution and that of the barium ions when barium chloride was used as the coagulant. This is characteristic of chemical reactions in which a practically insoluble precipitate is formed allowing the reaction to go to completion. The evidence of these investigators as concerns the point under question seems rather conclusive.

Duclaux[2] reports that when a colloidal solution of arsenious sulphide was precipitated by the addition of barium chloride there appeared in solution a quantity of arsenic corresponding closely to the chlorine in solution and the barium taken up. He believed that the colloidal arsenious sulphide contained some arsenious oxide, the arsenic of which exchanged places with the barium of barium chloride. On the basis of Duclaux's contention, the acidity of the resulting solution as reported by Whitney and Ober[3] may be explained by the hydrolysis of the $AsCl_3$ which is formed. Like Picton and Linder, Duclaux believed the taking up of the base to be due to a chemical reaction.

The phenomenon of adsorption previously defined is

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[1] Jour. Am. Chem. Soc., 23, 842 (1901).

[2] Jour. Chim. phys., 6, 592 (1908).

[3] Jour. Am. Chem. Soc., 23, 842 (1901).

reversible and exhibits no relation to chemical equivalence between adsorbent and absorbed substance even at maximum adsorption. This is just opposite to the phenomenon of the removal of cations by colloidal arsenious sulphide solutions on being coagulated by salts. This removal of cations is undoubtedly due to chemical reactions between the salt used and certain minor constituents of the hydrosulphide, and has nothing to do with the coagulation and precipitation of the colloid. Its magnitude is of the same order as the so-called selective ion adsorption of cotton and charcoal already referred to. Were it granted (there is not one reason for doing it) that colloids like arsenious sulphide adsorb cations, and that soil acidity is due to a similar phenomenon, it would still have to be explained why equal weights of soil colloids exhibit an adsorption, 25 to 100 times as great as that of colloidal arsenious sulphide as is indicated by the following:

1 g As_2S_3 took up 0.0060 g Ba — Picton and Linder[1]
1 g As_2S_3 took up 0.0062 g Ba — Whitney and Ober[2]

Av. = 0.0061

The 0.0061 g barium is equivalent to 0.00445 g of calcium carbonate. On this basis if a soil contained 10 percent of colloids and these had an average so-called adsorbing capacity for bases equal to that of colloidal arsenious sulphide, there would be accounted for, an acidity equivalent to 890 lbs. of calcium carbonate per acre, assuming 2,000,000 lbs. to be the weight of the cultivated layer over an acre. Soils that will take up an equivalent of 50,000 lbs. of calcium carbonate per acre are common and some take up much more. It appears conclusive that the colloid adsorption theory is entirely inadequate to explain soil acidity.

Because of the wide publicity and frequent acceptance given to the views of Harris, it is desirable and important to discuss these views in detail. The reader is referred to Mich. Agr. Expt. Sta., Tech. Bull. 19. On page 6, Harris states:

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[1] Jour. Chem. Soc., 67, 63 (1895).

[2] Jour. Am. Chem. Soc., 23, 842 (1901).

"Also in the action of the soil toward salt solutions, we may assume that the soil adsorbs the base in the same way that the arsenic trisulphide adsorbs the barium in Linder and Picton's experiment."

On page 8, Harris shows with a table of results that, when an acid soil is treated with various salt solutions, various amounts of free acid are liberated depending on the kind of salt used. His results also show that the reaction between soil and salt is one of equilibrium. These results as regards equilibria relations are in direct contradiction to the deportment of colloidal arsenious sulphide and hence rule out his contention that the acid soil acts like the colloid. In the removal of bases the soil acts like the colloid in that a chemical reaction probably intervenes in both cases. With the arsenious sulphide, a very insoluble precipitate is formed and hence equilibria relations are not pronounced. In discussing the results in this table, Harris states that if the acid set free is due to insoluble soil acids, then the amount should approach the same limit in each case. This indicates that he ignores secondary reactions, which as will be shown later play an important part and account for this discrepancy.

On page 7, Harris states that Linder and Picton have shown that the coagulation of a negatively charged colloid by a salt is accompanied by the adsorption of the negatively charged ion. As is well known this is not true, for the positively charged ion is removed from the salt in this case.

On pages 12 and 13, Harris describes an experiment which is evidently designed to give strong proof to his theory. He finds that the barium which an acid soil takes up from a barium chloride solution may again be almost completely recovered by treatment with hydrochloric acid. Harris states that if it is assumed that the soil acidity is due to insoluble acids the reaction of barium chloride with the insoluble humic acids (H_2A) may be represented as follows:[1]

$$H_2A + BaCl_2 \rightleftarrows BaA + 2HCl$$

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[1] Representation of humic acids by H_2A instead of HA as represented by Harris, seems preferable.

and the recovery of the barium by hydrochloric acid as follows:

$$BaA + 2HCl \rightleftarrows BaCl_2 + H_2A$$

Harris states that for the first reaction to go as far to completion as it really does means that the salts of the humic acids must be either far more insoluble or far less dissociated than is the humic acid, but to account for the second reaction going so near completion just the opposite must be true as to solubility and dissociation and hence the acidity cannot be due to an insoluble acid but is due to selective adsorption. Harris, apparently, forgets that in the first reaction an overwhelming mass of barium chloride was used and the reaction forced as a consequence to the right. In the second reaction the excess of barium chloride had previously been removed and now a large excess of hydrochloric acid is added and to be sure the reaction is reversed and forced to the right. The water solution also helps to force the reaction to the right. The results are entirely in accord with the law of mass action and serve as evidence in favor of the existence of true acids as the cause of soil acidity.

On page 14, Harris describes an experiment designed to show that the removal of cations from neutral salt solutions is not due to organic acids. The organic matter was destroyed by digestion with concentrated sulphuric acid, after which the soluble acid was washed out. He found that after this treatment the capacity of the soil for removing the cations from a potassium nitrate solution had been about doubled. He then concluded that the capacity of the untreated soil for removing bases cannot be due to organic acids at all. This is certainly a dangerous presumption. Is it not possible that the treatment of a complex mixture like a soil, containing many polybasic salts, with a strong acid, may, by the removal of bases, produce acid salts? The fact that the capacity of the soil for removing cations was increased, indicates that something of this kind took place, and it may be that the original capacity of the organic matter for taking up bases was more than offset by the production of acid salts. The writer agrees that the acidity in upland sandy soils is usually due largely to something else than organic acids but does not agree to Harris' method of proof.

Arguments have been presented in support of the contention that soil acidity is not due to selective adsorption of ions by colloids or finely divided material. If it is not due to these causes, but to true acids, then it should be possible to show that an acid soil will take up equivalent amounts of different bases. *The failure of investigators to realize this possibility has been the one strong argument for the selective ion adsorption theory, and against the existence of true acids as the cause of soil acidity. That this possibility may be realized is shown in what follows.*

True Acids as the Cause of Soil Acidity

In order to prove by experiment the existence of true acids as the cause of soil acidity, it is necessary to take cognizance of the probable solubility of the acids and neutralized products and adapt the methods accordingly. That most of the acids causing soil acidity in upland soils are quite insoluble may be gleaned from the following: Upland soils become acid primarily in humid regions. If the soil acids were soluble they would be leached out. As a matter of fact, usually, the more an acid upland mineral soil is leached with water the more acid does it become. In a consideration of soil acidity, soils should be divided into at least two classes, *viz.*, the well aerated and the poorly aerated. In the following two paragraphs a brief outline is given of the writer's view regarding the formation of acid soils:

Acidity of Well Aerated Soils.—The cultivated upland soils make up the major part of these soils. Thoroughly drained and cultivated lowland mineral soils and even very sandy virgin soils also belong here. These soils consist of from 75 percent to over 95 percent of silicates and silica. Silicates are polybasic salts of various silicic and alumino-silicic acids. The water solution in the soil slowly reacts by hydrolysis, carbonation and base exchange, with these silicates, forming with the bases of the silicates soluble hydroxides and salts, which are taken up by plants or removed in the drainage water. Iron and aluminum, however, being quite insoluble are not removed to any great extent. The other products besides SiO_2 are acid silicates, which, being comparatively insoluble, accumulate in the soil and gives rise to an acid condition. The writer and assistants have treated powdered basalt, granite, feldspar and other minerals with carbonated water, and after filtering have obtained residues which are acid to litmus and other tests. Daikuhara[1] has obtained similar results. This is essentially comparable to the weathering process going on in soils. Acid soils treated in this way are made more acid.

What has just been said applies to soils in the humid region. In arid regions very little of the products of weathering are removed and the accumulation of soluble salts gives rise to alkali soils.

Organic acids are usually of minor importance as regards the acidity existing in well aerated soils. Some of them are almost devoid of organic matter and yet are extremely acid. Others containing considerable organic matter appear to retain all or nearly all of their acidity when the organic matter is destroyed with hydrogen peroxide. Being well aerated any organic matter applied in the form of manure or crop residues decomposes comparatively rapidly and the carbon splits off to form carbon dioxide without ever forming complex and rather inert organic compounds and acids of the type often designated as humic acids. Organic acids may be formed but the amounts at any one time are small and are to be regarded as transitory substances. This rapid decomposition is very favorable to the weathering of the mineral matter and consequent production of acid mineral substances as already explained.

Acidity of Poorly Aerated Soils.—The poorly drained peat and muck soils make up the major portion of these soils. In these soils the organic matter from plant residues goes through a radically different and much slower process of decomposi-

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[1] Bull. Imp. Centr. Agr. Expt. Sta., Japan, 2, 1 (1914).

tion than is the case in well aerated soils. The carbon, in place of splitting off to form carbon dioxide, accumulates, and compounds of higher and higher carbon content are formed. Coal is the final product of this sort of decomposition. Substances designated as humic acids and having an acid reaction are early products of this decomposition. In virgin clay and silt soils covered with prairie grass or hardwood timber, the return of dead grass and leaves furnishes a covering which prevents rapid oxidation and hence complex organic acids may be accumulated, unless neutralized, giving rise to acid conditions. When this type of soil is brought under cultivation the acid condition due to organic acids gradually disappears, as the acids are oxidized, but in time a new acidity due to mineral acids may be developed.

Peat and muck soils which have once become acid through the accumulation of considerable amounts of organic acids may lose this acidity at least partly on being drained and aerated, due to the fact that these acids gradually decompose and may wash out partially in the drainage water.

In the case of soils naturally containing limestone and those receiving carbonates in the seepage and drainage water from the surrounding country, the acids are neutralized as formed, giving rise to neutral or alkaline prairie, timber, muck and peat soils.

The Determination of Soil Acidity with Different Hydrates.—In a previous publication[1] the writer has shown that the acidity in a soil may be conveniently divided into two kinds, *viz.*, active and latent. The active acidity combines almost instantly with bases that are added in solution. The latent acidity acts comparatively slowly, but in contact with bases and salts it gradually opens up and takes up more and more base up to a certain limit which is usually several times the active acidity. It is possible that this latent acidity may be due largely to a peculiar condition of kaolinite and allied compounds. Free quartz may also influence the amount of latent acidity. Methods for determining the active and latent

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[1] Jour. Ind. Eng. Chem., 8, 341 (1916).

acidity have been described.[1] In these methods soluble reagents are used in order that they may react with the insoluble acids. In Table I are given the results for active acidity when different hydrates were used.

TABLE I

Active Soil Acidity in Tons $CaCO_3$ per Acre on Using Hydrates Indicated

Kind of soil	No.	$Ba(OH)_2$	NaOH	$Ca(OH)_2$
Sand	1	3.8	3.5	3.7
Sandy loam	2	6.2	7.9	6.5
Silt loam	3	6.3	6.4	5.7
Silt loam	4	8.5	9.1	7.7
Peat	5	11.2	11.5	11.3
Peat	6	5.6	5.6	5.3

The data in this table show that nearly equivalent amounts of the different bases were used. The reason that the sodium hydroxide sometimes gives a slightly higher result than barium hydroxide and calcium hydroxide a slightly lower one, is undoubtedly due to side reactions, such as action on organic matter, latent acidity, and phosphates, which may be different for the different hydrates. If the determinations of the latent acidity are made as outlined,[1] the different hydroxides are again used in practically equivalent amounts showing that the reaction is a chemical one.

Experiments with Salt Solutions.—The treatment of an acid soil with a neutral salt solution results of course in the liberation of a certain amount of free acid. It may be argued by the adherents of the selective adsorption theory of soil acidity that if soil acidity is due to true acids, then acid soils should take up equivalent amounts of the different bases from salt solutions having a common acid ion, since the law in this regard reads: The relative affinity of the acids is independent of the nature of the base. *It must be carefully noted that this law only holds when all the reacting substances are in a*

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[1] Jour. Ind. Eng. Chem., 8, 341 (1916).

true solution, or if there are partially soluble substances formed, then in any series of comparisons, the solubility of the corresponding substances must be of the same order. The opportunity for secondary or side reactions must also be eliminated or made comparable. In the soil there is almost unlimited opportunity for these side reactions to occur. If the active soil acids are represented by H_2X and the soil is treated with potassium or calcium chloride solutions, the resulting reactions may be represented as follows:

$$H_2X + 2KCl \rightleftarrows 2HCl + K_2X$$
$$H_2X + CaCl_2 \rightleftarrows 2HCl + CaX$$

The point of equilibrium of either reaction will depend upon the following: concentration of reacting substances, temperature, nature of solvent, solubility of soil acids and resulting neutralized products in solution used, and nature and extent of side reactions. If these factors can be equalized then the acidity of the extract secured in the two cases should be the same. The concentrations and solvent are easily chosen the same. The solubility of the soil acids and neutralized products are perhaps negligible in both cases. The greatest difficulty comes with side reactions, *e. g.*, the rate of hydrolysis of the K_2X may be different than CaX, the action of liberated acids on soil substances may be different in different salt solutions, and the opening effect of the different salt solutions on the latent acidity may vary. By using comparatively small amounts of finely powdered soil with large volumes of salt solutions, and allowing a very short period of contact these side reactions are prevented and equalized to a large extent. With these precautions in mind the following experiment was carried out:

A volume of 800 cc of normal salt solutions was placed in 1000 cc Erlenmeyer flasks. Water free from carbon dioxide was used, and after adding 5 drops phenolphthalein, each salt solution was made slightly alkaline with the respective hydrates, taking great care to get exactly the same intensity of faint pink color in each case. The finely powdered soil was added, the flask stoppered and shaken vigorously for 2 minutes. The solution was quickly filtered on an 8-inch Büchner funnel taking about one minute. Five drops of phenolphthalein were added and then $N/25$ sodium hydroxide till the solutions had all again regained the same faint pink color. Of silt loam soil 4 g were used and of peat 2 g. Results are given in Table II.

TABLE II

Acidity of Salt Extracts of Acid Soils in Cubic Centimeters of $N/25$ NaOH

Kind of soil	Acidic part of salt	Kind of salt used			
		Basic part of salt			
		Sodium	Potassium	Barium	Calcium
Silt Loam soil	Chloride	1.2	1.4	1.4	2.0
	Acetate	5.6	6.4	6.5	6.5
Peat soil	Chloride	1.9	1.9	1.9	2.7
	Acetate	21.7	21.8	25.6	26.0

The results of Table II are certainly difficult to explain on the basis of any selective ion adsorption theory. Competition of acids for bases appears to be the only satisfactory explanation. Lessened opportunity for side reactions has made these favorable results possible. Entire elimination of side reactions as is possible only with soluble monobasic acids, bases and salts would undoubtedly make the results still more favorable. If the soil acidity is due to selective adsorption of cations, then the nature of the cation should have the major or at least strong influence on the amount of cation taken up; if due to true acids then the nature of the anion should have the major influence. The reader may easily draw his own conclusions from Table II.

If soil acidity is due to adsorption then the grinding of a soil to an impalpable powder would be expected to increase adsorption of cations from salts. However, by experiment, the writer observed a slight decrease. This decrease is undoubtedly due to hydrolysis of fresh mineral surfaces exposed by grinding which changes the point of equilibrium. Brown and Johnson[1] have noted a decrease in lime requirements due to grinding.[2] The writer has also observed that soils remove more cation from alcoholic solutions of potassium acetate than from water solutions. This is contrary to most adsorption phenomena and bespeaks the intervention of chemical reactions.

It is sometimes maintained that the equilibria relations which result on treating soils with salt solutions are identical with those of adsorption and hence the two phenomena are identical. In this respect it is to be noted that a great many chemical reactions proceed only to partial completion depending on the concentration and solubility of reacting substances and hence exhibit the same kind of equilibria phenomena as adsorption and give similar curves. In 1878, Armsby[3] pointed out that the equilibria relations which obtain when soils are treated with salt solutions could be clearly explained on the basis of the law of mass action and hence true chemical reactions are involved.

The question may well be asked: What is the nature of the mineral substances causing soil acidity? The large amount and variety of polysilicates in a soil furnishes ideal conditions for the formation of acid silicates. Often[4] the treatment of an acid mineral soil with a salt solution results in the exchange of an equivalent amount of iron and aluminum for the base which is taken up. The iron and aluminum go into solution as salts and since their hydroxides are neutral they enter into the titration as an equivalent amount of acid. The common soluble salts of iron and aluminum react strongly acid in water solution due to hydrolysis and their effect in the soil is much the same as an equivalent amount of acid and hence it is right

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[1] Jour. Ind. Eng. Chem., 7, 776 (1915).

[2] Lately, R. C. Cook has noted an increase in lime requirements of sandy soils due to grinding. This may be due to the increased acidic action of the finely ground quartz. See Soil Science, 1, 95 (1916).

[3] Landw. Vers. Sta., 21, 397 (1878). See also Robertson: J. Biol. Chem., 4, 38 (1908).

[4] Bull. Imp. Centr. Agr. Expt. Sta., Japan, 2, 1 (1914).

that the acidity determination should measure them as acid. The fact that equivalent amounts of iron and aluminum are displaced is further evidence of true chemical reactions and not selective ion adsorption. Parker evidently realized this as serious evidence against the selective ion adsorption theory. In an effort to show that the iron and aluminum come into solution not because they are displaced by the base of the salt solution, but because the liberated acid attacks iron and aluminum oxides and compounds, Parker[1] added a little free sodium hydroxide along with the salt to neutralize the free acid as formed and then found no iron and aluminum in solution. This, however, is absolutely no proof of the point, since a slight excess of sodium hydroxide will precipitate out the iron and aluminum no matter how they come into solution. The fact that this equivalent displacement is obtained with acetates indicates that it is true displacement, since it is improbable that the dilute acetic acid would dissolve iron and aluminum compounds to saturation. The knowledge of the particular silicates and acid silicates that cause soil acidity is still very incomplete, but as indicated in the following paragraphs at least some are known.

Kaolinite and Allied Compounds

In the weathering of silicates the alkali and alkaline bases go into solution and are partially leached away. The sodium and calcium are usually leached to a greater extent than the potassium and magnesium. Under good aeration nearly all of the iron goes over to ferric oxide. Part of the silicon and aluminum split off as oxides and remain in the soil although considerable silica may leach away if the soil solution is alkaline. A large portion of the silica and alumina usually split off in combination as acid silicates, *e. g.*, kaolinite. These acid silicates may combine in part with the bases that are liberated in weathering as just explained. They seem to have a decided preference for potassium and prevent its undue leaching. If insufficient alkali and alkaline bases are present then

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[1] Jour. Ind. Eng. Chem., 6, 831 (1914).

iron and aluminum may supply at least part of this base demand as is the case in acid soils. When treated with salt solutions of alkali and alkaline bases the iron and aluminum are displaced as already noted. In the formation of acid silicates of the type just referred to there is complete breaking down and rearrangement of the molecule. It is possible that mere removal of bases from the original silicates may give rise to acid silicates which cause soil acidity.

In samples of kaolinite tested by the writer it was found that some reacted decidedly acid, and others very nearly neutral. All became decidedly acid on being extracted with carbonated water. A ten gram sample of acid kaolinite was put into an Erlenmeyer flask with 100 cc of water and 5 drops of phenolphthalein. Calcium hydrate was added till a distinct pink color developed. On shaking and standing for some time the color entirely disappeared and more calcium hydroxide was needed to produce the pink color. This can be repeated and continued for weeks, the kaolinite gradually taking up more and more base. The addition of a neutral salt naturally increases the rate of this reaction. The use of alcohol as a solvent, in which case the hydrolysis of neutralized product is lessened, also increases the rate of the reaction.

This gradual taking up of bases by kaolinite is similar to a phenomenon exhibited by soils and termed by the writer as latent acidity. It may be due to rearrangement of the molecule, polymerization, or perhaps to the slowness of the reaction occasioned by the insolubility of one of the reacting substances. Asch and Asch[1] regard kaolinite as an acid and have advanced a theory regarding the polymerization and change of one form of kaolinic acid over to another form, which has considerably different physical and chemical properties.

The acid character of kaolinite is further supported by the work of Pukall[2] and Lemberg.[3] These two investigators have shown that kaolinite combines with potassium and

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[1] Asch and Asch: "The Silicates in Chemistry and Commerce," 114.

[2] Ber. deutsch. chem. Ges., 43, 2107 (1910).

[3] Zeit. deutsch. geo. Ges., 37, 960 (1885).

sodium according to definite chemical ratios. Gans[1] in an extensive treatment of the secondary silicates of the soil regards the exchange and taking up of bases by such silicates as chemical reactions. He states that the reaction of the soil is dependent upon the ratios of silica, alumina, and base present as previously stated. The existence of substances in soils that take up bases according to definite chemical ratios seems ample proof of the existence of true acid substances as the cause of soil acidity. Since the so-called adsorption compounds contain at maximum adsorption, a ratio of base to acid which bespeaks chemical equivalence, it must be concluded that this is a true chemical compound rather than an adsorption compound. However, before the maximum amount of base has been taken up there arises a complex or physical mixture of the unneutralized acid with the neutralized part. Whether or not this is to be called an adsorption compound, is largely a matter of definition. The use of the term adsorption compound is not conducive to clear thinking and hence it is better avoided.

The term colloid is being used very freely by many investigators of soils, and often, apparently, without a clear conception as to its meaning. Various properties having no existence in either pure chemistry or physics are ascribed to colloids in order that certain phenomena may be explained without going to the trouble of finding the real cause. The old idea that colloids form a separate world of matter is no longer in accordance with known facts, and investigators[2] now hold that matter or compounds may exist in two states, *viz.*, the crystalloidal and colloidal state. When a substance is changed from the crystalloidal to the colloidal state, the physical makeup changes but the chemical composition undergoes absolutely no change. The physical change causes a marked increase in surface and hence affects surface phenomena. As has been emphasized, the surface phenomenon of adsorp-

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[1] Int. Mitteil f. Bodk., 3, 529 (1913).

[2] P. P. von Weimarn: "Grundzüge der Dispersoidchemie;" Wo. Ostwald; "Grundriss der Kolloidchemie," 44.

tion of common salts deals with whole molecules and the existence of selective adsorption of ions from common salt solutions has never been proven. Common acids in the solid state may exist either as a crystalloid or colloid and the same may be said to be true of the soil acids which are acid not because they are in the colloidal state but because of their acid chemical nature.

Summary

In the adsorption of a substance the molecules as a whole are adsorbed or concentrated at surfaces. A certain substance may be adsorbed more than others, depending on the conditions, and this may be designated as selective adsorption. The existence of selective adsorption of ions from the common alkali and alkaline earth salts is questionable. The phenomenon observed with these salts and designated as selective adsorption of ions is small in extent and commensurate with chemical reactions that might be expected of impurities in the adsorbent. The phenomenon observed in acid soils and often designated as selective adsorption of ions is of an entirely higher order in extent, and comparable in every way to chemical reactions between acids, bases, etc. The failure of investigators to demonstrate that acid soils take up chemically equivalent amounts of different bases has been the one strong argument against the existence of true acids as the cause of soil acidity. This argument no longer holds, since it is shown in this paper that when the conditions are properly controlled, it can be demonstrated that the reactions due to soil acidity take place according to chemical equivalence and exhibit all the properties of true chemical reactions. The possibilities for the formation of true acid substances in soils of the humid region are manifold and it would be extremely difficult to explain why such substances should not be formed. In most upland soils mineral acids, *e. g.*, kaolinite, and other acid silicates are the main cause of soil acidity. Soils high in organic matter may contain considerable amounts of organic acids. These acid substances may be either in the crystalloidal or colloidal condition, and their acid reaction is due to their chemical nature and not colloidal condition.

In conclusion the writer wishes to state that the subject is being investigated further, especially as regards the specific substances causing soil acidity.

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SOME EXPERIMENTS ON THE EXTRACTION OF RADIUM FROM CARNOTITE ORES WITH CONCENTRATED SULFURIC ACID

BY HERMAN SCHLUNDT

At the present time the carnotite ores of southwestern Colorado and eastern Utah constitute the principal source of radium in the United States. The carnotites consist of a sandstone with a clay binder variably impregnated with the mineral carnotite, a hydrous potassium uranium vanadate containing barium and calcium.

By boiling carnotite ores with concentrated sulfuric acid the barium and radium compounds present are converted into bisulfates which remain in solution in an excess of the acid, and may then be separated from the insoluble components by filtration followed by washing the residue with concentrated sulfuric acid. From the acid liquors thus obtained the radium is recovered by diluting with water, whereby barium-radium sulfate is precipitated. The experiments outlined in this paper are based upon the preceding principle.

Partial Analysis of the Ores

Experiments were conducted with a low grade and a high grade ore. Both lots of ore came from the carnotite deposits in the Paradox Valley, southwestern Colorado. A stock of 250 kg. of low grade ore was available and 5 kg of high grade. The low grade ore was sampled and ground to pass through a 20 mesh sieve in the plant of a commercial ore grinding and sampling firm. The high grade lot of ore was ground and composited with the ordinary laboratory appliances until it passed through a 40 mesh sieve.

Determinations of the valuable constituents of the ore —radium, uranium and vanadium—seemed sufficient for our purpose. These analytical results appear in the following table, and refer to the air-dry ore as it was used in the experiments. Uranium and vanadium are reported in the customary way as the oxides U_3O_8 and V_2O_5 without implying that these elements are found in this form in the ore.

TABLE I—URANIUM, VANADIUM, RADIUM CONTENT OF ORES

Carnotite[4]	Percent U_3O_8	Percent V_2O_5	Moisture at 110°	Radium parts per billion	Radium calculated
Low grade	1.66	4.03	1.36	4.88	4.69
High grade	14.39	9.67	—	42.78	40.66

The method of analysis followed in the determination of uranium and vanadium in the ores is described in Bulletin No. 70, U. S. Bureau of Mines,[1] and by Lind and Whittemore in their investigations on the radium: uranium ratio in carnotites.[2] I am indebted to Mr. H. H. Barker for the uranium and vanadium determinations in the sample of low grade ore.

The determination of radium in the ores and the crude barium-radium sulfates separated from them in the course of the experiments was conducted electroscopically by the emanation method. The emanation was generally separated from the ore samples by boiling suitable quantities with nitric acid after the samples had been sealed up for a month or longer to attain equilibrium with the emanation that diffuses away continuously under ordinary conditions. Proper measurements of the ionization current produced by the emanation in a standardized air-tight electroscope furnish the data required for computing the quantity of radium.

The radium values found directly by experiment appear in the fifth column, and it is seen that these are approximately five percent higher than the calculated quantities of the last column, which were computed by multiplying the uranium content by the equilibrium ratio[3] of radium to uranium,—3.33×10^{-7}. Differences of this magnitude are not at

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[1] Moore and Kithill: Bureau of Mines, Bull. 70, 88 (1913).

[2] Jour. Am. Chem. Soc., 36, 2076 (1914).

[3] Heimann and Marckwald: Jahrb. d. Radioakt u. Electronik, 10, 299 (1913).

all uncommon for small lots of ore, and have been shown to occur occasionally in ton lots of well sampled ore.[1]

Our ore samples exhibit the characteristic high emanating power of carnotites; at room temperatures the low grade ore continuously loses 35.2 percent of its emanation, the high grade ore 20.2 percent.

The determination of radium in the crude sulfates and a few of the ore residues (tailings) was conducted for the most part by fusion of weighed samples with mixed carbonates of sodium and potassium followed by solution of the products in nitric acid, or a second fusion, after the lapse of a known period of storage extending over a few days. The emanation that accumulates during the interval, when collected quantitatively and transferred to a standardized electroscope, can be accurately determined by properly measuring the ionization current produced. From the data thus obtained the quantity of radium in the sample is readily deduced.[2] In a few of the radium determinations potassium bisulfate was substituted as a flux for the mixed carbonates. In most of the experiments the percentage extraction of radium from the ore was determined by comparison of the alpha radiation from equal surfaces of ore and tailings spread out in thin layers on very shallow trays.

Treatment of the Ores

Various experiments of a preliminary character were conducted with 100 g charges of ore to ascertain the conditions under which a high extraction of radium is obtained. These established the influence on the efficiency of the process of such factors as concentration of acid, temperature, period of digestion, fineness of division of the ore, and grade of ore. The experiments were then extended to ore charges of a kilogram, and later to ten kilos.

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[1] Cf. Lind and Whittemore: Jour. Am. Chem. Soc., 36, 2080 (1914).

[2] For details of operation, apparatus, and formulas used in the calculations see among other references: Schlundt and Moore: Jour. Phys. Chem., 9, 320 (1905); Randall: Trans. Am. Electrochem. Soc., 21, 463 (1912); Lind and Whittemore: Jour. Am. Chem. Soc., 36, 2062-5 (1914); Schlundt: Trans. Am. Electrochem. Soc., 26, 163 (1915).

Inasmuch as the addition of water to a solution of barium bisulfate in concentrated sulfuric acid results in the partial precipitation of normal barium sulfate, it might be expected that treatment of the ore with acid somewhat diluted would materially reduce the percentage of radium extracted. By boiling 100 g charges of the low grade ore for half an hour with acid containing, respectively, 96, 84, 78, 63, 49, and 35 percent of H_2SO_4, corresponding extractions of 95, 93, 92, 78, 52, 42 percent were obtained. It was thus established that digestion of the ore with crude sulfuric acid containing 78 or more percent H_2SO_4 (60° Baumé acid or stronger) removes fully 90 percent of the radium. Acid containing 35 percent H_2SO_4 effectively removes the vanadium and uranium from the ore leaving a light gray sandy residue.

The temperature of digestion appears to be of less influence than the concentration of acid employed. For example, an extraction of 84 percent was obtained by treating the low grade ore with 90 percent acid at room temperatures, but the digestion period was extended to twenty-four hours.

Working with low grade ore, it was found that the period of digestion could be reduced to fifteen minutes by adding the ore to boiling concentrated acid and stirring the mixture vigorously. The extractions exceeded 90 percent whenever 60° Baumé acid or stronger was employed. The decomposition of the high grade ore with hot concentrated acid progressed more slowly. Boiling the ore sample with 90 percent acid for an hour and until a temperature of 290° was reached resulted in an extraction of 89 percent of the radium. The sandy residue after drying still retained a faint yellow color characteristic of very low grade carnotites. By extending the digestion period to three hours an extraction of 92 percent was finally obtained.

With ore coarser than 20 mesh the acid fails to penetrate the larger grains fully. An experiment with low grade ore sized to pass through a 10 mesh sieve and held by 20 mesh resulted in an extraction of only 74 percent of radium when boiled with 85 percent acid for half an hour.

In the experiments with larger quantities of ore the digestions were conducted mainly with the crude acid known commercially as 60° Baumé, which contains approximately 78 percent of H_2SO_4.

A brief description of a typical experiment will illustrate the process. Eighteen liters of 60° acid are heated to 190° in a cast iron kettle of fifty liters' capacity. Ten kilos of the low grade ore, ground to pass a 20 mesh sieve, are then gradually added to the hot acid with occasional stirring of the mixture with an iron ladle. A vigorous interaction occurs accompanied by considerable frothing and evolution of carbon dioxide. The hot acid converts the uranium, vanadium, and some of the iron and aluminum constituents of the ore into water-soluble compounds. Calcium, barium and radium are converted to bisulfates which remain in solution in excess of hot acid. The sands, consisting of silica and silicates, are not materially acted upon by the hot acid and so remain as an insoluble residue.

The ore is boiled with the acid at least fifteen minutes and until the temperature rises to approximately 220°. When the contents of the kettle have cooled to 130° the material is transferred to a stoneware suction filter previously heated to 100° by steaming it for an hour to prevent cracking of the heavy walls when the hot ore and acid mixture is dumped on the filter. A circular suction filter 40 cm in diameter with a capacity of about 30 liters in each compartment when fitted with a "Filtros"[1] filter serves admirably for separation of the acid from the ore residue. By spreading the coarse portion of the ore residue on the filter first, the fine particles in the supernatant liquor do not clog up the filter, and filtration under a diminished pressure of 5 to 10 cm of mercury is then quite rapid. In less than half an hour the residue on the filter is dry and nearly ten liters of clear acid liquor have been separated. The ore residue is then washed by stirring it up

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[1] "Filtros" is a mineral filtering medium unaffected by hot concentrated sulfuric acid. It is produced by The General Filtration Co. of Rochester, N. Y. Grades 7-R and 5-3, four cm thick, were used.

thoroughly on the filter with five liters of hot concentrated acid. After separation of the first wash acid the ore residue is given a second washing with five liters of hot acid. It is desirable to conduct the filtrations while the acid is hot to avoid the separation of crystals of acid sulfates of iron, uranium and vanadium, which are slowly deposited when the acid liquors attain room temperatures.

From the combined acid liquors, amounting to nearly 20 liters, the radium is recovered by pouring the acid into fully eight times its volume of hot water contained in a wooden or stoneware tank. Ordinary tap water may be used for diluting the acid. The resulting green solution contains a portion of the vanadium and uranium compounds. It should be well stirred to promote the solution of calcium sulfate. The ore contains sufficient barium compounds for the precipitation of the radium as radium-barium sulfate. The recovery of radium is however increased nearly two percent by diluting with water containing a small quantity of some soluble barium salt. In most of the experiments water containing five grams of barium chloride per 100 liters was used.

After standing at least three days to complete the precipitation of the radium-barium sulfates the supernatant liquor is siphoned off, the precipitate of sulfates is collected on a filter, washed twice with hot water containing a trace of barium chloride, and is then dried. The crude sulfates thus obtained are designated *acid* sulfates in the tabulated results given below.

The residue on the filter contains a portion of the vanadium, uranium and iron sulfates, which are readily soluble in water. The acid in the residue also retains some radium. By washing the residue several times with hot water on the filter with thorough stirring a nearly white sand remains which is covered with a thin layer of drab-colored clay. The deep blue filtrate, however, is always slightly turbid, and upon standing a white precipitate settles out which contains three to nine percent of the radium recovered. The precipitate consists largely of finely divided silica and silicates, but also contains a small quantity of radium-barium sulfate which is precipitated in such finely divided form, when the ore residue is leached with water, as to pass through the filter. This radioactive precipitate is designated *water* sulfates.

The experiments with one kilogram lots of ore were conducted with similar apparatus of very much smaller dimensions. The filtrations were made with a large filter flask and Büchner funnel fitted with a "Filtros" filter, and extended in height by means of a cylinder of copper. Asbestos fiber was used as a packing material. The cast iron kettle of the smaller unit is still in service after having been used in at least forty extractions and in a few experiments boiling was continued three hours. The record of the larger kettle is less gratifying: In the fifth run, acid trickled out at two places, evidently due to blow holes in the casting. Repairs were made with iron plugs which have not required further attention in four subsequent runs.

Instead of recovering the radium from the concentrated acid liquor separated after treatment of one charge of ore, this liquor may be used for the extraction of radium from a second and even a third charge of ore before the radium is recovered by dilution of the acid liquor with water. By treating several charges of ore with the same acid its radium content is correspondingly increased, and some saving in acid is effected. The radium extraction, however, is thereby decreased to some extent, as shown by the data in the last column of Table 2 below.

Some typical experimental data are given in the following table. Items 17 and 18 have reference to the radium remaining in solution after dilution of the strong acid liquors.

The concentration of radium in the crude sulfates precipitated from the acid liquor varied somewhat in different experiments with the same grade of ore. The acid sulfates obtained from the low grade ore averaged 1.15×10^{-6} g radium per gram, *i. e.*, 1150 parts per billion. A comparison with the radium content of the ore, 4.88×10^{-9} g radium per gram, shows that the concentration of radium has been increased

TABLE 2—EXPERIMENTAL DATA

No.	Datum	Low grade ore	Low grade ore	High grade ore	Low grade ore
1	Ore charge	1 kg	10 kg	1 kg	3 × 1 kg
2	Ore residue (Tailings)	808 kg	8.22 kg	585 g	2497 g
3	Soluble portion	19.2%	17.8%	41.5%	16.8%
4	Acid used for digestion	1.8 l., sp. gr. 1.81	18 l., sp. gr. 1.72	20 l., sp. gr. 1.82	3.4 l., sp. gr. 1.81
5	Wash acid used	1.1 l., sp. gr. 1.81	10 l., sp. gr. 1.72	1.1 l., sp. gr. 1.82	
6	Final temperature	250°	210°	285°	270°
7	Digestion periods	1 hour	15 min.	30 min.	20 min. each
8	Acid sulfates	3.697 g	34.88 g	15.33 g	9.33 g
9	Water sulfates	1.754 g	32.5 g	3.22 g	8.57 g
10	Radium in acid sulfates	4.28×10^{-6} g	39.28×10^{-6} g	35.59×10^{-6} g	11.64×10^{-6} g
11	Radium in water sulfates	0.29×10^{-6} g	4.25×10^{-6} g	1.37×10^{-6} g	0.97×10^{-6} g
12	Total radium recovered	4.57×10^{-6} g	43.53×10^{-6} g	36.96×10^{-6} g	12.61×10^{-6} g
13	Total radium in ore	4.88×10^{-6} g	48.80×10^{-6} g	42.78×10^{-6} g	14.64×10^{-6} g
14	Radium recovered	93.6%	89.2%	86.4%	86.1%
15	Radium in acid sulfates	87.7%	80.5%	83.2%	79.5%
16	Radium in water sulfates	5.9%	8.7%	3.2%	6.6%
17	Radium in acid liquors	18.2×10^{-9} g	20.5×10^{-8} g	—	—
18	Radium in wash water	10.1×10^{-9} g	9.5×10^{-8} g	—	—
19	Total radium in liquors (17 and 18)	28.3×10^{-9} g	30.0×10^{-8} g	2.22×10^{-8} g	10.39×10^{-8} g
20	Radium loss in liquors	0.58%	0.61%	0.52%	0.71%
21	Ra left in ore residue	3.52×10^{-7} g	4.0×10^{-6} g	2.62×10^{-6} g	18×10^{-7} g
22	Ra in ore residue	7.2%	8.2%	10.8%	12.3%
23	Ra loss (20 + 22)	7.78%	8.81%	11.32%	12.91%
24	Recovery based on losses	92.2%	91.2%	88.7%	87.2%
25	Actual recovery	93.6%	89.2%	86.4%	86.1%
26	Difference	+1.4%	—2.0%	—2.3%	—1.1%

approximately 235 times. The acid sulfates from the high grade ore on the other hand contained 2.32×10^{-6} g radium per gram, a concentration double that of the sulfates separated from the low grade ore, but the concentration ratio of radium in sulfate to radium in ore is only 55.

It is seen that less than one percent radium remains in solution in the combined solutions after dilution. However, it should be stated that values as high as five percent were obtained in some experiments when the solutions were filtered off after standing for only six to ten hours. The low values represent the quantities remaining in solution after a period of at least three days.

Although more radium was actually recovered in a few experiments than was to be expected on the basis of the combined radium losses in tailings and solutions, in general the recovery fell short from two to five percent. I am inclined to ascribe this loss largely to retention of radium-barium sulfate in the thick filter plate. Likewise the quantities of insoluble material that appear in the filtrate when the ore residue is leached with water depend primarily upon the porosity of the "Filtros" filter used.

The sediment that appears in the water filtrate consists largely of finely divided silicates. A qualitative examination showed the presence of aluminum, calcium, magnesium and much silica. The sulfates of the alkaline earths constitute a relatively small proportion of the sediment.

The acid sulfates even after ignition are not pure white but retain a gray color. The acid sulfates separated from three kilos of low grade ore were found to contain 6.63 percent of lead sulfate, 3.83 percent of iron and aluminum weighed as oxides, and 2.27 percent of silica. The relatively high percentage of lead sulfate is largely introduced with the crude acid used in treatment of the ore. Barium of course predominates in the sulfates of the alkaline earths but calcium and strontium are also present.

We realize that this investigation is incomplete in several respects. It should be extended to carnotites from other localities and to ores of different composition. The recovery of acid from the liquors and the separation of uranium and vanadium from the solutions have been given but scant attention. The distribution and recovery of the other radioactive constituents of the ore would be of interest. More important, however, would be a comparative study of methods to ascertain the industrial possibilities of this method of extraction.

Preliminary experiments conducted with samarskite indicate that fully seventy percent of the radium of the mineral can be extracted by treatment with concentrated sulfuric acid.

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SOLUBILITY OF OXYGEN IN SALT SOLUTIONS AND THE HYDRATES OF THESE SALTS

BY C. G. MACARTHUR

Introduction

In another investigation, data on the solubility of oxygen in solutions of several of the ordinary salts were needed. The literature contained determinations for a few acids and bases and one salt, sodium chloride.[1] It, therefore, became necessary to find out how soluble oxygen (in the presence of the other gases of the air) was in different molecular concentrations of several typical salts. Incidentally, it will be possible to use these data to calculate the degree of hydration of these salts in solution.

Experimental

The salt was made up to a definite concentration in tall cylinders and placed in a thermostat at 25° C. The cylinders were shaken by hand several times a day for about four days. The solution was then poured into a 250 cc measuring flask that was also graduated to 252 cc and had a neck of such length that the bottom of a rubber stopper came just to the 252 cc mark. To the 250 cc of solution in the flask was added simultaneously 1 cc of the alkaline potassium iodide (33 grams NaOH + 10 grams KI dissolved in water and diluted to 100 cc) and 1 cc of the manganous chloride solution (40 grams $MnCl_2.4H_2O$ made up to 100 cc with H_2O). The flask was stoppered to the 252 cc mark, thoroughly shaken, and the precipitate allowed to settle. 3 cc of strong hydrochloric acid was added. The flask was again stoppered and shaken. The contents were then poured into a 700 cc flask and titrated with $N/100$ sodium thiosulfate solution, using starch as indicator. By the above method the amount of oxygen in distilled water at 25° C and at a pressure of 760 mm of mercury was found to be 5.78 cc. Dupli-

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[1] Geffcken: Zeit. phys. Chem., 49, 257 (1904).

Salt and concentration	Density at 25° C	Solubility of oxygen in cc per liter	Hydration
H_2O	1.000	5.78	—
m/8 LiCl	1.0004	5.63	9.2
m/4 LiCl	1.0035	5.49	9.5
m/2 LiCl	1.0091	5.17	10.6
m LiCl	1.021	4.59	10.3
2*m* LiCl	1.044	3.63	8.9
3*m* LiCl	1.113	1.97	6.1
4*m* LiCl	1.22	1.12	2.9
m/8 NaCl	1.0022	5.52	17.5
m/4 NaCl	1.0067	5.30	16.1
m/2 NaCl	1.017	4.92	15.2
m NaCl	1.038	4.20	14.0
2*m* NaCl	1.075	3.05	11.7
3*m* NaCl	1.112	2.24	10.0
4*m* NaCl	1.149	1.62	8.5
m/8 KCl	1.003	5.52	17.6
m/4 KCl	1.0086	5.30	16.0
m/2 KCl	1.020	4.98	13.6
m KCl	1.042	4.26	12.7
2*m* KCl	1.086	3.21	10.4
3*m* KCl	1.134	2.36	8.9
4*m* KCl	1.170	1.86	7.3
m/8 RbCl	1.0094	5.65	7.6
m/8 CsCl	1.014	5.67	5.3
m/8 NaBr	1.007	5.65	7.5
m/4 NaBr	1.017	5.52	7.8
m/2 NaBr	1.036	5.15	10.2
m NaBr	1.075	4.47	11.0
2*m* NaBr	1.150	3.37	8.9
3*m* NaBr	1.219	2.57	8.0
4*m* NaBr	1.305	2.02	6.5
6*m* NaBr	1.455	1.28	4.8
m/4 KBr	1.019	5.29	16.2
2*m* KBr	1.079	3.27	8.8
4*m* KBr	1.162	1.84	5.3
m/8 KI	1.013	5.65	6.0
m/4 KI	1.027	5.49	8.9
m/2 KI	1.056	5.20	8.1
m KI	1.116	4.75	7.0
2*m* KI	1.23	3.77	6.4
5*m* KI	1.46	1.81	1.5

$m/4$ KNO_3	1.015	5.49	9.4
$m/2$ KNO_3	1.029	5.11	10.5
m KNO_3	1.059	4.61	8.9
$2m$ KNO_3	1.110	3.65	7.6
$m/8$ Na_2SO_4	1.014	5.04	54.0
$m/4$ Na_2SO_4	1.032	4.60	43.5
$m/2$ Na_2SO_4	1.063	3.97	33.6
m Na_2SO_4	1.13	3.00	25.3
$m/8$ K_2SO_4	1.016	5.11	48.1
$m/4$ K_2SO_4	1.032	4.66	39.6
$m/2$ K_2SO_4	1.060	3.89	32.0
$m/8$ $MgCl_2$	1.011	5.35	31.9
$m/4$ $MgCl_2$	1.022	5.04	27.8
$m/2$ $MgCl_2$	1.044	4.37	26.2
m $MgCl_2$	1.085	3.18	24.0
$2m$ $MgCl_2$	1.160	2.22	15.6
$4m$ $MgCl_2$	1.284	0.78	9.3
$5m$ $MgCl_2$	1.343	0.54	6.8
$m/8$ $BaCl_2$	1.019	5.40	25.9
$m/4$ $BaCl_2$	1.042	5.04	26.2
$m/2$ $BaCl_2$	1.082	4.27	26.2
m $BaCl_2$	1.177	3.10	22.0
$m/4$ $CaCl_2$	1.022	5.08	25.3
m $CaCl_2$	1.084	3.71	18.2
$5m$ $CaCl_2$	1.34	2.14	3.5
$m/8$ NH_4Cl	1.0015	2.31	
$m/4$ NH_4Cl	1.0025	1.16	
m NH_4Cl	1.014	0.07	
$m/8$ Sucrose	1.015	5.40	
$m/4$ Sucrose	1.033	4.82	
$m/2$ Sucrose	1.068	4.39	
m Sucrose	1.147	3.20	
$2m$ Sucrose	1.336	1.84	

cate experiments were not run except on the *m*/8 concentration of each salt. Controls with distilled water were run along with each series of salts. Therefore, barometric pressure could be neglected because it would have practically the same effect on the control as on the solution.

The densities of the solutions were taken or calculated from the density tables in the International Tables of physicochemical constants.

The degree of hydration was calculated from the following formula:[1]

$$\frac{a-b}{a} \times \frac{100-c}{c} \times \frac{m}{m'} = \text{Hydration}$$

a = cc of O in liter of H_2O.
b = cc of O in 1000 grams of the water in the solution = $\dfrac{\text{cc oxygen per liter of solution}}{\text{density} - \text{grams of salt per cc of solution}}$.
c = per cent of salt in solution.
m = molecular weight of the salt.
m' = molecular weight of water.

Discussion of Data on Solubility of Oxygen

From the above data one will notice that in all cases the solubility of oxygen decreases with an increase in the concentration of the salt. The decrease per molecule of salt in solubility is greatest in the most dilute solutions. If one constructs a curve for the solubility of oxygen in increasing concentrations of salt, the curve flattens and becomes parallel with high concentration, indicating that all the oxygen would be removed only from concentrations that are much higher than are possible.

The solubility of oxygen in $m/8$ solutions of the chlorides does not decrease regularly from that of caesium to lithium with a decrease in molecular weight as one would expect. The figures are caesium chloride 5.67, rubidium chloride 5.65, potassium chloride 5.52, sodium chloride 5.52, lithium chloride 5.63. This irregularity can probably best be explained by the difference in potential of the ions in solution. It can not be due simply to the fact that there are ions present because the difference in number of ions in $m/8$ solutions does not thus vary with the different salts. It must be due to specific differences between the ions.

Another fact to be noted is the marked effect of ammonium chloride on the solubility of oxygen. It varies with the concentration, but the decrease in solubility is extremely large. At first it was thought to be due to a combination of the am-

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[1] Philip: Trans. Faraday Soc., 3, 123.

monium chloride with the manganous chloride, thus preventing the manganous compound from being oxidized by the oxygen in solution. This was shown not to be true by adding the ammonium chloride to water containing the usual amount of the alkaline iodide and manganous chloride solutions and finishing the determination as usual. This gave the amount of oxygen that distilled water usually contains. Though it is more likely that the ammonium chloride so influences the oxygen that it is not available to oxidize the manganous hydroxide, it is still possible that the ammonium chloride markedly decreases the amount of oxygen in solution.

By adding the manganous chloride solution and the alkaline iodide solution simultaneously and allowing the precipitate to stand about two hours before adding the hydrochloric acid, it is believed the insolubility of the hydroxides of barium, calcium and magnesium did not affect the completion of the oxidation of the manganous hydroxide.

In determining the amount of oxygen in sucrose solutions a difficulty was encountered that renders the results given in the table somewhat low. It was noticed that the sugar slowly uses the oxygen in the solution to oxidize itself, even at 25° C. The error in the figures of the table is not large because it was found that if the solutions were shaken vigorously immediately before adding the manganous chloride and alkaline iodide solutions rather constant maximum results were obtained that agreed fairly well with each other and with the results from the salts.

Discussion of Hydration Data

If one considers that a substance dissolves in water because it forms a hydrate, it would seem that the force causing the ionization is the one causing the combination between solute and water. When the pull of the water on the molecule is great enough to overcome the force holding the parts of the molecule together, it will split into parts. Thus when NaCl is placed in contact with H_2O the attraction of the water for the salt to form a hydrate will cause a separation of the salt crystals into molecules which are surrounded by water of hydration. The amount of this water of hydration is continually changing. When enough of this water pulls on the salt molecule it will cause its ionization. According to the kinetic theory, some of these hydrated ions will lose part of these loosely combined water molecules; then the ions will recombine to form molecules. The larger the dilution the greater the percent of molecules that will be separated into ions, because the chances are then greater, kinetically, that enough water will be influencing the molecule to ionize it.

Data on the degree of hydration of ions or molecules will indicate their average hydration. Any particular ion or molecule may be hydrated considerably more or less than the average. It is the molecules that become largely hydrated that will part into ions.

It is very probable that the molecules in a dilute solution have a hydration nearly as great as the sum of the hydration of their ions.

When oxygen dissolves in water it combines in a similar way to form a hydrate. The water will be saturated with oxygen molecules moving at a given rate at a given temperature and pressure, when the attraction of the water for the oxygen molecules is just large enough to hold that number (not the same molecules continually, of course) from flying back into space above the water. Other molecules or ions, like those of sodium chloride, which also form hydrates will decrease the amount of water that will influence the oxygen molecules; therefore, the number of dissolved oxygen molecules will decrease. It is possible that the number of water molecules attached to the salt molecule determines simply and definitely the amount of oxygen that can remain in the water. In this case a definite proportion would exist between the amount of oxygen in a solution and the degree of hydration of the salt added.

By consulting the data it will be seen that in the case of potassium chloride this definite proportion exists. This is also to a certain extent true of potassium bromide, sodium sulfate, potassium sulfate, magnesium chloride, calcium chloride, and probably barium chloride. In all the other salts studied the degree of hydration does not increase with a decrease in concentration, at least not consistently. It is probable then that in these salts that do not give a proportional increase in hydration with an increase in ionization, the ions that are present influence the amount of oxygen dissolved in the solution. In the higher concentrations, where the percentage of ionization is small, there is fairly good agreement between the hydration data obtained for these concentrations and results calculated from data obtained for dilute solutions by other methods.[1] However, when the ionized particles begin to predominate the expected increase in hydration, as calculated from the oxygen solubility, does not appear. It is conceivable that the oxygen in the solution does decrease the hydration of the ions more than it does that of the molecules. But it is probable that the sum of the hydration of the ions is somewhat larger than the hydration of the molecules that are made up of these ions. It is easier to believe that the difference in potential between the ions (because some ions do not have this effect) cause an increase in the solubility of the oxygen by attracting it, thus giving data for low hydration values.

If the data are studied in the light of what has just been stated and the assumption is made that the hydration of the chlorine ions calculated from the diffusion coefficient is correct (9.6 at infinite dilution)[2] the hydration of a potassium ion in an $m/8$ solution becomes 8. If 9.6 H_2O is correct for potassium, the data give the bromine ion 6.6 H_2O in $m/4$ solution. If chlorine is 9.6 H_2O, calcium equals 6.1, barium 6.7 and magnesium 12.7. These are minimal values, of course. With potassium hydration 9.6, the sulfate radicle is calculated to be 28.9. These values are not far from those calculated from the diffusion coefficient, nor from those obtained by the more reliable experimental methods.

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[1] Smith: Jour. Am. Chem. Soc., 37, 722 (1915).

[2] Smith: Ibid., 37, 722 (1915).

By comparing the hydration of a particular concentration of one salt with the same concentration of another, it will be noticed that sodium hydration is greater than potassium, potassium than rubidium, rubidium than caesium. The chlorides are more hydrated than the bromides; the bromides than the iodides.

Summary

The solubility of oxygen in various concentrations of the following substances was determined by the manganous hydroxide method: the chlorides of lithium, sodium, potassium, rubidium, caesium, ammonium, barium, calcium, magnesium; the bromides of sodium and potassium; the iodide of potassium; the nitrate of potassium; the sulfates of sodium and potassium, and sucrose.

From the data for the solubility of oxygen the hydration of the above named salts was calculated.

In all cases it was found that an increase in concentration of the substance decreased the solubility of oxygen in a regular manner.

Ammonium chloride has a very large effect on the solubility of oxygen.

Sucrose is slowly oxidized by the dissolved oxygen. This interferes with the determination of oxygen in sugar solutions.

Potassium chloride, potassium bromide, potassium sulfate, barium chloride, calcium chloride, and magnesium chloride seem to give hydration values that are approximately correct.

The other salts studied give low values for the highly ionized solutions, indicating that the particular ions increase the solubility of oxygen to a definite extent which is specific for that particular ion; or that it is the potential difference between the two ions present that causes this increase in oxygen solubility.

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DETECTORS IN WIRELESS TELEGRAPHY

BY WILDER D. BANCROFT

Pierce[1] classifies the detectors used in wireless telegraphy under the following heads: electrolytic detectors, crystal rectifiers, coherers, magnetic detectors, thermal detectors, vacuum detectors. This paper deals with the first three cases, beginning with the electrolytic detector.[2] "The electrolytic detector for electric waves, as described by Fessenden and shortly after by Schloemilch, consists of a cell containing an electrolyte and having one electrode of very small area, usually in the form of an extremely fine wire of platinum, and as the other electrode a larger area of platinum or some other metal. When used in wireless telegraphy the two electrodes are connected in a circuit upon which the electric oscillations are impressed, so that the rapidly oscillating electric currents in the circuit are made to traverse the cell of the detector. The electrolyte employed in the electrolytic detector is usually 20% nitric acid though almost any electrolytically conductive liquid (dilute sulphuric acid, common salt solution, caustic soda, etc.) may be used. For a highly sensitive detector the fine platinum wire employed as the sensitive point may be as small as one or two ten-thousandths of an inch in diameter. For a less sensitive detector, which is not so likely to be destroyed by strong signals, wire as large as one-thousandth of an inch or even larger may be used."

The usual way is to polarize the detector cell by means of an external circuit. When the electrical waves strike the detector a current passes. This is a case of depolarization by electrical waves,[3] which tend to remove the adsorbed gas from the surface of the electrode, thus cutting down the overvoltage and the polarization.

In the crystal detector a crystal of carborundum or other

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[1] "Principles of Wireless Telegraphy," 143 (1910).

[2] Ibid., 201 (1910).

[3] Cf. Bancroft: Jour. Phys. Chem., 20, 402 (1916).

suitable substance is wrapped or plated on one side with copper or platinum. A conducting point is brought practically into contact with the other side. When electrical waves pass, a better contact is made and a current passes. The gas film is removed more or less completely under the electrical stress thus decreasing the insulation. Different points in the same surface of the same carborundum or molybdenite crystal show great differences in sensitiveness. This is probably due to localized impurities in the crystal. Similar differences have been observed in the thermoelectric behavior[1] of the same crystals.

"Some of the specimens [of molybdenite] are thermoelectrically negative with respect to copper while other specimens are thermoelectrically positive with respect to copper. The great variability among the specimens studied may be due to an admixture of small quantities of some other substance with the molybdenite, or it may be due to structural differences from point to point in the crystal. The differences in the specimens could not have arisen from the copper-plating or from the heat employed in soldering the junctions, because [four of] the specimens were tested before the copper-plating and soldering was done, and by means of the preliminary test were classified as positive, negative, positive and negative, respectively, which agrees with the determination after soldering. The preliminary test was made by touching the specimens with two copper wires attached, respectively, to the two terminals of the galvanometer, one of the wires being slightly warmer than the other. *This preliminary test proved very interesting in that it showed that one may find, all over many of the pieces cut from a crystal of molybdenite, points where the substance is thermoelectrically positive and other points where it is thermoelectrically negative.* These positive and negative points sometimes lie so near together that, with a fine-pointed exploring electrode attached to a galvanometer and warmed by heat conducted from the hand, one may find the deflec-

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[1] Pierce: "Principles of Wireless Telegraphy," 192 (1910).

tions of the galvanometer reversed from large positive values to large negative values on making the slightest possible motion of the pointer over the crystal. Explorations of this kind failed to show any definite orientation of the thermoelectric quality with respect to the crystallographic axes."

According to Pierce[1] molybdenite, MoS_2, is the most sensitive of the crystal rectifiers thus far investigated. This is especially interesting because the experiments on ore flotation show that the sulphide ores have a marked tendency to adsorb gases. According to Wood[2] molybdenite ores are now being concentrated by flotation.

Carborundum crystals show unilateral conductivity,[3] since "the current through the crystal in one direction under a given electromotive force was found to be different from the current in the opposite direction under the same electromotive force." In terms of our hypothesis this means that the thickness of the adsorbed gas film is decreased more when the crystal is charged positively than when charged negatively or *vice versa*. This is not without analogy. Twomey[4] has shown that chloroform adsorbs air less readily in alkaline solutions where the chloroform is charged negatively by adsorbed hydroxyl ions than in acid solutions where the chloroform is charged positively by adsorbed hydrogen ions. I cannot agree entirely[5] that "when suitable crystals are employed, the crystal contacts are *detectors* for electric waves because they are *rectifiers* for rapid alternating currents." It is quite true that the crystals must conduct unilaterally if they are to be used as detectors without a battery in the local circuit; but this requirement is not necessary if a battery is used.

Since the action of the crystal detectors merely involves the temporary decrease in the thickness of the adsorbed gas film, it is not surprising that carborundum crystals should

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[1] "Principles of Wireless Telegraphy," 178 (1910).

[2] Eng. and Min. Jour., 93, 227 (1912).

[3] Pierce: "Principles of Wireless Telegraphy," 164 (1910).

[4] Jour. Phys. Chem., 19, 360 (1915).

[5] Pierce: "Principles of Wireless Telegraphy," 175 (1910).

show little or no change with time when used as detectors or rectifiers.[1]

"In confirmation of the absence of electrolytic polarization, a durability test of the carborundum rectifier has been made as follows: A crystal of carborundum enclosed in a glass tube with a few drops of oil and held between brass electrodes, one of which was pressed forward by a spiral spring, was kept under almost daily observation[2] from October 23, 1907, until March 18, 1908. During these five months more than 1200 measurements were made of the direct current obtained through the crystal under different direct and alternating voltages. The rectifier was kept in a temperature bath and was subjected to various long periods of heating and cooling ranging from 0° to 80° C. Notwithstanding the long continued exposure of the crystal to large changes of temperature, and notwithstanding the frequent loading of the rectifier with current, it was found at the end of the series that the values of the direct current obtained from the crystal under a given applied alternating voltage over a range of current from 4 to 400 micro-amperes (direct) and a range of voltage between 1 and 6 volts (alternating) did not differ from the corresponding values at the beginning of the series by an amount exceeding the limit of accuracy of the experiment, which was about $^1/_3$ of 1 percent. This experiment shows that, if there is any kind of electrolytic action, it must be of such a character as to change the nature of the electrodes or of the crystal only very slowly, if at all."

In another passage Pierce[3] compares the electrolytic and the crystal detectors. "The resemblance of the oscillograms with the electrolytic detector to those with the crystal rectifiers is close, in so far as depends on the fact that both classes

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[1] Ibid., 176 (1910).

[2] This series of measurements was carried out by Mr. K. S. Johnson, to whom the writer wishes to express his sincere thanks. The experiment was finally discontinued on account of the accidental melting of the cement holding in the end of the tube.

[3] "Principles of Wireless Telegraphy," 212 (1910).

of rectifiers are nearly perfect[1] rectifiers when employed under their best conditions. The electrolytic rectifier, in order to approximate perfection[2] as a rectifier must be polarized by the superposition of a direct current, while the use of the direct current with the crystal rectifier, does not always materially improve the rectification. Also *the two rectifiers are different, in that the electrolytic rectifier shows evidence of electrolytic polarization capacity, which, so far as may be judged from the oscillograms, is absent with the crystal rectifier.* The experiment with the electrolytic detector, since it shows in the matter of polarization capacity the integrative action of this detector which was sought for and not found with the crystal rectifier is thus an interesting 'control' experiment. In the matter of sensitiveness the best crystal rectifiers are about equal to the electrolytic detector."

All the statements in the preceding passage are in accordance with the theory as outlined. While Pierce does not give the true theory of the electrolytic detector and the crystal detector, his conclusions in regard to the latter are interesting, especially in view of the fact that many people have believed that thermoelectric phenomena play an essential part. His conclusions follow:[3]

1. An examination of the characteristics of contact detectors using carborundum, anatase, brookite, hessite, iron pyrites, and silicon shows that we are dealing with the same kind of a phenomenon in the case of all these crystal substances. The various other crystal-contact detectors which I have not examined probably act in the same way.

2. At the contact between the crystal and a common metal, or between two different crystals, or between two apparently similar crystals, there is asymmetric conductivity, permitting a much greater current to flow in one direction than in the other under the same applied voltage.

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[1] A rectifier is called "nearly perfect" when the ratio of the current in one direction to that in the other is large.

[2] The current through the electrolytic rectifier is slightly asymmetric when no polarizing current is used.

[3] Pierce: "Principles of Wireless Telegraphy," 199 (1910).

3. These contacts all have a rising current-voltage characteristic.

4. These crystals all have a large thermoelectric force against the common metals, and the amount and direction of the thermoelectric force is different at different points on the crystalline bodies.

5. The rectifying effect is also different in amount and direction at different points of the crystalline body; the direction of the rectifying effect is often opposite to the effect that would be obtained by heating the contact.

6. Thermoelectricity does not explain the phenomenon of rectification, but the two effects, since both exist in such marked degree in the same bodies, may be related in that both may have their seat in some common property of the materials employed. *For example, if we suppose that a surface of separation between the crystalline body and some other body permits the passage of electrons more easily in one direction than in the other, this would account for the rectifying effect, and would also account for the thermoelectric effect, provided the velocity of the electrons is suitably different at different temperatures.*

7. The thermoelectric explanation of the rectifying effect, if we had found it to be supported by the experiments, would have correlated the phenomenon of rectification at a solid contact with the body of information that we already have in regard to thermoelectricity, but we should still have had by no means a complete knowledge of the action, because our knowledge of thermoelectricity is very incomplete.

8. From experiments with thermoelectricity we are familiar with the fact that the energy of an oscillatory electric current passing through a high-resistance contact is partially converted into heat energy, and that the heat energy so obtained, if produced at a thermal junction, is again partially converted into electric energy manifesting itself as a direct current. It is, perhaps, after all, more simple to suppose the alternating current to be converted into heat energy without the intermediation of heat; and this seems to be the case with the crystal-contact rectifiers. This result opens up a new field for investi-

gation, which may contribute to a better understanding, not only of thermal electricity, but of the much larger question of the mechanism of electrical conductivity in solid bodies.

Under coherers, Pierce[1] includes only those detectors which employ a loose contact and require to be shaken, tapped or otherwise moved to restore the contact to its sensitive condition after the receipt of a signal. A great many modifications of the Branly coherer have been made, including the use of a single contact or a few contacts in series or parallel, between metallic balls or points to take the place of the filings.

"These various forms of coherer have their importance in the fact that, on the receipt of electric waves, a sufficiently large current is started in the local circuit to operate a relay, ring a bell, or give other form of alarm that can be heard at a distance from the operator's desk. Also the current permitted to flow in the local circuit of the coherers during the receipt of electric waves is sufficiently large to start machinery and control a mechanism (for example, a torpedo or dirigible craft) at a distance. This kind of result is not easily attained with the other forms of detectors, which do not permit of the use of sufficiently large currents in the local circuit to sound an alarm or start electrical machinery. Thus the coherer, though lacking in sensitiveness to feeble waves and not now generally employed in the receipt of messages, has still a field of usefulness.

"Besides the filings coherer we shall describe here another interesting form of coherer—that devised in 1902 by Lodge, Muirhead and Robinson. This instrument consists of a small steel disc, rotated vertically by a clockwork, so that the disc is just separated from a column of mercury by a thin film of oil on the surface of the mercury. One electrical contact is made to the wheel through a brush, and the other connection is made to the mercury well through a binding post. The impulse of the electric oscillations breaks down the oil film and establishes momentary cohesion between the steel disc

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[1] "Principles of Wireless Telegraphy," 143 (1910).

and the mercury. A current from a local battery passes through the disc and mercury contact, and operates a siphon recorder, which is used in series with the battery and the coherer. After the impulse ceases, the motion of the disc brings continuously a fresh oil film into the contact and causes decoherence. The siphon recorder gives a written record of the dots and dashes of the message. A felt brush serves to keep the rotating disc free from dust before and after contact with the mercury.

"A generally accepted theory as to the reason for the coherence of the filings, or other form of imperfect contact used in the coherers, has not been established. I shall state briefly some of the views presented in explanation of the phenomenon. Before the arrival of the waves, the high resistance of the contact is generally supposed to be due to the presence of some kind of poorly conductive film at the contact. In the case of the Lodge-Muirhead coherer, the insulating film is evidently present in the form of a film of oil. In many of the coherers a poorly conductive film is present in the form of an oxide of the metal. This is evident from the fact that in some cases the metallic particles (*e. g.*, iron or steel) are artificially prepared by oxidizing them in order to make of them a good coherer. The poorly conductive film may also be present in some cases in the form of a sulphide of the metal. On account of the readiness with which many metals (called the baser metals) enter into combination with the oxygen or sulphur dioxide of the air, a thin film or sulphide is always present on the surface of most of the baser metals, unless special care is taken to remove it.

"Apart, however, from the existence of such films of foreign matter at the contact, it seems not impossible that the high resistance before the arrival of the waves may be a property of the surfaces of even pure metals when these surfaces touch only very lightly. If we assume the presence of the poorly conductive film at the contacts of the coherer, we may suppose that, on the arrival of the electric waves, the poorly conductive film is removed by the heat developed by the oscillatory currents. This starts the local current which, developing further heat, still further improves the contact and permits the passage of further current. Instead of heat being the chief agency in removing the oxide or other poorly conductive film, or in bringing together the loose contacts, it may be that this is done by the electric attraction between the filings, which before the current starts will be charged with opposite signs of electricity, and which under the added electromotive force produced by the electric oscillations may attract each other strongly enough to pull the contacts together."

According to the theory advanced in this paper, the air film is the essential thing and the oxide film is more or less secondary. The thicker the oxide film is, up to a certain limit, the thicker will be the air film and the higher the voltage necessary to cut down the resistance markedly. That the conducting particles should cohere is not surprising. The only reason why two pieces of the same metal or two pieces of porcelain do not become one piece when pressed together is because of the adsorbed air on the surfaces. As Breuer[1] says: "All solids condense on their surfaces certain amounts of gases from the air and hold them with great force. The new surfaces, which are formed when a porcelain plate is broken, are covered instantaneously with particles from the surrounding atmosphere, and these are held in place powerfully as a thin, adherent elastic cushion. The portion of this layer which is next to the porcelain is believed nowadays to be as solid and dense as the porcelain itself, while the outer surface has the density of the air. A simple mechanical pressure, no matter how strong, is, therefore, not sufficient to bring the porcelain surfaces into intimate contact."

When the air film is removed more or less completely, the solid particles stick to one another more or less tightly and have to be separated by tapping, shaking, or other means. Depending on the conditions of the experiment we may have

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[1] Kitte and Klebstoffe, 23 (1907); cf. Bancroft: Jour. Phys. Chem., 20, 3 (1916).

the oxide films coalescing or the metals themselves. If sufficient energy is expended at the contacts we may have fusion;[1] but this is not a necessary part of the theory. From this point of view the essential difference between the coherer and the crystal detector is that coalescence does not take place readily in the latter case and does in the former. Experiments on welding by pressure give independent confirmation of this fact.

While Robinson[2] gives quite a different theory of the coherer, it only calls for a slight change in the wording of his argument to make it applicable to the theory I have outlined. In connection with the action of the Lodge-Muirhead coherer, it is interesting to note that Lenard[3] found, nearly thirty years ago, that mercury wets platinum only when a current is flowing. At other times there is evidently an air film.

Brown[4] superposed an alternating current on a cell, Zn | H_2SO_4 | C, and found that the polarization was decreased thereby. "By making the surface of the anode in contact with the electrolyte small in area, the action of the alternating current will be concentrated and the ions will be correspondingly increased in chemical activity. In one case the anode was constructed of a fine platinum wire dipping about one-tenth of an inch into the dilute sulphuric acid and an external battery of two volts applied. When the alternating current was superimposed the platinum started to oxidize, and in a short time the whole of the wire in contact with the liquid was turned into a black powder. The same thing happened with gold, the wire turned into a yellow insoluble powder. With the filament of a carbon lamp as anode the carbon was completely dissolved or turned into gas; and, in fact, no conducting material could be found that would resist the combined action of the two currents when applied in this concentrated manner.

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[1] Sundorph: Wied. Ann., 68, 594 (1899).

[2] Drude's Ann., 11, 770 (1903).

[3] Wied. Ann., 30, 212 (1887).

[4] Proc. Roy. Soc., 90A, 26 (1915).

"These experiments were carried out with alternating currents at a frequency of 12,000 periods per second, as it was thought that the stimulating effects were much greater at high frequencies but no tests were made to prove this point. The function of the alternating current is to stimulate the chemical changes; it may be to produce oxidation as in the foregoing experiments, or in other cases it may be to reduce the oxide, although no direct test was made to prove this supposition.

"I think that these experiments explain the action of the Branly filings coherer—a device in which the group of granules act normally as an insulator, but become conductive when high-frequency currents such as Hertz waves pass through them. Iron or nickel filings are insulated from each other by a thin film of oxide, but the coherer has a small capacity, with the oxide as dielectric, and the waves are thus allowed to pass. The rapid alternating currents act upon the oxide dielectric and, by stimulating chemical action, reduce the oxide at the points of contact to a metallic or conducting form and allow a continuous current to flow. When the tube is shaken the oxide again intervenes and another application of the alternating current is required to produce conduction."

There is a charming vagueness about the words "by stimulating chemical action, reduce the oxide." Also one would have liked to know just what the "insoluble yellow powder" was which was obtained from a gold electrode. From the context one would suppose it to be an oxidation product of gold, but the properties are more like those of disintegrated gold.

The general results of this paper are:

1. The coherer, the electrolytic detector, and the crystal detector act as they do because an electrical stress decreases the thickness of the adsorbed gas film and, therefore, decreases the resistance.

2. The unilateral conductance of the crystal detectors is essential when there is no battery in the local circuit; but it is of no theoretical importance when a battery is used.

3. The essential difference between the coherer and the

crystal detector is that coalescence takes place readily in the first case and not in the second.

4. It is not necessary that the oxide film of some coherers should be removed by the current though this may happen.

5. In the crystal detectors the marked changes in the behavior of adjacent portions of the same crystal face are probably due to localized impurities.

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THE PRODUCTION OF AROMATIC HYDROCARBONS FROM PARAFFIN WAX

BY GUSTAV EGLOFF AND THOMAS J. TWOMEY

The cracking of paraffin wax into lower boiling hydrocarbons has been made a study of in a number of investigations which are widely quoted. The first workers in this field were Thorpe and Young,[1] who cracked paraffin wax by distillation under pressure. In the distillate there was identified pentane, hexane, heptane, octane, nonane, probably also decane and undecane, as well as amylene, hexylene, etc., up to nonylene. Gawalowski[2] has found recently that paraffin wax (m. p. 45° C) by prolonged heating in an autoclave may be decomposed into gaseous and liquid products which in both cases are said to belong to the ethylene and acetylene series. At any rate the decomposition oils contain also methane and homologues, cyclical saturated (naphthenes) and unsaturated hydrocarbons. Brooks and co-workers[3] cracked pure commercial paraffin wax at temperatures not exceeding 420° C and under 100 pounds' pressure, thus obtaining gasolene entirely aliphatic in composition. The phenomena of the decomposition of wax is also very familiar to those persons who have distilled crude petroleum, as well as to the refiners of the oil. The cracking of paraffin wax in the oil takes place usually between 300 and 400° C under ordinary conditions of distillation at atmospheric pressure. These conditions do not produce such extensive cracking as distillation under pressure and only yield increased amounts of kerosene and not an appreciable amount of gasolene.

There is found nowhere in the literature that aromatic hydrocarbons such as benzene, toluene and xylenes have been produced in the decomposition of pure paraffin wax. The

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[1] Liebig's Ann., 165, 28; Chem. News, 23, 174 (1871).

[2] Oesterr. Chem. Techn. Ztg., 70 (1910).

[3] Jour. Ind. Eng. Chem., 7, 180 (1915); Jour. Franklin Inst., 180, 653 (1915); Jour. Am. Chem. Soc., 38, 393 (1916).

products of the reaction were always found to be those of the aliphatic group. Special effort to find aromatic compounds, especially by Brooks and co-workers[1] showed that they were not produced by distillation under 100 pounds' pressure and 420° C.

In view of these results and the development of cracking processes for the production of benzene and toluene from petroleum at the present day, the question has arisen whether or not oils containing paraffin wax are suited for the production of benzene and toluene. That such oils are adapted for gasolene formation is universally accepted. If oils containing paraffin wax are to be used, it should be known if the wax is desirable, otherwise the wax should be removed.

The authors saw no apparent reason why benzene and toluene should not be formed when paraffin wax is cracked, provided the proper conditions for the formation reaction were obtained. It was realized that the decomposition of paraffin wax by distillation under pressure as conducted by other investigators would produce only aliphatic compounds since the proper conditions were not obtainable by this method. It was also recognized that other investigators were seriously handicapped by using this liquid-gas phase method of cracking which automatically fixes both conditions of temperature and pressure, as is well known from the laws of physical chemistry.

From a study[2] of the kinetics of the decomposition of the paraffin series, it is indicated that decomposition of paraffin wax would tend toward the formation of aromatic hydrocarbons such as benzene, toluene and xylene. The formation was also foreseen by Kramer and Bottcher.[3] In commenting on the work of Thorpe and Young, they stated that if a higher temperature had been used, the higher boiling olefins would have changed into benzene hydrocarbons but not naphthenes.

For this reason the cracking of paraffin wax by the gas

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[1] Loc. cit.

[2] Rittman: Jour. Ind. Eng. Chem., 7, 945 (1915).

[3] Ber. deutsch. chem. Ges., 20, 604 (1887).

phase method, that is, the cracking of paraffin wax by passing through a heated tube, was undertaken to confirm the authors' opinion that it is possible to form benzene, toluene and xylenes from paraffin wax under similar conditions which result in the formation of the same compounds from petroleum cracking. As might be expected, positive data to this effect were obtained. The results are interesting in that they show (1) that oils containing paraffin wax are adapted for the production of aromatic hydrocarbons as far as the wax is concerned, (2) that there is a close relationship between the members of the aliphatic and aromatic series of hydrocarbons, (3) that the production of aromatic hydrocarbons formed by the cracking of petroleum may not be ascribed entirely to the presence of compounds in the petroleum containing the phenyl radical, and (4) the advantage of cracking in the gas phase system for the obtaining of desired results.

For the experiments pure commercial paraffin wax, m. p. 47° C, and containing 0.05% of oil, was used. It was cracked by passing through a heated tube, in an apparatus which has been described in detail in other articles.[1] The wax was melted and placed in the lubricator in this condition. It was kept in this state by heating the lubricator gently with a flame. It was admitted to the cracking area at a constant rate of 246 grams per hour, a rate of flow which has been used in all of the experimental work on the cracking of oils.

Only two temperatures and pressures were employed —500 and 600° C and atmospheric and 150 pounds' pressure. The work was undertaken primarily for the purpose of showing that it was possible to produce aromatic hydrocarbons from paraffin wax and not in order to show the effect of temperature and pressure. These effects in view of the present knowledge of the cracking reaction may be readily deduced from the results produced by experiments at a few temperatures and pressures.

The accompanying tables show the effect of temperature

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[1] Rittman: Jour. Ind. Eng. Chem., 6, 472 (1914).

and pressure on the percent of recovered oil, the percent to 170° C of the recovered oil with the specific gravities, the distillation with gravities of the cuts of this light oil fraction, and the percentage of benzene, toluene and xylenes in the recovered oil as well as on the basis of wax required for the production.

TABLE 1

The Effect of Temperature and Pressure on the Percent of Recovered Oil

Temp.	Pressure	Percent recovered
500° C	Atmospheric	92.3
600° C	Atmospheric	46.3
500° C	150 lbs.	78.0
600° C	150 lbs.	39.7

TABLE 2

The Effect of Temperature and Pressure on the Distillate to 170° C and the Specific Gravity

Temp.	Pressure	Percent to 170° C	Specific gravity
500° C	Atmospheric	0.08	0.723
600° C	Atmospheric	15.40	0.762
500° C	150 lbs.	12.90	0.753
600° C	150 lbs.	28.80	0.830

TABLE 3

The Effect of Temperature and Pressure on the Specific Gravity and Percent of the Benzene Cut to 95° C, on the Specific Gravity of the Toluene Cut 95° C to 120° C and the Specific Gravity of the Xylene Cut 120° C to 150° C

Temperature	Pressure	Percent to 95°	Sp. gr.	Percent 95° to 120° C	Sp. gr.	Percent 120° to 150°	Sp. gr.
500° C	Atmospheric	0.0	—	0.0	—	0.0	—
600° C	Atmospheric	2.96	0.747	3.84	0.768	5.0	0.773
500° C	150 lbs.	5.80	0.762	3.14	0.788	1.8	0.790
600° C	150 lbs.	10.60	0.820	7.20	0.835	3.8	0.824

TABLE 4

The Effect of Temperature and Pressure on the Percent of Benzene, Toluene and Xylene in the Recovered Oil

Temp.	Pressure	Percent benzene	Percent toluene	Percent xylene
500° C	Atmospheric	0.0	0.0	0.0
600° C	Atmospheric	0.5	1.0	0.6
500° C	150 lbs.	1.5	1.3	0.5
600° C	150 lbs.	6.6	5.4	2.3

TABLE 5

The Effect of Temperature and Pressure on the Percent of Benzene, Toluene and Xylene on the Basis of Paraffin Wax Used for Their Production

Temp.	Pressure	Percent benzene	Percent toluene	Percent xylene
500° C	Atmospheric	0.0	0.0	0.0
600° C	Atmospheric	0.2	0.5	0.3
500° C	150 lbs.	1.2	1.7	0.4
600° C	150 lbs.	2.6	2.2	0.9

The analysis of the recovered oil was made by means of fractional distillation and specific gravities.[1] However, the benzene, toluene and xylene formed were also identified by chemical means. The fractions were first deolefinized completely with concentrated sulphuric acid, and then nitrated to the mononitro stage. The paraffins associated with the mononitro compounds were separated by dissolving the mixture in concentrated sulphuric acid. A two-layer system resulted —paraffins and a mixture of mononitro compounds and sulphuric acid. The mixture of sulphuric acid and mononitro compounds was then nitrated to the dinitro state. The dinitro compounds were washed free from acid, recrystallized from alcohol and then identified by means of their melting point.

No attempt was made to distil or analyze the fraction of

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[1] Rittman, Twomey and Egloff: Met. and Chem. Eng., 13, 682 (1915).

oil boiling above 170° C, as it was considered that no naphthalene or anthracene was formed.

At atmospheric pressure and 500° C under the conditions of the experiment, but very little cracking of the paraffin wax took place, and to all appearances what cracking occurred produced members only of the aliphatic series. Under the other conditions which were obtained, benzene, toluene and xylene as shown by physical and chemical tests were formed in appreciable amounts, although contaminated to a large extent by other compounds such as olefins and paraffins. The aromatic formation increased with increase of temperature and pressure. This phenomena is shown by all cracking experiments in the gas phase method.

The temperatures and pressures used in these experiments do not necessarily represent the critical temperatures and pressures for the formation of aromatic hydrocarbons from paraffin wax. They represent only a few of the many conditions possible for production. Due to the rate at which the paraffin wax was admitted to the tube, it did not necessarily reach equilibrium. With a lower rate of feed, conditions approaching the true equilibrium would have been obtained, and in this way, data would have been obtained from which the absolute conditions of temperature and pressure required for the formation might have been deduced. At the present time, we are not so intensely interested in this side of the question. Hence a rate was employed which has been made the standard for a comparative study of oils.

Compared to a distillate oil boiling between 250 and 350° C derived from Pennsylvania petroleum, the paraffin wax is not so stable, and does not produce as much benzene, toluene and xylene. No explanation is offered at the present time.

The results of this paper may be summarized as follows:

1. It is possible to produce benzene, toluene and xylene by the cracking of paraffin wax at 600° C and atmospheric pressure; and at 500 and 600° C and 150 pounds' pressure.

2. Under the same conditions of cracking aromatic hydro-

carbons also result from petroleum oils of the paraffin type.

3. That the formation of aromatic hydrocarbons produced by the cracking of petroleum may not be ascribed entirely to the decomposition of the constituents of the petroleum which contain the phenyl group.

4. That there is a very close relationship between the members of aliphatic and aromatic series of hydrocarbons.

5. That oils containing paraffin wax are adapted for the commercial production of benzene and toluene.

Pittsburgh Division
Aetna Chemical Co.
Pittsburgh, Pa.
April 9, 1916

WASHING PRECIPITATES FOR PEPTIZATION

BY HARRY N. HOLMES AND R. E. RINDFUSZ

The peptization of insoluble compounds has become an interesting part of laboratory work with colloids. A common annoyance in such work is the difficulty of removing adsorbed ions. Unless the precipitate can be purified its subsequent peptization is complicated.

The flocculent or semi-gelatinous ferric arsenate and ferric phosphate are examples of precipitates difficult to free from their adsorbed ions. In the course of an investigation on the peptization of these two compounds we found it necessary to develop a working method of securing rather pure ferric arsenate and ferric phosphate and we believe the results may be of value to those interested in colloids.

For peptization purposes we precipitated ferric arsenate of the formula $Fe_2(HAsO_4)_3$ by adding an excess of dipotassium arsenate solution to ferric chloride solution. The precipitate, transferred to the filter, could not be washed free from the excess of dipotassium arsenate or the potassium chloride. Even when fresh washings gave weak tests for the arsenate ion if the precipitate was allowed to stand for some time under water and then filtered the washings contained plenty of soluble arsenate. The fresh precipitate was flocculent or semi-gelatinous and light yellow in color. With washing on the filter the color deepened and the arsenate became almost gelatinous. Cracks developed. The physical condition of the ferric arsenate was very favorable to powerful adsorption of ions.

It was thought that the washing out of adsorbed ions could be facilitated if the precipitate was disintegrated by suitable mechanical means. Violent shaking with water and clean sand was tried with interesting results. Sea sand was sifted on a 60-mesh screen and the grains sifting through rejected. The rest was heated with pure 6 *N* hydrochloric acid for ten hours on the water bath. The acid was changed three times and finally washed out with water. This treatment removed most of the magnetite.

In all our experiments the ferric arsenate was precipitated by adding 30 cc of a solution of dipotassium arsenate containing 1.7226 grams of arsenic and 10 cc of solution ferric chloride containing 0.1396 gram of iron to 160 cc of water. These proportions insured the presence of a large excess of dipotassium arsenate. For the sand shaking experiments the total volume of 200 cc, precipitate and all, was placed in a 500 cc cylinder with 10 grams of the clean sand. The cylinder was rubber stoppered as glass stoppers permitted sand to work in between stopper and neck. The shaking (by hand) continued for three minutes at a uniform rate of 100 shakes per minute. After standing over night, or 14 hours, 100 cc of the clear supernatant liquid was drawn off with a pipette, filtered and the filtrate analyzed for soluble arsenate. The filter paper was then perforated and any small particles of ferric arsenate washed back into the 500 cc cylinder with 100 cc of water. This maintained the volume of 200 cc exclusive of the 10 grams of sand. The operation of shaking for three minutes, letting stand one hour to settle, removing 100 cc of clear supernatant liquid, filtering, analyzing the filtrate for soluble arsenate and replacing the 100 cc by enough water to maintain the volume at 200 cc was repeated ten times. At this point it was necessary to let the material stand over night, or 14 hours. The usual operation was repeated ten times the next day. The last time the contents of the cylinder were thrown on the filter paper and the filtrate analyzed for the twentieth determination. It was not difficult to tilt the cylinder so that the wet sand stuck to the wall while the precipitate ran out.

The results are tabulated with those of similar experiments in shaking without sand, in decanting without shaking and in washing the precipitate on the filter paper. The procedure for the shaking without sand was exactly the same as above. The disintegrating action of the sand was absent but the results show considerable breaking down of the larger masses of ferric arsenate.

The experiments with washing the precipitate on the filter took less time. The 30 cc of potassium arsenate solution were added to 10 cc of ferric chloride solution and the mixture immediately thrown on the filter. Enough hot water was quickly poured on the filter to give 100 cc of filtrate. In practice about 75 cc was found sufficient. The aim in getting 100 cc of wash water was to make the different series comparable. This filtrate was set aside to be analyzed for soluble arsenate. As soon as 100 cc of wash water ran through 100 cc of hot water was immediately added to the ferric arsenate on the filter paper. This was continued for twenty washings allowing no time to elapse between washings. All these wash waters were analyzed at the same time.

In the decanting series the 200 cc total volume of precipitate and solution was allowed to stand over night or 14 hours. There was no shaking, merely the stirring caused by pouring one solution into the other. With a pipette 100 cc of clear supernatant liquid was drawn off, filtered and analyzed for soluble arsenate. As usual, a hole was punched in the filter paper and any traces of ferric arsenate washed back into the cylinder with 100 cc of water. This restored the original volume of 200 cc. After settling for an hour another 100 cc of clear liquid was removed by the pipette and the whole procedure repeated hourly for ten washings or decantings. For the eleventh the precipitate settled over night or 14 hours. Ten more hourly decantings the next day gave a total of twenty wash waters to analyze for arsenate. For the twentieth washing the usual 100 cc of water was not added but the cylinder emptied on the filter. About 85 cc filtered through and this was analyzed.

In all these experiments hot water was added. The method of analysis used was the precipitation of silver arsenate, its solution in nitric acid and titration with ammonium thiocyanate using ferric alum as an indicator.

In the following table the amount of arsenate removed by each washing is added to the amount removed by all previous washings. In other words, each number represents the total amount removed up to and including that treatment. No. 3, for example, represents the total amount of arsenate removed by the first, second and third washings.

Table I

Increasing Totals of Adsorbed Potassium Arsenate Removed by Successive Washings

Estimated as Arsenic

No.	Shaking with sand Grams	Shaking without sand Grams	Washing on filter Grams	Decanting without shaking Grams
1	0.6683	0.6218	0.9856	0.5362
2	1.0180	0.9793	1.2561	0.8145
3	1.1944	1.1627	1.3276	0.9441
4	1.2861	1.2591	1.3548	1.0356
5	1.3366	1.3112	1.3662	1.0994
6	1.3655	1.3422	1.3699	1.1475
7	1.3816	1.3600	1.3730	1.1836
8	1.3926	1.3710	1.3753	1.2106
9	1.4004	1.3791	1.3776	1.2318
10	1.4060	1.3850	1.3804	1.3460
11	1.4102	1.3999	1.3838	1.2569
12	1.4129	1.3935	1.3857	1.2659
13	1.4160	1.3967	1.3869	1.2709
14	1.4188	1.3995	1.3883	1.2754
15	1.4212	1.4023	1.3899	1.2798
16	1.4244	1.4046	1.3913	1.2825
17	1.4266	1.4065	1.3938	1.2851
18	1.4290	1.4084	1.3953	1.2879
19	1.4304	1.4102	1.3966	1.2907
20	1.4324	1.4118	1.3983	1.2943

Naturally the first "Washing on the filter" removed much more than the other treatments because most of the wash water filtered through. In the other experiments only half of the wash water was removed each time. In spite of this on the seventh treatment the total amount of adsorbed but soluble arsenate removed was greatest in "Shaking with sand" series and this lead was maintained to the end. The total removed in twenty treatments was 1.4324 grams (estimated as arsenic) by the "Shaking with sand" series, 1.4118 grams by the "Shaking without sand" series, 1.3983 grams by the "Washing on filter" series, and 1.2943 grams by the "Decanting without shaking" series. The excess arsenic to be washed out was 1.4371 grams.

It is evident that to secure the purest precipitate of a flocculent or semi-gelatinous nature the method of shaking with sand and water is the most effective. For rapid work in securing only a moderately pure precipitate the usual method of washing on the filter is probably most satisfactory.

The results of the preceding experiments suggested three more. Using the same quantities of potassium arsenate and ferric chloride solutions as before, enough water was added to make the total volume 1900 cc. This was shaken in a flask with 10 grams of clean sand as previously described and transferred to a tall cylinder. The flask was rinsed twice with 50 cc of water, making the total volume 2000 cc. After settling 12 hours 1800 cc of the clear supernatant liquid was drawn off and analyzed as usual. The removal of 1.2147 grams of soluble arsenate (estimated as arsenic) was more effective than in any of the previous experiments for the first treatment. Of course the gain was due to the removal of nine-tenths of the arsenate solution as compared with half in the other experiments. Such a fraction was not possible with a total volume of 200 cc because the flocculent precipitate occupied too great a volume.

An experiment similar to the above, using a volume of 2000 cc but without sand as a disintegrator, showed the removal of 1.1826 grams of the excess arsenate in a single treatment, also a much better showing than those in the table.

The final experiment was the addition of 10 grams of clean sand and 80 cc of water to the usual 40 cc volume of the mixed potassium arsenate and ferric chloride solutions. This was then shaken as indicated and everything but the sand thrown on a large filter. The filtrate, 100 cc., was analyzed and showed the removal of 1.2687 grams of excess arsenate. This extremely effective removal of adsorbed ions was plainly due to the disintegrating effect of the shaking with sand.

The conclusion is that the colloid student anxious to free a flocculent precipitate from adsorbed ions has two good methods at his disposal. The precipitate may be shaken in a large flask with nearly two liters of water, transferred to a tall cylinder, let settle over night, all the clear supernatant liquid removed and the treatment repeated as often as desired.

A better method is to shake the precipitate with a few grams of clean sand and as much hot water as the filter paper will hold, throw everything but the sand on the filter to drain, again transfer the precipitate to the shaking bottle, add hot water, shake, filter and repeat as many times as may seem necessary. This is the most rapid and the most effective method. If desired, the shaking may be managed without the sand. The washing will still be very rapid and effective.

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THE RELATIVE DENSITIES OF ALKALI-METAL AMALGAMS AND MERCURY[1]

BY JAMES R. WITHROW

Attention is called to erroneous impressions, concerning the relative densities of alkali-metal amalgams and mercury, which are encouraged by descriptions of the preparation of such amalgams in the literature and standard handbooks.

Arlt,[2] F. W. Goldby,[3] Nernst[4] and Kerp,[5] each used a falling stream of mercury as cathode in producing alkali amalgams. Kerp was aiming at the production of a solid alkali amalgam by ultimately separating the spongy mass, a mixture of solid and liquid amalgam, which he obtained in the receiver of the apparatus, by means of a Gooch crucible. He[6] gives an illustration of his apparatus. A noticeable feature of this illustration is that the solid potassium amalgam is pictured and *labeled,* as settling or collecting in the bottom of the receiver *beneath* the layer of mercury and dilute amalgam. Later E. S. Shepherd[7] described his lecture table experiment for the production of solid sodium amalgam in which he uses a special device to overcome the fact, pointed out by him, that sodium amalgam is *lighter* than mercury and floats on the top. Shepherd cited the work of Kerp but did not call attention to the anomalous behavior imputed to potassium amalgam by the latter. Although Shepherd's work should raise serious question concerning

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[1] Contribution from the Chemical Laboratory, The Ohio State University.

[2] A Process and Apparatus for Effecting Electrolysis. (Liquid Electrodes.)

[3] From O. Arlt, Goerlitz, Germany, Eng. Pat. 15,129, July 8 (1896); Jour. Soc. Chem. Ind., 16, 908 (1896); Zeit. Electrochemie, 3, 300 (1897).

[4] Zeit. Electrochemie, 3, 309 (1897).

[5] Zeit. anorg. Chem., 17, 300 (1898).

[6] Ibid., 17, 301 (1898).

[7] Jour. Phys. Chem., 7, 29 (1903).

the relative densities of all alkali-metal amalgams and mercury, the Handbuch der anorganischen Chemie by Abegg[1] copies the picture given by Kerp just as he gave it in his original article, indicating that the solid amalgam settles to the bottom with a layer of dilute amalgam remaining above it.

There appear to be no actual values in the literature for the density of these various amalgams. The work of Maey,[2] tables from which appear in Abegg itself,[3] gives specific volumes for alkali amalgams of different concentrations, which are the only series of values in the neighborhood of the range of composition in Kerp's work. From these values densities may be calculated and it is seen that the heaviest potassium amalgam given (0.184 percent K) has a density of 13.3707, the heaviest sodium amalgam (0.103 percent Na) a density of 13.448 and lithium amalgam (0.0301 percent Li) of 13.5116 when mercury has a density of 13.5956. These values calculated from the work of Maey show the amalgams to be distinctly lighter than metallic mercury. These calculated values are for highly dilute amalgams which are probably solutions of solid amalgams in mercury so that an actual solid amalgam might be heavier than these specifically light dilute amalgams. That this is *probably* not true at any point appears from an inspection of Maey's complete table of specific volumes, which runs up to high alkali concentrations. The values become progressively greater, showing that the densities corresponding must get progressively lighter. No overlapping or displacement of the curve takes place as would be the case if any solid amalgam separating should contract sufficiently to make it specifically heavier than the mother liquor or more dilute amalgam. Vanstone[4] condemns Maey's results as not accurate, but like Shepherd, he worked with sodium only and gives but one observation in the neighborhood of Kerp's operation zone. The results

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[1] Vol. 2 II, 579.

[2] Zeit. phys. Chem., 29, 127 (1899).

[3] Vol. 2 II, 582.

[4] Chem. News, 103, 207 (1911).

over Vanstone's whole range, however, agree so closely with Maey's that they do not alter the above deductions from Maey's results. For instance, a recalculation of Vanstone's data for his heaviest amalgam (2.26 percent Na) which was a solid amalgam, gives a density of 11.733 at 17° C, which is much lighter than mercury and confirms Shepherd.

These apparent contradictions of the illustrations in the work of Kerp and Abegg do not insure that even some outside factor was not reversing the probable natural properties of these amalgams in Kerp's case. Elevation of temperature might possibly reverse the relative densities of mercury and some of these amalgams. There is perhaps no reason why there should not exist some alkali amalgams heavier than mercury, but in the writer's experience with these amalgams he has never noticed such cases. Isolated crystals of amalgam, for instance, might grow attached to the walls or bottom of the vessel and beneath the mercury, in spite of their lighter density. A spongy mass of mixed solid and liquid amalgam might appear to rest on the bottom.

When, in investigating these possibilities, one placed the mercury and amalgam mixture in a suitable vessel and forced his hand or a scoop below the surface, he could feel the pasty amalgam at or just under the surface, and could lift some of it out. Solid alkali amalgam, both potassium and sodium, made by the method of both Kerp and Shepherd, in pieces an inch or more in diameter were placed in mercury. These firm pieces floated in the mercury like ice in water and are distinctly visible, projecting just above the surface, and can be felt with a rod or the finger for the mercury is not transparent as is the liquid in the ice and water case. When the solid amalgam is in isolated crystals or paste form it does not project above the surface of the mercury. No grounds of any kind were, however, found for assuming that solid amalgam ever stayed on the bottom beneath a layer of mercury or dilute amalgams. The ease, however, with which amalgam adheres to glass could readily deceive one into thinking when he poured out a mixture of solid and liquid amalgam, that the solid amalgam adhering to the sides and bottom of the vessel had always been there and therefore was heavier than mercury.

The fact that sodium amalgam is distinctly lighter than metallic mercury has long been the conscious basis of experimental effort among industrial chemists who have worked in the field of mercury cathode cells. This rising of sodium amalgam to the top, in a mixture with mercury, causes certain engineering difficulties in the otherwise simple manipulation of the Castner-Kellner Processes for making sodium hydroxide. Great trouble is encountered in endeavoring to circumvent the difficulties caused by this very fact. Complicated industrial chemical machines have been devised to overcome this factor, such, for instance, as the Whiting Cell,[1] which operates on the separatory funnel principle, or the Wildermann Cell, and others.

The recalculated data of Maey's are so well supported by the experiments presented here, as to indicate strongly that potassium amalgam is not anomalous in its effective density but, like sodium amalgam, is lighter than mercury. It seems, therefore, that when a book of the value of Abegg assists in giving the impression that solid amalgam settles to the bottom, attention should be called to the matter.

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[1] Trans. Am. Electrochem. Soc., 17, 327 (1912).

A MODIFIED VICTOR MEYER APPARATUS FOR THE DETERMINATION OF VAPOR DENSITIES

BY HARRY B. WEISER

The apparatus commonly used in the Victor Meyer displacement method of determining vapor densities consists of a cylindrical bulb of about 100 cc capacity attached to the end of a long tube. Near the upper end of the latter a side tube is attached which serves to conduct to a measuring vessel the air expelled during a determination. The bulb and a portion of the long tube are surrounded by a jacket in which a suitable liquid is boiled for regulating the temperature of the enclosed tube. The assembled apparatus is almost four feet tall exclusive of the eudiometer tube in which the expelled air is caught. Because of its height the apparatus is open to certain objections, the most serious of which is that it is very inconvenient to operate on the ordinary laboratory table.

Schwarz[1] has modified the Victor Meyer apparatus in such a way as to overcome this objection by employing a combustion furnace containing a deep iron trough fitted with a lid in which is placed a wide combustion tube closed at one end and connected at the other with the apparatus for collecting the displaced gas. In making a determination the temperature of the furnace is first allowed to become constant, after which the weighed substance is introduced in a boat into the front cold part of the tube, the cork replaced and the front end of the furnace raised so as to allow the boat to slide down into the hot portion of the tube, where vaporization takes place. This modification is not so good either in principle or applicability as the original apparatus. In a vapor density apparatus of this type, it is desirable to have a large gas space and a small neck space in order to minimize diffusion. For this reason also the vertical is preferable to the horizontal position. It is particularly important to have a constant

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[1] Ber. deutsch. chem. Ges., 16, 1051 (1883).

temperature and for easily decomposable substances it is advantageous to know that temperature. The temperature of an air bath is not so easy to control or regulate as that of a steam jacket and whenever possible a transparent jacket is to be preferred. The conditions mentioned are more completely fulfilled in the original Victor Meyer apparatus than in the Schwarz modification and render the latter less suitable than the former except in special cases.[1]

A compact modification has been devised by Harrington.[2] Two forms similar in principle were constructed. In one the cylindrical bulb in which vaporization of the substance takes place is horizontal and the long tube is bent upon itself a half dozen times; the other is similar except that the bulb is vertical. While such a construction obviously shortens the apparatus it does it by increasing the width to such an extent that it is not feasible to regulate the temperature by enclosing it in a glass jacket in which a suitable liquid is boiled. Instead the apparatus is enclosed in a box of copper or tinned iron. This opens it to certain of the same objections as the Schwarz apparatus and renders it less applicable than the original. However, it possesses the distinct advantage of being compact.

An apparatus has been designed and used in this laboratory which is not only more compact than the Harrington modification but possesses all the other desirable features of the original Victor Meyer apparatus along with certain additional advantages. The form of the apparatus is shown in Fig. 1.

A is the vaporization bulb which is 3 cm in diameter and 24.5 cm in length. The volume is approximately 125 cc exclusive of the space occupied by the tube B. The latter which corresponds to the stem attached to the top of the vaporization bulb in the original Victor Meyer apparatus is 0.9 cm in diameter and 51 cm in length from C to D where the capillary delivery tube E is attached. It is sealed into A at F and at C it is constricted to about 3 mm to prevent the

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[1] Cf. V. Meyer: Ber. deutsch. chem. Ges., 17, 1334 (1884).

[2] Am. Jour. Sci., (4) 20, 225 (1905).

little vial of substance whose vapor density is to be determined subsequently, from dropping into B. The bend at G is made so that B is close to A in order to make the apparatus firm and strong. The neck H is 4 cm in length and shaped as shown. The lower portion is 1 cm and the upper portion 1.3 cm in diameter. This is supplied with a one-hole stopper that extends at least 1 cm into E. In the hole in the stopper is inserted a short capillary stopcock tube I, that ends exactly flush with the bottom of the stopper. The stopcock of a broken burette will serve for this purpose. This portion of the apparatus is supported in the outer jacket J by the narrow snug-fitting cork K. Holes are bored to fit H and E and a groove is cut in the top in which the horizontal portion of E rests. An exit tube for steam is also supplied. The cork is then split vertically, the tubes inserted and the two portions fastened firmly together by a wire around the top. The jacket is about 6 cm in diameter and 32 cm in length preferably with a bulb blown on the end, although this latter is not essential. The jacket designed by Henderson[1] which utilizes a straight tube of suitable diameter and a beaker would serve admirably in place of J.

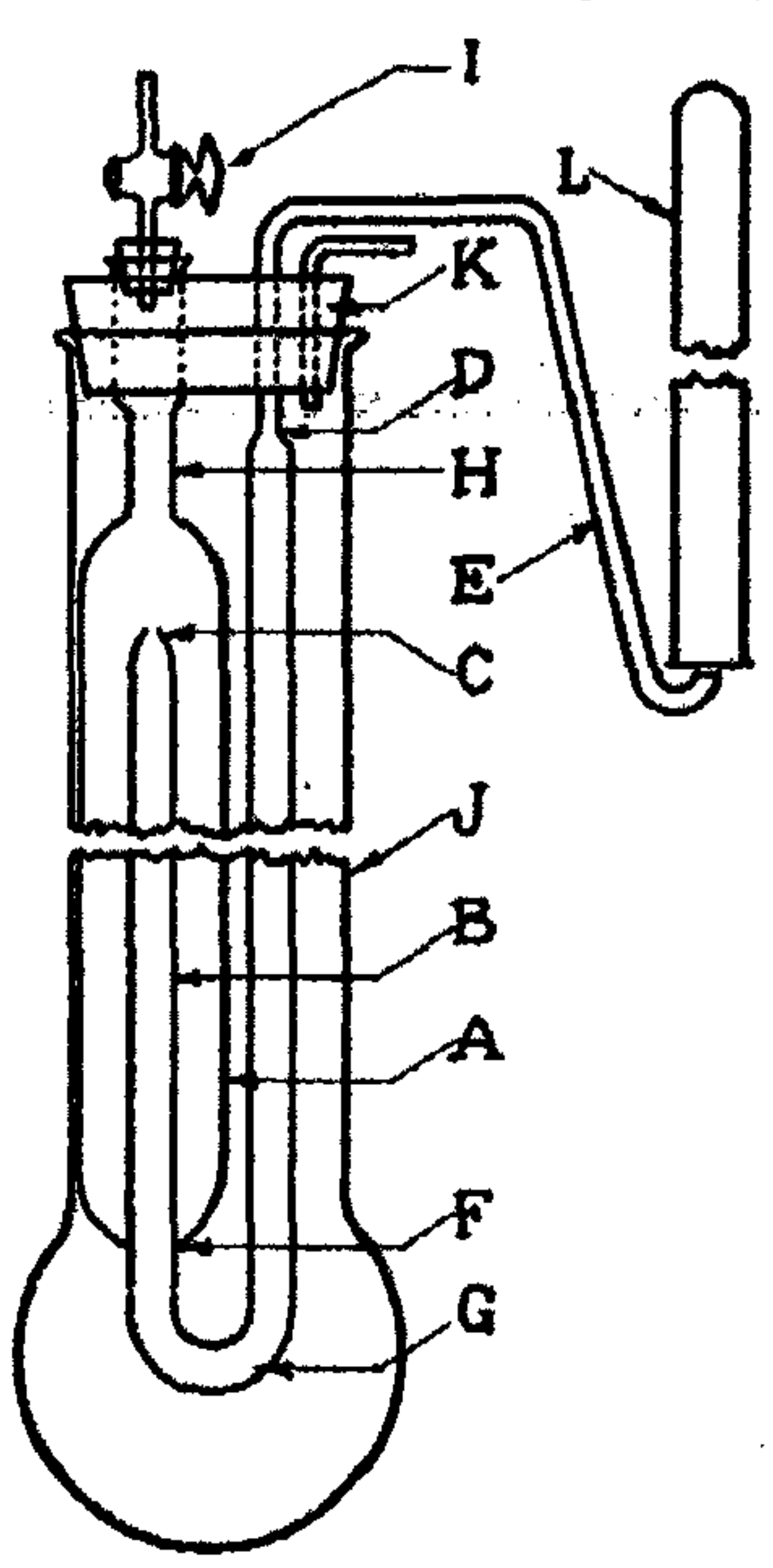

Fig. 1

A determination is carried out in the following manner: The bulb of the jacket is filled two-thirds full of water (or other liquid suitable for the specific determination), and is supported on a wire gauze out of the region of air currents. The inner tube is adjusted and a beaker of water is so arranged that the end of the delivery tube E dips into the surface of the water. A graduated tube L filled with water is inverted

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[1] Jour. Am. Chem. Soc., 34, 522 (1912).

in the same beaker and is clamped near the delivery tube in such a way that it can be easily and quickly moved over the tip. After inserting the stopper in the inner tube and closing the stopcock the water is started to boil and this is continued regularly until there is no visible condensation within the jacket and no bubbles of air are forced over through E. The measuring tube is then adjusted, the stopcock opened, the stopper removed and the sample contained in a little glass-stoppered vial dropped into A. The stopper is inserted immediately and the stopcock turned off. The bottle falls to the bottom of A where the sample vaporizes and drives air from B and the upper part of A into the measuring tube.

Another procedure may be followed for introducing the sample in case no stopcock is employed in the stopper. This consists simply in dropping in the vial with one hand and immediately inserting the stopper with the other, after which the eudiometer tube is quickly moved over the tip of E and finally adjusted firmly. This latter method has one slight advantage in that the inserting of the stopper forces a few bubbles of air over through E and in consequence empties it of water so that at the beginning and at the end of the experiment E is filled with air. If the former method is employed that portion of E immersed in the water and an additional portion due to capillarity, is filled with water at the beginning and with air at the end of the determination. The error introduced in this way is not great, however, since the tube E is of capillary dimensions. The closing of the apparatus without forcing any air through E is accomplished somewhat more quickly by the use of the stopcock.

Several methods have been recommended for the introduction of the sample into the vaporization tube without opening the apparatus.[1] Since one of the above procedures ordinarily suffices, these only complicate the apparatus and are of doubtful value except in special cases. In case the boiling point of the substance whose vapor density is to be determined,

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[1] L. Meyer: Ber. deutsch. chem. Ges., 13, 991 (1880); Bott and Macnair: Ibid., 20, 916 (1887); Bitz and Meyer: Zeit. phys. Chem., 2, 189 (1888).

is so low that a sealed tube instead of a glass-stoppered vial must be employed for introducing the sample, the device used by Chapin[1] is particularly commendable. By extending H a few centimeters outside of the jacket the Chapin device could be used with the apparatus described in this paper for the special case of a very low boiling liquid, since vaporization would be so rapid under these conditions that no diffusion would take place into the unjacketed portion of the tube.

The apparatus described has many decided advantages:

It is simple in construction, compact and easy to operate.

The entire inner tube with the exception of a portion of the capillary delivery tube is surrounded by the vapor jacket so that the air contained in the apparatus can be brought to the same temperature throughout, before the introduction of the sample. This is not the case in the original apparatus since a portion of the inner tube is not immersed in the jacket and the air in this portion is colder. Consequently the expelled air in the latter case is not all at the same temperature which introduces an error that is eliminated in the modified apparatus. It is further advantageous to have the inner tube completely jacketed in order to minimize any danger of diffusion and subsequent condensation of the vapor of the sample in a cold portion of the tube.

The time required to bring the air in the inner tube to the same temperature as the vapor in the jacket is much longer in the tall apparatus than in the compact one. Experience has shown that in the old apparatus about 45 minutes of constant boiling are required while in the modified one not more than 15 minutes are required.

It is necessary to place a pad of asbestos fiber or glass wool in the bottom of the tall vaporization tube in order to secure it against breakage when the little vial is dropped into it. This precaution need not be taken in the shorter apparatus and in consequence cleaning is facilitated.

The following series of molecular-weight determinations

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[1] Jour. Ind. Eng. Chem., 4, 684 (1912).

made with the apparatus show that very consistent results are obtainable. Pure chemicals were employed and were redried and redistilled before making the determinations. Particular care was taken to remove all vapor from the vaporization tube after each determination. Failure to do this is a frequent source of error.

Correction was also made for the water vapor in the air which filled the apparatus at the time determinations were made. In determining vapor densities by the Victor Meyer method it is usual to correct for the vapor tension of water when correcting the volume of the expelled air to standard conditions. Evans[1] has pointed out that this is correct only when the original air in the apparatus is quite dry, a condition which rarely obtains provided, as is usually the case, the apparatus is filled with the air of the room. If the air is moist, the corrected barometric pressure is $B - \left(\frac{100 - H}{100} \cdot w\right)$, in which B is the barometric reading, H is the percentage saturation at room temperature and w the pressure of aqueous vapor.

In the following tables S represents the weight of sample taken, V the volume of expelled air at a temperature t and a barometric pressure B. H is the relative humidity of the air of the room with which the apparatus is filled, V_0 the volume corrected to standard conditions and M the molecular weight. In the last column is given the percentage deviation from the theoretical molecular weight.

TABLE I

Benzol (78)

S	V	t	B	H	V_0	M	Percent error
0.0869	26.50	23.8	763.9	60	24.17	80.4	3.0
0.0879	27.13	24.4	768.6	50	24.81	79.2	1.0
0.1039	31.83	24.3	762.3	49	28.87	80.6	3.0
0.0877	27.45	25.0	762.2	44	24.78	79.2	1.0

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[1] Jour. Am. Chem. Soc., 35, 958 (1913).

Table II
Chloroform (119.38)

S	V	*t*	B	H	V_0	M	Percent error
0.1489	31.30	25.6	762.8	34	28.11	118.3	0.9
0.1748	36.36	23.1	770.0	40	33.40	117.3	1.7
0.1734	36.92	26.0	758.0	62	33.19	117.1	1.8

Table III
Methyl Alcohol (32.0)

S	V	*t*	B	H	V_0	M	Percent error
0.0596	45.40	23.5	770.1	44	41.57	32.1	0.3
0.0575	43.61	24.0	769.1	48	39.95	32.3	1.0
0.0559	43.52	25.2	760.4	38	39.09	32.05	0.0
0.0557	43.98	25.6	760.0	38	39.40	31.7	1.0
0.0490	38.58	25.2	758.1	56	34.74	31.6	1.2

Table IV
Diethyl Ether (74)

S	V	*t*	B	H	V_0	M	Percent error
0.0655	22.20	25.0	758.0	54	19.99	73.4	0.8
0.0752	25.62	26.0	758.1	60	23.02	73.2	1.1
0.0763	26.20	26.0	758.1	62	23.56	72.6	2.0

Table V
Ethyl Acetate (88)

S	V	*t*	B	H	V_0	M	Percent error
0.1071	29.60	21.5	773.0	40	27.49	87.3	0.8
0.0915	25.34	21.6	772.4	38	23.5	87.3	0.8
0.0911	25.56	21.7	772.0	38	23.68	86.2	2.0
0.1068	28.90	19.0	774.0	45	27.19	87.9	0.01

The above series of molecular-weight determinations show that even better and more consistent results are obtainable with the modified apparatus described than with the original.

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NEW BOOKS

Color and Its Applications. *By M. Luckiesh. 24 × 17 cm; pp. vii + 357. New York: D. Van Nostrand Company, 1915. Price: $3.00.*—The aim of this book is to present a condensed treatment of the science of color. The chapters are entitled: light; the production of color; color mixture; color terminology; the analysis of color; color and vision; the effect of environment on pigments; theories of color vision; color photometry; color photography; color in lighting; color effects for the stage and displays; color phenomena in painting; color matching; the art of mobile color; colored media. The following extracts, pp. 70, 78, 118, 148, 160, 169, 252, 276, will give some idea of the contents of this very interesting book.

"The quality of any color can be accurately described by determining its hue, saturation or purity, and its brightness. (The latter term is analogous to the term 'value' as used by the artist.) In the broadest sense, white, gray, and black are here considered as colors, and a mere change in brightness alone is considered as a change in color. It appears necessary to assume this broad definition of color, inasmuch as brightness is distinctly one of the products of color analysis. Hue is suggested in the name applied to the color. The dominant hues of most colors are accurately represented by the spectral colors; however, there are composite colors—the purples, which consist of red and violet, for which no spectral colors are found to represent their hues. In these cases it is satisfactory to determine the dominant hue of the complementary colors. The saturation or purity is a measure of the relative amount of white light in the color. In other words, all colors excepting purples can be matched by diluting spectral light of a definite wave-length with white light. The greater the percentage of white light required in the mixtures, the less saturated the colors are said to be. The brightness of a color can be found by comparing it by means of a photometer with a surface of known brightness. It is well to note that in the analysis of a color its absolute brightness is measured by comparing it with a brightness of known value. Inasmuch as its brightness depends upon the intensity of illumination of a given spectral character, its reflection coefficient for a standard white light should be determined in order to compare it with other colors in this respect."

"Other sciences have exact and practically universally accepted terminology. Music has its well-developed notation, which is definite and descriptive [not when one considers tone] and quite universal in adoption; but there is no universal scheme of color notation. Colors are named in very inexact, unwieldy, and often totally non-descriptive terms. We have rose, Indian red, Alice blue, pea green, olive green, cerise, taupe, baby blue, Copenhagen blue, king's blue, royal purple, invisible green, etc. Thus flowers, vegetables, cities, the savage and the royal family, are used to describe colors. Is there a more ridiculous instance of neglect? Those who work in color find themselves helpless in describing colors to others. Surely a color notation based upon color science should be acceptable, even though somewhat empirical. Musical notation is somewhat arbitrary, yet it has met with almost universal adoption. An acceptable color notation must involve the factors which influence the quality of a color, namely hue, saturation, and brightness."

"A very striking experiment is found in focusing a line spectrum—that of mercury will suffice—upon a ground glass. On viewing it at normal distance (14 inches), the yellow and green lines will appear sharply focused, but the blue and violet lines will appear hazy,and quite out of focus. On bringing the eye closer the latter lines will begin to appear clearer, and finally, when the eye is within about six inches of them, they will still appear clear-cut, while it will be quite impossible to accommodate the eye sufficiently to focus the yellow and green lines. In other words the eye is near-sighted (myopic) for blue rays and far-sighted (hyperopic) for red rays. On viewing a narrow continuous spectrum at some distance the blue appears to flare out. Another simple demonstration is found in viewing an illuminated slit through a dense cobalt glass which transmits extreme red and violet rays. On accommodating the eye for a point behind the slit a red image with a violet halo is seen. On accommodating for a point in front of the slit a violet image with a red halo is seen. This defect plays a prominent, though usually unnoticed, part in vision. A lens can be made practically achromatic by combining a convergent lens of crown glass with a divergent lens of flint glass. The former is more strongly convergent for blue than for red rays, while the latter is more strongly divergent for blue than for red lights. It is thus possible to bring the red and blue rays in coincidence at a focus. Inasmuch as it is only possible to bring two rays exactly into coincidence by a two-piece lens, such a lens is not truly achromatic, though practically so for most purposes."

"It is interesting to note that on a certain modern battleship a lighting system of blue lamps has been installed for use at night when in action. The reason given for installing blue lights is that they are invisible to the enemy. No information was obtainable as to whether the short range is due to the faintness of the blue lights or to a supposed lower range for blue than for yellow light of equal intensity."

"In using field glasses, distant vision can be improved sometimes by the use of a light yellow screen which eliminates the blue haze from the visual image. In connection it is well to note also that blue rays are normally out of focus at the retina. The author has experimented with colored screens for use with field glasses for detecting colored objects at a distance by altering their contrast with their surroundings by the use of colored screens. For instance a khaki uniform (yellow-orange in color) can be made to appear either lighter or darker than the green foliage surrounding it by respectively using a yellow-orange screen or one of a complementary hue. For instance if the ratio of the brightness of a piece of khaki cloth to that of a certain green leaf be taken as unity under daylight illumination, through an ordinary orange filter this ratio became 1.5 and through a blue-green filter, 0.7. With care the contrast can be made practically a maximum. In the case of objects more striking in color the problem is not as difficult. Whether or not the reduction of brightness more than offsets the advantage of increased contrast in distinguishing distant objects can be solved by actual trial. The point is mentioned here to illustrate the possibilities in the use of colored glasses as an aid to vision."

"Owing to the surface character of colored media the distribution of light is of some importance in the consideration of the appearance of colors. Few pigments are applied in such a manner as to be perfectly diffusing, therefore some light is specularly reflected without having penetrated the pigment. This light is unchanged by selective absorption and dilutes the light that is colored by penetrating the pigment and being selectively reflected. That is, when the light is distributed in such a manner that an appreciable amount is specularly reflected into the eye of the observer the color appears less saturated. In the extreme case of high specular reflection the pigment appears the same as a gray. A striking illustration of the effect of distribution of light is found in the case of the so-called changeable silks. Such fabrics have a nap, and when the fibers end in the direction toward the light the latter penetrates the fabric and is deeply colored by multiple selective reflections. The light that comes from other directions is more or less specularly reflected, thus undergoing less change by selective absorption, with the result that various portions of the surface appear differently. Adding to the foregoing another property of aniline dyes and the colors of changeable silks are accounted for. For instance, a dye which in solution appears pink or purple in color is often found to reflect green light predominantly in the solid state. Thus the specularly reflected light in the case of the changeable silk is sometimes roughly complementary to the light that penetrates the fabric and is returned after multiple reflections which in effect correspond to traversing a certain depth of an aqueous solution of the dye. A color will often appear different by reflection than when examined 'over-hand' by looking through the fibers by glancing along the surface at a grazing angle."

"North rooms, or those shielded from direct sunlight, are in general more satisfactory when colored in rose, cream, yellow, buff—the 'warm' colors. Yellowish tints in the window curtains aid in giving the effect of sunshine. On the sunny side, rooms will be more satisfactory when colored pale blue, gray-green, or shades and tints of other 'cool' colors. In introducing color into the illuminant by means of colored shades or lamps, the color scheme of the room should be considered. Apparently many prefer bright red wall coverings, if one may draw conclusions from observations. This again is a matter of personal taste, but extremely pure and bright colors in lighting effects in interiors are to the author like living with a brass band. Many of the lighting effects in pure colors certainly arise from a lack of study of the use and influence of color. If a room is decorated for natural lighting theoretically it should receive the same artificial lighting both as to direction and spectral character. Yet the change in the lighting—from natural to artificial—may be just the thing to relieve monotony. There are many statements on this subject that cannot be reconciled with the facts. For instance, a person may be satisfied with daylight living under it from day to day without any other comment than that it is ideal. The same person, however, may object to the increasing 'whiteness' of modern artificial illuminants. He insists that we must go back to the color of the carbon incandescent lamp or even further to that of the candle flame. Is there a dual standard? Can daylight be satisfactory and the light of the tungsten lamp or Welsbach mantle be too 'white.' As a matter of fact modern illuminants used in ordinary interiors—the gas and incandescent filament lamps—are in the same class and far yellower than daylight that enters interiors. Color is certainly the keynote of lighting in many interiors, but let us not base its use upon incorrect premises. If we prefer 'warmer' colors in our artificial illuminants, let us have them, but let us attribute this desire to the proper cause which may be a love for change in color. Slight tints of rose and yellow may add something pleasing to the complexion, but deep yellow, orange, or red have an obliterating effect upon the flesh tints of the face. They also tend to make colors appear further from their daylight appearance than untinted artificial lights. Using color for color's sake is a legitimate procedure, and in the absence of sufficient physiological and psychological data the use of color must remain, for the present, largely a matter of taste."

"The modern tendencies toward the use of color and color effects point to great future possibilities in the application of the science of color. Already in some European theaters the stage scenery has been revolutionized, and lighting effects are playing a greater part in the drama than heretofore. The experiments described below suggest the possibility that rays of light, swift and noiseless, might take the place of some of the present-day cumbersome methods of scene-shifting. Possibilities are also suggested for representing the supernatural, heretofore unrealized on the stage. In Fig. 114 are shown, as well as can be represented in black and white, two appearances of a mountain scene. The mountain and entire background can be made to disappear at will by changing the color of the illuminant. The appearance on the left is that under the ordinary yellowish light from tungsten incandescent lamps. The other appearance is that under an orange-red light. The colors in the foreground are violets, grays, blues, greens, and touches of yellow. Those in the background are white, yellow, orange, red, and pink. Lighting effects can be obtained by flashing reddish light on the painting. No attention was paid to the congruity in the use of colors, for the painting was designed merely to illustrate the possibilities of the scheme. Further striking effects can be obtained by the use of illuminants of other colors especially pale blue-green light. Thus a scene can be changed by rays of light. It is also possible to make the mountain disappear and in its place to have some other scene appear, for instance a seascape.

"In Fig. 115 the first picture appears to be a Japanesque arrangement of foliage. This is the appearance under a deep orange-red light. Gradually, by introducing blue light, the figure appears, and on adding green light or clear light it appears fully in view. On extinguishing the red component in the illumination the figure, and especially the flowing robe, stands out in strong contrast and beautiful effects are produced by changing gradually from blue-green to a deep blue. By gradually introducing orange-red light and extinguishing the other components the figure slowly disappears. Such effects show the possibility in scenic effects, in fairyland plays. It is well to understand that the photographic reproductions just shown only illustrate the brightness contrast. In the originals the contrasts are more striking because they are due to differences in hue as well as in brightness. In fact, it is difficult to illustrate in black and white the effects produced with this particular subject, because in the center illustration most of the contrast is due to differences in hue alone.

"Another changing scene that was produced is that of a summer landscape gradually merging into a snowy wintry scene. By painting the body and branches of the trees a gray, and covering these and the ground with a bluish green foliage, they appear in their abundant garb of summer under ordinary light. By changing the color of the illuminant to a 'cold' pale blue-green the summer foliage disappears from the trees and from the ground, and barren trees and a ground covered with snow appears. These are the chief features of this scene. Of course touches of color added judiciously here and there greatly enhance the beauty of the scene. Many other effects have been produced, but no attempt has as yet been made in applying them on a large scale in stage scenery. However, the problem in the theater is comparatively simple owing to the perfect control of the illumination. Certainly the possibilities of such applications of the science of color are very extensive. Only the simpler ones have been described here, owing to the necessity for demonstrating the principle as simply as possible. The more elaborate effects require more perfect interrelation of colors and illuminants. A field not to be overlooked is that of legerdemain, in which such disappearing and changing effects should prove valuable."

Wilder D. Bancroft

The Physical Properties of Colloidal Solutions. *By E. F. Burton. 23 × 16 cm; pp. vii + 200. New York: Longmans, Green & Co., 1916. Price: $1.80.* In the preface the author says: "The present attempt to give an outline of the study of colloidal solutions has to do particularly with its interest to the student of physics. Both by aim and necessity the writer has kept in mind the relation of colloids to the development of physics. For this reason rather extended treatment is given to the development of the ultramicroscope and the confirmation of the kinetic theory of matter afforded by the theoretical and experimental study of the Brownian movement. When we come to deal with the phenomena of the charge possessed by the colloidal particle and the surrounding medium, and the mechanism of coagulation, we approach the most important problem of physics and chemistry, namely, the unfolding of the interaction of the ultimate particles of matter on one another."

In the introduction, p. 4, the author says: "The theoretical importance of colloidal solutions is wide-spread; to the physicist, probably their chief interest may be summed up under three heads. In the first place, the work of Einstein, Smoluchowski, and Langevin, in offering exact mathematical formulae whereby the Brownian movement may be quantitatively tested, and the investigations of Perrin on the distribution of the particles throughout the volume of a liquid, afford most striking evidence of the truth of the fundamental hypotheses of the kinetic theory of liquids and gases, and of the existence of the molecule. Secondly, Faraday's work on the optical effects of such solutions has been recently supplemented by many researches which have been attempted to solve the riddle of the form and structure of the particles. Thirdly, the perennial question as to the reason for the stability of these solutions remains. The various physical forces which may be involved—electrical attractions or repulsions, surface tension, molecular shocks—suggest a puzzle, the solution of which will undoubtedly give us most valuable information regarding the forms of energy involved in the liquid and solid states."

The subject is treated under the general headings: preparation and classification of colloidal solutions; the ultramicroscope; the Brownian movement; the optical properties of colloidal solutions; measurement of the sizes of ultramicroscopic particles; motion of colloidal particles in an electric field; the coagulation of colloids; theory of the stability of colloids; practical application of the study of colloidal solutions.

Though the book is published in 1916, the manuscript was apparently finished before the middle of 1914. Consequently there is no general theory, and the author states explicitly that attempts to account for the stability of suspensoids and emulsoids by the same theory have been so unsuccessful that we are forced to treat these as two distinct classes. The chief value of the book therefore is in showing what parts of colloid chemistry interest the physicist.

Wilder D. Bancroft

Rubber Machinery. *By Henry C. Pearson. 23 × 17 cm; pp. viii + 419. New York: The India Rubber World, 1915. Price: $6.00.* In the preface the author says: "For more than fifty years mechanical and inventive ingenuity has been producing machinery for use in rubber manufacture. In crude rubber washing, mixing and calendering the problems were once thought to be comparatively simple and their solution about the same the world over. Today, however, scores of new and more efficient machines handle new gums and intricate compounds, and the simplicity disappears. Even in the preparation of the crude material for market, machinery is to a marked degree supplanting hand labor."

The headings of the chapters are: the washing of crude rubber; crude rubber drying; dry-sifting and batching of compound ingredients; the mixing or compounding of rubber; preparing fabrics for calendering and spreading; calenders; clutches, drives, and safety stops for mills and calenders; molds, metal and rubber; vulcanizers, general types; vulcanizing presses, screw and hydraulic; tube making machinery; spreaders, doublers, and surface finishers; cement and solution machinery; extraction of rubber and gutta percha from shrubs, vines, roots and leaves; extraction of resin from rubber and gutta percha; reclaiming; temperature recording and controlling devices; rubber laboratory equipment.

The book is illustrated profusely, averaging slightly over one cut to a page. The reviewer cannot speak for the rubber manufacturer; but the book is certainly helpful to the student. Its value would be increased by a more complete index, and it is not quite clear why the chapters on vulcanizing should come before those on spreaders, etc. *Wilder D. Bancroft*

Le Hasard. *By Émile Borel. Second Edition. 19 × 12 cm; pp. iv + 312. Paris: Félix Alcan, 1914. Price: 3.50 francs.* In the statistical sciences we make great use of the theory of probability. We cannot predict with any accuracy how long any particular man will live; but we know the average length of life of a man and the insurance companies work out tables which are sufficiently accurate when applied to a large number of men. We cannot predict whether any given child is to be a boy or a girl but we know that out of a thousand children the probability is very strong of there being 510 boys. Throughout the biological sciences the theory of probabilities is of great value. The author points out that the kinetic theory of gases is chiefly a theory of probabilities and that its quantitative development really dates from the explicit recognition of this fact by Maxwell. The book is distinctly an interesting one, though its value lies more in the possible broadening of the point of view than in any concrete results that may be obtained from it. *Wilder D. Bancroft*

THE INFLUENCE OF STRONG SALT SOLUTIONS ON THE SPONTANEOUS OXIDATION OF PYROGALLIC ACID, FERROUS SULFATE AND FRUCTOSE

BY C. G. MACARTHUR

In one of Mr. A. P. Mathews' papers[1] on the oxidation of cystein, he states that upon the addition of salts to the solutions the rate of oxidation was decreased. He was uncertain whether this effect was caused by the salts decreasing the solubility of the oxygen or by a specific action of the salts on the oxidizing substance. At his suggestion this work was started to see which of these two theories was correct.

Method

The quantity of salt that would make a certain molecular concentration was dissolved in 50 cc. of $N/10$ sodium hydroxide. This was placed in a 400 cc. flask[2] that was provided with a ground glass stopper carrying a mercury thermometer and a glass cock. To this solution was added a definite amount of the substance to be oxidized. The contents were shaken rapidly in a mechanical shaker. The amount of oxygen absorbed was determined by the negative pressure in the flask as measured by the manometer. The barometer and thermometer were read at the same time as the manometer. The variations in temperature during any one experiment were not greater than one degree. As a rule the difference in temperature between any two experiments was not greater than three degrees. The results are not materially affected by these irregularities in temperature. During any experiment the barometric pressure did not vary more than two millimeters.

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[1] Jour. Biol. Chem., 6, 312 (1909).
[2] A. P. Mathews: Ibid., 6, 1 (1909).

In this work no attempt was made to work in concentrations of alkali that give maximum speeds. The amount of alkali that would give a desirable reading on the manometer in a reasonable period of time was chosen. This amount was kept constant during the experiments on any one oxidizable substance.

For the calculations of the velocity constant (k) it was assumed that one-fifth of the initial atmospheric pressure was due to oxygen. The oxygen pressure would therefore be about 150 mm mercury. The negative readings on the manometer subtracted from 150 indicate the millimeters of oxygen pressure remaining.

Though it is approximately true, as a rule, that the amount of oxygen dissolved in a solution is directly proportional to the oxygen pressure above the solution, it was noticed in these experiments that slight variations resulted from irregularities in shaking caused by changes in speed of the electric motor. This probably accounts for some of the irregularities in the data. It is believed, however, that the speed of shaking was great enough to keep the solution so nearly saturated at the then existing oxygen pressure that no serious errors were introduced.

The velocity constant was calculated from the monomolecular equation:

$$k = \frac{2.302}{t} \log_{10} A - \log_{10} (A - x)$$

In this expression t is the time in minutes, A the initial oxygen pressure (the barometric pressure divided by five), and x equals the manometer reading.

The values for the solubility of oxygen are to be found in a recent article on the solubility of oxygen in various concentrations of several of the ordinary salts.[1] The figures in the table are the number of cc of oxygen per liter of salt solution.

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[1] MacArthur: Jour. Phys. Chem., 20, 495 (1916).

Pyrogallic Acid

5 grams pyrogallic acid + the amount of salts given below, dissolved in 50 cc $N/10$ NaOH

Barometric pressure = 748. Temperature = 20.6° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	110 min.
No salt	5.78	0.0155	40	73	95	121
$M/2$ NaCl	4.92	0.0146	38	70	92	120
M NaCl	4.20	0.0099	27	50	70	100
$2M$ NaCl	3.05	0.0087	24	44	60	92
$3M$ NaCl	2.24	0.0053	15	28	40	68
$4M$ NaCl	1.62	0.0042	12	22	32	58

5 grams pyrogallic acid + the amount of salts given below, dissolved in 50 cc $N/10$ NaOH

Barometric pressure = 750.7. Temperature = 20° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	110 min.
No salt	5.78	0.0168	43	73	92	120
$^1/_2M$ MgCl$_2$	4.37	0.0079	22	45	65	105
$1M$ MgCl$_2$	3.18	0.0045	13	28	40	82
$2M$ MgCl$_2$	2.22	0.0013	4	6	9	26
$3M$ MgCl$_2$	1.50	0.0010	3	4	5	13

5 grams pyrogallic acid + the amount of salts given below, dissolved in 50 cc $N/10$ NaOH

Barometric pressure = 751.8. Temperature = 20° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	120 min.
No salt	5.78	0.0192	48	79	98	122
$^1/_2M$ KNO$_3$	5.11	0.0164	42	74	94	122
$1M$ KNO$_3$	4.61	0.0141	37	63	85	115
$2M$ KNO$_3$	3.65	0.0099	27	46	63	100

5 grams pyrogallic acid + the amount of salts given below, dissolved in 50 cc *N*/10 NaOH

Barometric pressure = 751.8. Temperature = 20° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	120 min.
No salt	5.78	0.0192	48	79	98	122
1*M* NaBr	4.47	0.0075	21	39	53	88
2*M* NaBr	3.37	0.0060	17	34	47	83
3*M* NaBr	2.57	0.0035	10	18	29	59
4*M* NaBr	2.02	0.0020	6	12	19	42

5 grams pyrogallic acid + the amount of salts given below, dissolved in 50 cc *N*/10 NaOH

Barometric pressure = 748.2. Temperature = 20° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	90 min.
No salt	5.78	0.0182	46	72	90	110
$^1/_2M$ KCl	4.98	0.0141	37	65	83	102
1*M* KCl	4.26	0.0095	26	46	64	82
2*M* KCl	3.21	0.0075	21	39	55	72
3*M* KCl	2.36	0.0067	19	37	51	70

5 grams pyrogallic acid + the amount of salts given below, dissolved in 50 cc *N*/10 NaOH

Barometric pressure = 748.2. Temperature = 20° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	90 min.
No salt	5.78	0.0192	48	72	99	114
$^1/_2M$ Na_2SO_4	3.97	0.0103	28	48	66	87
1*M* Na_2SO_4	3.00	0.0056	16	30	42	59

The effect that the *N*/10 alkali would have on the solubility of oxygen has been neglected. In the smaller concentrations of salt to neglect the effect of the alkali introduces an appreciable error, for alkali influences the solubility of oxygen to about the same extent as sodium chloride. This error decreases, however, with an increase in salt concentration.

These experiments show greater manometer readings with an increase in time, for all concentrations of salt. This is to be expected if the salts do not have a direct influence on the substance oxidizing.

At the end of any given period of time, the readings decrease from the solutions containing no salt to those of the highest concentrations. This decrease is largest between the more dilute solutions and becomes less and less with an increase in amount of salt, showing that the addition of a given amount of salt has more influence on the decrease in oxygen pressure than any subsequent like amounts.

The velocity constants decrease with an increase in salt concentration at about the same rate as the oxygen solubility. Some irregularities are to be noticed among them, but probably no more than is to be expected from the conditions under which these experiments were carried out. If one constructs a curve for k, and another for oxygen solubility against salt concentration, it will be seen that the two curves have a similar form. It may be concluded that the principal factor influencing the rate of oxidation of pyrogallic acid in salt solutions is the decrease in solubility of oxygen caused by these salts.

That k is a fairly good constant for the oxidation of pyrogallol for any particular concentration of salt is evident from the following table. The data were chosen largely at random:

Time in min.	No salt	$3M$ NaCl	M $MgCl_2$	$1/2M$ KCl	$3M$ KCl
20	0.0168	0.0053	0.0045	0.0141	0.0067
40	0.0166	0.0052	0.0051	0.0142	0.0070
60	0.0159	0.0052	0.0052	0.0134	0.0069

Ferrous Sulfate

5 grams ferrous sulfate + the amount of salts given below, dissolved in 50 cc $N/1$ NaOH

Barometric pressure = 753.4. Temperature = 20.4° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			10 min.	20 min.	40 min.	60 min.
No salt	5.78	0.0187	27	47	89	104
$1/_2M$ NaCl	4.92	0.0163	25	44	88	103
$1M$ NaCl	4.20	0.0128	22	34	78	93
$2M$ NaCl	3.05	0.0075	9	21	54	69
$3M$ NaCl	2.24	0.0063	7	18	48	63
$4M$ NaCl	1.62	0.0031	2	9	31	45

5 grams ferrous sulfate + the amount of salts given below, dissolved in 50 cc $N/1$ NaOH

Barometric pressure = 751.5. Temperature = 20.5° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	90 min.
No salt	5.78	0.0228	55	90	109	126
$^1/_2M$ NaBr	5.15	0.0192	48	82	101	120
$1M$ NaBr	4.47	0.0173	44	76	97	115
$2M$ NaBr	3.37	0.0107	29	50	72	91
$3M$ NaBr	2.57	0.0067	19	34	52	75
$4M$ NaBr	2.02	0.0031	9	21	35	54

In ferrous sulfate also the manometer readings decrease with an increase in salt. The velocity constant decreases with an increase in concentrations of salt at about the same rate as the solubility of oxygen does. The most marked influence is in the smaller concentrations. It would seem that the decrease in oxygen solubility produced by the salt is the most important factor in decreasing the rate of oxidation of ferrous sulfate.

Fructose

2.0 grams fructose + the amount of salts given below, dissolved in 50 cc $N/1$ NaOH

Barometric pressure = 740.4. Temperature = 20.2° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	130 min.
No salt	5.78	0.0059	19	38	55	99
$^1/_2M$ NaCl	4.92	0.0056	18	37	50	95
$1M$ NaCl	4.20	0.0052	17	36	50	95
$2M$ NaCl	3.05	0.0045	15	32	40	77
$3M$ NaCl	2.24	0.0029	8	17	25	52
$4M$ NaCl	1.62	0.0017	5	12	19	40

2.0 grams fructose + the amount of salts given below, dissolved in 50 cc $N/1$ NaOH

Barometric pressure = 752.8. Temperature = 21° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	80 min.
No salt	5.78	0.0079	22	43	62	76
$^1/_2M$ NaBr	5.15	0.0079	22	42	60	75
$1M$ NaBr	4.47	0.0067	19	37	51	65
$2M$ NaBr	3.37	0.0031	9	21	32	40
$3M$ NaBr	2.57	0.0024	7	17	25	33
$4M$ NaBr	2.02	0.0009	3	8	14	20

2.0 grams fructose + the amount of salts given below, dissolved in 50 cc $N/1$ NaOH

Barometric pressure = 736.3. Temperature = 20.4° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	90 min.
No salt	5.78	0.0073	20	40	60	82
$^1/_2M$ Na_2SO_4	3.97	0.0054	15	32	47	66
$1M$ Na_2SO_4	3.00	0.0032	9	21	32	50

2.0 grams fructose + the amount of salts given below, dissolved in 50 cc $N/1$ NaOH
Barometric pressure = 736.3. Temperature = 20.4° C

Conc. of salt	Sol of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	90 min.
No salt	5.78	0.0073	20	40	60	82
$1M$ KCl	4.26	0.0073	20	40	57	79
$2M$ KCl	3.21	0.0054	15	30	46	63
$3M$ KCl	2.36	0.0046	13	26	38	55

2.0 grams fructose + the amount of salts given below, dissolved in 50 cc $N/1$ NaOH
Barometric pressure = 744.7. Temperature = 20.6° C

Conc. of salt	Sol. of O	*k* at 20 min.	Manometer readings			
			20 min.	40 min.	60 min.	100 min.
No salt	5.78	0.0076	21	40	59	91
$1M$ KNO_3	4.61	0.0076	21	40	56	86
$2M$ KNO_3	3.65	0.0060	17	35	50	82

In fructose it was noted that small concentrations of salt had little effect on the manometer readings,[1] compared with the differences observed for pyrogallol and ferrous sulfate. With the exception of sodium sulfate molecular concentrations caused practically the same decrease in oxygen pressure in the flasks as when no salts were present. In fact in a few instances it was observed that a slightly larger negative reading was obtained for $^1/_2$ molecular salt solutions than for the no salt controls. The differences, however, were so small that they were attributed to irregularity in the conditions present in each of the flasks. It is certain that the amount of dissolved oxygen is markedly decreased in $^1/_2$ molecular salt solutions. It is difficult then to see why small amounts of salt have no effect on the rate of oxidation of fructose. If small amounts of salts catalyzed the reaction

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[1] Mathews: Jour. Biol. Chem., 6, 310 (1909).

one would not expect the close approach to the controls. If the salt influenced the fructose in any way larger differences from the control would be expected. In higher concentrations of salt marked effects on the rate of oxidation are seen.

From the following data another difference from pyrogallic acid and ferrous sulfate will be observed. Instead of *k* being a constant it gradually increases.

Time in minutes	No salt	2*M* NaBr	4*M* NaCl	2*M* KCl
20	0.0079	0.0031	0.0017	0.0054
40	0.0084	0.0037	0.0021	0.0056
60	0.0088	0.0040	0.0024	0.0062

It is very probable that the alkali present increases the number of active reducing particles as the reaction progresses. This would cause a gradual increase in the velocity constant.[1]

Conclusion

The tables bring out the fact that sodium chloride, potassium chloride, potassium nitrate have about the same effects on the rate of oxidation of pyrogallol, ferrous sulfate and fructose. Sodium bromide decreases the solubility of oxygen more than the above salts and consequently decreases the rate of oxidation more. Sodium sulfate and magnesium chloride affect both the oxygen solubility and the rate of oxidation more than sodium bromide, even when normal concentrations instead of molecular are compared.

In all experiments with increase of salt there is a decrease in the rate of oxidation. The rate of oxidation parallels the solubility of oxygen in all cases except those on fructose in dilute salt solutions.

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[1] Mathews: Jour. Biol. Chem., 6, 10 (1909).

THE RELATION OF MOLECULAR COHESION TO SURFACE TENSION AND GRAVITATION; WITH A METHOD OF DETERMINING "*a*" OF VAN DER WAALS' EQUATION WITHOUT ASSUMPTIONS; AND THE EXPLANATION OF THE MEANING OF THE CONSTANTS IN THE SURFACE TENSION LAW OF EÖTVÖS, AND THE LATENT HEAT FORMULAS OF DIETERICI AND MILLS

BY A. P. MATHEWS

This paper is a revision and extension of the studies already made and published on molecular cohesion.[1] The principal contributions in this paper are (1) a method of computing "*a*" of Van der Waals' equation from the internal latent heat of vaporization, which is free, I believe, from all assumptions; (2) the proof that the values of "*a*" thus found are proportional, as already published, to the two-thirds power of the product of the molecular weight and the number of valences in the molecule. Cohesion of a molecule depends, therefore, on the molecular weight and valence; (3) the cohesive attraction of two molecules at unit distance is shown to be equal to the two-thirds power of their gravitational attraction at this distance, multiplied by the two-thirds power of the ratio of the number of valences to the molecular weight; or if M^2K, which is "*a*" for a single pair of molecules, is the cohesional attraction at unit distance and m^2k, the gravitational attraction of the two molecules at the same distance, then the relation exists: $M^2K = (m^2k \times \text{valences}/\text{molecular weight})^{2/3}$; (4) a brief discussion of the meaning of this relationship between cohesional and gravitational attraction; (5) the theoretical derivation of the relation of cohesion to surface tension, and the derivation of Eötvös' surface tension law $sV_1^{2/3} = C(T_c - T)$, showing what C really is

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[1] Mathews: "The Internal Pressures of Liquids," Jour. Phys. Chem., 17, 603 (1913).

and why it varies from substance to substance; (6) an expression showing the number of layers deep the surface film is; (7) the partial derivation of the relationship $[T_c/(T_c - T)]^{1/3} = d_o/(d_l - d_v)$; (8) the meaning of the constant, C′, in Dieterici's expression of the relationship between the internal latent heat of vaporization, or L — E, and the work done in expanding from the density of the liquid to that of the vapor, or $L - E = C'RT ln_e d_l/d_v$; and (9) the meaning of the constant μ', in Mills' expression of the relation of the internal latent heat to the difference between the cube roots of the density of liquid and vapor, or $L - E = \mu'(d_l^{1/3} - d_v^{1/3})$.

As the results which are included in this paper have come from the study of the Eötvös surface tension law in an attempt to discover its meaning, I have decided to make that the central part of the discussion which follows.

In 1886 Eötvös[1] published the discovery that the surface tension energy of a gram mol of any pure, non-associating liquid in contact with its saturated vapor was a linear function of the temperature counting downward from the critical temperature. If s is the surface tension in dynes per cm at any temperature, T, and V_l the volume of a gram mol of the liquid, then $sV_l^{2/3}$ is proportional to the surface energy of a gram mol of the liquid, expressed in ergs; or it is equal to the surface energy of one face of the cube containing the gram mol of substance. This value, $sV_l^{2/3}$, Eötvös found to be equal to a constant, C, multiplied into the value $(T_c - T)$, where T_c is the absolute critical temperature, or a temperature differing but little from it, and T is the absolute temperature at which the surface tension is measured. Eötvös' law is then

$$sV_l^{2/3} = C(T_c - T). \tag{1}$$

Eötvös measured the surface tension of various liquids and condensed gases, when they were in contact with their saturated vapors, by a reflection method which did not involve the angle of contact of the liquid with the glass, and

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[1] Eötvös: Wied Ann., 27, 458 (1886).

hence was free from this uncertainty. By these measurements he found C to vary in non-associating liquids from 2.26 to 2.32. For several substances it was very close to 2.27 and he believed it probable that 2.27 was the constant for all pure, non-associating substances, and that the observed, slight deviations from this value were accidental. For all associating substances such as water, alcohol, and acetic acid, "C" was not constant, but diminished as the temperature fell, and while in some cases it might be 2.27 at temperatures not far from the critical, it might fall even below 1 at low temperatures. For water at ordinary temperatures it was somewhat lower than 1. What this constant "C" was, that is, what elements it had in it, Eötvös did not know since the law was discovered empirically and not derived by theory.

Some years later in 1893, Ramsay and Shields[1] and later Ramsay and Aston[2] carried out an extensive investigation of this law. They determined the surface tension of a large number of pure liquids in contact with their saturated vapors from temperatures close to 0° clear to the critical temperatures, or to very high temperatures. They used the capillary rise method of determining surface tension, a method which involves the assumption, which is certainly not justified, that the angle of contact of the liquid with the glass is zero. This method gave lower values for the surface tension than those obtained by Eötvös, so that the constant "C" did not have as high a value as he had ascribed to it, but varied in non-associating substances from about 2.0 to 2.23, and was correspondingly lower also for associating substances. They confirmed, then, Eötvös' discovery and found his law applicable to a great variety of substances. But they found it necessary to modify the original simple formula which he had given, so that instead of taking the critical temperature as

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[1] Ramsay and Shields: Zeit. phys. Chem., 12, 433 (1893); Phil. Trans., 184A, 602 (1893).

[2] Ramsay and Aston: Zeit. phys. Chem., 15, 89 (1894); Proc. Roy. Soc., 66, 162 (1894).

the point of departure, a point about 6° below was taken. Eötvös' law became in their hands:

$$(2) \qquad sV_1^{2/3} = C(T_c - T - t)$$

The correction, t, had to be determined empirically and was about 6° for most substances. The expression in this form gave very good correspondences between the observed and computed values except within about 40° of the critical temperature. At temperatures nearer than this to the critical the formula gave results lower than the observed values and to get agreement with these values it was necessary to introduce a second complicating, correcting term in the formula. They found that the surface tension became zero at the critical temperature, and not at 6° below as the formula implied. The law in the form they gave it is obviously, then, an empirical expression less simple and satisfactory than that of Eötvös. They believed, however, that the capillary method really gave reliable results for the surface tension, the contact angle being actually zero, and that the deviation of their results from the law as proposed by Eötvös could not be ascribed to a fault of the method. Recent work has, however, confirmed the earlier doubts of the correctness of the assumption that the contact angle is zero, particularly at high temperatures, and most observers are of the opinion that the capillary rise method gives, for this reason, results which are somewhat lower than they should be, and that the error is greater at higher temperatures. The law in the form suggested by Ramsay and Shields has been the one generally adopted and it has displaced the original simple expression of Eötvös, which I hope to show in this paper is really the correct form.

Surface tension measurements of many other substances have been made by various investigators of whom Renard and Guye,[1] Morgan and his colleagues,[2] Turner and Merry,[3]

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[1] Renard and Guye: Jour. Chim. phys., 5, 81 (1907).

[2] Morgan, *et al.;* Jour. Am. Chem. Soc., 35, 1821 (1913).

[3] Turner and Merry: Jour. Chem. Soc., 97, 2069 (1910).

Richards and Coombs,[1] Walden,[2] and Jaeger[3] may be mentioned. The general result of the work has been to confirm the law in the form given it by Ramsay and Shields. Most of these investigators have used the capillary method with the exception of Morgan and his collaborators who used the drop weight method. This method as used by Morgan has, however, been seriously criticized by Lohnstein[4] since the tips were standardized simply by comparing the drop weights obtained with benzene, with the surface tension of benzene as given by the capillary rise method. They did not make determinations, either, at temperatures near the critical. The capillary pressure method was used by Jaeger and by this method at low temperatures always considerably higher values of the surface tension were obtained than by the capillary rise method. The results of the last observer did not follow the law of Ramsay and Shields, or that of Eötvös, except in some cases; very often the constant, C, was high at low and low at high temperatures, and often it was low at low and higher at high temperatures. It is not to be supposed that the results by this capillary pressure method would follow accurately Eötvös' law, since one of the cardinal conditions made in that law is that the liquid shall be in contact always with its saturated vapor, whereas in the capillary pressure method, in which the maximum pressure is measured necessary to blow air or nitrogen gas from a capillary tube the end of which dips below the surface of the liquid, the liquid is not in contact with its saturated vapor.

As a result of the work in which the surface tension is measured when the liquid is in contact with its saturated vapor it has been found that some substances have constants a good deal higher than 2.0 or 2.27. Thus very complex substances have been found in many cases to have constants

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[1] Richards and Coombs: Jour. Am. Chem. Soc., 37, 1656 (1915).

[2] Walden and Swinne: Zeit. phys. Chem., 79, 700 (1912); Ibid., 82, 271 (1913).

[3] Jaeger: Proceedings Amsterdam Acad. Sci., (II) 17, 329, 1203 (1915).

[4] Lohnstein: Zeit. phys. Chem., 64, 686 (1908); 84, 410 (1913).

"C" as high as 2.35 and even 3, and in many of these cases as the temperature rises the constant falls, so that at higher temperatures it approaches the usual 2.20 or thereabout. The reason for these very high constants has been puzzling, and it has been suggested that in some cases dissociation, in place of association, occurs as the temperature falls, or that certain mechanical properties of these substances at low temperatures, such as their viscosity, have made the surface tension measurements at such temperatures apparently too high.

In the present paper I wish to show what the constant "C" of the law really is, and how the law is derived theoretically. In the course of the discussion the depth of the surface film, the density at absolute zero, and a relationship between the difference in density of the liquid and vapor and the temperature will be considered. Since the last relationship underlies the other parts of the discussion we may begin by considering it.

1. The Relationship: $d_{\text{liquid}} - d_{\text{vapor}} = C''(T_c - T)^{1/3}$

The relationship that the difference in density of the liquid and saturated vapor is equal to a constant multiplied into the cube root of $T_c - T$, T_c being the absolute critical temperature, was discovered empirically by Goldhammer[1] and appears to be true for all kinds of non-associating substances from the simplest to the most complex, and from very low clear to the critical temperature. Its validity is much greater than the so-called rectilinear diameter law which expresses the relationship between the sum of the densities and the temperature. The relationship, $d_l - d_v = C''(T_c - T)^{1/3}$, appears to be valid, indeed, over the whole range of temperature from absolute zero to the critical temperature, as is shown in the curves and tables which follow. I have computed it for a great variety of substances from oxygen on the one hand to octane and complex esters on the other.

The significance of this law is sufficiently clear. Since

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[1] Goldhammer: Zeit. phys. Chem., 71, 577 (1910).

TABLE I—$C'' = (d_1 - d_v)/(T_c - T)^{1/3}$

Octane. (t_c = 296.2) (Densities from Young)		Oxygen. (t_c = —118.8) (Densities Mathias and Onnes)		CCl_4. (t_c = 283.15) (Densities from Young)	
t°	C''	t°	C''	t°	C''
0	0.1078	—210.4	0.2827	0	0.2487
40	0.1080	—182.0	0.2853	40	0.2492
80	0.1087	—154.1	0.2847	120	0.2514
120	0.1094	—140.2	0.2859	160	0.2536
160	0.1105	—129.9	0.2896	200	0.2555
200	0.1117	—120.4	0.2848	240	0.2562
240	0.1125	Mean	0.2855	270	0.2523
280	0.1120			280	0.2754
290	0.1097			Mean	0.2524
Mean	0.1100				

Fluorbenzene. (t_c = 286.5)		Ethyl acetate. (t_c = 250.1)		Argon. (t_c = —122.44)	
t°	C''	t°	C''	t°	C''
0	0.1587	0	0.1467	—189	0.3512 (Baly and Donnan)
80	0.1602	40	0.1474	—140.8	0.3486 (Crommelin)
120	0.1612	80	0.1482	—134.72	0.3345
160	0.1626	120	0.1496	—129.83	0.3338
200	0.1640	160	0.1511	—125.49	0.3251
240	0.1654	200	0.1527	Mean	0.3373
280	0.1656	220	0.1517		
Mean	0.1625	245	0.1510		
		249	0.1503		
		Mean	0.1509 (Omitting lowest two)		

Note: d_v was neglected in computing the first. The result is evidently high.

Pentane. (t_c = 197.2)		Methyl formate. (t_c = 214.0)		Chlorbenzene. (t_c = 359.2)	
$t°$	C′	$t°$	C′	$t°$	C′
0	0.1107 (Young)	0	0.1677	—45	0.1592
40	0.1117 (Young)	40	0.1686	0	0.1587
100	0.1134 (Young)	80	0.1700	80	0.1594
140	0.1142 (Young)	120	0.1716	140	0.1605
190	0.1127 (Young)	160	0.1723	220	0.1632
—6.2°	0.1106 (Timmermans)	200	0.1715	270	0.1643
—45	0.1101	210	0.1682	Mean	0.1609
—83.4	0.1101	213	0.1647		
—123.3	0.1104	Mean	0.1700 (Omitting last)		
—136.5	0.1107				
Mean	0.1125 (Young)				
	0.1105 (Timmermans)				

SnCl$_4$. (t_c = 318.7)		Benzene. (t_c = 288.5)		Ether. (t_c = 193.8)	
$t°$	C′	$t°$	C′	$t°$	C′
0	0.3335	0	0.1362	—117.6	0.1266 (Timmermans)
40	0.3330	80	0.1369	—83.4	0.1266
120	0.3348	160	0.1390	0	0.1271 (Young)
200	0.3394	200	0.1403	40	0.1279
240	0.3404	240	0.1408	80	0.1297
280	0.3390	270	0.1398	120	0.1304
Mean	0.3367	280	0.1398	160	0.1317
		Mean	0.1390	180	0.1306
				190	0.1309
				193	0.1388
				Mean	0.1298 (Omitting last)

Isopentane. (t_c = 187.8)		Carbon dioxide. (t_c = 31.35)	
$t°$	C''	$t°$	C''
—158.05	0.1120 (Timmermans)	—188	0.2703
—104.85	0.1110	0	0.2594
—53.6	0.1109	10	0.2606
—6.2	0.1115	20	0.2563
0	0.1116 (Young)	30	0.2389
80	0.1137	31.25	0.1616
160	0.1150	Mean	0.2565 (Omitting last two and first)
180	0.1129		
185	0.1113		
187	0.1103		
187.4	0.1100		
Mean	0.1109		

Acetic acid. (t_c = 321.6)		Methyl alcohol. (t_c = 240.0)		Ethyl alcohol. (t_c = 243.1)	
$t°$	C''	$t°$	C''	$t°$	C''
0	0.1561	—94.9	0.1392 (Solid)	—140	0.1279
100	0.1583	—94.9	0.1299 (Liquid)	—80	0.1274
150	0.1601	—94.5	0.1301 (Timmermans)	0	0.1292
200	0.1628	—53.6	0.1296	80	0.1342
250	0.1649	—6.2	0.1302	160	0.1407
300	0.1658	0	0.1303	200	0.1443
310	0.1637	50	0.1329 (Young)	220	0.1441
		100	0.1368	240	0.1447
		150	0.1415	242.5	0.1488
		200	0.1469		
		230	0.1496		
		238	0.1606		

Methyl isobutyrate. (t_c = 267.55)		Methyl propionate. (t_c = 257.4)	
$t°$	C''	$t°$	C''
0	0.1414	0	0.1476
50	0.1421	50	0.1485
100	0.1433	100	0.1494
150	0.1448	150	0.1515
200	0.1470	200	0.1535
220	0.1472	240	0.1538
260	0.1464	250	0.1529
266.5	0.1497	256	0.1509
Mean	0.1446 (Omitting last)	Mean	0.1513

at the critical temperature the liquid and vapor densities are equal, this is taken as the point of departure. As we proceed downward from the critical temperature the density of the liquid increases, and that of the vapor decreases, so that the difference between them will steadily increase. It might be thought that it would increase according to the first power of the temperature interval from the critical temperature, or as $(T_c - T)$, but since only the vertical component of the molecular motions tends to carry the molecules from the liquid to the vapor, the increase will be proportional to the cube root of the temperature interval from the critical.

That $\log (d_l - d_v) = \log C'' + {}^1/_3 \log (T_c - T)$ is shown very plainly in the plots in Figs. 1 and 2, and Table I. Attention is particularly directed to isopentane since the density of this substance has been determined more accurately than for any other from the critical temperature to the point of solidification. The critical temperature is also accurately known. It will be seen that C'' has a very constant value throughout this great interval of 345 degrees and that the law holds even within a fraction of a degree of the critical temperature. C'' is constant in pure, non-associating substances, but in the associating substances, such as acetic acid, alcohol and methyl alcohol, it is not constant throughout, but shows a tendency, more or less marked, to fall with the temperature. Thus from 0° to 300° in acetic acid there is a gradual advance in the constant, so that at the higher temperature the constant is about 7 percent higher than at zero. In methyl alcohol the constant is constant from —95° to 0° but from zero degrees on it increases steadily to the critical temperature. Evidently association makes no difference in the calculation at the low temperatures where the vapor may be neglected. At temperatures above zero association must either make the liquid density too great, or, perhaps, the vapor density is too small for the rule to hold exactly. The same fact is shown in ethyl alcohol. At temperatures below zero the formula gives a constant; from about zero to two hundred degrees the constant steadily advances, but

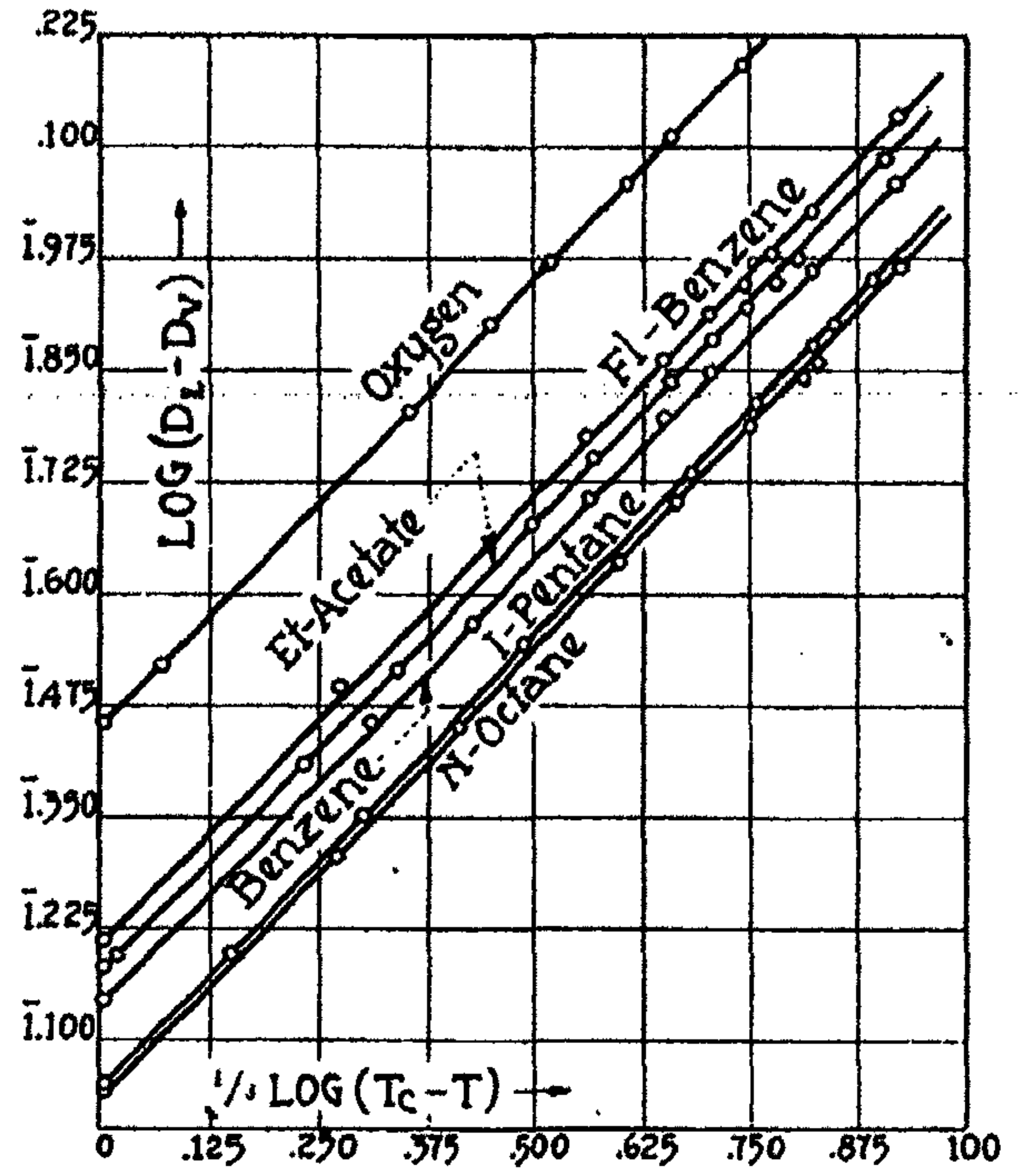

Fig. 1

Plot of relationship, $\log (d_l - d_v) = \log C' + {}^1/_3 \log (T_c - T)$

Ordinate $= \log (d_l - d_v)$

Abscissa $= {}^1/_3 \log (T_c - T)$

from there for the next forty degrees to the critical temperature it is constant. Presumably from about 200° on, the alcohol is normal. The constant changes on passing from the liquid to the solid state.

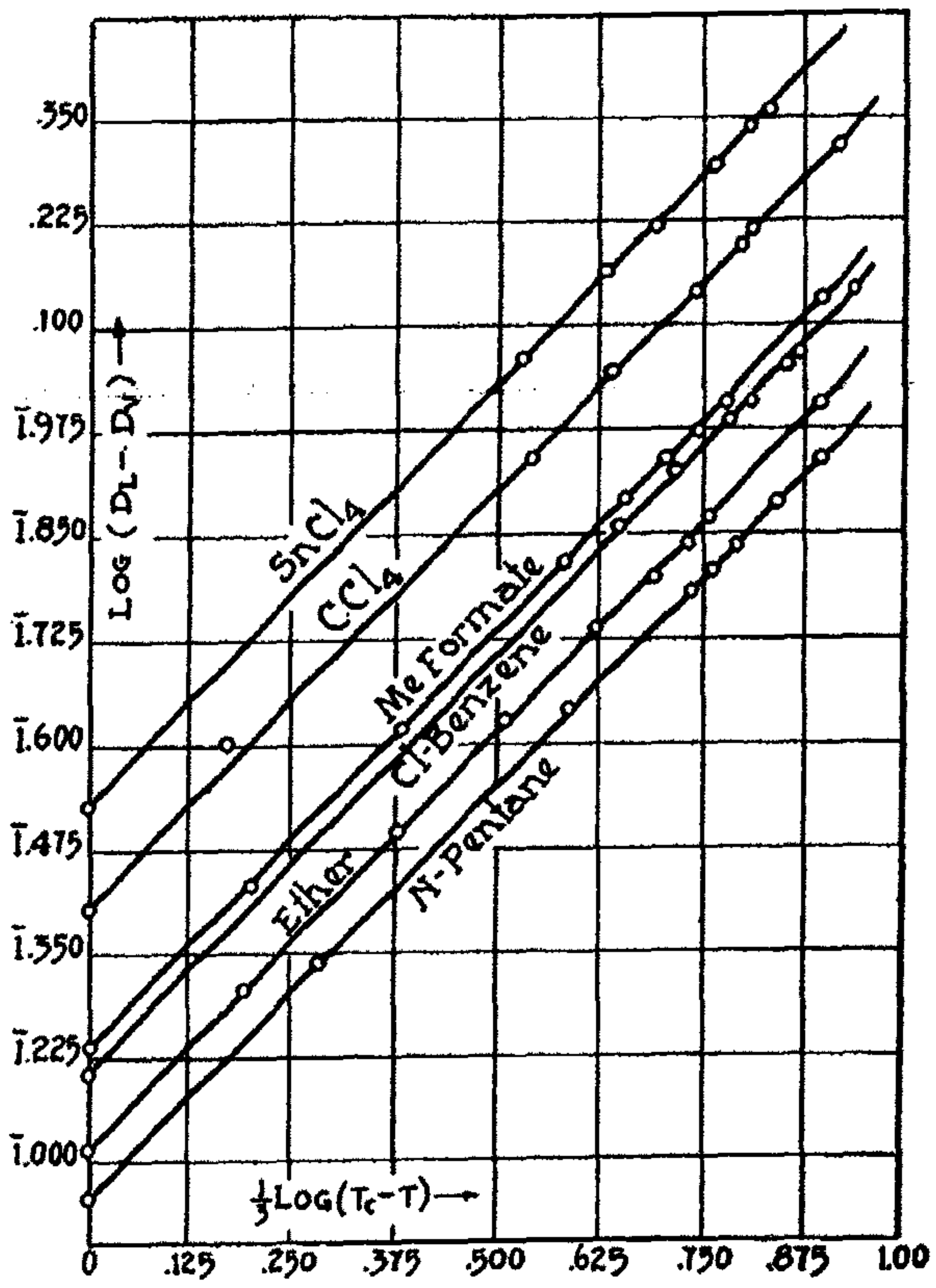

Fig. 2

Plot of relationship, $\log (d_l - d_v) = \log C'' + {}^1/_3 \log (T_c - T)$
Ordinate $= \log (d_l - d_v)$
Abscissa $= {}^1/_3 \log (T_c - T)$

Occasionally within a degree, or a few degrees, of the critical temperature the constant may appear to vary a little, but I do not doubt that this is due to a slight inaccuracy in the critical temperature. Few substances have their critical temperatures determined within a tenth of a degree. Many of them are uncertain within half a degree.

2. Calculation of the Density at Absolute Zero

The relationship $d_1 - d_v = C''(T_c - T)^{1/3}$ allows us to calculate the density at absolute zero without difficulty because "C''" is nothing else than $d_0/T_c^{1/3}$ as is evident if d_v and T are zero. Hence if T_c is known and if at any other temperature d_1 and d_v are known, C'' can be determined and from this d_0. The results obtained are, I believe, accurate for non-associating substances and agree very closely with those of Timmermans obtained by extrapolation from density determinations at low temperatures on certain substances. They are always lower than the results obtained by calculating

TABLE II—DENSITIES AT ABSOLUTE ZERO

Substance	d_0 Timmermans	d_0 Rectilinear diameter	$d_0 = Sd_c$ $S = RT_c/P_cV_c$	$d_0 = C'T_c^{1/3}$
Argon	—	—	1.746	1.729–1.854
Nitrogen	—	—	1.064	1.104
Oxygen	—	—	1.470	1.531
Carbon dioxide	—	—	1.658	1.725
Isopentane	0.8744	0.8961	0.8761	0.8687
Pentane	0.8703	0.8880	0.8736	0.8751
Chlorbenzene	—	1.3918	1.3780	1.3808
Benzene	—	—	1.1433	1.1464
Fluorbenzene	—	—	1.3445	1.3392
Ether	0.9968	1.0148	1.0001	1.0066
Hexane	—	—	0.8978	0.9071
Octane	—	—	0.9006	0.9119
Methyl formate	—	—	1.3680	1.3373
Methyl acetate	—	—	1.2822	1.2770
Ethyl acetate	1.2274	1.2406	1.2160	1.2161
Propyl acetate	—	—	1.1633	1.1790
Methyl propionate	—	—	1.2214	1.2250
Methyl iso-butyrate	—	—	1.1640	1.1780
Methyl butyrate	—	—	1.1720	1.1820
Carbon tetrachloride	—	—	2.0494	2.0757
Stannic chloride	—	—	2.7860	2.8264

from the law of the rectilinear diameter, and they agree on the whole fairly well in the case of complex substances with the assumption made by van der Waals that the density at absolute zero is approximately equal to Sd_c, where S is equal to RT_c/P_cV_c. In simple substances like O_2 the agreement is not so good. Considering the uncertainty of the critical data upon which the calculation of S is based, and in particular the uncertainty in the critical density, it may be said that the value of d_0 is within the limits of error of Sd_c except possibly in very simple substances where the deviation may be 4-5%. Table II illustrates the value of d_0 as calculated in various ways.

Having established these relationships and the value of the density at absolute zero, we may now proceed with the derivation of Eötvös' law.

3. Derivation of Eötvös' Law

The surface tension, s, is the force which is required to rupture the surface film along a line 1 cm in length and drag one or more molecules from the layer beneath the surface into the surface. If this force act over one cm it gives the surface tension energy in ergs per square cm. That is, it represents the work necessary to increase the surface by a square centimeter. If V_1 is the volume of a gram mol of the liquid, v_1 may be taken as the volume at the disposal of each molecule of the liquid. This volume is a little cube. Then $v_1^{2/3}$ is the area of one face of the cubical space at the disposal of the molecule. $sv_1^{2/3}$ is, then, the energy consumed or required to move a single molecule from the layer beneath the surface into the surface film. To get the whole gram mol into the surface the work required will be N times $sv_1^{2/3}$, since N is the number of molecules in a gram mol. Since $N^{2/3}v_1^{2/3}$ is equal to $V_1^{2/3}$, where V is the volume of a whole gram mol, $v_1^{2/3}N$ is equal to $V_1^{2/3}N^{1/3}$. Now it is probable that the surface layer is more than a single molecular diameter deep at all temperatures above absolute zero. That is, the surface layer, in which there is a diminishing density as one passes outward to the vapor, is several molecular diameters deep, at least at high temperatures. At the critical temperature it must become infinitely deep, since at that temperature it becomes coexistent with the vapor itself. If we assume that the density diminishes uniformly in the surface layer, each molecular layer being less dense than the one lying behind it nearer the liquid, evidently the same amount of work will be required to move a molecule from each inner layer to the next outer layer, since the difference in density determines how much work must be done in moving from each layer to the next outer until the uniform density of the vapor is reached. If there are *n* layers in the surface film, the total amount of work necessary to move a molecule through the surface will be $sv_1^{2/3}n$; and to move the whole gram mol through the surface it will be $sV_1^{2/3}N^{1/3}n$.

a. The Depth of the Surface Layer

We have now to enquire into the value of *n*, that is, the depth of the surface film in molecular layers. It is clear that the molecules which have a certain amount of kinetic energy above the average of that of the molecules of the liquid will be able to move into the surface film where they are unequally attracted outward and inward. The density is diminishing as they pass outward so that they are attracted inward with a greater force than they are outward. Some molecules can pass clear through the film into the vapor, but those moving less slowly will rise a greater or less distance above the inner core of uniform density. Each step they take outward is against the differential of attraction outward and inward. Now the simplest assumption which we can make is that the number of steps upward, that is, from layer to layer of the surface film, which they can take under these circumstances will be inversely proportional to the differential of pressure due to the molecular attraction. Since this attraction is proportional to the square of the density, the differential force against which the molecules are moving will be equal to the square of the difference of the densities or $(d_1 - d_v)^2$.

The number of steps, then, which a molecule can take when passing outward from layer to layer in the surface film will be inversely proportional to this pressure, or $n = K/(d_1 - d_v)^2$. And at any two temperatures, t and t', $n : n' = (d' - d_v')^2/(d_1 - d_v)^2$. If we take n' as the absolute zero then the depth ratio will be equal to $d_\circ^2/(d_1 - d_v)^2$. The question is, then, what is n' at absolute zero? How deep is the surface layer at absolute zero? The simplest assumption which we can make is the one I have made, namely, that the surface film at absolute zero is one molecular layer deep. We are guided to this assumption by several circumstances. One is that the surface layer certainly diminishes in depth with the fall of temperature, and, at ordinary temperatures, measurements have shown that it is not more than two or three molecular diameters in thickness. Another is that the radius of action of the cohesive forces is apparently but a single molecular diameter, and with the molecules in contact, as they presumably are at absolute zero, and as there is no vapor, it is probable that only the peripheral layer of molecules is under a different attraction outward and inward, so that the surface layer will be only this deep. Furthermore the assumption that the layer is but a single molecule deep works out well. The surface layer is then $[d_\circ/(d_1 - d_v)]^2$ molecular layers deep. At the critical temperature the layer will be an indefinite number of such layers deep, that is, n is infinite. At ordinary temperatures, that is, at temperatures about $^3/_5$ of the critical temperature, the surface layer will be about two molecular layers deep.

The total energy then required to pass a gram mol through the surface so that the gram mol is expanded to a vapor in one direction, but is still a liquid in the other two dimensions, will be $sV_1^{2/3}N^{1/3}(d_\circ/(d_1 - d_v))^2$.

It will be observed that this is not the energy necessary to vaporize a gram mol. I correctly inferred before that this was but one-third the energy necessary to vaporize the gram mol, but I incorrectly explained this as I ascribed it to the surface tension measuring the difference in cohesive pressure in one direction only. The real explanation appears now to me to be that in the factor $V_1^{2/3}$ we have assumed that we have not increased the surface. That is, we have assumed that we have moved the molecules into the surface film, diminishing their density in a direction perpendicular to the film, but keeping it unchanged in the plane of the film. This is as if we had separated the layers of molecules in a direction perpendicular to the surface to the distance they are apart in the vapor, but we have not separated the individual molecules in each layer in the plane of the surface to the distance they are apart in the vapor. In other words, we have expanded the liquid to a vapor in one dimension, but left it a liquid in the other two. This requires evidently only one-third the work that will be necessary to expand it in the other two dimensions, that is, to the state of the vapor.

The work necessary to expand a liquid gram mol to a vapor gram mol is the work necessary to overcome the cohesive energy of the liquid and reduce it to that of the vapor. The cohesive energy of the liquid is a/V_1, and of the vapor a/V_v, where a is van der Waals' constant, and as we have done only one-third of this work we have the equation:

$$(3) \qquad sV_1^{2/3}N^{1/3}(d_o/(d_1 - d_v))^2 \underset{\cdot}{=} a(1/V_1 - 1/V_v)/3$$

This equation is in reality the Eötvös surface tension law with the value of C written out, as I shall presently show. Before doing that, however, I wish for a moment to go back to the depth of the surface film.

We can express the depth of the surface film also as being equal to $(T_c/(T_c - T))^{2/3}$. This can be done for the reason that this fraction is equal to $(d_o/(d_1 - d_v))^2$ as has been already shown in the first division of the paper. But we may also come at the same conclusion in another way. At the critical temperature, where the density in liquid and vapor become equal, the conditions are such that all the molecules are able to lie in the surface film; the surface film becomes coextensive with the vapor and liquid. The critical temperature is then the point of departure. Now at temperatures below the critical only a portion of the molecules will have a kinetic energy sufficient to carry them into the surface film and keep them there and we may assume if we have a gram mol of the substance so that the number of molecules in $V_1^{2/3}$, that is, in one face of the cube, remains the same, that the number of layers of molecules in the surface film will vary inversely as the two-thirds power of the distance from the critical temperature. The reason that we have to take the two-thirds power is, I presume, that only two components of the kinetic motions of the molecules tend to keep the molecules in the surface, the third component takes them into or out of the surface, but the motions in the plane of the surface counteract the contractile action of the surface and tend to keep the molecules in the surface. Hence n, the number of layers, will be inversely proportional to $(T_c - T)^{2/3}$. And in the same way assuming that at absolute zero there is but a single layer in the film, we have $n = (T_c/(T_c - T))^{2/3}$. As we have already seen, this is equal to $(d_0/(d_1 - d_v))^2$.

I shall now show that the equation just derived expressing the relation between the cohesion and the surface tension is in reality Eötvös' law. The equation is:

$$(3) \qquad sV_1^{2/3}N^{1/3}(d_0/(d_1 - d_v))^2 = a(1/V_1 - 1/V_v)/3$$

Changing to density in place of volume in the right term of the equation and putting $(T_c/(T_c - T))^{2/3}$ in place of $(d_0/(d_1 - d_v))^2$ in the left hand side we have:

$$(4) \qquad sV_1^{2/3}N^{1/3} = a(d_1 - d_v)(T_c - T)^{2/3}/MT_c^{2/3}3$$

and since $(d_1 - d_v)/d_0$ is equal to $[(T_c - T)/T_c]^{1/3}$ we have, on substituting this value,

$$(5) \qquad sV_1^{2/3} = ad_0(T_c - T)/3MN^{1/3}T_c = C(T_c - T).$$

This expression is Eötvös' law and C of that law is shown to have the value:

$$(6) \qquad C = ad_0/3MN^{1/3}T_c$$

In this expression "a" is van der Waals' constant; M is the molecular weight; d_0 is the density at absolute zero; N is the number of molecules in a gram mol; and T_c the absolute critical temperature. C, it will be remembered, has the empirical value of something between 2.0 and 2.3.

In a former paper C was supposed to have the value:

$$C = K_cR/3P_cN^{1/3} \tag{7}$$

K_c having the value of a/V_c^2 and R being the gas constant for a gram mol. Formulas 6 and 7 are identical provided that the density at absolute zero has the value of S times the critical density. This relationship is at least approximately true for most substances, although there is some doubt, as already said, whether it is true for the simplest substances. S is, of course, equal to RT_c/P_cV_c.

We shall now proceed to test relationship (6). The value of d_0 is that computed in the preceding section of the paper; T_c is the critical temperature; M is the molecular weight; N, the number of molecules in a gram molecule, is not known with absolute certainty but I have used the value determined by Millikan which appears to have been determined with the most accuracy, namely, 6.062×10^{23}. The value of "a" is, however, uncertain and it was necessary to find some method of computing this value which should relieve it of uncertainty. After some consideration two methods were devised for finding "a" and these we shall now consider.

4. A Method Computing "a" of van der Waals and the Meaning of the Constants in Dieterici's and Mills' Formulas

a. Dieterici's Formula

Dieterici[1] showed that if a liquid is expanded to the state of its saturated vapor, then, if the molecules remain the same in vapor and liquid, there being neither dissociation nor association, and if the molecules do not expand or contract or change their energies of rotation, all the work that is necessary to bring about the expansion will be done in over-

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[1] Dieterici: Wied. Ann., 25, 569 (1908).

coming molecular cohesion. This work must then be equal to the internal latent heat of vaporization, or L — E, where L is the total latent heat of vaporization and E the part represented by the external work done in lifting the external pressure from V_l to V_v. The relationship should hold, then,

$$(8) \qquad L - E = RTLn_e \frac{d_l}{d_v}$$

d_l and d_v are the densities of liquid and saturated vapor, respectively.

As a matter of fact this relationship was never found to hold experimentally, since in all cases there is some change in the energy content of the molecules themselves when they escape from liquid to vapor, for Dieterici found that the heat rendered latent was greater than $RTLn(d_l/d_v)$, some of the heat evidently passing into the molecules so as to increase their size, or their rotational energy. He discovered the interesting fact that while L — E was not equal to $RTLn(d_l/d_v)$ it was proportional to it over a considerable range of temperature, so that

$$(9) \qquad L - E = C'RTLn(d_l/d_v).$$

In other words for a considerable temperature interval below the critical temperature, always the same proportion of the total internal heat of vaporization goes into the molecules at different temperatures in the case of the same substance. C′ varies somewhat in different substances, but lies, generally, between the values 1.66 and 1.82, most substances coming not far from the mean of 1.71.

Mills[1] has pointed out that it is very doubtful if this formula holds at low temperatures, since in all cases in which he examined it for substances of a critical temperature of 200° C and over, C′ is lower at zero degrees than at higher temperatures. It cannot be expected that the formula will hold over the whole temperature interval from absolute zero to the critical, since it is obvious that if dissociation or

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[1] Mills: Phil. Mag., (6) 22, 97 (1911).

association or chemical change occur as the temperature falls or rises, or if the molecules get so close together that they cannot revolve freely, more or less heat will be liberated or rendered latent on vaporization so that the proportion of the internal latent heat which is going into the molecules will probably not remain precisely the same fraction of the total internal latent heat. But from that temperature or density at which the molecules are sufficiently far apart to revolve freely, where they are not too much compressed, and at a temperature sufficiently high so that association does not occur, but not so high that new molecular dissociation occurs, then the proportion of energy going into the molecules is for a considerable period always the same fraction of the total internal latent heat. If, for example, at low temperatures association occurs in the vapor, then the constant will be lower than it should be; as is found to be the case almost always. And if at high temperatures near the critical, molecular dissociation occurs, then the constant will rise. And as a matter of fact it is found to rise in the case of octane, methyl butyrate and heptane in all of which the critical temperature is high, lying between 280° and 300° C, temperatures at which some molecular decomposition is not improbable.

For most substances, then, of not too high a critical temperature the relationship holds very closely for a temperature interval of about 200° from the critical temperature downward, that roughly about 0.6 of the total internal latent heat is used in overcoming molecular cohesion; and about 0.4 is used in increasing intra-molecular energy, either by expansion or increased speed of molecular revolution.

If all the internal latent heat was used in overcoming molecular cohesion then this would be precisely equal to the difference in the cohesive energy in the liquid and vapor, respectively, or, since a/V_l is the cohesive energy in the liquid and a/V_v that in the vapor and M is the molecular weight, the relation would hold:

$$(10) \quad L - E = a(1/V_l - 1/V_v) = a(d_l - d_v)/M$$

Hence we would have:

$$(11) \qquad L - E = a(d_1 - d_v)/M = C'RTLn(d_1/d_v)$$

Relationship (11) will, of course, not hold except at the critical temperature, since as already stated not all the internal latent heat is used in overcoming molecular cohesion. But as one approaches the critical temperature, where the conditions of the molecules in vapor and liquid approach equality, $a(d_1 - d_v)/M$ must indeed approach more and more closely the value $L - E$; and at the critical temperature $a(d_1 - d_v)/M$ must be precisely equal to $L - E$ and so to $C'RTLn(d_1/d_v)$. Hence we have at the limit, namely the critical temperature,

$$(12) \qquad a = MC'RTLn(d_1/d_v)/(d_1 - d_v).$$

The fraction $Ln(d_1/d_v)/(d_1 - d_v)$ has the indeterminate form of $\frac{0}{0}$ at T_c, but it has the finite value of $1/d_c$. Hence at the limit we have:

$$(13) \qquad a = MC'RT_c/d_c$$

or since M/d_c is equal to V_c,

$$(14) \qquad a = C'RT_cV_c.$$

From Equation 14 we may compute "a," since C' is experimentally determined. We see that C' of Dieterici is the simple expression

$$(15) \qquad C' = a/RT_cV_c.$$

In other words since a/V_c is the cohesive energy at the critical temperature, and RT_c is two-thirds of the kinetic energy at the critical temperature, C' is really nothing else than $^3/_2$ of the ratio of the cohesive energy to the kinetic energy at the critical temperature. If there were no external pressure and if the molecules had no extension, then a/V_c should equal RT_c and C' should be 1, but since the molecules have extension and there is external pressure, C' represents the correction involved in P_c and in $(V_c - b_c)$ of van der Waals' equation.

This is the simplest formula for calculating "a" of van der Waals' equation, since C′ is determined by the relationship $(L - E)/(RTLn(d_l/d_v))$. In Table III, Column 3 contains the values of "a" calculated by Formula 14, using the values of C′ given in Column 2, which were taken from Mills'[1] paper. The values for d_c are those published by S. Young

TABLE III—"a" COMPUTED FROM DIETERICI'S FORMULA

Substance	C′	$a = C'RT_cV_c \times 10^{-12}$	Substance	C′	$a = C'RT_cV_c \times 10^{-12}$
Carbon dioxide	1.762	4.27	Diisopropyl	1.725	25.61
Nitrous oxide	1.513	3.77[2]	*n*-Hexane	1.752	27.15
	—	4.18[3]		1.680[4]	26.04
Sulphur dioxide	1.707	7.50	Chlorbenzene	1.714	27.74
Carbon bisulphide	1.516	13.28	Methyl isobutyrate	1.814	27.62
Methyl formate	1.706	11.28	Methyl *n*-butyrate	1.824	28.57
Ethyl formate	1.747	16.91	Propyl acetate	1.850	29.16
Ether	1.724	18.87	Ethyl propionate	1.837	28.69
Methyl acetate	1.784	17.11	Stannic chloride	1.741	30.12
Benzene	1.690	19.17	Brombenzene	1.691	30.48
Isopentane	1.688	19.88	*n*-Heptane	1.814	34.80
n-Pentane	1.707	20.69		1.685[4]	32.32
Carbon tetrachloride	1.667	21.27	Iodobenzene	1.687	35.48
Propyl formate	1.774	22.57	*n*-Octane	1.858	43.10
Ethyl acetate	1.812	22.56		1.695[4]	39.30
Methyl propionate	1.803	22.42	Diisobutyl	1.813	39.95
Hexamethylene	1.694	23.94		1.669[4]	36.80
Fluorbenzene	1.711	24.18			

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[1] Mills: "The Relation of Temperature and Molecular Attraction," Phil. Mag., (6) **22**, 94–97 (1911).

[2] (d_c = 0.454).

[3] (d_c = 0.41).

[4] At 0°.

except for the simpler gases. The values for "*a*" are for gram mol quantities and expressed in dynes.

If we take Dieterici's modification of van der Waals' equation, namely

$$P = \frac{RT}{V - b} e^{-\frac{a}{VRT}}$$

we obtain by transposing and taking natural logarithms:

$$(16) \qquad Ln(RT/P(V - b)) = a/VRT$$

and at the critical temperature this becomes:

$$(17) \quad Ln(RT_c/P_c(V_c - b_c)) = a/V_cRT_c = {}^3/_2 \text{ cohesive pressure/kinetic energy}$$

Now it has just been shown that C' of the other equation of Dieterici is equal to a/V_cRT_c. Hence we have the relationship:

$$(18) \qquad Ln(RT_c/P_c(V_c - b_c)) = C'$$

Dieterici's equation, like van der Waals', is derived on the assumption that "*a*" and "*b*" are constants. Van der Waals' equation gives, on these assumptions, the result that V_c is equal to $3b_c$. If we take this value for b_c and substitute it in Dieterici's equation, we have:

$$(19) \qquad Ln(3RT_c/2P_cV_c) = C'$$

or since RT_c/P_cV_c is equal to S

$$(20) \qquad Ln(3S/2) = C'.$$

S is usually between 3.5 and 3.9, and C' is between 1.60 and 1.82. As a matter of fact $Ln(3S/2)$ does equal C' fairly closely in a great many cases, particularly in complex substances such as ether and diisopropyl, but in nitrogen the relation does not appear to hold. For example, C' in CO_2 is about 1.76, and S is very nearly 3.5. In nitrogen S is 3.42 which would require that C' should be 1.635, whereas it was found to be not constant, but to advance with the temperature and at 91° Abs. it was 1.535. If this relationship shall be found to hold more generally than appears at present, it would be possible to compute C′ readily from S. It is singular that taking b_c equal to $V_c/3$ should give an approximately correct value for C′ in complex substances in which V_c really equals $2\ b_c$, approximately, and not $3\ b_c$.

5. The Method of Computing "a" from Mills' Formula and the Meaning of the Constant of That Formula

Mills[1] found empirically a relationship between the internal latent heat of vaporization and the difference between the cube roots of the densities of the liquid and vapor, respectively:

$$L - E = \mu'(\sqrt[3]{d_l} - \sqrt[3]{d_v}) \tag{21}$$

L — E in this equation is that for one gram of substance.

Mills has studied this equation very carefully and believes that it means that molecules attract each other inversely as the square of the distance. He believes that the constant, μ', has the mass factor of cohesion in it, and that the cube root of the density signifies that the molecules attract as the square of the distance between the centers of the molecules. In place of using the density the volume may be used instead and written in the form:

$$L - E = \mu'(\sqrt[3]{1/V_l} - \sqrt[3]{1/V_v}) \tag{22}$$

I have elsewhere[2] shown that this conclusion of Mills is, in my opinion, unwarranted and I pointed out that the constant, μ', for a gram mol appeared to have the value $3a/M^{1/3}V_c^{2/3}$. I have now discovered that this value of the constant is the correct one and accordingly μ' has in it not only the mass factor "a" but also the critical volume. The formula probably possesses a different significance from that attributed to it by Mills.

If all the internal latent heat of vaporization was used

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[1] Mills: "The Relation of Temperature and Molecular Attraction," Phil. Mag., 22, 84 (1911).

[2] Mathews: Jour. Phys. Chem., 17, 531 (1913).

in separating the molecules then the difference in cohesive energy of liquid and vapor should be equal to this or, for a gram mol

$$(23) \qquad M(L - E) = a(d_1 - d_v)/M.$$

At temperatures below the critical, $M(L - E)$ will be larger than $a(d_1 - d_v)/M$ for the reason, which has already been stated, that some of the heat passes into the molecules. But as the critical temperature is approached, Equation 23 holds more and more nearly and at the critical point it will hold exactly. Hence at the critical temperature we shall have for a gram mol:

$$(24) \quad M(L - E) = a(d_1 - d_v)/M = \mu'(\sqrt[3]{d_1} - \sqrt[3]{d_v})M$$

and for "*a*" we shall have:

$$(25) \qquad a = \text{limiting value } \mu' M^2 \left(\frac{\sqrt[3]{d_1} - \sqrt[3]{d_v}}{d_1 - d_v}\right)$$

The fraction $\frac{\sqrt[3]{d_1} - \sqrt[3]{d_v}}{d_1 - d_v}$, although it has at T_c the indeterminate value of $\frac{0}{0}$, has a finite value, which is equal to $1/3d_c^{2/3}$, d_c being the critical density. Substituting this value we have for the value of "*a*":

$$(26) \qquad a = \mu' M^2/3d_c^{2/3}$$

This expresses the value of "*a*" in calories; to convert it into dynes it is necessary to multiply by 4.185×10^7. Since $M^{2/3}/d_c^{2/3} = V_c^{2/3}$, the constant μ' has the value:

$$(27) \qquad \mu' = 3a/M^{4/3}V_c^{2/3}$$

Or if μ' is taken for a gram mol and written $M\mu'$, we have:

$$(28) \qquad M\mu' = 3a/M^{1/3}V_c^{2/3}$$

This is just the value I stated that it appeared to have in my former paper but at that time I could not prove that this was its true value. Now since μ' is determined from the relation $\mu' = L - E/(\sqrt[3]{d_1} - \sqrt[3]{d_v})$ we may, from this equation, calculate "*a*" and the results are shown in Column 3 of Table IV.

TABLE IV—CALCULATION OF "*a*" FROM MILLS' FORMULA

Substance	μ'	$a = \mu' M^2/3d_c^{2/3} \times 10^{-12}$	μ''	$a = \mu'' M^2/3d_c^{2/3} \times 10^{-12}$
Carbon dioxide	95.2	4.315	91.8	4.160
Nitrous oxide	88.3	4.04	93.6	4.28
		($d_c = 0.454$)		($d_c = 0.454$)
		4.32		4.58
		($d_c = 0.41$)		($d_c = 0.41$)
Sulphur dioxide	85.5	7.56	85.4	7.55
Carbon bisulphide	82.4	12.84	98.8	15.39
Methyl formate	119.86	12.14	119.8	12.14
Methyl acetate	108.8	17.58	103.6	16.73
Ethyl formate	107.14	17.38	103.9	16.85
Ether	103.8	19.34	102.0	19.01
Benzene	109.23	20.48	110.5	20.72
Isopentane	105.5	20.08	107.0	20.36
Pentane	110.0	21.05	109.4	20.94
Carbon tetrachloride	44.29	21.57	45.3	22.06
Propyl formate	98.79	23.33	93.7	22.13
Ethyl acetate	98.0	23.23	91.7	21.73
Methyl propionate	99.02	23.27	92.4	21.71
Hexamethylene	103.63	24.21	104.5	24.41
Fluorbenzene	85.65	22.00	85.2	22.00
Diisopropyl	97.53	25.96	96.5	25.68
n-Hexane	102.8	27.90	99.2	26.93
Chlorbenzene	81.42	28.10	81.5	28.00
Methyl isobutyrate	87.78	28.68	82	26.49
Methyl *n*-butyrate	91.31	29.56	84.3	27.29
Propyl acetate	93.12	30.45	84.8	27.50
Ethyl propionate	91.59	29.22	80.8	26.38
n-Heptane	98.64	36.23	90.8	33.35
Stannic tetrachloride	26.51	30.69	25.9	29.99
Brombenzene	55.37	30.81	56.3	31.33
Iodobenzene	43.37	36.09	43.8	36.45
Diisobutyl	87.72	41.56	80.7	38.24
n-Octane	92.78	44.46	84.2	40.35

In that table Column 3 shows the values of "*a*" using the mean values of μ' found by Mills in the paper already cited, and Column 5 gives the values of "*a*" calculated from a value of μ'' computed by him from the equation $dP/dT = 2R/V_c$. It will be noticed that the values of "*a*" thus calculated agree very closely with the values computed from Dieterici. A particularly good agreement is obtained between Formulas 26 and 14 if for μ'' the values computed from the relation $dP/dT = 2R/V_c$ are employed in place of μ' which is actually observed. For most substances μ' and μ'' agree closely but the deviations are marked in octane, diisobutyl, heptane, hexane and the more complex esters such as methyl butyrate and its isomers. These are the substances of the highest critical temperatures; the rise of Dieterici's constant near the critical temperature in some of these possibly may mean a slight decomposition.

We thus have two methods of computing "*a*" neither of which involves any assumption as to the value of *b* of van der Waals, both methods theoretically grounded, or at least that of Dieterici is so grounded, and no assumptions are made at any point in the calculation. The two methods yield closely agreeing values of "*a*" and these values, as we shall presently see, are practically identical with those computed from the molecular weight and the number of valences.

a. The Meaning of Mills' Equation

Having found that the significance of the constant μ' is:

$$\mu' = 3a/M^{1/2}V_c^{2/3} \tag{27}$$

in which "*a*" is expressed in calories for a gram mol of the substance or, if "*a*" is in dynes:

$$\mu' = 3a/M^{1/2}V_c^{2/3}(4.185 \times 10^7) \tag{28}$$

we see that μ' has in it, indeed, the mass factor of the molecular cohesion, or "*a*," as Mills supposed, but it also has in it the two thirds power of the critical volume. Just what this equation means I am not able to say but it may be transposed into the form:

$$(29)\quad M(L - E) = \mu' M(\sqrt[3]{d_1} - \sqrt[3]{d_v}) = 3ad_c^{2/3}(\sqrt[3]{d_1} - \sqrt[3]{d_v})/M^2(4.185 \times 10^7) = \frac{3a}{V_c(4.185 \times 10^7)}\left(\sqrt[3]{\frac{V_c}{V_1}} - \sqrt[3]{\frac{V_c}{V_v}}\right)$$

In other words the molecular internal latent heat is equal to three times the cohesional energy at the critical temperature multiplied into the difference of the cube roots of the ratios of the critical volume to the liquid and vapor volumes, respectively. I do not yet see why this should be so. It is, however, clear that the internal latent heat involves not only the heat used in overcoming cohesion, but also heat used in increasing the intra-molecular energy. The interpretation given the formula by Mills is for this reason, I believe, unwarranted.

From Dieterici's equation we see that for a considerable temperature interval the heat used in expanding from liquid to vapor while not equal to the difference in cohesive energy in the liquid and vapor respectively, as it would be were all the heat used in overcoming cohesion, is, nevertheless, a constant proportion of it. Hence we may write the formula:

$$(30)\qquad M(L - E) = C'a(1/V_1 - 1/V_v)$$

In this formula M is the molecular weight, L — E the internal latent heat for a gram of the substance, C′ is Dieterici's constant, "*a*" the usual constant and V_1 and V_v the volume occupied by a gram mol of the substance in the liquid and vapor form. From this we may get another formula for the calculation of "*a*," namely,

$$(31)\qquad a = M^2(L - E)(4.185 \times 10^7)/C'(d_1 - d_v).$$

This formula may be used when the critical data are not known. The result is given in dynes for a gram mol quantity.

If we combine Dieterici's and Mills' equations we have:

$$(32)\qquad C'RTLn(d_1/d_v) = L - E = \mu'(\sqrt[3]{d_1} - \sqrt[3]{d_v})$$

And if gram mol quantities be taken

$$(33)\qquad RTLn(d_1/d_v) = 3RT_c[(V_c/V_1)^{1/3} - (V_c/V_v)^{1/3}].$$

Now $RTLn(d_1/d_v)$ is the amount of work which is necessary to expand the gas from the liquid to the vapor density provided all the work is done in separating the molecules and no energy is absorbed by the molecules. This, for some reason, is exactly equal, for a considerable temperature interval, to twice the kinetic energy of the molecules at the critical temperature multiplied by the fraction $(\sqrt[3]{d_1} - \sqrt[3]{d_v})/\sqrt[3]{d_c}$. Why this should be I do not see.

6. Molecular Attraction Is Determined by the Molecular Weight and the Number of Valences in the Molecule

There was some uncertainty about my former proof that cohesion was a function of the molecular weight by the number of valences. This uncertainty was due to the uncertainty of the values of "*a*." I had to make some assumption at some point in all the various methods of calculating "*a*" and this, of course, weakened the proof. That uncertainty has now been removed and the results of the computation of "*a*" by these new and certain methods show that the agreement between the values of "*a*" computed from the molecular weight and the number of valences and the values computed from the internal latent heat of vaporization in the way just stated is much better than was obtained in my former papers. By the new and improved method the values obtained for "*a*" for the simpler substances especially are somewhat lower than the old, and in nearly all the substances they are lower than the values given in my paper on the Internal Pressures of Liquids, but somewhat higher than those in my first paper on the value of "*a*." The values of "*a*" given in this paper are intended to supplant my former values.

In Table V I have put down the values of "*a*" calculated from Dieterici's and Mills' formulas and compared them with the values calculated from the molecular weights and number of valences by the formula:

$$a = N^2\left(m^2k\,\frac{\text{val.}}{M}\right)^{2/3} \tag{34}$$

In this formula N is the number of molecules in a gram mol and is equal to 6.062 × 10^{23}; m^2k is the gravitational attraction of the molecules at 1 cm distance, m being the

TABLE V—COMPARISON OF "a" COMPUTED FROM MILLS AND DIETERICI WITH THE RESULTS OBTAINED FROM THE MOLECULAR WEIGHT AND THE NUMBER OF VALENCES. $a \times 10^{-12}$

Substance	By Mills a	By Dieterici a	By molecular weight and valences a	Weight (used in computation)	Valences (used in computation)
Hydrogen	—	0.298[1]	0.296	2	2
Nitrogen	—	1.72[1]	1.73	28	2
Carbon dioxide	4.32	4.27	3.69	44	4
	—	—	4.84	44	6
Nitrous oxide	4.04[2]	3.77[2]	3.37	44	4
	4.32	4.18	4.84	44	6
Sulphur dioxide	7.55	7.50	7.53	64	8
Carbon bisulphide	12.84	13.28	13.40	76	16
Methyl formate	12.14	11.88	11.45	60	16
	—	—	12.38	60	18
Ethyl formate	17.38	16.91	16.28	74	22
	—	—	17.25	74	24
Ether	19.34	18.87	19.12	74	28
Methyl acetate	17.30	17.11	16.28	74	22
	—	—	17.25	74	24
Benzene	20.72	19.17	20.73	78	30
Isopentane	20.36	19.88	20.52	72	32
n-Pentane	20.94	20.69	20.52	72	32
Carbon tetrachloride	21.57	21.27	21.44	153.8	16
Propyl formate	23.33	22.57	21.46	88	28
	—	—	22.47	88	30
Ethyl acetate	23.23	22.56	21.46	88	28
	—	—	22.47	88	30
Methyl propionate	23.27	22.42	21.46	88	28
	—	—	22.47	88	30
Hexamethylene	24.21	23.94	24.30	84	36
Fluorbenzene	22.00	24.18	23.81	96	30
Diisopropyl	25.96	25.61	25.90	86	38
n-Hexane	26.93	27.15	25.90	86	38
Chlorbenzene	28.10	27.74	27.62	112.45	32
Methyl isobutyrate	28.68	27.62	26.97	102	36
	—	—	28.00	102	38
Methyl butyrate	29.56	28.57	26.97	102	36
	—	—	28.00	102	38
Propyl acetate	30.45	29.16	28.00	102	38
Ethyl propionate	29.22	28.69	28.00	102	38
Stannic chloride	30.69	30.12	30.49	260.8	16
n-Heptane	36.23	34.80	31.58	100	44
Brombenzene	30.81	30.48	33.05	156.96	30
Iodobenzene	36.09	35.48	39.34	203.85	30
n-Octane	44.46	43.10	37.54	114	50
Diisobutyl	41.56	39.95	37.54	114	50

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[1] The values of hydrogen and nitrogen are computed by the method described presently. I have incorporated them for purposes of comparison.

[2] The two values for a of nitrous oxide are from different critical densities.

gravitational mass of the molecule; val. is the number of valences in the molecule, and M is the molecular weight. *k* is the gravitational constant. The formula may also be written, as I formerly wrote it:

$$a = 3.201 \times 10^{-37} N^2 (M \times \text{val.})^{2/3} \tag{35}$$

The factor 3.201×10^{-37} is the value of the two-thirds power of the gravitational attraction of two molecules of molecular weight of unity and at one cm distance between their centers.

If we examine Table V we see, indeed, how exactly the values of "*a*" thus obtained agree with those computed from Mills' and Dieterici's equations. The deviation is seldom more than two or three percent and very many agree within one percent. The deviations are due, possibly in part, to there being extra or residual valences on some of the molecules. Thus for the esters "*a*" comes close to the theoretical if there be two extra valences on one of the oxygen atoms of the ester, a conclusion which has been reached from the chemical behavior of these esters. The deviation of iodobenzene and brombenzene may be disregarded since the critical data of these were extrapolated from a long distance and are probably somewhat incorrect. In the case of diisobutyl some decomposition probably occurs near the critical temperature, since Mills found on examining the specimen used by Young for his determination of the critical data and densities that it was not a homogeneous substance. As regards octane and heptane the latent heat from 200–270° does not fall in a normal manner but behaves as if some decomposition were occurring. Dieterici's constant C′ in octane shows the following course (Mills):

120°	92.6
150	92.5
170	92.4
200	93.0
220	93.6
240	93.7
260	94.6
270	94.3
280	93.4
290	91.0
296.2	Critical

Heptane shows a similar increase from 200–240°. Neither pentane nor hexane behaves in this way. Methyl butyrate shows a somewhat similar behavior but methyl isobutyrate does not. It is probable, also, that there is some residual valence on the carbon atoms of octane, since it behaves somewhat as an unsaturated body, Professor Gomberg tells me.

The calculation of the values of "a" for nitrogen and hydrogen which are given in Table V were not made in the usual way but as follows: For nitrogen the latent heat figures which I have employed are those of Planck.[1] At first I attempted to compute "a" in the usual way from the formulas of Dieterici and Mills, but I found that neither C′ nor μ' was constant, but both advanced steadily in value.

T	d_l	d_v	L — E	C′	μ'
62.5	—	—	47.05	1.472	—
77.0	0.8087	0.00448	42.67	1.498	55.5
85.0	—	—	40.04	1.521	—
91.0	0.7485	0.01626	37.98	1.535	58.03

Even the highest of these values gave results for "a" which were considerably lower than the theoretical. Thus using the recently published critical data of Mathias, Crommelin and Onnes[2] of $T_c = 125.96$, $d_c = 0.311$, and $P_c = 33.49$, "a" would equal $1.535RT_cV_c$ or 1.421×10^{12}. The same value is obtained by the use of Mills' formula with μ' equal to 58.03. 1.722×10^{12} is the theoretical value for "a" required by the formula $a = N^2(m^2k \times \text{val.}/M)^{1/3}$. On attempting to compute L — E for temperatures nearer the critical, hoping that C′ would there be constant, I found that the formula of Planck did not allow such an extensive extrapolation. The following temporary expedient suggested itself. The internal latent heat is composed of two parts, namely, a part consumed in overcoming molecular cohesion, and a part which goes into

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[1] Planck: Phys. Zeit., 11, 633 (1910).

[2] Mathias, Onnes and Crommelin: Proc. Amsterdam Acad. Sci., 17, 953 (1915).

the molecules. So we can write the formula: $L - E = x + y$. Now y is evidently equal to the difference in cohesive energy, or $a(d_1 - d_v)/M$, or if $L - E$ is taken for a gram it is equal to $a(d_1 - d_v)/M^2$. Or since $d_1 - d_v = d_0((T_c - T)/T_c)^{1/3}$

$$L - E = x + ad_0(T_c - T)^{1/3}/M^2T_c^{1/3}.$$

To find x I made the guess that it was proportional to $(T_c - T)^{4/3}$

$$L - E = K(T_c - T)^{4/3} + ad_0(T_c - T)/M^2T_c^{1/3}.$$

Substituting the values of $(T_c - T)$, $(T_c - T)^{1/3}$ and $L - E$ from the temperatures 62.5° and 77° and taking d_0 as Sd_c, S being 3.421, we find the value of "a" to be 1.734×10^{12}. If d_0 had been taken as computed from the equation $d_1 - d_v = d_0((T_c - T)/T_c)^{1/3}$, or as 1.104 in place of 1.064, the value of Sd_c, it would have made "a" equal to 1.703×10^{12}. Of course, this whole determination is in the nature of only an approximation in the case of nitrogen.

To determine the value of "a" for hydrogen I put "a" of nitrogen as equal to 1.722×10^{12} and computed b_c of van der Waals' equation at the critical temperature. It turned out to be equal to $V_c/1.897$. This is a matter of considerable interest that b_c is so large a fraction of V_c in the simple substances and we shall return to it in a moment. To return to the calculation of "a" for hydrogen. T_c of hydrogen is 31.95, P_c, 11.5, and d_c, 0.033. Substituting these values in van der Waals' equation, and making b_c equal $V_c/1.897$ we have for "a" of hydrogen the value 2.978×10^{11} in place of the theoretical from the valence and weight formula of 2.964×10^{11}. The critical temperature cited of hydrogen is that of Buller, the density from Dewar, the pressure of 11.5 is intermediate between the values of Buller and Olszewski.

The foregoing values for "a" require that the value of b_c shall be somewhat higher than $V_c/2$ which is the value in the more complex substances. This is contrary to the hypothesis that in simple substances such as these gases the value of b_c approaches that of $V_c/3$ as a limit. The latter supposition is, I think, unwarranted and incorrect. It does not consider the fact that in these simple substances the value of "a"

is extremely small. The result of this is that it is necessary for the molecules to separate only a short distance in the simple substances for the cohesion to be reduced to so small a proportion of the total pressure that the critical state is reached and the substance can exist only in the state of a gas. In the more complex substances with their greater value of "*a*" it is necessary for the molecules to separate much farther before they have sufficiently reduced the cohesion to permit the substance to become a gas. Consequently when the critical state is reached the molecules will make a larger proportion of the total volume in the simpler than in the complex substances, and not the reverse as has been so generally concluded. It is clear that if we had a substance without any cohesion, that is, a monatomic gas without any valence at all, it could not be condensed to a liquid and the critical state would be absolute zero and the value of V_c and b_c would be identical. Simple substances approach V_c as the limit for b_c and not $V_c/3$.

7. The Relation of Cohesional and Gravitational Attraction

The cohesional and gravitational attractions of two molecules are related in the manner shown in Formula 34, namely,

$$a = N^2\left(m^2k\,\frac{\text{val.}}{M}\right)^{2/3}. \tag{34}$$

Or, if "*a*" is taken for a single pair of molecules and written M^2K, M being the cohesional mass of a molecule to correspond with the gravitational mass,

$$M^2K = \left(m^2k\,\frac{\text{val.}}{M}\right)^{2/3}. \tag{36}$$

That is, the cohesional attraction at unit distance will be equal to the two-thirds power of the gravitational attraction multiplied by the two-thirds power of the ratio of the number of valences in the molecule to the molecular weight. The total attraction of two molecules will be, then, at the distance *r* between their centers presumably equal to the sum of the gravitational and cohesional attractions; or, if F is the force of attraction, and *m* the gravitational mass,

$$(37)\quad \mathrm{F} = m^2k/r^2 + \mathrm{M}^2\mathrm{K}/r^4 = m^2k/r^2 + \left(m^2k\,\frac{\text{val.}}{\mathrm{M}}\right)^{2/3}/r^4.$$

In a former paper it was suggested in discussing this relationship that it indicated that the cohesional attraction was of the nature of magnetism, the movement of the valence electrons generating some kind of a magnetic field. Inasmuch, however, as the valence effect is additive, we should have to assume, it seems to me, that the orbits of the valences should be in parallel planes, otherwise the effect of the movement of one valence might neutralize the effect of another. The way this uniformity of movement could be secured would be by the molecules revolving as wholes and thus the electrons would all revolve in the same direction and in parallel orbits. If this were the case, then since the cohesion does not vanish or diminish in the neighborhood of absolute zero, we should have to make the further assumption that the revolution of the molecule was independent of the temperature. Furthermore it is probable that at low temperatures the molecules lie so close together in a solid that they cannot revolve freely. In fact the melting point may be nothing else than that temperature at which the molecules are sufficiently separated to be able to revolve freely. For this reason I have also thought of the possibility that the effect of the valences is electrostatic rather than electromagnetic, and the following possibility occurred to me, which is, of course, only a tentative suggestion.

It looks, from the fact that the cohesion contains the gravitational attraction multiplied by the ratio of the number of valences to the molecular weight, as if there were a certain number of gravitational lines of force running between the molecules, the number being proportional to the molecular weight, and that these gravitational lines of force were electrified by the valence electrons. Perhaps being thus electrified the gravitational lines of force do not run straight, but repel each other and this repulsion is a powerful factor in bringing the molecules together. It is as if the ether lying between the molecules was rarefied by this electrification and its density decreased and the molecules were forced together by the unequal densities of the ether, that lying behind the molecules being denser than that between them. The effectiveness of this repulsion is determined by the ratio of the number of electrifying valence electrons to the number of gravitational lines of force to be electrified, hence the value of the ratio val./M. Obviously a large or heavy molecule with a large number of gravitational lines of force would be but slightly influenced by a small number of valences, as these would produce but a small amount of electrification. We can picture the lines of force as running from the faces of the cubical molecules. They are repelled from each other and curved as in Fig. 3, this curvature tending to bring the ends of the lines of force closer together and thus increasing the gravitational attraction so that it becomes cohesional attraction. When the molecules are far apart the curvature due to their repulsion will have little effect, but as the molecules approach more closely this curvature has a greater and greater effect so that the cohesional attraction shows itself only when the molecules are close together, and appears to vary inversely with a much higher power than the square of the distance.

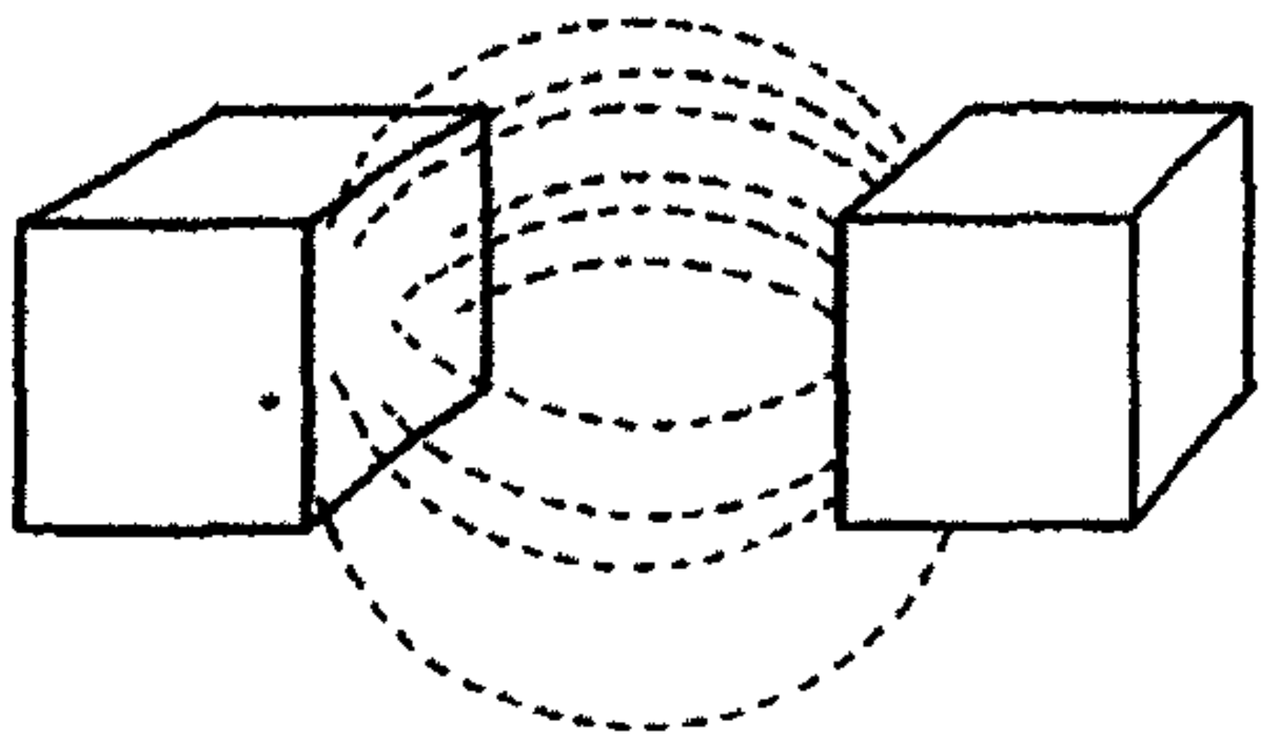

Fig. 3

Two cubical molecules showing hypothetical curvature of the lines of gravitational force running between two adjacent faces. The curvature is supposed to be due to mutual repulsion due to the electrification of the lines by the valence electrons, and the intensification of the gravitation thus produced is supposed to be the cohesion.

The exponent of two-thirds would have reference, perhaps, to the area of the cross section containing the lines of force lying between the two adjacent faces of the molecules.

8. The Relation of the Internal to the External Pressure at the Critical Temperature

We may pause for a moment at this point to consider another interesting relationship which has appeared from the discovery of the meaning of the constant C′ of Dieterici, namely, the relation between the internal and external pressures at the critical temperature. From Formula 15 and the formula: $S = RT_c/P_cV_c$ we may find the value of this ratio. Multiplying the values of S and C′ we have the result:

$$C'S = a/V_cP_c^2 = K_c/P_c. \tag{38}$$

K_c is the internal pressure at the critical temperature. The value of this fraction varies from about 7 in the case of more complex substances to about 6 in the simplest substances, as S tends to approach 3 in the simplest compounds, being 3.23 in helium and 3.5 in oxygen. The value for hydrogen is still uncertain but is probably not far from 3.4. Table VI gives the values of C′, S and K_c/P_c.

In a former paper[1] this ratio of K_c/P_c was expressed as equal to $(S^2 - S + 2)/(S - 2)$. This formula was based on two assumptions, namely, that b_c was always $2V_0$ and that V_c was equal to SV_0. The first of these assumptions is, I think, clearly incorrect for simple substances. While the formula used gave values for K_c/P_c which were close to 7, just as the present formula, namely C′S, does, yet in more simple substances such as CO_2, O_2 and N_2 the ratio of K_c/P_c is undoubtedly less than $(S^2 - S + 2)/(S - 2)$ which approaches 8 as a limit, whereas the formula C′S makes it nearer to 6. The values of "*a*" computed from the formula $a = (S^2 - S + 2)/(S - 2)P_cV_c^2$ are, hence, all too high in the simpler substances and will need revision accordingly. The formula $a = C'SP_cV_c^2$ gives, of course, the same values of "*a*" as those already computed from Formula 14.

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[1] Mathews: Jour. Phys. Chem., 17, 614 (1913).

TABLE VI—RATIO OF INTERNAL TO EXTERNAL CRITICAL PRESSURES

Substance	C′	S	C′S or K_c/P_c	K_c/P_c observed
Ether	1.724	3.814	6.575	—
Diisopropyl	1.725	3.742	6.453	6.536
Isopentane	1.688	3.734	6.303	—
Diisobutyl	1.813	3.810	6.908	—
n-Pentane	1.707	3.762	6.422	6.384
n-Hexane	1.752	3.830	6.710	—
n-Heptane	1.814	3.945	7.154	—
n-Octane	1.858	3.864	7.179	—
Hexamethylene	1.694	3.798	6.434	—
Benzene	1.690	3.755	6.346	—
Fluorbenzene	1.711	3.797	6.497	—
Chlorbenzene	1.714	3.776	6.472	—
Brombenzene	1.691	3.813	6.447	—
Iodobenzene	1.687	3.778	6.373	—
Carbon tetrachloride	1.667	3.677	6.130	—
Stannic chloride	1.741	3.755	6.537	—
Methyl formate	1.706	3.921	6.689	—
Ethyl formate	1.747	3.895	6.804	—
Methyl acetate	1.784	3.943	7.034	—
Propyl formate	1.774	3.869	6.863	—
Ethyl acetate	1.812	3.885	7.040	—
Methyl propionate	1.803	3.908	7.046	—
Propyl acetate	1.850	3.934	7.278	—
Ethyl propionate	1.837	3.922	7.205	—
Methyl butyrate	1.824	3.903	7.119	—
Methyl isobutyrate	1.814	3.865	7.011	—
Carbon bisulphide	1.516	—	—	—
Chloroform	1.706	—	—	—
Carbon dioxide	1.762	3.486	6.142	—
Sulphur dioxide	1.707	—	—	—
Nitrous oxide	1.513	3.401	5.146	$T_c = 38.8$; P_c, 77.5; d_c, 0.454

9. Comparison of the Observed and Computed Values of the Constant C of Eötvös' Law

After this long digression we may now return to the point of departure, namely, Eötvös' law. We have found how to calculate the density at absolute zero, the depth of the surface film, and also how to get the value of "*a*." We will now substitute the values thus found in formula

$$C = ad_0/3MN^{1/3}T_c \tag{6}$$

and see how the values thus obtained agree with those determined directly from the surface tension measurements by the formula:

$$(1) \qquad sV_1^{2/3} = C(T_c - T)$$

TABLE VII—COMPARISON OF THE FOUND AND COMPUTED VALUES OF THE CONSTANT OF EÖTVÖS' SURFACE TENSION LAW

Substance	C computed	C found
Nitrogen	2.045	1.95
Oxygen	2.20	1.92--2.03
Ether	2.195	2.160 (Ramsay)
Ethyl formate	2.144	2.01–2.08
Benzene	2.138	2.163 (Morgan and S.)
	—	2.142 (Richards and Coombs)
Methyl acetate	2.182	2.11–2.17
Ethyl propionate	2.22	2.23
Ethyl acetate	2.23	2.16 (2.24 Ramsay and Aston at —89°)
Methyl isobutyrate	2.268	2.25
Hexane	2.12	2.11–2.27
Methyl butyrate	2.22	2.22
Propyl formate	2.14	2.12–2.11
Methyl propionate	2.21	2.18
Stannic chloride	2.20	2.20 (Kistyakovsky)
Propyl acetate	2.23	2.23
Methyl formate	2.06	2.00
Hydrogen	1.60	1.47 (Onnes)

The values under "C found" have been taken for the most part from the values of the results of Morgan and his colleagues corrected by the method of Lohnstein. But in some cases I have used the values of Ramsay and Aston, or Ramsay and Shields. Where more than one figure was available I have generally taken the higher values, as the errors in the capillary rise method tend to lower the observed values and the higher values are more apt to be correct. I attach especial importance to the excellent agreement in the case of benzene of which the surface tension has recently been determined with great accuracy by Richards and Coombs. It will be noticed that the two results agree within a fraction of a percent.

It will be obvious from this excellent agreement that we can use the surface tension measurements to compute "a" of van der Waals' equation by the formula given in my former paper:

(39) $$a = sV_1^{2/3}3MN^{1/3}T_c/(d_0(T_c - T))$$

or if the critical temperature is unknown

(40) $$a = 3sV_1^{2/3}N^{1/3}M[d_0^2/(d_1 - d_v)^3]$$

a. Relation of Dieterici's Constant to That of Eötvös

The constant of Dieterici has the value: $C' = a/RT_cV_c$; and that of Eötvös has the value: $C = ad_0/3MN^{1/3}T_c$. From these two equations we see that the constant of Dieterici may be readily found from that of Eötvös since the following relationship exists between them:

(41) $$C' = 3Cd_cN^{1/3}/d_0R$$

In this d_c and d_0 are the densities at the critical temperature and the absolute zero, respectively, R the gas constant for a gram mol, and N the number of molecules in a gram mol. C/C' will equal $Rd_0/3N^{1/3}d_c$. The surface tension constant, C, is obviously one-third the ratio of the cohesive energy at the absolute zero to the critical temperature, the ratio being divided by $N^{1/3}$, or $C = a/3V_0N^{1/3}T_c$.

It is clear that if desired the ratio d_0/d_c can readily be found from the two constants C and C′.

10. Thomas Young's Formula Expressing the Relation of Cohesion and Surface Tension

One more feature of the general formula expressing the relation between cohesion and surface tension and which has just been given may be pointed out. It is the general formula expressing this relation of which the formula of Thomas Young is the limiting case at absolute zero. It will be recalled that Young, in his classical papers on cohesion and surface tension published over a century ago, by the most ingenious reasoning concluded that the relation between the surface tension energy and the cohesion was expressed by the formula

(42) $$s = Kr/3.$$

In this equation, K was the cohesive pressure, represented later by van der Waals as a/V^2; and r was the radius of action of the cohesive attraction. Now since this formula expresses the surface tension as the function of the cohesion of the liquid alone it will only hold at that temperature at which the cohesion in the vapor can be neglected. If r is equal, as appears probable, to a single molecular diameter, then at absolute zero the formula becomes

(43) $$s = av_o^{1/3}/V_o{}^{2}3.$$

Multiplying both sides of the equation by $V_o^{2/3}$ we have:

(44) $$sV_1^{2/3} = av_o^{1/3}/V_o{}^{4/}3$$

Multiplying both numerator and denominator of the right-hand expression by $N^{1/3}$, where N is the number of molecules in a gram mol, we have

(45) $$sV_1^{2/3} = aV_o^{1/3}/3V_o{}^{4/}N^{1/3}$$

Changing to density in place of volume we have:

(46) $$sV_1^{2/3} = ad_o/MN^{1/3}3$$

This, as will be seen, is nothing else than the general Formula 5 at the limit of absolute zero where $(T_c - T)/T_c$ becomes equal to unity. The law of Eötvös and the law of Young are hence the same law a little differently expressed.

10. Conclusion

This paper brings one phase of the work which van der Waals began in his celebrated paper on the transition of liquids to gases in a certain sense to a conclusion. By following the road he marked out we now have arrived at the expressions of the relationship between cohesion and surface tension on the one hand and between cohesion and gravitation on the other. By the first relation we can compute either the cohesion from the surface tension, or the surface tension from the cohesion; and the latter relation shows in clear light and for the first time the properties of the molecule which determine its cohesional attraction. It promises, indeed, to clear up the very nature of molecular cohesion and gravitation itself. The equation of van der Waals has, indeed, been a torch to light the way of the physicist and the physical chemist through some of the darkest regions of the physical world. Of the many discoveries to be attributed to it not the least interesting, I believe, is the discovery of the relation of cohesion and gravitation, and the relation of cohesion and surface tension. The constant "*a*" of van der Waals has shown itself to be one of the most fundamental constants in nature, as fundamental, indeed, as the constants of gravitation and the molecular weights. From it we can determine the number of valences in a molecule more surely than in any other way, and in this respect alone it will be invaluable in its future service to constitutional chemistry.

With the value of "*a*" thus established, the value of "*b*," the other correction for the molecular volume, can now be determined and from it such important facts as the volumes of the molecules and the atoms, and their behavior under compression can be determined in a very simple way. Such work van der Waals, in his recent papers, has already begun. There can be no doubt of the rich harvest to be had in this field. We can not close this paper without expressing again our admiration of the fruitful work of this great physicist which has resulted in so many valuable discoveries springing from his formulation of the relationship between the cohesional attraction, the extension, and the kinetic energy of molecules in his well-known equation.

University of Chicago

THE RECRACKING OF A CRACKED OIL PRODUCED FROM PETROLEUM

BY GUSTAV EGLOFF AND THOMAS J. TWOMEY

Introduction

In the cracking of petroleum, either for gasoline or aromatics, by the gas phase method, a cracked oil representing a percentage of the oil pumped into the cracking tube is recovered in the condensers and in the carbon trap. Whether the operation has been conducted for either gasoline or aromatics, the cracked oil is distilled to 170° C. The distillate up to this point contains the gasoline or the aromatic hydrocarbons, benzene, toluene and xylenes produced. The question arose as to the disposition of the residue above 170° C. This residue from commercial operations contains, besides oil, approximately 20 percent pitch and one to two percent of naphthalene. Would it be advisable to crack it again for the production of aromatics or gasoline, and what yields would be obtained in comparison with those obtained by the first decomposition of the petroleum oil? By experience it has been learned that a petroleum oil which has a relatively high pitch content—in this case represented by the residue with its 20 percent pitch content—is not especially desirable as a starting oil for the production of benzene and toluene on account of the resulting carbon formation. Whenever possible, the carbon formation as controlled by the composition of the starting oil is avoided. For this reason, the residue is distilled and an oil is obtained free from pitch.

The problem then limited itself to the advisability of using the distillate from the cracked oil for further cracking and to ascertaining the yields of either gasoline or aromatics which might be obtained. Seeking this information constituted the grounds for the present communication. The questions which were to be answered were as follows:

1. What value has a cracked oil for either the production of gasoline or aromatic hydrocarbons?

2. Will the recracking of a cracked oil result in amounts of carbon sufficient to make commercial operations not feasible?

Theoretical

There can be but one answer as to results which will be produced by thermolizing a cracked oil. These are deduceable from the nature of a cracked oil itself and from data obtained in the cracking of different types of oils.

Depending upon the extent to which the decomposition produced by temperature and pressure has taken place, a recovered oil is obtained which contains aliphatic and aromatic hydrocarbons in proportions corresponding to these conditions. If the reaction is carried far enough, it is possible to obtain a recovered oil which consists almost entirely of aromatic compounds. The cracked oil studied in this paper was made under conditions which gave a mixture of these two types. The aromatic hydrocarbons resulted from the breaking down of the aliphatic compounds present in the petroleum: the aliphatic compounds are composed of low boiling compounds produced by the cracking and high boiling compounds unaffected by the cracking reaction due to incomplete equilibrium. In any distillate from a cracked oil boiling above 200° C—similar to the one employed in these experiments—it is not a simple matter to show chemically that there are aromatic hydrocarbons present. In this case, the presence of naphthalene and anthracene, the determination of which is simple, was not considered. A physical constant, however, such as that of specific gravity, may be safely used as a qualitative indication. This method is recommended by Engler.[1] The specific gravity of aromatic compounds is so much higher in value than those of the aliphatic compounds that mixtures of these types of hydrocarbons are shown by a gravity midway between the two extremes. The gravity of the distillation cut from the cracked oil is between that known for similar distillation cuts from many petroleums, and that generally associated with dead or creosote oils from which the

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[1] Engler-Höfer: Das Erdöl, 1914.

naphthalene and anthracene salts have been removed. On these grounds, the conclusion was drawn that the distillate derived from the cracked oil was a mixture of aliphatic and aromatic hydrocarbons or, perhaps better stated, a mixture of unchanged petroleum and aromatic hydrocarbons produced by cracking.

There are sufficient data at hand to show what happens when a petroleum or aromatic oil is cracked by itself. The literature in regard to the decomposition of the first type of oil is extensive, the tendency of this reaction being as follows: Aliphatic to aromatic hydrocarbons to hydrogen and carbon. On the other hand, there are less accessible data on the cracking of aromatic compounds boiling above 200° C. In a series of cracking experiments,[1] using dead oils, *i. e.*, distillation cuts from coal tar above 200° C, it was found that these types of oils—almost aromatic entirely in composition—did not tend to break down to any considerable extent to lower boiling hydrocarbons.

An oil containing such a mixture of aliphatic and aromatic hydrocarbons will break down into lower boiling compounds only in proportion to the amount of aliphatic hydrocarbons —unchanged petroleum—present. Since the cracked oil only contains a percentage of unchanged petroleum, the cracking will not produce as much gasoline or aromatic hydrocarbons such as benzene and toluene as did the cracking of the original petroleum oil. It is also to be expected that more carbon will be produced because whatever cracking of the aromatic constituents takes place tends to produce carbon and gas.

The Results of This Paper

Experimental data were obtained directly in accord with the theoretical considerations. From a study of the results produced by the thermal decomposition of a petroleum oil and a cracked oil derived from the petroleum oil, it is possible to show that a cracked oil is not so well adapted for the production of gasoline as is the petroleum oil; that the cracked

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[1] Rittman and Egloff: Met. and Chem. Eng., 24, 52 (1916).

oil is adapted for the production of aromatic hydrocarbons, but then only yielded much smaller percentages of these compounds as compared to those made from the petroleum oil, and that carbon formation is greater when the cracked oil is recracked than when the petroleum oil is subjected to the same factors of decomposition.

Experimental

a. *Oils Used*

The two oils employed for the cracking experiments were (1) a distillate or gas oil from Pennsylvania Crude Petroleum, and (2) the distillate between 170 and 360° C from the recovered oil produced by the cracking of the distillate from the Pennsylvania Crude Petroleum. The analysis of these two oils by distillation in a standard Engler flask of 100 cc capacity and by specific gravities follows:

Distillation Analysis

A = Petroleum Oil
B = Cracked Oil

	Sp. gr.	To 170° C		170–230° C		230–270° C		270–360° C		Residue %
		%	Sp. gr.	%	Sp. gr.	%	Sp. gr.	%	Sp. gr.	
A	0.817	0.0	—	0.0	—	21.4	0.798	78.6	0.826	0.0
B	0.892	3.0	0.824	19.3	0.857	26.9	0.879	45.0	0.900	5.3

The main difference in these two oils is that the gravity of distillation cuts of the cracked oil are considerably higher than those of the distillate from the Pennsylvania Crude Petroleum. This indicates, as has already been mentioned, that the cracked oil is a mixture of unchanged petroleum and aromatic hydrocarbons which were formed by the first cracking.

b. *Furnace Employed*

The cracking of the two oils was conducted in an electrically heated furnace which has been described. Briefly, it consisted of a one and one-half inch diameter steel tube, thirty-two inches in length, and which was operated in a vertical position. To the top of the tube was attached a lubricator through which the oil was admitted to the tube. Connected at the bottom was a condenser and a receiver. The tube was heated over a length of 22 inches by conducting 110 volt D. C. current through 18 gage nichrome wire wound three times to the inch and insulated from the tube by three layers of asbestos paper. The temperature of the cracking was recorded by a pyrometer inserted through a weld and a stuffing box into the center of the tube. A natural gas line conducted through a compressor led into the top of the tube. The gases formed during the cracking were led out by means of a pipe line to the gasometer from the top of the receiver.

c. *Experiments Conducted*

The oils were cracked at atmospheric and 150 lbs. pressure at temperatures 550, 600, 650 and 700° C, under identical conditions. The temperature of the tube as recorded by the pyrometer was controlled accurately by means of resistance in the electrical circuit and varied only ±5° C during an experiment. The oil was admitted from the lubricator at a constant rate of three drops per second which represented a flow of approximately 246 grams per hour. The regularity of the rate was controlled by comparison with a metronome which oscillated three times to the second. When operating at 150 lbs. pressure, the pressure in the system was built up by means of compressed natural gas.

For each experiment 546 grams of oil were used. Three or more runs were made at each temperature and pressure in order to obtain checking results and for the purpose of obtaining sufficient oil for analysis. In the experimental data the average of these runs are reported.

d. *Method of Analysis*

The cracked oil recovered from the receiver was filtered to remove any suspended carbon and then analyzed for benzene, toluene and xylenes by a method devised by the authors.[1] The naphthalene and anthracene salts were frozen from the distillation cuts and thoroughly dried before weighing. The cut to 170° C was taken as indicative of the amount of gasoline produced. All analytical results are expressed in percents by weight. Specific gravities were taken by means of a Westphal balance at 15.5° C.

Experimental Data

The results found from the cracking of the distillate oil from Pennsylvania Crude Petroleum and the cracked oil derived from it, under similar conditions of temperature and pressure are shown in the following manner:

Table 1 and Figs. 1 and 2.—The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of recovered oil and the specific gravity of the recovered oil from the petroleum and cracked oils.

Table 2 and Figs. 3 and 4.—The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of benzene, toluene, xylenes, naphthalene and anthracene in the recovered oils produced from the petroleum and cracked oils.

Table 3 and Figs. 5 and 6.—The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of benzene, toluene, xylenes, naphthalene and anthracene on the basis of petroleum and cracked oils used for production.

Table 4 and Figs. 7 and 8.—The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of distillate to 170° C, on the specific gravity of the distillate to 170° C, and on the distillation cuts of the recovered oils from the petroleum and cracked oils.

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[1] Rittman, Twomey and Egloff: Met. and Chem. Eng., 13, 682 (1915).

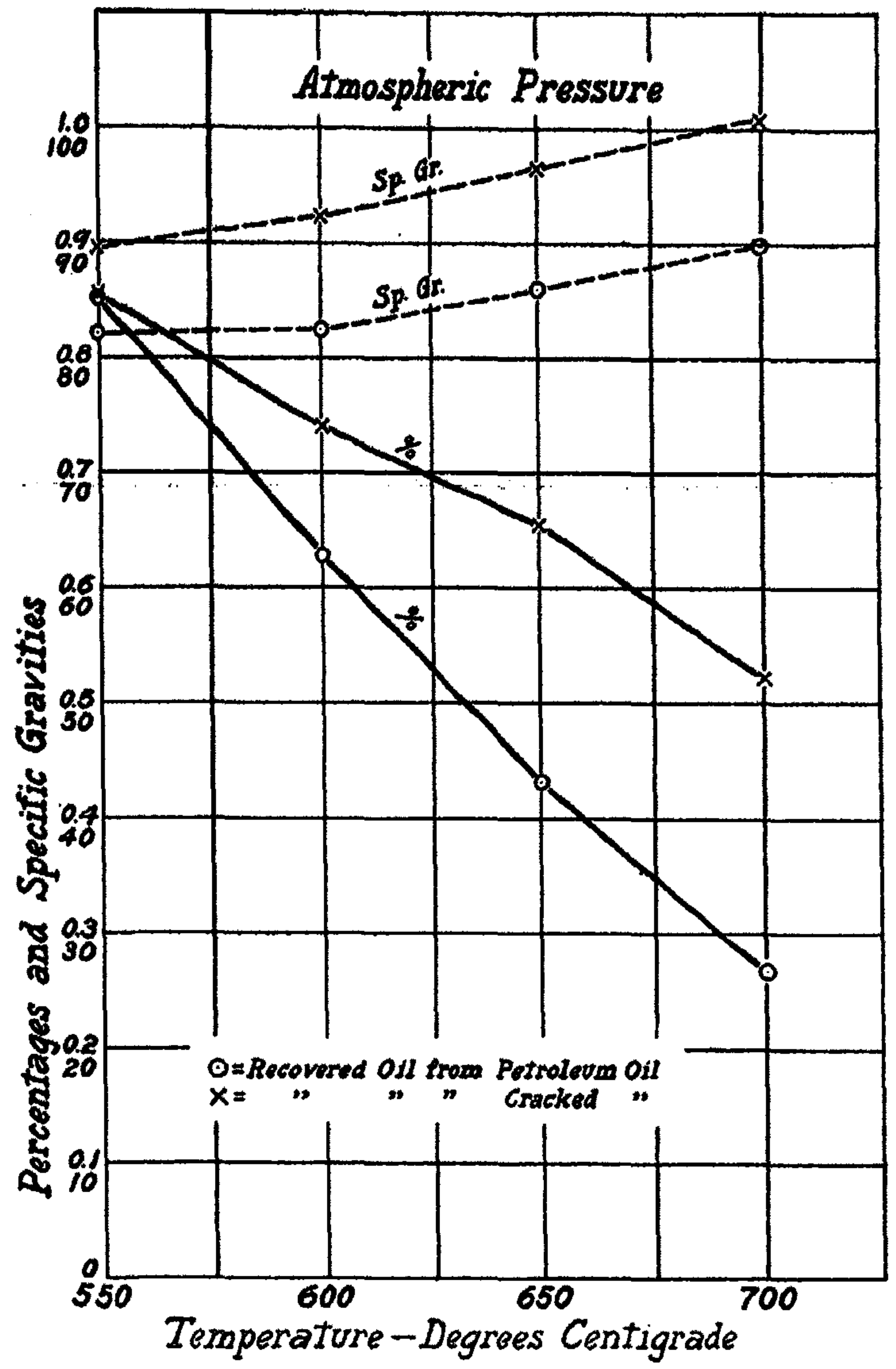

Fig. 1
The effect of temperature at atmospheric pressure upon the percent of recovered oil, and the specific gravity

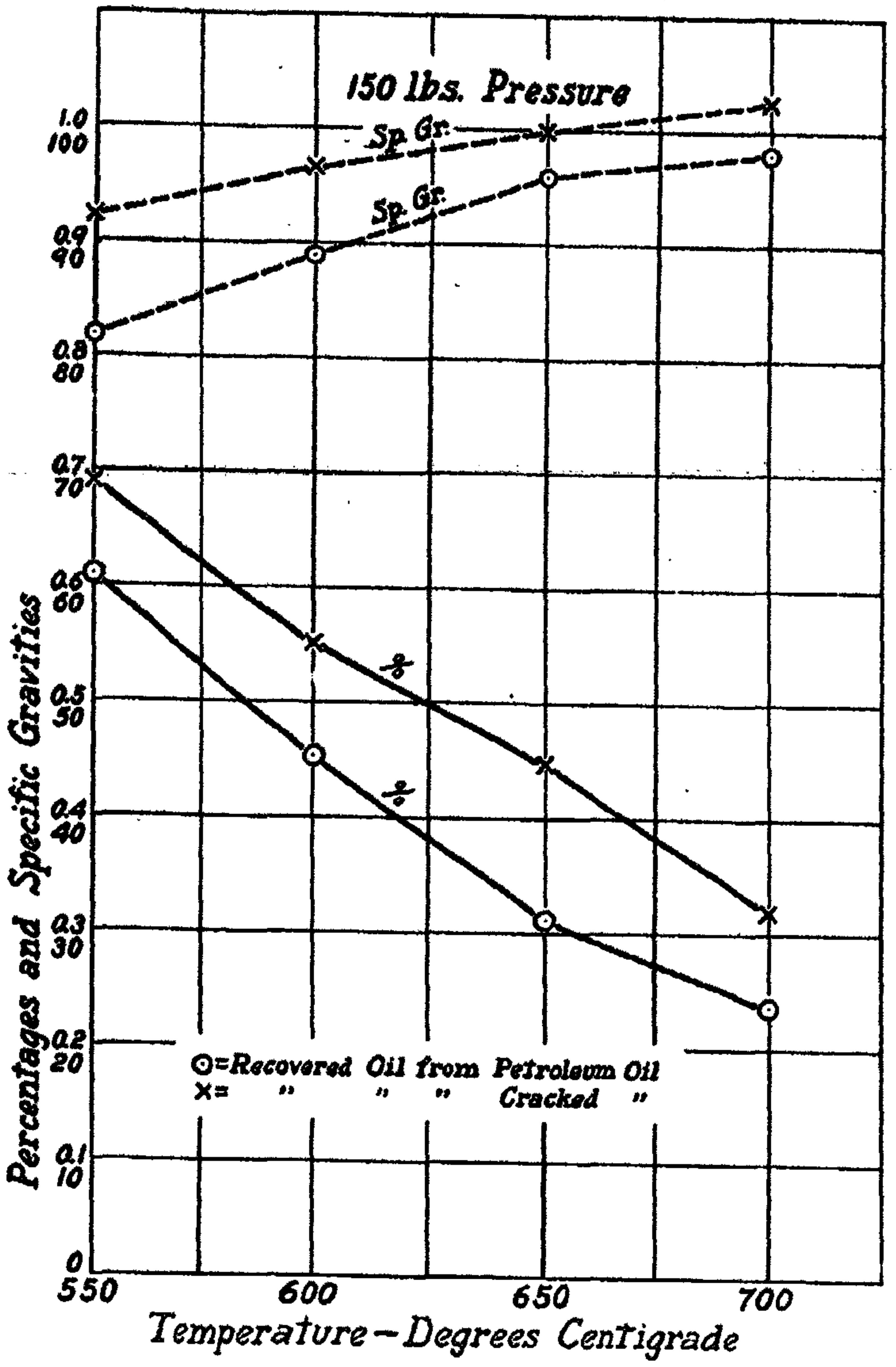

Fig. 2
The effect of temperature at 150 pounds pressure upon the percent of recovered oil and the specific gravity

TABLE I

A comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of recovered oil, and the specific gravity of the recovered oil from the Petroleum and Cracked Oils

Atmospheric Pressure

Temp. (°C)	550		600	
	Pet. oil	Cracked oil	Pet. oil	Cracked oil
% recovered	85.1	85.5	62.8	74.0
Sp. gr. recovered oil	0.820	0.895	0.824	0.922
	650		700	
% recovered	43.1	65.5	26.7	52.2
Sp. gr. recovered oil	0.860	0.965	0.899	1.009

150 Lbs.

	550		600	
% recovered	60.9	69.0	45.2	55.0
Sp. gr. recovered oil	0.818	0.921	0.888	0.964
	650		700	
% recovered	31.1	44.5	23.6	31.9
Sp. gr. recovered oil	0.958	0.998	0.978	1.022

TABLE 2

A comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of Benzene, Toluene, Xylenes, Naphthalene and Anthracene in the recovered oils produced from the Petroleum and Cracked Oils

Atmospheric Pressure

Temp. (°C)	550		600	
	Pet. oil	Cracked oil	Pet. oil	Cracked oil
% Benzene	0.0	0.1	0.8	1.4
% Toluene	0.7	1.5	2.3	2.8
% Xylene	0.3	1.9	1.5	3.2
% Naphthalene	0.0	0.0	0.0	0.0
% Anthracene	0.0	0.0	0.0	0.0

	650		700	
% Benzene	5.0	2.9	12.3	5.1
% Toluene	7.0	3.3	8.3	4.1
% Xylene	3.2	4.5	7.2	4.7
% Naphthalene	0.0	0.0	0.0	2.6
% Anthracene	0.0	0.0	0.0	1.1

150 Lbs.

	550		600	
% Benzene	1.1	0.5	10.0	4.5
% Toluene	4.5	2.0	10.2	6.2
% Xylene	3.3	2.6	6.7	6.3
% Naphthalene	0.0	0.0	0.0	0.0
% Anthracene	0.0	0.0	0.0	0.0

	650		700	
% Benzene	24.5	6.4	28.7	10.2
% Toluene	10.3	6.3	9.3	4.2
% Xylene	4.6	6.3	6.0	3.6
% Naphthalene	9.2	Trace	9.2	13.3
% Anthracene	0.0	Trace	0.9	2.6

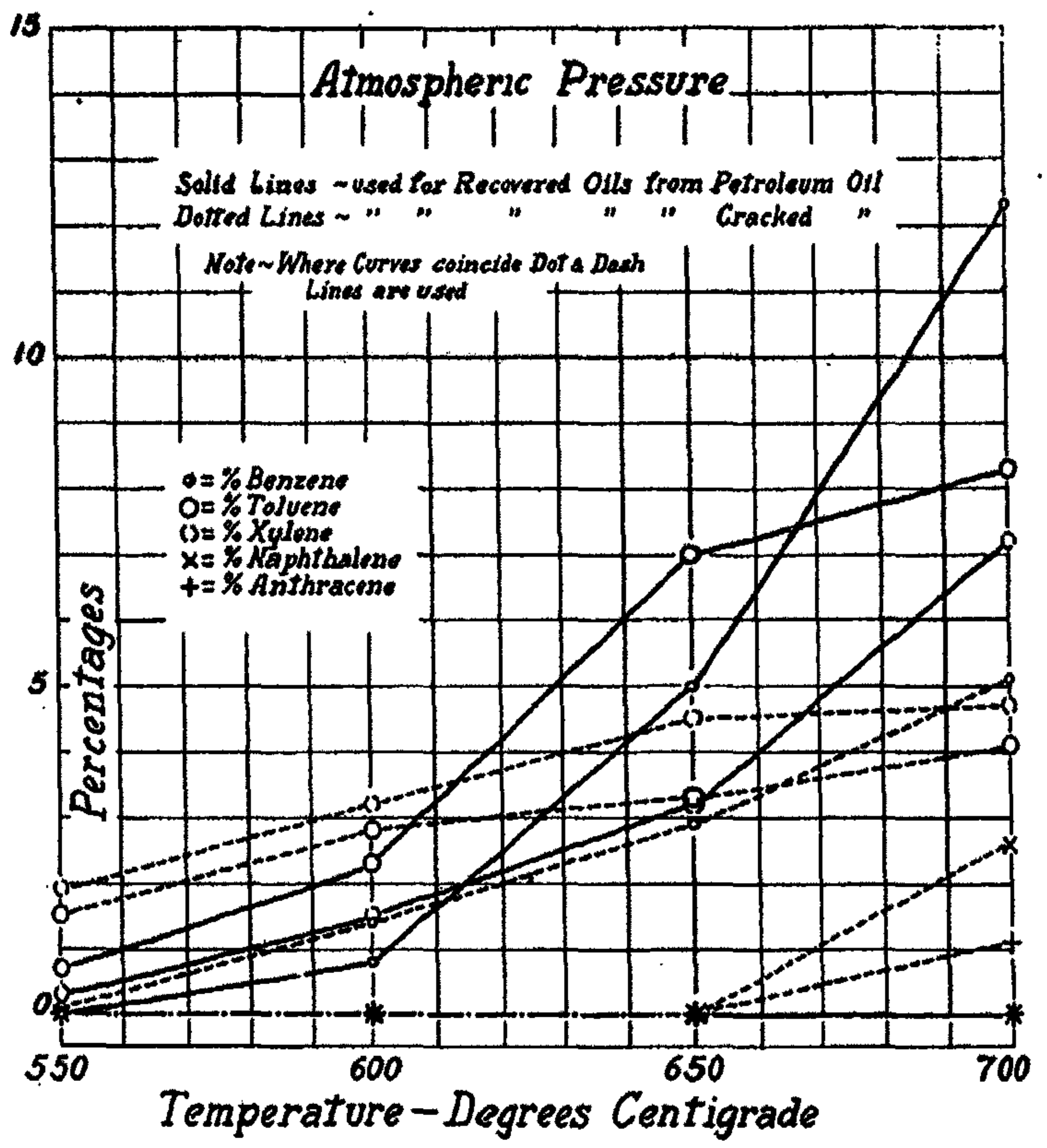

Fig. 3
The effect of temperature at atmospheric pressure on the percent of benzene, toluene, xylenes, naphthalene and anthracene in the recovered oil

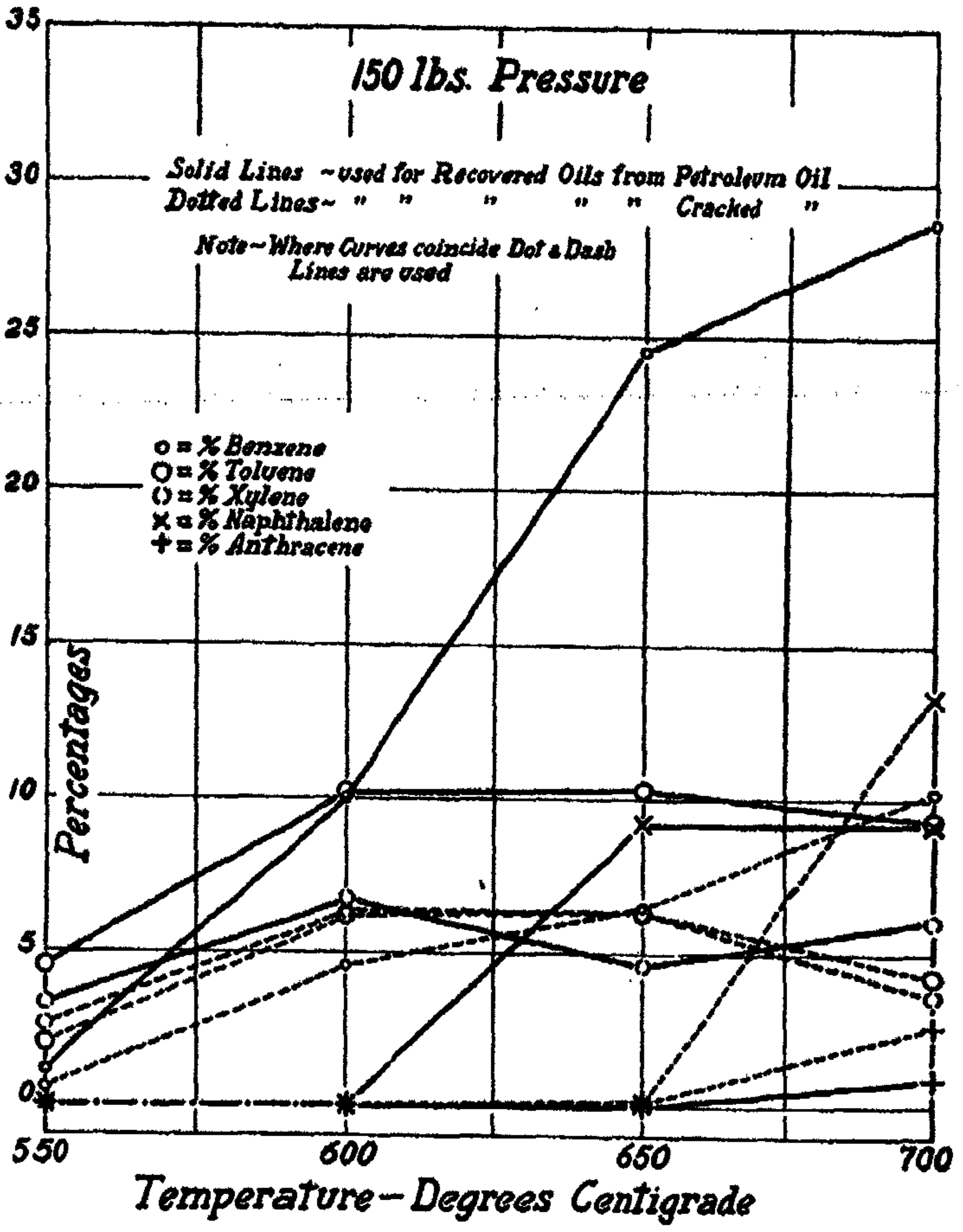

Fig. 4
The effect of temperature at 150 pounds pressure on the percent of benzene, toluene, xylenes, naphthalene and anthracene in the recovered oil

TABLE 3

A comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of Benzene, Toluene, Xylenes, Naphthalene and Anthracene on the basis of Petroleum and Cracked Oils used for production

Atmospheric Pressure

Temp. (°C)	550		600	
	Pet. oil	Cracked oil	Pet. oil	Cracked oil
% Benzene	0.0	0.1	0.5	1.0
% Toluene	0.6	1.3	1.4	2.1
% Xylene	0.3	1.6	1.0	2.4
% Naphthalene	0.0	0.0	0.0	0.0
% Anthracene	0.0	0.0	0.0	0.0
	650		700	
% Benzene	2.5	1.9	3.3	2.7
% Toluene	3.1	2.2	2.2	2.1
% Xylene	1.4	3.0	1.9	2.4
% Naphthalene	0.0	0.0	0.0	1.4
% Anthracene	0.0	0.0	0.0	0.6

150 Lbs.

	550		600	
% Benzene	0.7	0.4	4.5	2.5
% Toluene	2.7	1.4	4.6	3.4
% Xylene	2.0	1.8	3.0	3.5
% Naphthalene	0.0	0.0	0.0	0.0
% Anthracene	0.0	0.0	0.0	0.0
	650		700	
% Benzene	7.6	2.9	6.8	3.3
% Toluene	3.2	2.8	2.2	1.3
% Xylene	1.4	2.8	1.4	1.2
% Naphthalene	2.9	Trace	2.2	4.2
% Anthracene	0.0	Trace	0.2	0.8

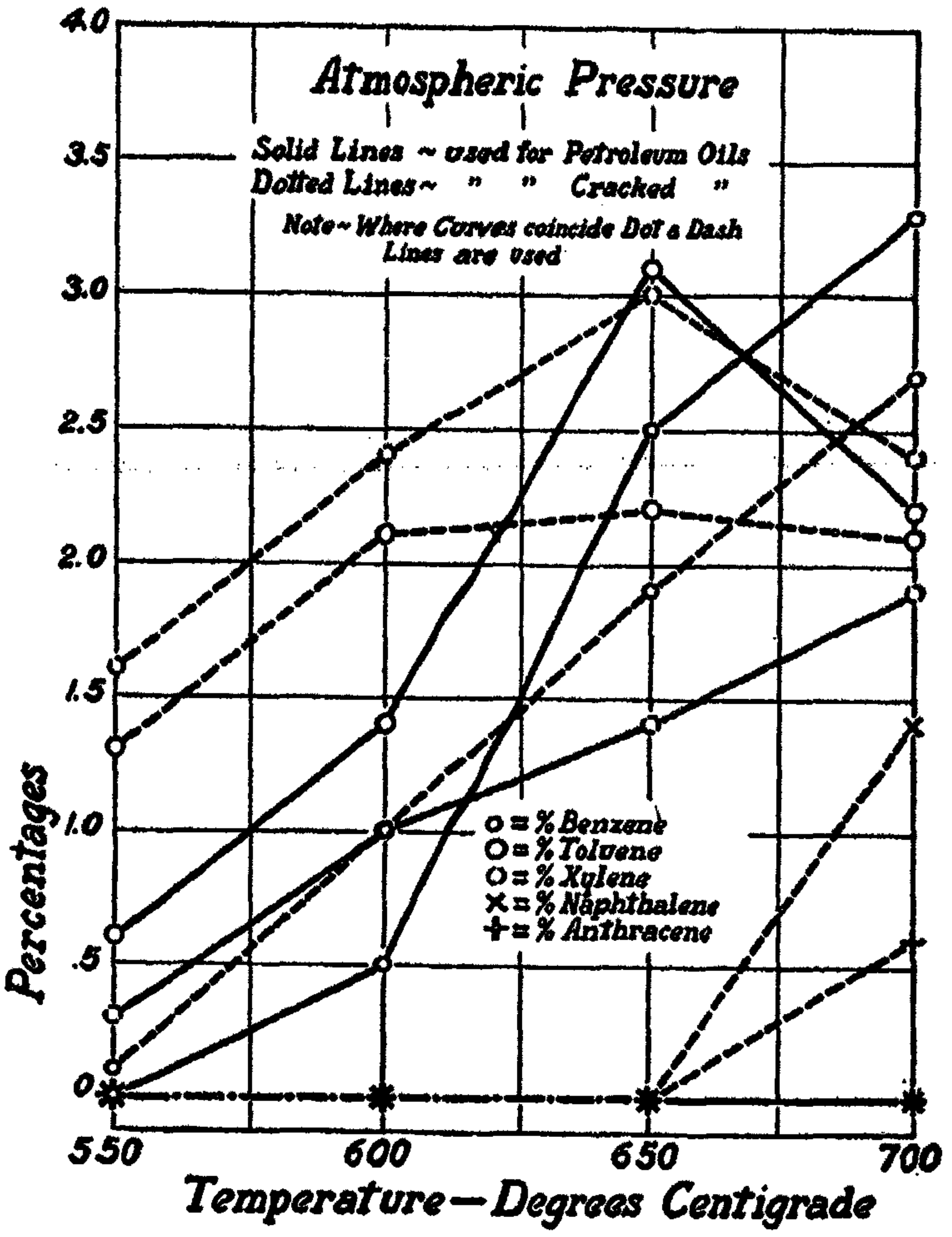

Fig. 5
The effect of temperature at atmospheric pressure on the percent of benzene, toluene, xylenes, naphthalene and anthracene on the basis of oil used for production

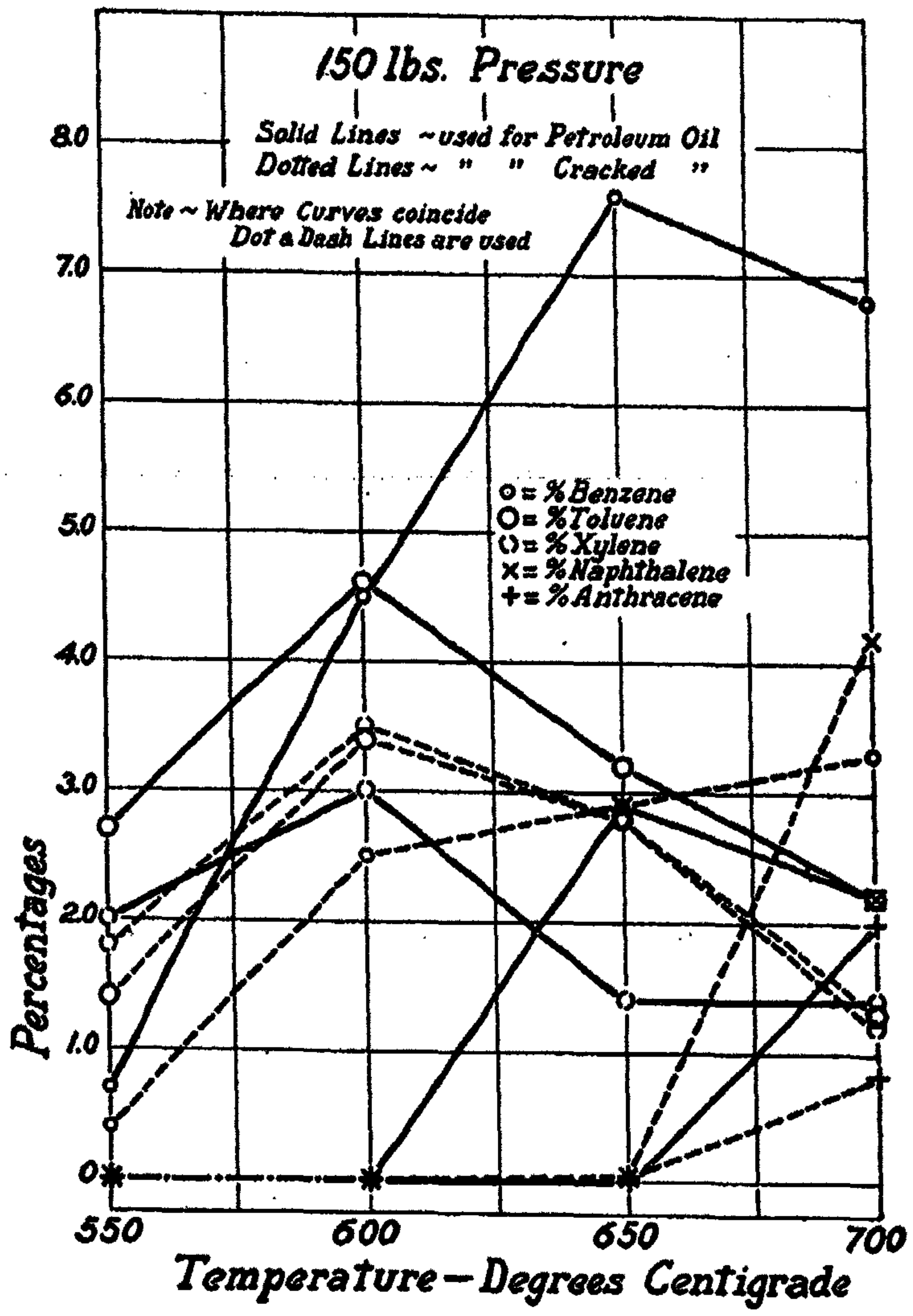

Fig. 6
The effect of temperature at 150 pounds pressure on the percent of benzene, toluene, xylenes, naphthalene and anthracene on the basis of oil used for production

Table 4

A comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the Distillate to 170° C, on the specific gravity of the Distillate to 170° C, and on the specific gravity of the distillation cuts from the Petroleum and Cracked Oils

Atmospheric Pressure

Temp. (°C)	550		600	
	Pet. oil	Cracked oil	Pet. oil	Cracked oil
% to 170° C	14.8	14.1	26.2	17.3
Sp. gr. to 170° C	0.742	0.795	0.766	0.809
Sp. gr. to 95° C	0.711	0.728	0.733	0.762
Sp. gr. 95–120	0.762	0.802	0.786	0.822
Sp. gr. 120–150	0.771	0.817	0.792	0.832

	650		700	
% to 170° C	31.9	19.0	42.7	17.4
Sp. gr. to 170° C	0.806	0.832	0.828	0.860
Sp. gr. to 95° C	0.784	0.794	0.828	0.856
Sp. gr. 95–120	0.824	0.846	0.850	0.865
Sp. gr. 120–150	0.825	0.850	0.850	0.870

150 Lbs.

	550		600	
% to 170° C	34.1	16.7	40.7	27.8
Sp. gr. to 170° C	0.772	0.795	0.833	0.835
Sp. gr. to 95° C	0.734	0.738	0.815	0.800
Sp. gr. 95–120	0.809	0.809	0.852	0.853
Sp. gr. 120–150	0.816	0.826	0.850	0.858

	650		700	
% to 170° C	44.8	23.7	49.0	22.8
Sp. gr. to 170° C	0.867	0.856	0.866	0.868
Sp. gr. to 95° C	0.870	0.845	0.867	0.864
Sp. gr. 95–120	0.869	0.860	0.868	0.868
Sp. gr. 120–150	0.867	0.862	0.868	0.868

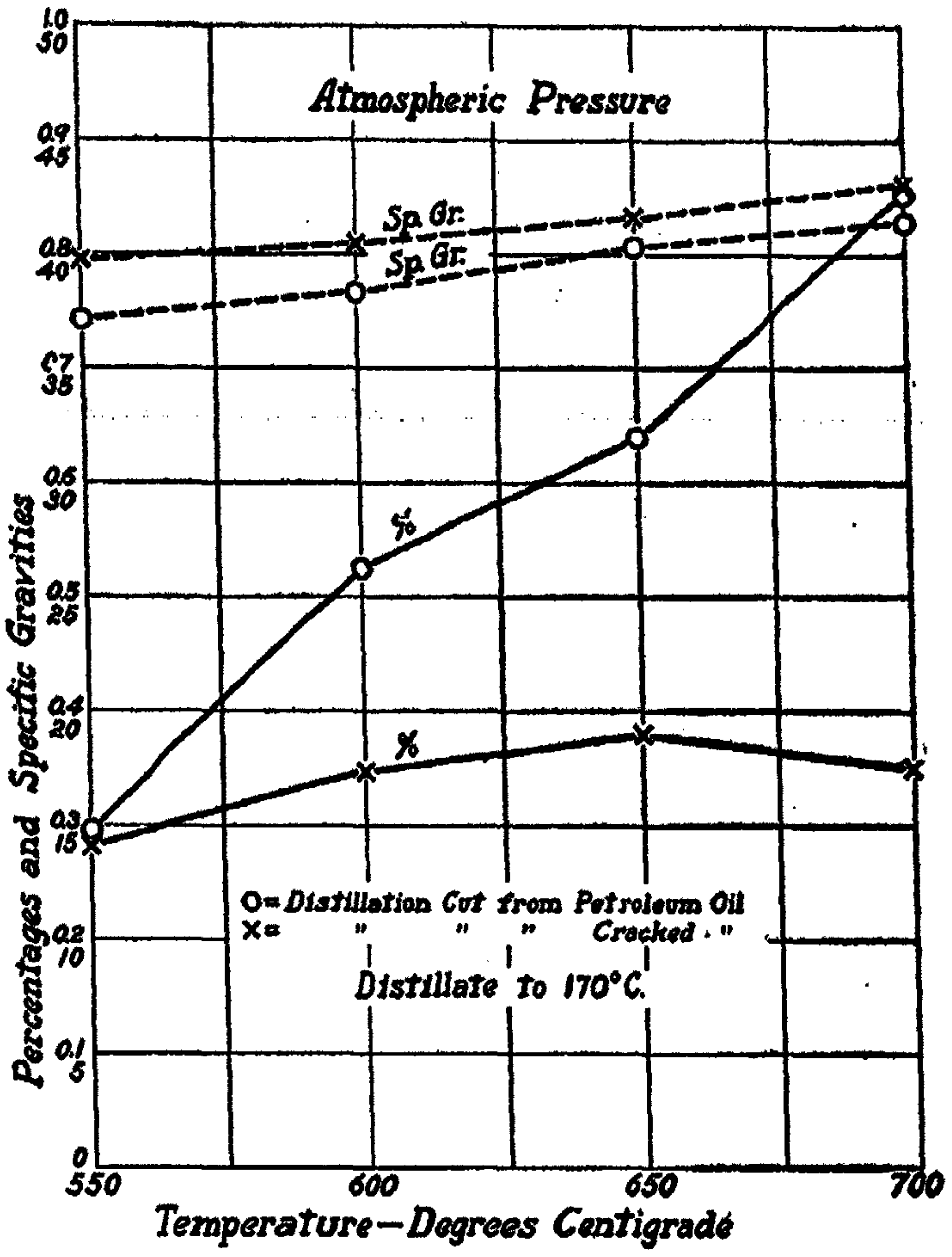

Fig. 7

The effect of temperature at atmospheric pressure on the distillate to 170° C, on the specific gravity of the distillate to 170° C, and on the distillation cuts from the petroleum and cracked oils

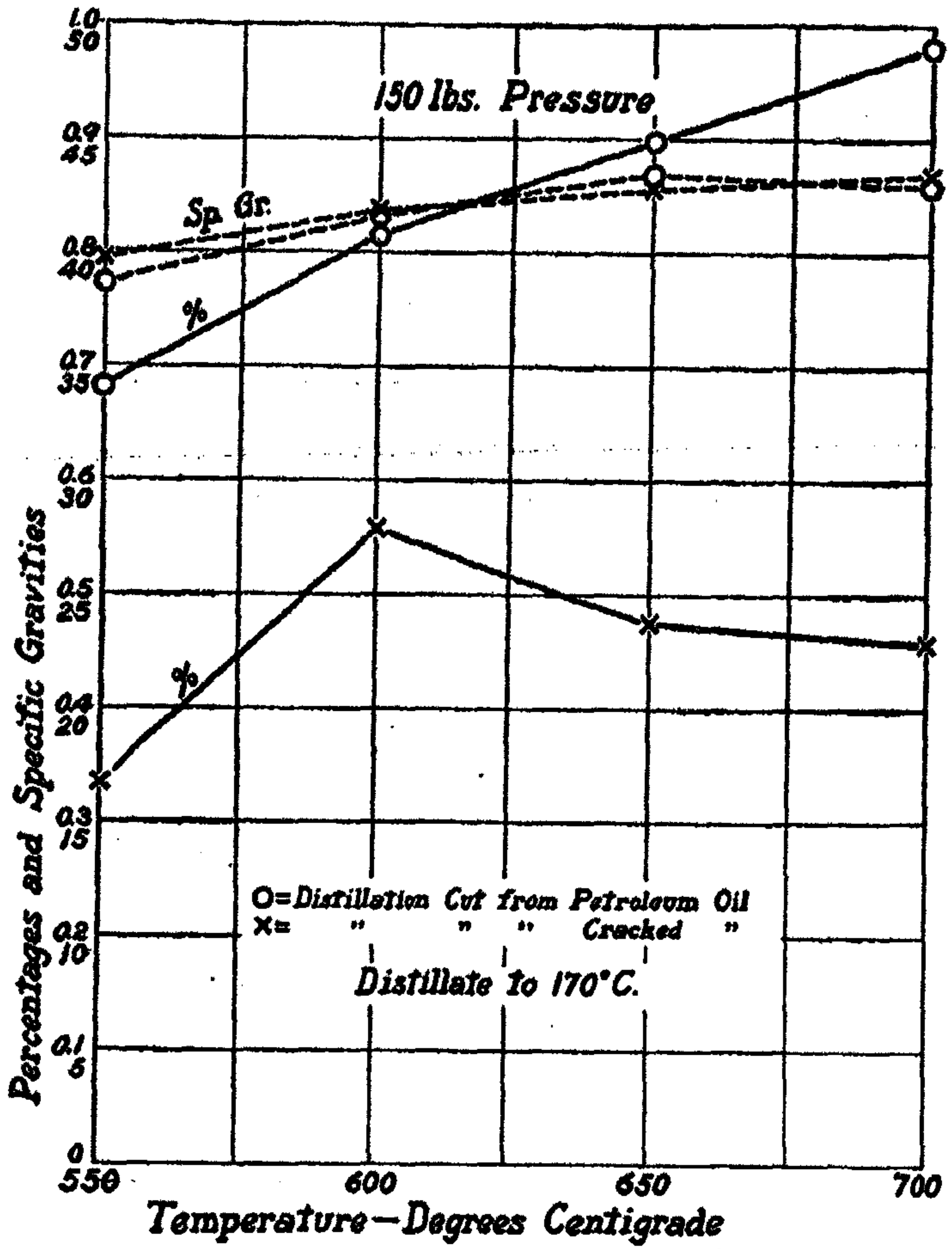

Fig. 8
The effect of temperature at 150 pounds pressure on the distillate to 170° C, on the specific gravity of the distillate to 170° C, and on the distillation cuts from the petroleum and cracked oils

Discussion of the Experimental Results

a. The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of recovered oil and the specific gravity of the recovered oil from the petroleum and cracked oils

At all temperatures and pressures employed, the percent of recovered oil obtained by the decomposition of the cracked oil is larger than that from the petroleum oil. Since the cracked oil is the product of primary thermal decomposition at approximately the same temperatures and pressures employed in these experiments, it does not break up to gases and lower boiling compounds to the same extent as does the original distillate oil. It contains aromatic hydrocarbons formed by temperature and pressure effect which are, therefore, more or less stable when again subjected to the same cracking conditions. The decomposition which took place may be attributed in the main part to the presence of the unchanged petroleum. This is very similar to what has been shown in the cracking of dead oils[1] from coal tar, where the percent of recovered oil was larger than that obtained from petroleum oil cracked under the same conditions. The decomposition of the cracked oil proceeded in this case to a larger degree than was found with dead oils, but yet not the extent noticed with a petroleum oil.

There are no new points of particular interest in regard to the specific gravities of the recovered oils except that the gravity of the recovered oil from both sources increased fairly regularly with increase of temperature and pressure.

There is another regularity which seems to be characteristic of these data. The percent of recovered oil and the specific gravity of the recovered oil from both the petroleum and cracked oils produced at atmospheric pressure and 600° C corresponds to that produced at 150 lbs. pressure and 550° C; likewise, the results at atmospheric pressure and 650° C are similar to those found at 150 lbs. pressure and 600° C.

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[1] Loc. cit.

Or, the amount of decomposition produced by increasing the pressure 150 lbs. corresponds to that produced by increasing the temperature 50° C.

While no quantitative data were recorded as to the amount of carbon and gas produced, it was noted for particular reasons that the cracking of the cracked oil yielded more carbon and less gas than did the cracking of the petroleum oil. On account of the carbon formation, when the cracked oil was recracked, an extra amount of time and labor was required to remove the carbon from the tube after each run. No such difficulties were experienced in operating with the petroleum oil. Neither was it necessary to release the excess gases formed in order to keep the pressure constant when the cracked oil was recracked as often as it was when the petroleum oil was thermolized.

b. The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of benzene, toluene, xylenes; naphthalene and anthracene in the recovered oils produced from the petroleum and cracked oils

The percentage of benzene, toluene and xylenes in the recovered oil from the petroleum oil is almost uniformly twice as large as that found in the oil resulting from the cracked oil. Naphthalene and anthracene formation are apparent exceptions to this observation. At atmospheric pressure, and 550 and 600° C, it appears from the data that the cracked oil gives a recovered oil which contains more aromatic hydrocarbons than does the petroleum oil, but the differences are so slight that no conclusions may be deduced.

In all cases the petroleum oil produces the larger quantities. The conclusion may, therefore, be drawn that the cracked oil is not so well adapted for aromatic formation as is the petroleum oil. The effect of temperature on the formation of benzene, toluene, xylenes, naphthalene and anthracene at atmospheric pressure has been shown in a previous communication.[1] A part of the data in this table, that of the

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[1] Egloff and Twomey: Jour. Phys. Chem., 20, 122 (1916).

petroleum oil, is used in the present connection. The data from the cracked oil at atmospheric pressure also illustrate the points which have been previously pointed out, but in a manner more in accord with the theory of the cracking reaction. At temperatures 550, 600 and 650° C, there is more xylene than toluene, but more toluene than benzene. At 700° C, the percent of benzene is the largest. At this temperature in this series of experiments, toluene should have been present in a larger quantity than xylene, but the experimental data do not show this.

The fundamental reaction of xylene to toluene to benzene to naphthalene to anthracene is well illustrated by the data at 150 lbs. pressure from both the petroleum and cracked oils. The results from the cracked oil are slightly better than those from petroleum. At the lower temperatures employed, 550 and 600° C, the percentages of xylene and toluene exceed that of benzene. Above these temperatures, benzene increased very rapidly, apparently at the expense of the toluene and xylene, and this increase was accompanied by naphthalene formation.

Higher temperatures than 700° C were not used in the present work because it was judged from the data obtained that these temperatures would have only produced results similar to those already found at atmospheric pressure.

That is, higher temperatures would have produced recovered oils in which the percentage of benzene has fallen off together with that of the toluene and xylene, and in which the amounts of naphthalene and anthracene predominate.

It might be well at this time to call attention to the effect of pressure on the aromatic formation. This has been done by another investigator, but the results expressed in distillation cuts are only qualitative indications of the direct effect of pressure on the benzene and toluene formation. Pressure increases the aromatic formation. While all the data show the effect, that at 650° C will be mentioned. At atmospheric pressure there was formed from the petroleum oil 5.0 percent benzene as compared to 24.5 percent at 150 lbs., 7.0 percent toluene compared to 10.3 percent, 3.2 percent xylenes as compared to 4.6 percent and 0.0 percent naphthalene as compared to 9.2 percent.

Pressure is favorable for aromatic formation, since the reaction which results in the formation of the aromatic hydrocarbons is without doubt one primarily of polymerization.

c. The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the percent of benzene, toluene, xylenes, naphthalene and anthracene on the basis of petroleum and cracked oils used for production

The results in this table are obtained by multiplying the percent of aromatic hydrocarbons in the recovered oil by the percent of recovered oil. The figures represent the number of pounds of aromatic compounds which are produced from 100 pounds of oil subjected to the cracking. The petroleum oil yields more aromatic hydrocarbons on this basis than does the cracked oil. The data simply bring out what has already been stated—the cracked oil is not so well adapted for aromatic formation as is the petroleum oil.

d. The comparison of the effect of temperature at atmospheric and 150 lbs. pressure on the distillate to 170° C, the specific gravity of the distillate to 170° C, and the specific gravities of the distillation cuts from the petroleum and cracked oils

Up to the present we have been dealing entirely with the question of aromatic formation. The data in this section permit the consideration of the possibility of gasoline formation from a cracked oil, as compared with that from the petroleum oil. The gasoline from the recovered oils in both cases are represented by the percent of distillate to 170° C, and by the specific gravities.

The gasoline formation is greater by far from the petroleum than from the cracked oil; in fact there was formed approximately twice as much in one case as in the other. Strictly speaking, the experiments at 550 and 600° C are the only ones which may be taken as typifying the production of gasoline. These results indicate that the cracked oil even at low temperatures does not form much gasoline. The main change is one producing aromatic hydrocarbons. The results of these experiments should not be taken as indicating that in commercial operations it would not be possible to produce gasoline by the second cracking of the oil. The cracked oil used in these experiments is the result of a cracking reaction mainly for the production of aromatic hydrocarbons, where a large change into aromatic hydrocarbons is produced. This does not happen when the cracking is conducted for the production of gasoline. When cracking for gasoline, the distillate from the cracked oil which would be used for recracking will contain only a very small percentage of aromatic hydrocarbons and will differ in composition but slightly from the starting petroleum. Consequently, gasoline will be formed on the recracking, but in slightly less amounts than from the original petroleum oil, due to the small change produced by the first cracking reaction in the composition of the oil. The number of times that recracking will produce gasoline may only be determined by actual experiment for each individual oil. With each recracking, the distillate from the recovered oil or the residue becomes more and more aromatic in composition and, therefore, less and less valuable as a starting oil for gasoline production. The data in these experiments represent in a measure the extreme which would be obtained. When cracking for gasoline similar conditions would probably result after two recrackings of the recovered oil from which the gasoline has been removed by distillation.

Similar results in regard to the value of residues from cracked oils for the further production have been found by Hall[1] in commercial operations. He states "The liquid residues are usually run through a second time, but they are seldom of the same value for the purpose as the original oil."

In an excellent paper on studies of pressure distillation of petroleum hydrocarbons, A. P. Bjerregaard[2] produced 4.8 percent gasoline boiling up to 150° C at 400 lbs. pressure at a cracking temperature of 433° C. The residue was recracked

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[1] The Inst. Petroleum Technologists, 1914.

[2] Jour. Ind. Eng. Chem., 7 573 (1915).

and a yield of 4.5 percent was obtained. In this case, there was but little difference between the amounts produced from the original petroleum oil and the residue. In any commercial operation, however, the first cracking to be of commercial value must yield several times 4.8 percent. When the cracking has taken place to this extent, the residue, it will be found, will have changed enough to make it less valuable for the second cracking. The results of Bjerregaard are what would be expected, as the first cracking produced but very little cracking as judged by the gasoline formation, and hence but very little change in the composition of the starting petroleum oil.

Summary

Under identical conditions, the cracking of a petroleum oil and a cracked oil derived from this petroleum oil gave results from which the following conclusions may be drawn:

1. The cracked oil does not decompose to the same extent as does the petroleum oil.
2. The cracked oil is not so well adapted for either aromatic or gasoline production as is the petroleum oil.
3. That whatever cracking takes place to lower boiling hydrocarbons from a cracked oil may be attributed to a large extent to the unchanged petroleum in the cracked oil and not to its aromatic constituents.
4. There is a limit to the number of times which an oil can be recracked, because the tendency of the reaction is to form aromatic compounds which decompose neither to gasoline nor to members of the benzene series appreciably, but toward the ultimate products, carbon and hydrogen.

ABNORMAL ADSORPTION BY FILTER PAPER

BY RUBY RIVERS MURRAY

Evans[1] has reported a number of cases of apparently abnormal adsorption by filter paper. With hydrochloric acid the amount adsorbed was apparently independent of the concentration of the solution from 0.007 *N* to 0.08 *N*. It then increased to double the amount as the concentration of the solution rose to 0.28 *N* and dropped off apparently to zero with 0.36 *N* HCl and with normal acid. In a second series the maximum adsorption was found at about 0.2 *N* HCl and there was apparently no adsorption with *N*/2 acid. A similar behavior was observed with copper sulphate solutions, the maximum adsorption occurring at about 0.04 *M* $CuSO_4$ and the adsorption dropping to zero for a 0.13 *M* solution. There seemed to be two possible explanations for these phenomena. The filter paper might undergo a change which cuts down the adsorbing power. In that case treating filter paper with a half-normal solution of hydrochloric acid and then diluting should not give the same result as treating originally with a dilute solution. The other possibility was that the solution might be adsorbed without change of concentration, in which case the method of analysis would show no apparent adsorption.[2] As a matter of fact neither of these hypotheses accounted for the data. The first thing to do was evidently to repeat Evans' results.

Five grams of filter paper (No. 597, 9 cm, washed) were torn in shreds and added bit by bit to 100 cc hydrochloric acid in order to ensure complete wetting. The stoppered flask was shaken thoroughly but not too vigorously, because too violent shaking tends to disintegrate the paper. The bottles were allowed to stand at ordinary temperatures for lengths of time varying from one hour to ten days before titrating. Since it was found that there were always some

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[1] Jour. Phys. Chem., 10, 290 (1906).

[2] Leighton: Jour. Phys. Chem., 20, 32 (1916).

particles of paper which did not settle out of the supernatant liquid, the solution was filtered through a single paper of the same sort as that used in the adsorption tests. Except when otherwise stated, 10 cc of the filtered solution were drawn off in a pipette, the same pipette being used in all determinations. The solutions were titrated with caustic soda solutions slightly less in strength than the corresponding acid solutions. An ordinary burette was used which was cleaned carefully and was allowed to drain one minute before reading. Evans used phenolphthalein as an indicator; but methyl orange is safer for this sort of work, so runs were made both with methyl orange and with phenolphthalein. Evans states that "the amount of adsorption in a particular case was identical after various periods ranging from five minutes to a week." This has been found not to be quite accurate.

TABLE I

5 grams filter paper and 100 cc HCl. 25 cc portions titrated in 7-day runs and 10 cc portions in other runs. Methyl orange as indicator

G. equiv. HCl per liter	Diff. in cc NaOH	Mg HCl adsorbed	Mg HCl adsorbed per gram paper	Time of standing
0.986	0.31	116.0	23.2	1 hour
0.489	0.21	32.5	6.5	1 hour
0.216	0.20	19.5	3.9	1 hour
0.986	0.33	123.4	24.7	3 days
0.489	0.22	35.7	7.1	3 days
0.216	0.20	19.5	3.9	3 days
0.986	0.32	119.7	23.9	3 days
0.489	0.21	35.0	7.0	3 days
0.216	0.19	13.9	2.8	3 days
0.986	0.32	47.9	9.6	7 days
0.489	0.20	14.3	2.9	7 days
0.216	0.10	7.3	1.5	7 days
0.986	0.13	50.3	10.1	10 days
0.489	0.07	11.7	2.3	10 days
0.216	0.05	3.7	0.7	10 days

In Table I are given the data with methyl orange as indicator. In order to call attention to the experimental error in this sort of work, the difference in the cubic centimeters of NaOH required to neutralize before and after adsorption is given in the second column. Since 25 cc portions were titrated in the seven day runs as against 10 cc portions in the other runs, the differences for those runs are not directly comparable with the corresponding data for the other runs.

In all cases the adsorption increases with increasing concentration. While the values for one hour are practically the same as those for three days, there is a marked change when we come to the seven day runs. The adsorption has dropped to less than half its original value. This cannot be due to a dissolving of alkali from the glass because that would produce an apparent increase in the adsorption. Some change must therefore take place in the filter paper which decreases its adsorbing power for hydrochloric acid. The experimental error is so large in the ten day runs that it is impossible to decide whether the change was still in process, though this seems probable. It would have been interesting to have made a study of the change in adsorption, with increasing time and also to have determined whether a similar phenomenon is to be observed with purified cotton wool; but such experiments were outside the scope of this investigation. It was not deemed desirable to centrifuge the solutions; but it was noted that only about 70 cc solution could be poured off, so that about 30 cc solution were held in and about the fragments of paper.

While Evans does not state what kind of filter paper he used, it seemed probable that the trouble was due to his choice of indicator. Nothing is said in his paper about the boiling off of carbon dioxide and therefore two runs were made using phenolphthalein as indicator and not driving out carbon dioxide. The data are given in Table II.

When using phenolphthalein as indicator the apparent adsorptions for the approximately normal and half-normal solutions are much less than when methyl orange is used. In the first run no change in titration could be detected with the most concentrated solution. This confirms Evans. In

TABLE II

5 grams filter paper and 100 cc HCl. 10 cc portions titrated.
Phenolphthalein as indicator

G. equiv. HCl per liter	Diff. in cc NaOH	Mg HCl adsorbed	Mg HCl adsorbed per gram paper	Time of standing
0.986	0.00	0.0	0.0	7 days
0.489	0.05	8.3	1.7	7 days
0.216	0.05	3.7	0.7	7 days
0.986	0.03	11.2	2.2	7 days
0.489	0.04	6.7	1.3	7 days
0.216	0.05	3.7	0.7	7 days

the second run the adsorption is apparently greater than for the more dilute solutions; but the total difference in titration before and after adsorption is only 0.03 cc NaOH, which is pretty close to the limit of experimental error. It would be legitimate to call the adsorption "doubtful" just as Evans did. Since we have duplicated Evans' results approximately by working under apparently similar conditions, it seems safe to conclude that the abnormal results obtained by Evans with hydrochloric acid were due to analytical errors.

The general conclusions to be drawn from this work are:

1. The adsorption of hydrochloric acid by filter paper increases with increasing concentration of the solution within the range studied.

2. When filter paper is allowed to stand with hydrochloric acid solutions for 7–10 days, some change occurs in the filter paper which decreases the adsorption to less than one-half its original value.

3. No experiments have been made to determine what changes take place on longer standing than ten days.

4. The abnormal results obtained by Evans with hydrochloric acid are due to analytical errors.

This work was suggested by Professor Bancroft and has been carried out under his supervision.

Cornell University

NEW BOOKS

Soils and Manures. *By E. J. Russell. 20 × 15 cm; pp. ix + 206. Cambridge: University Press, 1915. New York: G. P. Putnam's Sons. Price: 90 cts.*—The author discusses the subject under three general headings: an account of the soil; the control of the soil; fertilizers. The chapters are entitled: what the plant wants from the soil; the composition of the soil; the organic matter of the soil and the changes it undergoes; the effect of climate on the soil and on fertility; cultivation; the control of soil fertility; the nitrogenous fertilizers; phosphates; potassic fertilizers; farmyard manure; other organic manures; the purchase and use of artificial manures; chalk, limestone and lime.

The author's main thesis is given clearly on p. 2. "Six conditions or factors are known to be necessary before the plant will make good growth. The soil must supply a suitable amount of: (1) food, (2) water, and (3) air; (4) it must be at a proper temperature; (5) there must be enough of it to afford adequate root room; (6) it must be free from injurious substances or pests. What is exactly a suitable amount cannot be stated beforehand but can only be found out by trying; because different plants, and even different varieties of the same plants, have different requirements. Thus an azalea needs all the six conditions and so does a barley plant, but the suitable amount is very different in the two cases. It is unfortunate that no one has yet discovered any way of finding out the suitable amounts simpler than actual trial because this particular method, though it looks straightforward, is really very cumbersome and liable to give misleading results as we shall see later on.

"All these six conditions are wanted and no one of them can take the place of any other. If a plant is dying for lack of water, it will not recover by receiving more food or more air. A proper supply of *all* the factors must be maintained, and if any one is insufficient, the plant suffers. This proposition looks simple enough; but the student must fix it carefully in his mind because it really lies at the foundation of all our work. It is convenient to use a special name for the lacking condition, the insufficiency of which is preventing the plant from making better growth, and to speak of it as the 'limiting factor.' Thus on a dry chalky soil the water supply is often the limiting factor; if more water is got into the soil a bigger crop will be obtained. In the cold summer of 1912 the temperature was on many farms the limiting factor; had the days and nights been hotter, the plants would have made more growth. On poor soils the food supply is the limiting factor, and addition of more food in the form of manure will increase the crop. The problem of successful management of soil fertility resolves itself into finding out what is the limiting factor and then correcting it as cheaply and completely as possible. This is easy enough on paper but often difficult in practice."

On p. 22 the author says: "Clay is such a dominating substance that it impresses its properties on the soil to a considerable extent, hence when the clay is in the sticky state the whole soil becomes sticky, and conversely, when the clay is in the crumbly state the whole soil becomes crumbly. Practical men have long since learned that the crumbly state is good for plants while the sticky state is not, and they have also discovered how to change one into the other.

Addition of lime, chalk or limestone causes the change to take place rapidly: organic matter (such as farmyard manure or green crops ploughed in), frost, and good cultivation also have the same effect. On the other hand, alkaline manures such as liquid manure, and manures like nitrate of soda that leave an alkaline residue in the soil, tend to change the crumbly back into the sticky state, and if much clay is present they have a bad effect on the condition of the soil."

On p. 44 we read: "Under our climatic conditions the nitrates do not get the opportunity of persisting long but are either washed out by rain or taken up by plants. Once the stock is reduced a further quantity begins to be formed and so far no limit has been reached to the amount of nitrate a soil can be made to yield. One of the Rothamstead plots which had been cropped with wheat every year since 1843 and has had no manure since 1839 still goes on yielding nitrate and in September, 1913, contained nearly 35 lbs. of nitrogen as nitrate, equivalent to 210 lbs. of nitrate of soda in the top 18 inches of soil per acre. Another piece of land is kept bare of all vegetation and is undermined in such a way that the whole of the drainage water can be collected for analysis. Ever since 1872 when the experiment began, the land has yielded a large supply of nitrate, the amount being equivalent to 300 lbs. of nitrate of soda per acre every year for the first 20 or 30 years, and to some 200 lbs. in more recent years.

"A further change goes on in certain circumstances. When all air is excluded from the soil by flooding it for a long time with water the nitrates are liable to decompose to form nitrites and subsequently gaseous nitrogen. This change, known as denitrification, only goes on slowly in cold weather and probably is of rare occurrence under British agricultural conditions where land would only be waterlogged in winter, if at all. But it seems to go on in the wet rice fields of the East and in these circumstances nitrates are not used to manure."

On p. 66 the author says: "More important, however, than high mean temperature is the absence of spring or autumn frosts. Low-lying valley lands are peculiarly susceptible to frost on clear calm nights; the cold air drifts down from above and collects in the valley where it chills the trees and not infrequently kills the fruit blossoms and the tender shoots of early potatoes. Land lying above this stagnant pool of cold air escapes these frosts and is therefore a safer place for susceptible crops, even though its mean temperature may be lower than that of the valley. Where, however, the lowland adjoins the sea or any great body of water, it is protected from these frosts and is indeed better than land lying further off because it is warmer.

"We can now understand why fruit is so often grown in undulating country. Slopes are needed to give the desired shelter and aspect, but above all to avoid risks of late frosts. The 'lucky banks' of the Evesham district, on which crops can nearly always be got, are of this character. In the fruit-growing region of Kent, the fruit tends to collect on the middle slopes, hops on the lower ground (or wood, if the ground is wet) and woodland or nuts on the high ground. But near the sea—and this holds generally round the coast—fruit can be grown with advantage on the lower ground.'" *Wilder D. Bancroft*

The Structure and Properties of the More Common Materials of Construction. *By G. B. Upton. 23 × 15 cm; pp. v + 327. New York: John Wiley and Sons, Inc., 1916. Price: $2.50 net.*—In the preface the author says:

"This book is an outgrowth of the laboratory course in Materials of Construction given to juniors in Sibley college. For some time past the instructors in the course have been giving, during the first hour of each three-hour laboratory period, a lecture upon the theoretical side of the particular test being conducted with indication of the relation of the test to engineering practice. Then came the actual testing work in the laboratory, with further discussion during the conduct of the test. Both the theory and the conduct of the test and its relation to engineering practice were then discussed in the reports written by the students. In time it has become evident that we cannot by this method cover thoroughly as much ground as we desire. Hereafter the student will study the theory of each topic in this book, and discuss theory and practice with the instructor during the first part of the laboratory period. This discussion will replace the lecture formerly given."

The book is divided into two parts: the determination of properties of materials; the nature of materials and control of their properties. The second part is the one of special interest to the chemist. The chapters in this section are entitled: the nature and origin of the structure of alloys; the shaping of steel and the control of final properties during the shaping process; engineering properties of normal carbon steels as function of the carbon content, and effects of elements other than carbon; general theory of heat treatment; engineering heat treatments of carbon steels and properties obtained; cast irons; alloy steels; non-ferrous metals and alloys; cement and cement testing.

The author is very explicit in regard to fatigue breaks, p. 112. "This study shows that the fatigue break goes through the crystals in such a way that on the fractured surface the original crystal structure of the metal would be made evident to the eye or to the microscope. In this feature a fatigue break differs, if the material is ductile, from the fracture due to a single loading. In single loading to break of a ductile material the individual crystals are pulled out more or less to fibers so that the break cannot reveal to the eye the original crystal structure.

"The difference between fatigue break and the break under a single loading, in the way that the original crystal structure is revealed, has caused a very persistent misconception of the reason for fatigue failures in service. It has been said that the cause of the service failure was crystallization due to vibration or repeated stressing. The assumption is that the vibration caused the crystals to grow large and so weakened the piece. The truth of the matter is that in the case of the piece failing in service, when similar pieces stand up, the original crystal size of the piece which fails was larger. The crystals did not grow. The trouble originated in the manufacturing processes which left that particular piece coarse grained."

The general outline of the theory of heat treatment, pp. 171, 209, 212, is very clear. "By heating a carbon tool steel to a temperature above the critical, it changes spontaneously from the normal structure of α and Fe_3C, ferrite and cementite crystals, to $\gamma(C)$, austenite. If this steel were cooled slowly it would change back at the critical temperature to a mixture of α and Fe_3C. The time required at red heat for this change, after it starts, is from ten to thirty seconds. If the steel is cooled slowly the change is completed while the temperature is still high, and at the end of the cooling the steel will be soft. By taking the hot steel from the furnace and plunging the piece into water, it is possible to cool the steel to below a red heat in three or four seconds. By such quenching we deny the steel time to complete the change from γ(C) to α + Fe_3C. The quenched piece will be found to be very hard, and also brittle. At ordinary temperatures this hard brittle structure is practically permanent. If the hardened steel is warmed up, even to so low a temperature as that of boiling water, it begins to soften. The higher the reheating temperature the more rapid is this softening. As it softens, the hardened steel becomes less brittle or tougher. Because the fully hardened tool steel is too brittle to be used, we commonly apply this softening and toughening by reheating, calling it tempering. By a proper amount of tempering we can make the hardened steel tough enough to use in tools while still retaining a large part of its full hardness.

"Closer study of the hardening of steel discovers an apparent mystery. Austenite, γ(C), is soft and tough at any temperature. The ferrite and cementite mixture, α + Fe_3C, is also comparatively soft. The hardened steel is two or three times as hard as either γ(C) or α + Fe_3C. The quenching prevented the completion of the change from γ(C) to α + Fe_3C. It is evident that this change cannot be a simple one. From the microscopic examination and the accompanying measurement of the properties of the steel, we have found that the change from γ(C) to α + Fe_3C has four stages. These are technically known as the austenitic, martensitic, troostitic and sorbitic conditions of the steel."

"The austenitic and sorbitic stages are the chemically stable forms γ(C) and α + Fe_3C. γ(C) is stable above and unstable below the critical temperature. α + Fe_3C builds structures stable below and unstable above the critical temperature. The martensitic [non-crystalline β] and troostitic [non-crystalline α] stages are not stable under any conditions, from a theoretical standpoint; but if we can obtain them at ordinary temperatures they are practically permanent. The martensitic stage is the hard brittle stage. The hardness utilized in cutting tools comes from the martensite in the hardened steel. Troostite is similar in engineering properties to sorbite and pearlite. It is stronger and less ductile than sorbite, which in turn is stronger than pearlite. When, by quenching, we prevent the γ(C) from completing the change to α + Fe_3C, we usually catch a steel in the second stage of the change, the martensitic stage. Tempering changes the martensite to troostite or sorbite."

"The formation of troostite from the martensite is essentially a change of the non-crystalline β to non-crystalline α. With this change the steel suddenly becomes magnetically soft, while the electrical resistance drops from the high values of austenite and martensite nearly to that of soft steel. Simultaneously with the transformation of β to α the last of the γ in the martensite is disappearing. Neither β nor α will hold carbon in solid solution. The carbon of troostite is found neither as solution carbon nor combined carbon. Some idea as to its condition may be obtained from the microscopic appearance of the steel by working backwards from the known structures in cast irons with high carbon content to the steels with comparatively little carbon." The appearance of troostite in steel is characterized by peculiar round knots. The cast-iron structure cited for analogy is the temper graphite known from malleable cast iron. In the making of "black-heart" malleable cast iron a large portion of the temper graphite may appear at the same time with the appearance of magnetism and the disappearance of austenite just below the critical temperature. The circumstances are just those of the appearance of troostite in steels. The circumstances of the formation of a temper graphite knot in a very high carbon steel closely parallel the malleabilizing process in changing white cast iron to malleable.

"Perhaps we might reverse the statement, and say that the formation of temper graphite below the critical temperature in malleabilizing is an exaggerated case of setting free of carbon in troostite formation, made evident by the large quantities of carbon released." [81]

"The formation of sorbite from troostite may be considered as consisting of two simultaneous actions. One is the chemical combination of the α iron of the troostite with the adjacent carbon, forming the stable crystalline product Fe_3C. The non-crystalline α iron, like nascent hydrogen, ought to be chemically very active. The other is a crystallization of the outstanding α iron of the troostite. Both α and Fe_3C crystals of the structure then grow in size if the temperature and times of exposure permit. The sorbitic structure is chemically and physically stable at ordinary temperatures."

"In attempts to formulate explanations of the hardening of steel, controversy has generally raged round the part played by β iron. Often the very existence of β iron as an allotropic form of iron has been denied. The reasons for this are several. Crystalline β iron turns out to be very similar in crystal habit to α iron, while γ iron is markedly different from the other two. That the density of pure crystalline β iron is less than that of pure crystalline α iron at the same temperature has now been demonstrated. If curves are plotted against temperature for such properties of pure iron as magnetism, specific heat or electrical resistance, such curves are uniformly three branched, indicating that β has just as much right to recognition as an allotropic form as has α or γ iron. The main trouble has been a lack of knowledge of the relations of stable and metastable forms.......... A contributing factor has been the failure to recognize the austenite-martensite-troostite-sorbite as a sequence of overlapping chemical changes.......... Another source of confusion has been an insufficient allowance for the difference in physical and engineering properties between crystalline and non-crystalline conditions of the various allotropic forms or molecular kinds."

Wilder D. Bancroft

Atmospheric Circulation and Radiation. *By Frank H. Bigelow. 24 × 16 cm; pp. xi + 431. New York: John Wiley and Sons, 1915. Price: $5.00.*—The treatment is essentially mathematical and the subject is presented under the subheads: meteorological constants and elementary formulas; thermodynamic meteorology; the thermodynamics of the atmosphere; examples of the construction of vortices in the earth's atmosphere; radiation, ionization, and magnetic vectors in the earth's atmosphere; terrestrial and solar relations; extension of the thermodynamic computations to the top of the atmosphere.

The author writes the gas formula $P = \rho RT$ where ρ is the density. He states that this formula does not hold for air at different elevations and that consequently R varies with the height above sea-level. Since this is the starting point for all of the mathematical formulas, it would have been more satisfactory to the lay reader if the author had discussed this point somewhat in detail.

One would like to know whether this variation is due to the fact that the simplified gas law does not hold for pure oxygen or pure nitrogen under these circumstances, whether the simplified gas law does not hold for a mixture of nitrogen and oxygen, or whether the simplified gas law does not hold because the percentage composition varies with height above sea-level. It seems to the reviewer that the treatment of the subject would vary somewhat depending on the relative importance of these three possibilities. A reference to the van der Waals formula would not have been out of place.

There is an interesting paragraph on local circulations, p. 163. "The circulations of the earth's atmosphere can be conveniently analyzed under two classes: the first, or *general* circulation, including the largest movements that are primarily related to the axis of the earth as the line of reference for the angular motion, and the second, or *local* circulation, including the minor movements that are referred to axes which are wandering over the surface of the earth. The general circulation takes account of the great polar whirls covering the entire hemisphere, one north and one south of the equator, including the trade winds in the tropics, the eastward drifts in the temperate zones, and the minor circulations near the poles. These great zonal currents break up into localized circulations, as determined by the ocean and land areas, which constitute the first disintegration of the general circulation into smaller circulations. The true local circulations are commonly known as cyclones, anti-cyclones, hurricanes, tornadoes, and waterspouts, and these are referred to axes which move over the earth in paths that are determined by their relation to the breaks in the normal, general circulation. Finally there are very numerous minor whirls as eddies, small vortices of many types, which constitute the effectual internal friction through the operation of the law of inertia in the moving masses."

On p. 343, the author says: "The subject of the evaporation of water has been very extensively studied, and there is a large literature on the results. These, however, are unsatisfactory as concerns the terms and the coefficients of the proposed formulas........ The principal difficulty in arriving at conclusions has been due to the necessity of using pans for evaporation, in which case the wind in blowing over the pan greatly complicates the action of the evaporation. Pans of different sizes in the same wind evaporate different amounts during the same interval of time, because the wind carries away the evaporated vapor at different rates, according to the size of the pan, and thus produces a varying mixture of dry air and vapor. A large body of water in a wind, and a small pan in a calm, produce the same effect as an evaporating medium, because the vapor is actually the same in density near the water on a lake in a wind, which merely transports it from place to place without really removing it, as in a calm air over a small pan. The result is that lakes evaporate only at about two-thirds the rate from pans nearby in moderate winds. In certain places it was found that a small pan evaporates three times as much water as does a lake in the neighborhood."

Under polarization of sunlight in the atmosphere, we read, p. 349: "Besides the primary scattering and polarization on the small particles in a turbid atmosphere, it is found that the light is only partially polarized, so that a secondary polarization exists at right angles to each other, thus tending more or less to complete neutralization of plane polarized light as the primary and secondary components approach equality. There are several such points of neutralization: Babinet's neutral point about 15° to 25° above the solar point, Brewster's neutral point about the same distance below as the sun rises above the horizon, and Arago's neutral point about 15° to 25° above the antisolar point when the sun is on the horizon. The positions of these points vary with the position of the sun in the heavens, and the relative turbidity of the atmosphere. Since the dust particles accumulate chiefly in the lower atmosphere, in a stratum less than two miles thick, there is an apparent ring of special turbidity close to the horizon, which causes the light to be horizontally polarized within a few degrees of the horizon. Generally, polarization is a maximum in the zenith, and diminishes to the north and south horizon points, and from these to the east point, for a sun in the east and on the horizon. There are numerous variations of these principal results due to change in the intensity of solar light from radiation, and change in the contents of turbidity in the atmosphere."

There are, of course, other oases in the desert of thermodynamics; but these are the ones that appealed most to the reviewer. *Wilder D. Bancroft*

The British Coal-Tar Industry. *Edited by Walter M. Gardner. 21 × 15 cm; pp. ix + 437. Philadelphia: J. B. Lippincott Co., 1915. Price: $3.00 net.* —This volume contains a number of addresses on various features of the coal-tar industry during the last fifty years by different scientific men. There is consequently a great deal of repetition; but this is perhaps compensated by the multiplicity of the points of view. The general situation is put clearly by Meldola, p. 266, in an address on tinctorial chemistry, delivered in 1910.

"The question of the cause of the decline of the British industry resolves in reality into the question of the cause of the continental activity. The answer to this last question has been staring us broadly in the face for over thirty years. It is amazing that there should ever have been any doubt about, or any other cause suggested than the true cause, which is RESEARCH—writ large! The foreign manufacturers knew what it meant and realized its importance, and they tapped the universities and technical high schools and they added research departments and research chemists to their factories, while our manufacturers were taking no steps at all, or were calmly hugging themselves into a state of false security, based on the belief that the old order under which they had been prosperous was imperishable. It is true that when the effect of the new discoveries began to make themselves felt, one or two factories did add a research chemist to the staff, but the number and the means of work were totally inadequate. I happened to be one of them, and so I speak with some practical knowledge of the conditions. We were but a handful of light skirmishers against an army of trained legionaries. What could three or four—say half a dozen at a liberal estimate—research chemists, working under every disadvantage, do against scores, increasing to hundreds, of highly trained university chemists, equipped with all the facilities for research, and backed up by technological skill of the highest order? The cause of the decline of our supremacy in this color industry is no mystery—it is transparently and painfully obvious. In the early stages of its decadence it had little or nothing to do with faulty patent legislation or excise restrictions with respect to alcohol. The decay of the British industry set in from the time when the Continental factories allied themselves with pure science and the British manufacturers neglected such aid, or secured it to an absurdly inadequate extent in view of the strength of the competing forces."

It is interesting to note the point raised by Singer, p. 296, that the Englishman is interested only in production on a large scale. He claims: that in England inventions are disregarded unless or until they relate to objects for which there is an ample market; that, failing such condition, an invention is useless and hence an increase in the number of persons engaged in the making of such inventions mere waste of time and money; that inventions made in England are neglected locally while others, made abroad, are exploited successfully here. He concludes that want of education is not the deciding factor, but rather the tendency towards specialization which makes mass production a necessity.

Wilder D. Bancroft

Representative Procedures in Quantitative Chemical Analysis. *By Frank A. Gooch. 23 × 15 cm; pp. x + 262. New York: John Wiley and Sons, 1916. Price: $2.00 net.*—The author states in the preface that, "The book is an introduction to representative procedures in quantitative chemical analysis," and "that the arrangement of the book is such as to permit the selection of a narrower course or a broader course." Judging by the contents, the book might almost be entitled, "The Procedures in Quantitative Analysis Originating at Yale University." It is hardly fair to classify such research theses as: The Precipitation of Magnesium as Magnesium Ammonium Carbonate; The Precipitation and Weighing of Mercurous Oxalate; The Determination of Barium as Chloride; Electrolysis with Small Electrodes with a Weighable Cell, etc., etc., as representative procedures in quantitative analysis. The arrangement of the text leaves much to be desired. The student is led into the field of electrolytic processes after trying three different methods of determining the water of composition, four different methods of determining carbon dioxide (one by fusion with $Na_{10}W_{12}O_{41}$), one method for the determination of boric acid and two experiments in the determination of magnesium and manganese as sulphate. After the electrolytic work the student is led back to the ordinary gravimetric determinations of chlorides, etc. To summarize, the book is poorly suited for use as a laboratory manual, and not comprehensive enough for a reference book.

G. E. F. Lundell

The Elements of Physical Chemistry. *By Harry C. Jones. Fourth edition. 22 × 16 cm; pp. xiv + 672. New York: The Macmillan Company, 1915. Price: $4.00.*—In view of the tragical death of the author there is nothing to be gained by discussing ways in which a future edition might be improved. The reviewer has often disagreed with Mr. Jones' point of view in regard to many scientific matters; but he has recognized the extraordinary energy which has always characterized Mr. Jones and which has been made manifest in the volume of work from the Johns Hopkins laboratory. If Mr. Jones had been able to relax a little, his life would have been prolonged; but he felt that he would have accomplished less.

Wilder D. Bancroft

THE CONSISTENCY OF PECTIN GELS[1]

(PRELIMINARY COMMUNICATION)

BY JAS. B. McNAIR

Just what chemical substances are necessary and how they combine to form a fruit jelly of the proper consistency has been quite a subject of investigation and argument.

Fremy (1) claimed that jelly formed from a change of pectin into pectic acid. He considered pectic acid the essential part of jelly as fruit juice spontaneously gelatinized when pectin was transformed to pectic acid by the action of an enzyme pectase. This jelly, however, has no connection with fruit jelly for three reasons, *viz.*, 1. When a pectic acid solution and sugar are mixed no jelly forms, and secondly, pectic acid together with sugar and another acid or salt gives a syrupy liquid. A jelly of the proper consistency does not form because pectic acid is not soluble in this medium. 3. An analysis of fruit jelly does not disclose any pectic acid.

Tschirch (2) experimented with currants. He considered jelly as due to a pectin and sugar solution or a combination between pectin and sugar. Without sugar he could obtain no jelly. As a disproof of this theory we have the experience of von Fellenberg. Upon dialyzing currant jelly, he observed that it attracted water quickly. The liquid increased in the apparatus and in fifteen hours the jelly dissolved. No clear solution resulted, however; flocks of a body similar to cellulose remained which could be removed by filter or centrifuge. When the clear filtrate was dialyzed, flocks were formed during dialysis which were not present beforehand in the jelly. These flocks dissolved in a sugar solution and on successive heating and cooling a jelly formed. These flocks were considered by Tschirch as pectin. But this substance is not taken as pectin by von Fellenberg (3) first because the filtrate free from these

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[1] Contribution from the Rudolph Spreckels Physiological Laboratory and the Enology Laboratory of the University of California.

flocks when heated with sugar gives a jelly. Secondly, this flocking body in currants is not present in other fruits. Thirdly it differs from the pectin of von Fellenberg in not containing methoxyl groups. Lastly, Tromp de Haas and Tollens (9) analyzed this flocculating body to find it evidently a carbohydrate containing 54.4 percent carbon, and 5.05 percent hydrogen. It contains, therefore, a higher percentage of carbon than either cellulose or pectin.

To prove that pectin plays an important rôle in jelly formation von Fellenberg dissolved quince jelly in boiling water. From this mixture he precipitated pectin by adding alcohol. The filtrate would form only a syrupy solution, not jelly. If the precipitated pectin were added, jelly formed. A similar result was obtained when purified pectin was added to quince syrup.

A purified pectin and sugar solution alone gave no jelly. Pectin from various fruits and varying quantities when added to a sugar solution resulted in syrups only. He concluded, therefore, the formation of jelly is due to other substances than pectin and sugar.

If jelly formation be considered as a coagulation it might be supposed that a jelly would result by addition of mineral salts which coagulate pectin to a solution of pectin and sugar. This was not the case for when ferric chloride was added to a solution of pectin and sugar, flocks of a pectin-iron coagulum separated, no jelly formed.

Von Fellenberg obtained better results by using organic salts, *i. e.*, malates of calcium, magnesium, and aluminum. These gave jellies when added to a solution of pectin and sugar. Such jellies were not as stiff as those formed by the addition of pectin to pectin-free fruit syrups. In summarizing his work with jellies, von Fellenberg concluded that besides sugar and pectin certain salts are necessary to jelly formation. He considered the possibility of other parts of fruit juice playing active rôles in jelly making.

A previous investigator to von Fellenberg on jelly making, Miss Goldthwaite (4), noticed that jelly formation would occur when 0.5 percent tartaric acid solution, 1 percent pectin, and three-fourths volume of sugar were heated for not more than fifteen minutes. She considered the presence of free acid necessary for jelly. In fact she claimed that neutral juice would not gelatinize.

In considering earlier researches I believe that the malates of calcium, magnesium and aluminum may owe their virtue in gelatinization to the presence of the hydrogen ion. Acid malates may have been present as impurities in the salts used by von Fellenberg. It is doubtful if neutral malates would aid appreciably in gelatinization.

In commencing work on jelly I considered the principal factors in securing a fruit jelly of the proper consistency, pectin, sugar, and acid. The pectin used was obtained from Villa Franca and Eureka lemon rinds by the von Fellenberg process. 4 kg of lemon rinds were boiled in a reflux condenser 6–8 times (20 minute periods) with 4–6 liters of 95 percent alcohol. This process tended to free them from coloring matter, acids, etc. Between each boiling the material was pressed in a screw press. Three liters of water were added to the final press cake and the mixture heated in an autoclave for an hour at 110° C. At the end of this period the contents were pressed and the liquid was filtered through a Seitz asbestos filter until clear. The pectin was obtained from the filtrate by adding a double volume of alcohol to which 7 cc of concentrated hydrochloric acid had been added per liter. The coagulum was pressed in canton flannel and kneaded in several changes of alcohol until the acid reaction disappeared. Finally the pectin was washed with ether and dried in a vacuum desiccator over sulphuric acid.

Dr. Robertson suggested that a method might be evolved for the determination of pectin through use of its refractive index. The refractive index of a 2 percent water solution of lemon pectin was found to be 0.00130 per g percent when observed in a Pulfrich refractometer which indicates to within 1′ of the angle of total reflection. A sodium flame was employed as a source of light. The solution was adjusted to the temperature of the room so that the temperature of the refractometer prism and that of the solution used would be the same. It has been shown by Robertson (5) that in alkaline or acid aqueous solutions of proteins the change in the refractive index of the solvent is directly proportional to the concentration of the dissolved protein. In respect to its refractive index pectin acts similarly to protein. This relation can be expressed by the equation:

$$n - n_1 = a \times c$$

when n is the observed refractive index of the pectin solution, n_1 that of the solvent in which the pectin is dissolved, c the percentage of pectin in solution, and a a constant, expressing the change in the refractive index of the solvent by the addition of 1 g of pectin per 100 cc.

In the viscosity experiments a Redwood viscosimeter was used. The results will be found in Table I.

The results show: 1. That all three of the substances tested, when in aqueous solution, independently increase the viscosity of distilled water. 2. That mixtures of any two or all three of the substances result in an increase of viscosity greater than the viscosities independently. 3. That jelly will form when acid, pectin, and sugar are in solution of certain concentration. 4. That jelly will form from a solution of 3 g percent pectin and 65 g percent sugar. 5. The viscosities of the separate substances are not additive.

According to Hardy (6) and Robertson (7) jelly formation is analogous in some instances to emulsification and may, therefore, be dependent on surface tension phenomena. From the Tolman (8) theory of colloids, in the case of a lyophilic colloid in equilibrium with a dispersing medium, an increase in the concentration of the hydrogen ion in the dispersing medium lessens surface tension and hence increases dispersion. Thus an increase in hydrogen ion concentration would result in an increase in the total surface of the pectin and consequently the viscosity of the solution could be increased. Still further additions of acid might lead to such high degrees of dispersion

TABLE I
Viscosity results all obtained at 45° C

Citric acid (Baker's Analyzed) grams percent	Cane sugar (commercial) grams percent	Pectin grams percent	Specific gravity	Time of flow			
				Trial I min. sec.	Trial II min. sec.	Trial III min. sec.	Average min. sec.
—	65.0	—	1.3204 at 23.5°	1, 59.2	1, 58.1	1, 54.3	1, 57.2
0.5	—	—	0.995	25.2	25.4	25.4	25.33
1.0	—	—	0.996	25.4	25.5	25.4	25.43
2.0	—	—	0.999	25.8	26.6	25.5	25.63
4.0	—	—	1.012	27.2	26.8	26.8	26.93
—	—	1.0	1.002	27.2	27.6	27.4	27.4
—	—	2.0	1.005	28.4	28.4	28.6	28.4
—	—	3.0	1.007	29.8	29.8	30.0	29.8
—	—	4.0	1.012	32.0	32.4	32.0	32.2
—	65.0	1.0	—	9, 10.4	9, 45.0	9, 31.0	9, 28.8
—	65.0	2.0	—	13, 25.4	13, 25.2	14, 00.0	13, 36.8
—	65.0	3.0	—	Jelly			
—	65.0	4.0	—	Jelly			
0.5	—	1.0	—	1, 10.0	1, 5.4	—	—
0.5	—	2.0	—	1, 22.4	1, 22.6	1, 22.0	1, 22.3
0.5	—	3.0	—	1, 18.8	1, 20.0	1, 21.6	1, 19.44
0.5	—	4.0	—	1, 22.8	1, 25.0	1, 22.0	1, 23.2
0.5	65.0	1.0	—	Jelly			

that the condition of affairs in so-called true solutions would be approached and thus the viscosity again decreased.

The function of sugar may be that of a dehydrating agent. It also imparts a certain amount of viscosity to the jelly presumably by combining the water which would otherwise lead to fluidity. Glycerol acts similarly. The comparative anhydrous state of jelly may be shown by the addition of a small amount of either cupric chloride or cobalt chloride to the jelly. Green and red colors, respectively, result, which are the anhydrous colors of these salts. Upon dilution these colors change to blue and pink, the respective hydrous colors of the salts.

If the function of sugar is principally that of dehydration then a higher concentration of pectin together with the same concentration of acid and no sugar should give a jelly of equal firmness to the one in which sugar is present. Indeed experimental results indicate such to be the case.

Conclusions

1. The author considers pectin, acid, and sugar the principal factors in fruit jelly making.

2. Pectin was obtained from lemon rinds by boiling in several changes of alcohol, heating in an autoclave for 1 hr. at 110° C in the presence of water, filtering, precipitating by a double volume of acidified alcohol, removal of acidity with alcohol, and ether, drying in vacuum desiccator over sulphuric acid.

3. The combined refractive index of Villa Franca and Eureka lemon pectin in water solution was 0.00130 per g percent.

4. The results of the viscosity experiments indicate that:

(*a*) Pectin, acid, and sugar independently or combined increase the viscosity of water.

(*b*) Jelly will form from a mixture of acid, pectin and sugar when in certain concentration.

(*c*) Jelly will form when pectin and sugar are dissolved in certain concentration.

(*d*) The viscosities of the various substances are not additive.

(*e*) The increase of viscosity may be due to the presence of the hydrogen ion.

(*f*) That sugar may have two functions, *viz.*, that of a dehydrating agent and of increasing the viscosity.

The work is being continued.

I would like to express my gratitude to Professor T. Brailsford Robertson and Assistant Professor Wm. V. Cruess, under whom this work was done.

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Berkeley, California, April 20, 1916

THE PHYSICAL CHARACTER OF PRECIPITATED LEAD MOLYBDATE AND ITS IMPORTANCE IN THE ESTIMATION OF MOLYBDENUM AND LEAD

BY HARRY B. WEISER

For the determination of molybdenum in alkali molybdates Chatard[1] recommends that the solution of the molybdate be heated to boiling and lead acetate added in slight excess after which the liquid is boiled a few minutes. The liquid is at first very milky but the precipitate soon becomes granular and subsides readily, leaving a clear supernatant liquid. He calls attention to the fact that the thick milky fluid is very apt to boil over unless particular care is taken in heating. After settling, the precipitate is filtered, washed, and lastly ignited in a porcelain crucible.

Although some recognized text-books of analytical chemistry do not even refer to this method and others barely mention it, it seemed to me to be more simple and easy to carry out than any other method described for estimating molybdenum in alkali molybdates. As I was recently called upon to make a large number of such determinations I decided to test the ease, rapidity and accuracy of the method.

A solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (hereafter called ammonium molybdate), containing about 0.5 gram of the salt dissolved in 250 cc of water, was heated to boiling and a lead acetate solution added in slight excess. The liquid was very milky but after boiling for a few minutes, with constant stirring, and removing from the source of heat, the precipitated salt settled readily. Under these conditions the precipitate was bluish white in color, flocculent in appearance and was quite bulky showing that it had carried down with it a large amount of water. On examination with the microscope it was found to consist of very fine particles. After pouring the supernatant liquid rapidly

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[1] Am. Jour. Sci., (3) 1, 416 (1871).

through a Gooch funnel, the precipitate was washed in with a stream of hot water from a wash bottle. The bulky mass matted down tightly on the asbestos bottom, clogging the pores so that it required hours to filter and wash it free from lead. The crucible was next put in the oven to dry. The salt had carried down so much water that drying caused it to shrink and curl up, loosening the asbestos fiber from the bottom of the crucible. Final heating was done at a low red heat with a Bunsen flame. When the free flame was first applied, the white precipitate became dark blue in color. This color gradually disappeared as the temperature increased, leaving the salt perfectly white. At a dull red heat the salt assumed a decided yellow color that became almost white again on cooling.

The experiment showed that, because of the character of the precipitate, it was not at all feasible to use a Gooch crucible for filtration. Accordingly, the above described experiment was repeated substituting a funnel and filter paper for the Gooch crucible. In the hope of securing a less bulky precipitate the precipitant was added slowly to the boiling molybdate solution from a burette. The precipitate so obtained was quite as bulky as before but the filtration was somewhat more rapid. Even under these conditions the necessary period of washing was unduly long. The precipitate was dried as before and because of the shrinking it cracked loose from the paper and was very easy to remove. A portion was ignited, and darkening of the salt was again observed at the outset of the ignition. This procedure was repeated a number of times and each time the same phenomenon was noted. Attention was accordingly directed to finding out the cause of this transient coloration during ignition.

It is a well known fact that when molybdic acid or a soluble molybdate is treated with a reducing agent, the molybdic acid is converted into a blue oxide or oxides of molybdenum of doubtful composition intermediate between the dioxide and the trioxide. In hydrochloric acid solution this intermediate oxide is held in solution, imparting to it a blue to green color. With this information as a guide the first assumption was that the lead molybdate was partly reduced on heating, becoming dark blue; and on further heating in the presence of air it reoxidized completely to the white salt. To test this, some lead molybdate was made in the method above described and was placed in a hard glass test tube fitted with a two-hole rubber stopper, one hole of which was supplied with a glass tube for conducting in carbon dioxide and the other with an exit tube. After thoroughly washing out the air of the test tube, the salt was heated and became blue. Continued heating at a high temperature for several minutes failed to restore the white color. This tended to prove that the darkening on first heating was a reduction product of a molybdate and that subsequent heating in air resulted in oxidation to the white salt. A possible explanation of the cause of the phenomenon is, that lead molybdate adsorbs lead acetate which breaks up on heating with the formation of acetone and that the latter reduces the lead salt. Since the amount of acetone formed under these conditions would be very minute at the most and since it is not a very strong reducing agent, this explanation seemed altogether inadequate. Subsequent observations that will now be recorded have resulted in a more probable explanation.

A solution of ammonium molybdate containing about 3 grams of the salt was placed over a Bunsen flame to boil and was forgotten until it had boiled almost to dryness. The few cubic centimeters of solution that remained had a bluish green tinge as if the salt had been reduced. This was thought to have been caused by the possible presence of some non-volatile organic matter in the distilled water. Accordingly, some water was purified in the usual manner for making conductivity water and with this a concentrated solution of the molybdate was prepared. The solution was boiled with a reflux condenser for several hours, and it became darker and darker blue-green as the process was continued. A parallel experiment using a solution of the normal sodium molybdate ($Na_2MoO_4.2H_2O$) was carried out in exactly the same manner and this solution showed no tendency whatsoever to become colored. The blue color of the ammonium molybdate solution disappears if the solution is exposed to the air[1] for some time just as does the blue solution obtained by reduction with zinc and hydrochloric acid and it may be discharged immediately by the addition of dilute potassium permanganate solution. It is evident, therefore, that heating a solution of ammonium molybdate results in decomposition with the formation of a lower oxidation product.

Samples of the solid molybdate of ammonium and of sodium were then heated slowly on a sand bath and it was found that the sodium salts did not darken but that the ammonium salt darkened no matter how carefully the heat was applied. A blue oxide of molybdenum formed which oxidized at a higher temperature to the white trioxide. Some of the ammonium salt was heated very slowly in an electric furnace in a combustion tube through which a continuous stream of oxygen was conducted. Even under these conditions the decomposition of the salt resulted in the formation of a blue oxide which subsequently oxidized to the higher oxide. Some of the ammonium salt heated out of contact with air or oxygen became blue and the blue color did not disappear on continued heating at high temperature. Although I have found no statement in the literature to the effect that ammonium molybdate darkens on heating due to the formation of a blue oxide, this observation has doubtless been made by everyone who has prepared molybdic oxide by the decomposition of ammonium molybdate. Uhrlaub[2] and Berlin[3] claim to have prepared the oxide Mo_3O_8 by heating $(NH_4)_6Mo_7O_{24}.4H_2O$ with MoO_3.

Ammonium molybdate begins to darken at a temperature a little above 200° C. and it was noted that lead molybdate prepared as before described starts to darken at about

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[1] Cf. Manschke: Zeit. anal. Chem., 12, 384 (1873).
[2] Pogg. Ann., 101, 605 (1857).
[3] Jour. prakt. Chem., 49, 447 (1853).

the same temperature. It is reasonable to assume that the transient coloration of lead molybdate during ignition is due to the presence of ammonium molybdate adsorbed by the flocculent precipitate. This was confirmed in the following way: A gram sample of ignited lead molybdate was ground finely in an agate mortar and was thoroughly mixed with 5 drops of a solution containing 0.8 mg of ammonium molybdate. After drying, this was gently ignited and a darkening of the salt resulted, similar to that previously observed and described. In line with this explanation I have observed that the darkening of the lead salt on ignition was greater the higher the concentration of ammonium molybdate solution from which it was precipitated. This is the condition under which one would expect to get the greatest adsorption of the ammonium salt.

At the time it was thought that the presence of adsorbed lead acetate was indirectly responsible for the darkening of the precipitated lead molybdate, it was decided to avoid the use of lead acetate altogether and to substitute lead nitrate in its place. The same procedure was followed as when the acetate was used as precipitant and the precipitate so prepared did not darken when ignited. It was further noted that the physical character of the salt was markedly different under these conditions. The precipitate settled out in larger particles and consequently in considerably less time; it was less flocculent and carried down much less water than the salt using lead acetate as precipitant. In consequence, it was less bulky, more easy to filter and required less time to wash. A further difference in property was the color. As already stated, the salt precipitated with lead acetate was bluish white; in marked contrast, the salt precipitated with the nitrate was yellowish white. This difference in color is caused by the difference in size of the precipitated particles. The finer the state of subdivision and the more flocculent the precipitate the bluer it is and the larger the particles and more dense the precipitate the yellower it is. This fact is brought out quite clearly in the ignition of the salt. The latter is distinctly yellow when hot and white when cold. The yellow color is produced by the coalescing of the particles by heat and the return of the white color by the disintegration of the coalesced particles on cooling. If, however, the salt is heated sufficiently hot to cause noticeable fusion, it does not regain its white color on cooling. This is analogous to the experiments of Farnau[1] on zinc oxide. It also explains, in part at least, the fact that precipitated lead molybdate is white, while the native salt is yellow to yellowish red in color.

In general, the smaller the size of the particles of any precipitate the slower it will settle, likewise the more flocculent a precipitate the slower it will settle and the more bulky it will be. That lead molybdate precipitates in larger particles and in a much less flocculent condition with lead nitrate as precipitant than with lead acetate was shown clearly by the following experiments: Sufficient ammonium molybdate (0.4811 gm) to make 1 gram of lead molybdate was dissolved in 200 cc of water and heated to boiling. In 50 cc of boiling water in a separate beaker was dissolved slightly more than enough lead salt to precipitate all the molybdenum. The boiling solutions were poured quickly together into a tall cylinder 3.6 cm in diameter. The time was noted and the solutions were stirred vigorously and continuously for one minute. The precipitate was then allowed to settle and the distance from the top of the settling precipitate to the bottom of the cylindrical vessel was measured at certain intervals of time. The results are recorded in Table I. At the left of the table is recorded the time intervals. In the first column under the heading "Solutions Mixed" is recorded the thickness of the layer of suspended molybdate in centimeters for the corresponding time interval when the ammonium salt was precipitated with lead acetate. In the second column is recorded similar observations with lead nitrate as the precipitant:

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[1] Farnau: Jour. Phys. Chem., 17, 637 (1913).

TABLE I

Time interval (Minutes)	Solutions mixed		
	(1) Ammonium molybdate and lead acetate	(2) Ammonium molybdate and lead nitrate	(3) Ammonium molybdate 5 gm. NH_4NO_3 lead acetate
1	12.0	1.9	10.0
2	5.1	1.4	4.1
3	4.0	1.1	3.4
4	3.5	1.0	3.0
5	3.2	0.9	2.7
10	2.3	0.6	2.1
20	1.9	0.5	1.7
30	1.8	0.4	1.6

As seen from the above table, the larger more granular particles of lead molybdate, precipitated with lead nitrate, settle in one and one-half minutes to a bulk less than the particles of the more flocculent precipitate, obtained with lead acetate, settle in one-half hour. This is a significant fact of particular importance from the standpoint of the analyst. Since adsorption is a surface phenomenon, it follows that the more flocculent and the more finely divided a precipitate the greater is the tendency for adsorption to take place. This explains why, even after prolonged washing, the precipitate obtained with ammonium molybdate and lead acetate darkened on ignition, whereas the precipitate obtained using lead nitrate as precipitant did not darken when heated. Ammonium molybdate was adsorbed to a much greater extent by the flocculent precipitate than by the more granular one.

The question naturally arises as to why the precipitate is more flocculent and bulky in one case than in the other. It seems likely that the physical character of every precipitate may be affected by the presence of substances in the solution, the extent of the effect varying widely in different cases. A particular case in point is the precipitation of barium ion by sulphate ion in excess. This precipitate comes down in a more filterable condition in the presence of a large excess of hydrochloric acid. Krak[1] has pointed out that fine barium sulphate changes instantly into a coarse precipitate in the presence of a saturated solution of ammonium acetate. Osborne[2] has shown this to be due to the solvent action of the acetate. Small particles are more soluble than large ones and so the smaller particles dissolve first and reprecipitate on the larger. In this way the large particles grow larger at the expense of the smaller.[3] This same explanation might be given to account for the beneficial effect of hydrochloric acid in the precipitation of barium ion by sulphate ion in excess were it not for the fact that hydrochloric acid has an undesirable effect on the crystal size when sulphate ion is precipitated by barium ion in excess. Experiments are now being carried out in this laboratory in an attempt to account for these facts.

The physical character of a substance precipitated from colloidal suspension sometimes varies markedly, depending on the coagulant used. Oden[4] states that different salts cause colloidal sulphur to precipitate in different forms: with hydrochloric acid the coagulum is liquid; with barium salts a plastic mass; with cupric sulphate a fine grained precipitate and with certain other salts a slimy precipitate. Giolitti[5] finds that hydrochloric acid precipitates a certain suspension of ferric oxide as a brick-red powder while a similar suspension of ferric oxide is precipitated by sulphuric acid in a gelatinous form. Bancroft,[6] in discussing this phenomenon, says: "The precipitation of ferric oxide as a sandy mass by hydrochloric acid and as a gelatinous one by sulphuric acid is an important matter about which we know very little theoretically. The formation of the gelatinous precipitate cannot be a matter involving the hydrogen ion

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[1] Chemist Analyst, 1912, 26.

[2] Jour. Phys. Chem., 17, 629 (1913).

[3] Cf. Hulett: Zeit. phys. Chem., 37, 385 (1901); 47, 356, (1904).

[4] Oden: "Der Kolloide Schwefel," 157 (1912).

[5] Giolitti: Gazz. chim. ital., 35 II, 181 (1905).

[6] Jour. Phys. Chem., 19, 236 (1915).

because we get the effect with sodium sulphate and do not get it with hydrochloric acid. Since it occurs with a number of different acids and salts it cannot be due to a specific anion. The one common characteristic is that the anions precipitate in low concentration and are therefore adsorbed strongly, but this does not enable us to distinguish the possible hypothesis of the effect being due to the strongly adsorbed anion or the solvent action of the adsorbed salt. It has been shown by von Weimarn[1] that cellulose can be converted into a gelatinous mass by heating with concentrated salt solutions preferably under pressure. In the particular case of ferric oxide the salt concentrations are low which makes it a little more probable that we may be dealing with the effect of the anion rather than of the salt, but on the other hand it is open to anyone to postulate a high salt concentration in or at the surface of the ferric oxide."

It seemed possible that the more granular precipitate of lead molybdate obtained with lead nitrate as precipitant might be due to the presence of nitrate ions. To test this possibility 5 grams of ammonium nitrate were added to the ammonium molybdate solution before precipitating with lead acetate. The results are recorded in the third column of Table I. The character of the precipitate to outward appearances was the same as when no ammonium nitrate was added and the rate at which it settled was but little different.

Experiments were next tried using a different molybdenum salt and noting the effect on the physical character of the lead molybdate precipitated by lead nitrate and by lead acetate. The salt used was the normal sodium molybdate. For each experiment enough of this salt was dissolved to make .1 gram of lead molybdate and precipitation was carried out as above described for ammonium molybdate. The results are given in Table II.

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[1] Zeit. Kolloidchemie, 11, 41 (1912).

TABLE II

Time in minutes	Solutions mixed	
	Sodium molybdate and lead acetate	Sodium molybdate and lead nitrate
1	4.1	10.0
2	2.9	5.0
3	2.4	3.5
4	2.1	3.0
5	1.95	2.7
10	1.5	2.3
20	1.3	2.0
30	1.2	1.9

To outward appearances the character of the precipitates obtained from sodium molybdate solution is identical with that obtained with ammonium molybdate and lead acetate. As shown in the table the precipitate with lead nitrate as precipitant was more flocculent and bulky than that with lead acetate. Both precipitates were bulky, the particles were small and the mass had a blue-white color. These results were confirmed by several repetitions of the experiments.

The fact that a less bulky and more granular precipitate of lead molybdate was obtained with a solution of ammonium molybdate and lead nitrate than with any other combination tried, lead to a study of the reaction products obtained in each case and the possible effects these might have on the character of the precipitate obtained. With sodium molybdate the reactions involved may be expressed by the following equations:

$$Na_2MoO_4 + Pb(Ac)_2 = PbMoO_4 + 2NaAc \qquad (1)$$

$$Na_2MoO_4 + Pb(NO_3)_2 = PbMoO_4 + 2NaNO_3 \qquad (2)$$

and with ammonium molybdate:

$$(NH_4)_6Mo_7O_{24}.4H_2O + Pb(Ac)_2 = 7PbMoO_4 + 6NH_4Ac + 8HAc \qquad (3)$$

$$(NH_4)_6Mo_7O_{24}.4H_2O + Pb(NO)_2 = 7PbMoO_4 + 6NH_4NO_3 + 8HNO_3 \qquad (4)$$

As can be seen from Equation 4, nitric acid is formed as a reaction product in the solution from which the most compact precipitate is obtained. From this I deduce that reaction (4) is partly reversible, and that the larger particles obtained in this case are due in part to the solvent action of nitric acid which dissolves up the more readily soluble small particles that then reprecipitate on the larger ones. As a matter of fact lead molybdate in the moist condition is fairly soluble in nitric acid and in other strong acids; but after ignition, that is, after the more finely divided particles are sintered together, it is practically unattacked by nitric acid. Acetic acid which is very weak and hence gives but few acetate ions has no appreciable action. Ammonium acetate and sodium acetate have a slight solvent action on the freshly precipitated salt but not nearly so much as nitric acid. Lead molybdate dissolves in ammonium and sodium acetate for the same reason that lead sulphate dissolves in this reagent. The solvent action depends on the formation by metathesis of undissociated lead acetate, which is much less ionized than most other salts of the same type.[1]

It is not surprising that the physical character of a precipitate should be affected by the presence in solution of a small amount of a substance which possesses a slight solvent action. It is known that digesting small particles of a so-called insoluble precipitate in cold distilled water for some time or in boiling water for a short time, is conducive to the growth of the particles. This is due to the fact that different degrees of solubility exist among particles of different size.[2]

On the basis of the slight solubility of lead molybdate in nitric acid and in sodium and ammonium acetates may be explained the results obtained in the four experiments above tabulated. Nitric acid has considerable solvent action on lead molybdate, hence the particles obtained from solutions of ammonium molybdate and lead nitrate are larger and the precipitate more granular than in the other cases. The solvent action of ammonium acetate and sodium acetate has

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[1] Noyes and Bray: Mass. Inst. Tech. Quarterly, 19, 234 (1906).

[2] Foulk: Quant. Chemical Analysis, 46 (1914).

relatively a very slight effect and so the precipitates obtained in the presence of small amounts of these salts alone, are more flocculent and bulky. The precipitate obtained with sodium molybdate and lead nitrate is the most bulky of all, since sodium nitrate has no solvent action.

In line with the above explanation it follows that if any lead salt of a strong acid is used as a precipitant for ammonium molybdate the physical character should be similar to that obtained with lead nitrate as precipitant. It further follows, if a strong acid is added to ammonium molybdate before precipitating with lead acetate (in quantity equivalent to the amount of acetic acid subsequently formed), that the physical character of the lead molybdate should be similar to that obtained with lead nitrate as precipitant. Since ammonium acetate has a very slight solvent action on lead molybdate the addition of a large excess of this salt to the ammonium molybdate solution before precipitating with lead acetate should have an effect similar to that of adding a very small amount of strong acid. That these conclusions are correct was shown by observation and by the results of the experiments recorded in Tables III and IV. According to reaction (4) above, it was calculated that about 0.2 gram of nitric acid is formed during the formation of 1 gram of lead molybdate from $(NH_4)_6Mo_7O_{24}.4H_2O$.

TABLE III

Time in minutes	Solutions mixed		
	(1) Ammonium molybdate and lead chloride	(2) Ammonium molybdate and lead bromide	(3) Ammonium molybdate and lead formate
1	2.0	2.1	9.5
2	1.6	1.6	3.6
3	1.2	1.3	3.0
4	1.0	1.1	2.6
5	0.95	1.0	2.4
10	0.65	0.75	1.9
20	0.60	0.55	1.5
30	0.50	0.50	1.4

TABLE IV

Time in minutes	Solutions mixed			
	(1) Ammonium molybdate 0.2 g HNO_3 lead acetate	(2) Ammonium molybdate 0.12 g HCl lead acetate	(3) Ammonium molybdate 0.4 g HNO_3 lead acetate	(4) Ammonium molybdate 5.0 g NH_4Ac lead acetate
1	4.0	4.0	2.1	1.8
2	2.6	2.6	1.5	1.3
3	2.0	2.0	1.1	1.1
4	1.9	1.7	1.0	1.0
5	1.7	1.5	0.9	0.9
10	1.3	1.2	0.65	0.7
20	1.1	1.1	0.6	0.6
30	0.9	0.9	0.5	0.5

In Table III it is shown that when the lead salt of any strong acid is used as precipitant for lead molybdate from ammonium molybdate solution, the precipitate is more granular and less bulky than when the lead salt of a weak acid is used. The precipitate using lead formate as precipitant (Table III (3)) is somewhat less bulky than that with lead acetate (Table I (2)). This is in line with what we should expect since formic acid is a stronger acid than acetic. As can be seen from Table IV the addition of 0.2 gram of nitric acid or the equivalent of hydrochloric acid to the ammonium molybdate solution before precipitating with lead acetate has an effect on the character of the precipitate but it is still more flocculent than that obtained with lead nitrate as precipitant. This is due to the fact that the concentration of nitric acid is cut down by the presence of ammonium acetate as a product of the reaction. That this is the case, is evident from the experiment recorded in Table IV (3), in which 0.4 gram of nitric acid is added before precipitation. Under these conditions the precipitate is less bulky and more granular. The presence of 5 grams of ammonium acetate has the same effect as the presence of a very small amount of nitric acid, as shown in Table IV (4).

Experiments were next tried with solutions of sodium molybdate to which a trace of strong acid was added before the addition of the precipitant. As heretofore, 1 gram of lead molybdate was precipitated under the conditions recorded in Table V.

TABLE V

Time in minutes	Solutions mixed		
	(1) Sodium molybdate 0.2 g HNO_3 lead nitrate	(2) Sodium molybdate 0.2 g HNO_3 lead acetate	(3) Sodium molybdate 0.4 g HNO_3 lead acetate
1	2.0	12.0	2.5
2	1.5	4.6	1.8
3	1.1	3.7	1.4
4	1.0	3.3	1.2
5	0.9	3.0	1.1
10	0.5	2.3	0.85
20	0.45	1.8	0.65
30	0.4	1.5	0.55

As shown in the table, the presence of 0.2 gram of nitric acid in the solution when lead nitrate is used as precipitant for sodium molybdate, causes a precipitate to form that has the same properties as that obtained with ammonium molybdate and lead nitrate. This is in striking contrast to the more flocculent bulky precipitate obtained when no nitric acid is added. (See Table II (2).)

The addition of 0.2 gram of nitric acid with lead acetate as precipitant has practically no effect as can be seen by comparing the results in Table I (2) with Table V (2). The reason is that sodium acetate is formed in the solution and this cuts down the concentration of nitric acid as before explained. With 0.4 gram of nitric acid and other conditions the same, the precipitate is very much less bulky. (See Table V (3).)

In the precipitation of lead molybdate by the dropwise addition of a soluble lead salt to the boiling solution of alkali molybdate, it was noted that the solution was very milky indeed until an excess of the precipitant was added when the solution cleared. Just as in the case of the silver chloride precipitation this "clearing" was evidence of the fact that the precipitation was almost, if not quite, complete. The reverse procedure was tried, adding ammonium molybdate dropwise to a boiling solution of lead nitrate. Under these conditions the solution did not become milky until after the addition of a slight excess of ammonium molybdate, when it became decidedly so and the precipitate did not settle after boiling. This observation lead to other experiments.

A boiling solution containing 0.9 gram of lead nitrate was precipitated with a slight excess (0.5 gram) of a boiling solution of ammonium molybdate. The total volume of solution was 250 cc. The precipitate of lead molybdate settled but the supernatant liquid remained cloudy and ran through the filter even after standing 2 hours. The experiment was repeated adding 0.2 gram of nitric acid to the lead nitrate solution before precipitating with the molybdate. The solution could be filtered immediately. Solutions of 0.9 gram of lead nitrate were precipitated with 0.6 gram of ammonium molybdate with and without the previous addition of 0.2 gram of nitric acid. The solution to which the acid was added could be filtered readily after standing a few minutes. The solution to which no nitric acid was added remained milky and could not be filtered after standing for months.

In conformity with observations recorded at the beginning of this paper these experiments show that lead molybdate in the presence of an excess of a soluble molybdate adsorbs the ions of that salt; but it adsorbs one ion more strongly than it does the other. This preferential adsorption results in the peptization of the adsorbing salt and the consequent formation of a colloidal solution.[1] The suspended particles of the salt are charged either positively or negatively depending on which ion is adsorbed preferentially and consequently will move either to the anode or the cathode under electrical

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[1] Cf. Bancroft: Jour. Phys. Chem., 20, 85 (1916).

stress. Experiment showed that the colloidal particles moved to the anode and consequently had adsorbed the molybdate ion more strongly. This was to be expected inasmuch as it is a pretty general rule that insoluble electrolytes show a marked adsorption for their own ions. Lottermoser[1] found that silver chloride was peptized by the preferential adsorption of either silver ions or chlorine ions depending on which ion was in excess. Bancroft[2] has called attention to numerous cases of this kind.

Lead molybdate in the presence of a slight excess of molybdate ion is peptized with the formation of a colloidal solution; but this is not the case in the presence of a slight excess of lead ion. Experiments were next tried in which the lead ion was in great excess. Equivalent samples of lead acetate and lead nitrate sufficient to precipitate 0.5 gram of lead molybdate were dissolved in 100 cc of water in separate beakers. The solutions were heated to boiling and the same quantity of ammonium molybdate solution added to each, an amount sufficient to precipitate only about $^1/_3$ of the lead ions. The lead salt precipitated from the acetate solution was decidedly flocculent and of a blue-white color that reminded one of the more gelatinous aluminum hydroxide; from the nitrate solution it was of a yellowish white color before mentioned and was not more than $^1/_3$ as bulky as that from the acetate solution. Both solutions could be filtered at once as the supernatant liquid was clear.

Experiments were tried on the precipitation of colloidal lead molybdate. Solutions containing 0.502 and 0.450 gram of lead acetate and lead nitrate, respectively, were precipitated with 0.3 gram of ammonium molybdate. The total volume was 250 cc. The colloidal solutions formed contained the same quantity of lead molybdate but it was noted that the color was different in the two cases: The precipitate from the acetate solution was blue-white and that from the nitrate solution was yellow-white. It seems probable from

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[1] Jour. prakt. Chem., (2) 72, 39 (1905).

[2] Jour. Phys. Chem., 20, 97 (1916).

what has already been said, that the colloidal particles of lead molybdate precipitated from acetate solution were the smaller which gave rise to the slight difference in color. When 50 cc of the hot colloidal solution obtained with lead nitrate were treated with 2 drops of concentrated nitric acid, the particles coagulated immediately and settled to the bottom in a compact mass. This was due to strong adsorption of hydrogen ion, which neutralized the charge on the particles and they precipitated. Slightly more nitric acid was needed to coagulate immediately the same quantity of colloidal lead molybdate prepared with lead acetate. The addition of ammonium nitrate resulted in precipitation but ammonium ions are adsorbed much less strongly than hydrogen ions, so that a greater concentration of the former must be added in order to effect precipitation. When the colloidal solution obtained with lead acetate was precipitated with ammonium acetate the precipitate was more flocculent and bulky than when nitric acid was used. Acetic acid caused little agglutination (except after long standing), either in low or fairly high concentration, because it gives a relatively low concentration of hydrogen ion. Ammonium molybdate in *large* excess caused precipitation of the colloid. The large concentration of ammonium ion under these conditions neutralized the ions adsorbed preferentially.

A survey of this series of experiments shows that colloidal lead molybdate is obtained in the finest particles in the absence of hydrogen ion and that hydrogen ion is strongly adsorbed and hence precipitates colloidal lead molybdate in relatively low concentration. This raises the question whether the effect of hydrogen ion in neutralizing the peptizing action of the strongly adsorbed molybdate ion may not be the important factor in securing a more granular, less bulky precipitate of lead molybdate. If this is the important thing then the presence of an excess of the less strongly adsorbed ammonium ions should produce the same effect. As a matter of fact the same effect is produced when ammonium acetate is added, in excess, to the ammonium molybdate solution before precipitation, but the same effect is not produced by a like concentration of ammonium ions from ammonium nitrate, which has no solvent action on lead molybdate. However, the presence of ammonium ion in excess has a very slight effect even in this latter case. From this I conclude that the presence of a readily adsorbed cation may have a slight effect on the character of the lead molybdate precipitate but that the solvent action of substances in solution is the more important thing.

A colloidal solution of lead molybdate negatively charged can be precipitated by the addition of an electrolyte with a readily adsorbed cation. If the precipitating agent can be washed out the salt should again go into colloidal solution. The possibility of peptizing lead molybdate by washing out the precipitating agent was tested in the following way: Lead molybdate was prepared as previously described and the first washings tested for molybdenum by zinc and hydrochloric acid in the presence of ammonium thiocyanate. Negative results were obtained. Later washings, however, gave a slight test for molybdenum showing that the salt was going into colloidal solution. The test was repeated after the addition of ammonium nitrate to the wash water and under these conditions no molybdenum was found in the filtrate.

The above investigation has furnished data for working out the details of the lead molybdate method of estimating molybdenum whereby uniformly good results can be secured with the least difficulty and in the shortest time. The details of the procedure are as follows: The sample of soluble molybdate which should contain preferably about 0.4 gram of molybdenum as MoO_3 is dissolved in 180 cc of water in a 350 cc beaker. In case the molybdenum compound is the trioxide and this has been dissolved in ammonia, the solution is made neutral or slightly acid with nitric acid. No acid is added to neutral ammonium molybdate solution. To solutions of other alkali molybdates is added previous to precipitation, concentrated nitric acid in about the proportion of 8 drops for each 0.4 gram of MoO_3 present, as nearly as this can be conveniently estimated. The solution is heated to boiling and is kept almost at the boiling point over a small flame during the addition of the precipitant. For the latter is employed approximately a 4 percent solution of lead nitrate, which is added from a burette drop by drop with constant stirring. The constant stirring prevents bumping and is an aid in getting the precipitate in a good physical condition. With the addition of a slight excess of the precipitant the milky solution clears visibly. As soon as this is noted the solution is boiled for two or three minutes stirring all the while, after which the precipitate is allowed to settle. To the almost clear supernatant liquid is added another drop of precipitant and if this test shows precipitation is not complete a few drops more of the precipitant are added and the solution boiled a few minutes longer. In the interest of cutting down the time necessary for washing, it is inadvisable to add more than a slight excess of precipitant. The precipitate will settle in a compact granular condition. After precipitation is complete dilute ammonia solution is added *dropwise* from a *burette* until the solution is neutral or but faintly alkaline to litmus. It is then made acid with a few drops of acetic acid. By this procedure is removed the slight solvent action of the small amount of nitric acid added before precipitation in the interest of a more granular, less bulky precipitate. After allowing to stand for a few minutes the supernatant liquid is decanted off through an ashless filter. The precipitate is washed with a hot 2 to 3 percent solution of ammonium nitrate. Three or four washings are carried out by decantation using about 75 cc of wash water each time; the precipitate is then washed into the funnel. After this procedure the filtrate will ordinarily show but a faint test for lead with H_2S. Washing is continued on the filter if necessary until the filtrate gives no test for lead. The funnel with contents are then placed in a drying oven and dried above 100°. The precipitate can be removed readily from the paper so that the latter is best ignited separately in a porcelain crucible, after which the bulk of the precipitate is added and ignition completed at a dull red heat. $PbMoO_4 \times 0.2615 = Mo$.

The above procedure results in many decided advantages over the method described by Chatard. The precipitate obtained is more compact and granular, filtration is faster, washing is more rapid and thorough and contamination by adsorption is eliminated to a large extent. The method has been tried out carefully as above described using different molybdenum salts. Kahlbaum's chemicals were used throughout in the tests. The molybdic acid was dried and an attempt made to purify it entirely from traces of blue oxide by heating in a stream of oxygen. The sodium molybdate was prepared by thoroughly drying molybdic oxide and sodium carbonate, weighing out equivalent samples, thoroughly mixing and fusing them in a platinum dish. The sodium molybdate so formed was taken up with water and the salt recrystallized three times. A weighed amount of the dried sample was in each case dissolved, diluted with water to a liter and an aliquot part taken for analysis. The results of a series of analyses are given in Table VI.

TABLE VI

Salt analyzed	Quantity of salt analyzed	Quantity of $PbMoO_4$ formed	Percent Mo found	Percent Mo calculated
Na_2MoO_4	0.4075	0.7285	46.74	46.60
Na_2MoO_4	0.4657	0.8300	46.60	
Na_2MoO_4	0.4657	0.8290	46.55	
Na_2MoO_4	0.5822	1.0376	46.61	
Na_2MoO_4	0.5822	1.0359	46.53	
Na_2MoO_4	0.4376	0.7785	46.53	
MoO_3	0.4033	1.0273	66.61	66.67
MoO_3	0.4033	1.0284	66.68	
MoO_3	0.4033	1.0286	66.69	
MoO_3	0.4033	1.0257	66.51	

The reverse of the above procedure may also be carried out; that is, lead may be quantitatively precipitated by ammonium molybdate in slight excess and conveniently ignited and weighed as lead molybdate. The chief difficulty in the way heretofore was that lead molybdate is peptized by preferential adsorption of molybdate ion and is carried into colloidal solution. This may be prevented by the addition of a small amount of a substance with a cation that is readily adsorbed by lead molybdate. The addition of a small amount of nitric acid serves this purpose as well as promotes the precipitation of the salt in a good physical condition. The procedure is as follows: The solution of soluble lead salt containing preferably about 0.5 gram of lead is made up to about 200 cc and for this amount of lead approximately 8 drops of conc. nitric acid is added. The solution is heated to boiling and is kept near the boiling point during the addition of the precipitant. For the latter is used a 2.0 to 2.5 percent solution of ammonium molybdate. This should be added from a burette slowly and with constant stirring. Whether or not precipitation is complete may be told by boiling the solution for a minute, letting the granular precipitate subside and adding a drop of precipitant to the supernatant liquid. Too great an excess should be avoided both because the washing process is thereby lengthened and because too much tends to peptize the lead salt. After test shows that precipitation is complete the nitric acid added is just neutralized by ammonia and the solution made just acid with acetic acid as before described. Washing with hot ammonium nitrate solution is continued until the addition of lead acetate to the filtrate produces no clouding. The ignition is carried out in the same manner as above given. $PbMoO_4 \times 0.56415 = Pb$.

The procedure was tested out with pure carefully dried samples of lead chloride. The results are recorded in Table VII.

TABLE VII

Salt used	Wt. of sample	Wt. of $PbMoO_4$	Percent lead	Calculated Percent
$PbCl_2$	0.6	0.7918	74.50	74.49
$PbCl_2$	0.6	0.7929	74.55	
$PbCl_2$	0.6	0.7933	74.60	

This method of estimating lead has three very important advantages that no other one of the ordinary gravimetric methods for this element possesses:

1. Lead molybdate is so insoluble in water that there is no danger of loss in this way providing dilute ammonium nitrate solution is used for wash water. Lead carbonate, sulphate and chloride are slightly soluble.

2. Lead nitrate may be ignited without taking particular precaution to avoid loss by decomposition. This is not the case with lead sulphide and lead chromate.

3. The factor for lead in lead molybdate is lower than it is in lead oxide, sulphide, sulphate, chromate or chloride.

The results of this paper may be summarized as follows:

1. Lead molybdate precipitated from ammonium molybdate solution by a solution of lead acetate (or any lead salt of a weak acid), is finely divided, flocculent and bulky and is blue-white in color. A precipitate of similar character is obtained by mixing solutions of sodium molybdate and any soluble salt.

2. Lead molybdate precipitated from ammonium molybdate solution by a solution of lead nitrate (or any lead salt of a strong acid), is more granular and much less bulky than when precipitated with lead acetate. The color is yellowish white. A precipitate of similar character is obtained by the addition of a very small amount of nitric acid or an excess of sodium or ammonium acetate to the solution of either sodium or ammonium molybdate before precipitating with a solution of any soluble lead salt.

3. Freshly precipitated lead molybdate is fairly soluble in nitric acid and other strong acids and is slightly soluble in ammonium acetate and sodium acetate. It is insoluble in acetic acid.

4. The solvent effect of the small amount of strong acid formed in the process of the reaction between ammonium molybdate and a lead salt of a strong acid is largely responsible for the more granular character of the precipitated salt in this case. In the other cases, the addition of a very small

amount of strong acid or an excess of sodium acetate or ammonium acetate has a similar effect.

5. When heated to about 200° ammonium molybdate darkens, due to the formation of a blue oxide.

6. Lead molybdate adsorbs ammonium molybdate from the solution in which it is precipitated. In the case of the bulky precipitate obtained with lead acetate as precipitant, the extent of this adsorption is sufficient to cause a darkening of the precipitated salt when gently ignited.

7. In the presence of an excess of ammonium molybdate, lead molybdate is carried into colloidal solution. Peptization is caused by preferential adsorption of the molybdate ion.

8. A small amount of nitric acid suffices to precipitate lead molybdate peptized by molybdate ion. This is due to neutralization of the negative charges on the particles by hydrogen ions which are more strongly adsorbed than most cations and hence effect precipitation in relatively low concentration.

9. In the presence of a small amount of nitric acid lead may be precipitated almost quantitatively from its soluble salts by molybdate ions in slight excess. The presence of nitric acid promotes the precipitation of lead molybdate in a good physical condition from the analyst's standpoint as well as prevents peptization of the salt by the small excess of molybdate ion. The precipitation can be made completely quantitative by subsequent neutralization of the acid added.

10. Lead molybdate may be washed into colloidal solution in the absence of an electrolyte in the wash water.

11. The Chatard method for the estimation of molybdenum has been modified and detailed directions given.

12. A method for the estimation of lead as lead molybdate has been described.

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NEUTRAL SALT ACTION ON ACID SOLUBILITIES[1]

BY WILLIAM NOLAND HENDERSON AND HUGH STOTT TAYLOR

Introduction

A considerable correspondence may be shown to exist between the development of chemical theory and the change of ideas with regard to the nature of acids. Lemery's idea of sharply pointed particles capable of tearing asunder other particles of matter gave to alchemical thought a mechanical picture of the solvent power which acids exert. It contrasts sharply with the older concept of affinity between substances, a concept which originally postulated similarity of chemical origin, though later it became recognized that dissimilar substances display a greater tendency to combine. The important change of attitude toward chemical investigation at the close of the eighteenth century is associated with acids in the formulation by Lavoisier of the oxygen theory of acids. The researches of Davy and Gay-Lussac developed the hydrogen theory of acids which Liebig made definite in his dualistic theory. The theory of Grotthus, the experimental investigations of Hittorf on conductivity and the theories of Clausius paved the way for the ionic conception of acids put forward by Arrhenius in 1884.

In the development and establishment of the ionic theory reactions involving acids played an important rôle. The theory of Arrhenius that acids were substances which yielded hydrogen ions when in solution accounted immediately for the earlier thermochemical results obtained by Thomsen in his studies of the heats of neutralization of acids by bases and the distribution of a base between two acids of varying strengths, the relative strength of an acid finding a new interpretation as the relative concentration of hydrogen ions which it yielded in a given solvent. Further, the degree of ionization as cal-

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[1] Communication from the Laboratory of Physical Chemistry, Princeton University.

culated from the measurements of electrical conductivity was shown to be a measure of the acid strength in a variety of other reactions, notably the inversion of cane sugar and the hydrolysis of esters. To these reactions the researches of Ostwald added also the power of an acid to dissolve certain salts relatively insoluble in water, as for example calcium and zinc oxalates, zinc sulphides, etc., and also its power to decompose acid amides to their corresponding acid and ammonium salt of the acid used as hydrolytic agent.

In the ensuing studies—prompted by the interpretation of acid reactions in terms of the dissociation theory—the abnormal influence of neutral salts was noted. This varied with the strength of the acid employed. Thus, the addition of sodium acetate to acetic acid reduced the capacity of the acid to hydrolyze esters or invert cane sugar. A mixture of acetic acid and sodium acetate each present in a concentration of 0.25 normal possessed only 1/75th of the capacity to invert cane sugar which a 0.25 normal solution of acetic acid alone possessed. This fact was shown by Arrhenius to be in accord with the demands of the theory of mass action applied to the equilibrium of ions in a given solution, since, according to the law of mass action, it could be calculated that the concentration of hydrogen ions in a mixture of acetic acid and sodium acetate of the above concentrations was also just the same fraction of the concentration in acetic acid alone as would be required to account for the phenomenon described, *viz.*, 1/75th.

With strong acids, however, the observed facts were not so easily reconcilable with the theoretical conclusions. There was an absence of strict proportionality between catalytic activity and hydrogen ion concentration. It was also found, for example, that addition of sodium chloride to a solution of hydrochloric acid increased the catalytic activity of the acid toward sugar inversion and ester hydrolysis although from the mass-action standpoint the concentration of hydrogen ions was diminished. This abnormal behavior of salts of strong acids was termed neutral salt action. Considerable research has been undertaken to elucidate its nature and explain the cause of the deviation from the normal behavior.

In his researches on the solubility of certain salts in hydrochloric and nitric acids Ostwald[1] showed that neutral salts like sodium and potassium chlorides and nitrates also possessed the power to increase the solubility of certain salts in the respective acids. He demonstrated a certain amount of parallelism between the phenomena studied and those of the catalytic activity of strong acids. The experimental results suggested a variety of conclusions none of which were exactly satisfactory, however. For example, it could be assumed that the added salt strengthened the acid, and therefore its solvent power by taking up water from the solution. When it was attempted to apply this quantitatively, however, no mathematical formulation of the hydration of the salt could be obtained. It was shown further that, quantitatively, consideration could not be given to an assumption that the oxalic acid produced liberated, for example, nitric acid from the nitrate, the liberated acid then playing its part in dissolving more calcium oxalate. The suggestion that the insoluble substance possessed varying stabilities toward the solvent acid seemed to Ostwald a plausible hypothesis to account for the increase of solubility. According to the stability the salt would be dissolved in different quantities by the acid, and every cause that would change the stability would automatically change the solubility. One such cause seemed to be the presence of neutral salts. The known possibility of double decomposition by mass-action effect in a solution containing two salts whereby a relatively insoluble salt and a soluble salt might interact to form two soluble salts, as, for example, the formation of potassium oxalate and calcium nitrate from calcium oxalate and potassium nitrate, tended to support this idea of varying stability. This hypothesis had its parallel in that put forward by Arrhenius to account for the accelerating influence of neutral

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[1] Jour. prakt. Chem., (2) 19, 468 (1879); 22, 251 (1880).

salts in catalytic acid reactions, namely, that all the molecules of the substrate (sugar or ester) were not in a reactive condition, that in the solution an equilibrium existed between active and inactive molecules which equilibrium was shifted to the side of increased concentration of active molecules by addition of neutral salts. Such suggestions are, however, at best merely mental pictures which facilitate comprehension. They attribute to the operation of physical forces—stability and reactivity—what in reality may be normal, if unknown, chemical phenomena.

Since the researches of Ostwald the problem of solution of salts in acid solutions and in mixtures of acids and neutral salts has been neglected in favor of the corresponding phenomena in catalytic reactions. In this study considerable work has been done and many theories have gained prominence. Thus Arrhenius and Lunden[1] have shown that the phenomena could be mathematically formulated in terms of specific accelerating activities of the several ions, though the nature of the accelerating influence remained unformulated. Armstrong[2] and his co-workers have attempted to interpret the facts by what may for the sake of brevity be termed a hydrate theory in which it is assumed that salts can not fail to act as dehydrating agents both by directly withdrawing water from the solution and by altering the state of the solvent water. With such assumptions apparent hydration values have been obtained in various reactions. From the quantitative standpoint it seems just criticism to say that the suggested explanation does not carry conviction since high hydration values are assigned to salts which in the solid state seem to possess little affinity for water, while salts with considerable hydrate-water in the solid state do not cause abnormally high accelerating influence on the catalytic action.

Recently, considerable attention has been directed to the possibility that the accelerating influence of neutral salts of strong acids as well as the variation from strict pro-

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[1] Zeit. phys. Chem., 49, 189 (1904).

[2] Proc. Roy. Soc., 87A, 600 (1912).

portionality between activity and hydrogen-ion concentration in a series of varying strengths of a strong acid might find its explanation in a possible activity of the undissociated acid molecules. The possibility of the activity of molecules as well as ions has never been rigidly excluded from the ionic theory by its best exponents. Indeed references are frequent, both in the earlier literature and in more modern work, which definitely admit such possibility and adduce facts which could readily be reconciled to a theory of undissociated molecule activity. This idea has gained momentum recently, and researches[1] of Lapworth, Senter, Goldschmidt, Bredig, Acree, Snethlage, Taylor, Dawson and Powis, Dawson and Reiman, and McBain and Coleman, have indicated that the idea has found considerable favor. The researches of Taylor, of Dawson and Powis, of Dawson and Reiman, of Ramstedt, and of McBain and Coleman have shown that the facts of acid catalysis and of neutral salt action in aqueous solutions are capable of interpretation on a dualistic theory of acid catalysis whereby a specific activity is attributed to both hydrogen ion and undissociated molecule. Further, with such an assumption it has been shown that with a given reaction a constant and definite activity for the hydrogen ion is obtained with all acids, that for the undissociated molecule, however, the activity varies from acid to acid, is greatest with the strong acids and is negligibly small with acids of weak dissociating power. In the case of the strongest acids it is suggested that the activity of the molecule is greater than that of the hydrogen ion, hence arising the increased activity when neutral salts are added. For, these repress the hydrogen-ion concentration and simultaneously increase the concentration of the undissociated molecule which is assumed more active.

The object of the present investigation was therefore to re-examine the old work of Ostwald on the solubilities of difficultly soluble salts in acids and in mixtures of acids

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[1] For references consult Jour. Am. Chem. Soc., 37, 551 (1915).

and neutral salts in the light of recent work on the activity of the undissociated molecule, to trace out if possible any parallelism. The observations of Ostwald were extended to acids other than the strong acids, hydrochloric and nitric, both of similar salt effect. It was hoped that an investigation of other acids and their salts might yield some points of support for one or the other of the hypotheses which have been put forward.

Experimental

The method employed in the present investigation consisted essentially in rotating the system—acid, solute, and neutral salt—in sealed bottles in a well regulated thermostat until equilibrium had been established. Tests were made from time to time to insure that the equilibrium point had been reached. Half normal acid was found to be the most convenient strength for the purpose required. These acid solutions were originally of normal concentration in order to allow for the addition of the neutral salt solution and water sufficient to reduce the normality to one-half. Carefully prepared baryta of known strength was used in standardizing the acids.

The neutral salt solutions were made twice normal, from materials of the highest grade procurable, by weighing carefully the potassium salts and making up to the above normality with water. In the cases of potassium mono- and trichloroacetates the salt solutions were made up as follows: A four times normal solution of the acid was carefully prepared and neutralized in a white porcelain dish with concentrated carbonate-free potassium hydroxide solution using phenolphthalein as indicator. Two hundred and fifty cubic centimeters of the four times normal acid were, after neutralization, made up to five hundred cubic centimeters, thereby giving the desired twice normal solution of the potassium salt.

The salts—calcium oxalate and tartrate—used for the solubility determinations were of high grade and quality.

A detailed account of the procedure employed in the present investigation may here be given. Choosing the system—calcium oxalate, hydrochloric acid, and potassium chloride: 100 cc of the normal hydrochloric acid were drawn out by means of a pipette calibrated to deliver this amount and placed in a calibrated 200 cc flask which was used for mixing each solution. Now if 0.1 *N* neutral salt was desired, 10 cc of the twice normal potassium chloride solution were added to the acid in the flask. The mixture was then made up to 200 cc with distilled water and, after mixing thoroughly, was poured into a 250 cc reagent bottle which was fitted with a ground glass stopper. These reagent bottles were found to be very suitable as rotating flasks. A small and approximately constant quantity of calcium oxalate was then added, the bottle sealed with paraffine and rotated at 25° C, the temperature being kept constant to within 0.01 degree. The rotation was effected by attachment to spider wheel arrangements suitably fastened on a shaft placed in the thermostat at an angle of forty-five degrees, which shaft was itself driven by means of a worm wheel arrangement from the stirring gear of the thermostat. This rotation around an inclined shaft ensures a steady and efficient mixing of the several phases present in the flask. After the equilibrium point had been reached the bottles were removed from the rotator and suspended in the thermostat over night to allow the precipitate to settle, since the latter was light and did not settle readily. To prevent suspended particles from being drawn off with the liquid to be analyzed a piece of filter paper was placed over the end of a calibrated pipette and 150 cc of the clear solution were removed for analysis. Sufficient ammonium oxalate was added to insure complete precipitation of the calcium, and the latter was precipitated as the oxalate by neutralizing the hot acid solution with ammonium hydroxide. After standing over night the precipitated calcium oxalate was filtered, washed with dilute ammonia solution, ignited in a platinum crucible and weighed as the oxide.

The appended tables represent the most reliable data obtained with the several acids and their corresponding salts. All determinations which in any way seemed doubtful were carefully rechecked and, of the series communicated, several separate and distinct determinations were performed at each concentration of salt. The results obtained could readily be duplicated.

In the case of the weaker acids, in which the oxalate of calcium had too small a solubility to ensure accuracy of working and reproducibility of results, the more soluble tartrate was substituted. The general behavior towards solution in the acids and mixtures with salts was not expected to vary considerably though Tables IV and V indicate that the magnitude of the influence of the neutral salt varied.

The tables which follow represent a summary of the results obtained. Column I gives the normality of the salt in the half normal acid solution employed. The second column gives the weight in grams of CaO of the calcium oxalate or tartrate dissolved in 150 cc of the solution. In the last column the percentage change in solubility is given, the positive sign indicating increase, the negative sign a decrease. Originally the investigations were conducted to determine the variation in solubility produced by salt in increasing concentrations of 0.1 normal. The results with weak acids showed that special interest attached to the influence of very small concentrations of salt. Half normal acid was used in all cases and the tables refer to solubilities at 25 degrees Centigrade.

TABLE I—SYSTEM

Calcium Oxalate, Hydrochloric Acid and Potassium Chloride

Normality of neutral salt—KCl	Gram of CaO in 150 cc of sat. sol.	Percentage influence of neutral salt on solubility
0	0.1750	—
1/200	0.1756	+ 0.34%
1/100	0.1761	+ 0.63
1/50	0.1775	+ 1.43
1/20	0.1791	+ 2.34
1/10	0.1832	+ 4.69
2/10	0.1903	+ 8.74
3/10	0.1964	+12.23
5/10	0.2094	+19.66

TABLE II—SYSTEM
Calcium Oxalate, Hydrochloric Acid and Potassium Nitrate

Normality of neutral salt—KNO_3	Gram of CaO in 150 cc of sat. sol.	Percentage influence of neutral salt on solubility
0	0.1781	—
1/200	0.1796	+ 0.84%
1/100	0.1800	+ 1.06
1/50	0.1813	+ 1.80
1/25	0.1829	+ 2.70
1/10	0.1890	+ 6.12
2/10	0.1981	+11.23
3/10	0.2053	+15.27
4/10	0.2155	+21.00
5/10	0.2242	+25.90

TABLE III—SYSTEM
Calcium Oxalate, Trichloracetic Acid and Potassium Trichloracetate

Normality of neutral salt—CCl_3COOK	Gram of CaO in 150 cc of sat. sol.	Percentage influence of neutral salt on solubility
0	0.1330	—
1/200	0.1330	0%
1/100	0.1325	— 0.4
1/50	0.1330	0
1/20	0.1332	+ 0.1
1/10	0.1312	— 1.35
2/10	0.1314	— 1.20
3/10	0.1306	— 1.80
4/10	0.1289	— 3.08
6/10	0.1241	— 6.69
8/10	0.1179	—11.35

TABLE IV—SYSTEM
Calcium Oxalate, Monochloracetic Acid and Potassium-monochloracetate

Normality of neutral salt—$CH_2ClCOOK$	Gram of CaO in 150 cc of sat. sol.	Percentage influence of neutral salt on solubility
0	0.0154	—
1/200	0.0146	— 5.20%
1/100	0.0132	—14.29
1/50	0.0128	—16.88
1/25	0.0126	—18.18
13/200	0.0124	—19.48
2/10	0.0111	—27.92

TABLE V—SYSTEM

Calcium Tartrate, Monochloracetic Acid and Potassium Monochloracetate

Normality of neutral salt—$CH_2ClCOOK$	Gram of CaO in 150 cc of sat. sol.	Percentage influence of neutral salt on solubility
0	0.5543	—
1/100	0.5435	— 1.95%
1/50	0.5383	— 2.89
1/25	0.5216	— 5.90
1/10	0.4895	—11.69
3/20	0.4639	—16.31
2/10	0.4502	—18.78

TABLE VI—SYSTEM

Calcium Tartrate, Acetic Acid and Potassium Acetate

Normality of neutral salt—CH_3COOK	Gram of CaO in 150 cc of sat. sol.	Percentage influence of neutral salt on solubility
0	0.0755	—
1/200	0.0680	— 9.92%
1/100	0.0633	—16.16
1/50	0.0556	—26.36
1/20	0.0491	—34.97
1/10	0.0457	—39.47
3/10	0.0540	—28.48
5/10	0.0679	—10.07

TABLE VII—SYSTEM

Calcium Tartrate, Acetic Acid and Potassium Chloride

Normality of neutral salt—KCl	Gram of CaO in 150 cc of sat. sol.	Percentage influence of neutral salt on solubility
0	0.0710	—
1/200	0.0729	+ 2.68%
1/100	0.0739	+ 4.08
1/50	0.0781	+ 10.00
1/20	0.0840	+ 18.31
1/10	0.0921	+ 29.72
2/10	0.1068	+ 50.42
3/10	0.1306	+ 83.94
4/10	0.1612	+127.04

The following table shows the solubility of calcium oxalate in hydrochloric acid alone:

TABLE VIII—SYSTEM
Hydrochloric Acid and Calcium Oxalate

Normality of HCl	Gram of CaO in 150 cc of sat. sol.	Percentage influence of increasing the normality
0	0.0006	—
1/8	0.0471	—
2/8	0.0893	+ 89.60%
3/8	0.1327	+181.74
4/8	0.1734	+268.15
5/8	0.2181	+363.06
6/8	0.2578	+447.35
1	0.3424	+626.96

In the accompanying figure is plotted the influence of the neutral salt at different normalities, expressed in percentages of the slightly soluble salt dissolved by the acid in absence of neutral salt.

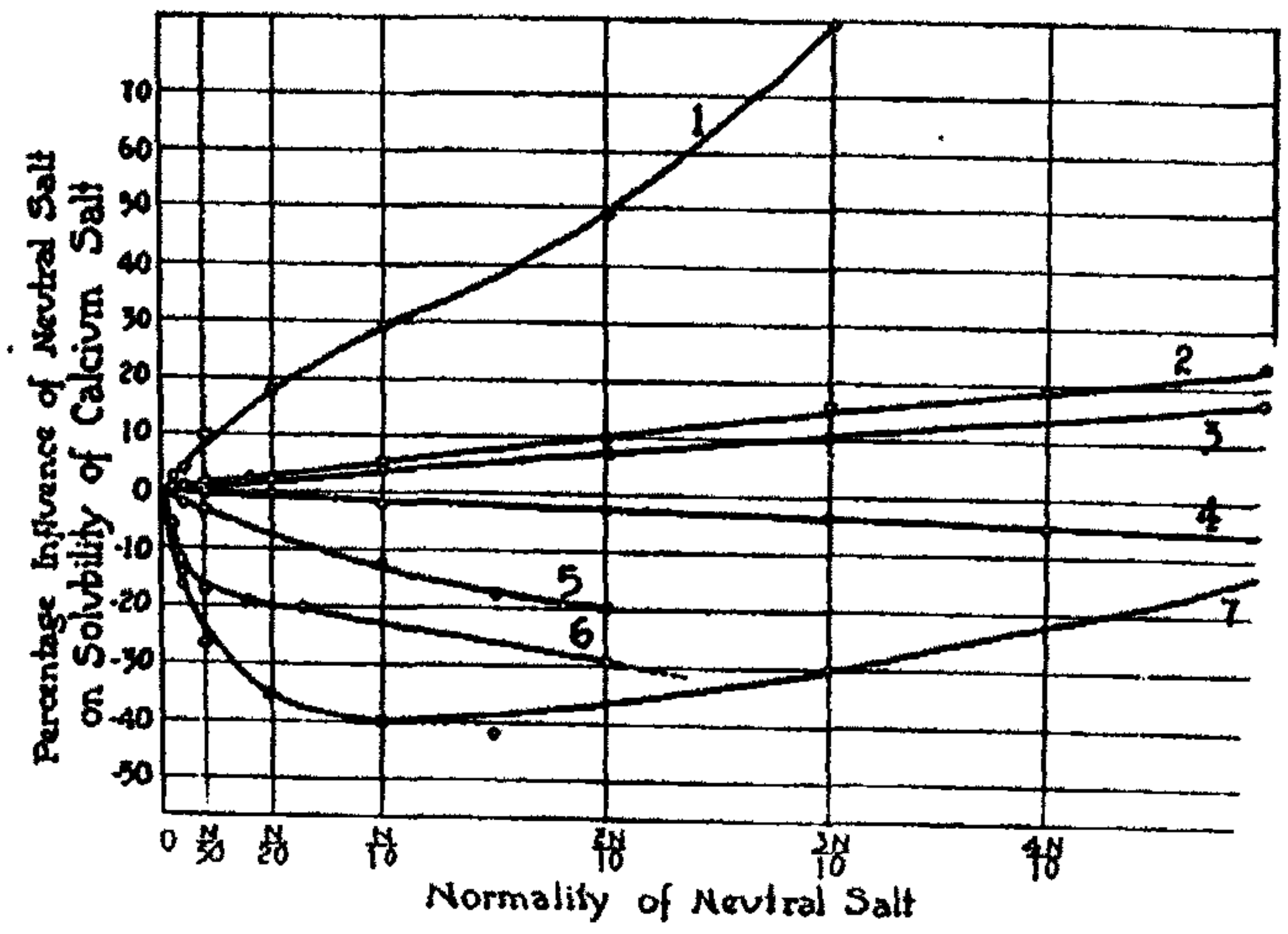

Fig. 1

1. CH_3CO_2H, KCl, Ca tartrate
2. HCl, KNO_3, CaC_2O_4
3. HCl, KCl, CaC_2O_4
4. CCl_3CO_2H, CCl_3CO_2K, CaC_2O_4
5. CH_2ClCO_2H, CH_2ClCO_2K, Ca tartrate
6. CH_2ClCO_2H, CH_2ClCO_2K, CaC_2O_4
7. CH_3CO_2H, CH_3CO_2K, Ca tartrate

Discussion of the Results

The results with the systems comprising acid, neutral salt with common ion and salt to be dissolved call for primary consideration. An examination of the figure or the tables from which the curves have been constructed will show a progressive variation in results as the acid changes from a strong acid like hydrochloric to the weakest acid employed, acetic acid. Addition of potassium chloride to the hydrochloric acid causes an increase of solubility of the calcium oxalate, which increase is greater the greater the concentration of salt. Trichloracetic acid is apparently little influenced in its capacity to dissolve the oxalate by addition of the corresponding potassium salt. Smaller concentrations of salt cause variations so small that they are masked by the experimental error and the results obtained at these concentrations show alternately trifling positive and negative influences. By increasing the concentration of salt considerably it is seen, however, that the effect of the salt is definitely negative on the power of the acid to cause solution so that a concentration of salt 0.8 normal causes a decrease in solubility of the oxalate to the extent of 11.35 percent of the solubility in the acid alone. With the next weaker acid, monochloracetic acid, the salt exercises considerable influence in inhibiting solubility so that already with a concentration of salt 1/5th normal the original solubility in acid alone has been diminished by 20 percent. It is in the case of this acid that the specific influence of the salt dissolved may be noted. The solubility of the oxalate is diminished 20 percent by 1/5th normal salt; that of the tartrate only 19 percent. The latter figure must be regarded as the more reliable index of the influence of addition of neutral salt. For, experimental error is considerable in the case of the solubility of the oxalate as the weights of lime determined only range from 0.0154 to 0.0111 gram and may therefore easily be subject to several percents of error. With acetic acid the influence of neutral salt is most pronounced. Salt of concentration 1/50th normal has already diminished the solubility by 25 percent and the diminution increases to a maximum somewhere in the neighborhood of 1/10th normal with a maximum depression of solubility of about 40 percent. Then increase of concentration of neutral salt brings about an increase in solubility again so that at a concentration of about 0.6 normal salt the acid has recovered its original capacity to dissolve the tartrate used in the determinations. Evidence for a similar minimum was obtained at higher concentrations of the monochloracetate but owing to some slight error in the normality of the acid or the salt the results obtained did not agree with those repeatedly verified at the lower concentrations of salt and so they have been neglected in the present communication. The significance of this minimum and of the subsequent increase will be discussed at a later stage.

The parallelism between the results recorded above and those of acid catalysis is striking. Taylor has shown that normal potassium chloride increases the reaction constant of the hydrolysis of ethyl acetate in 0.5 normal acid to the extent of 12 percent. In the present solubility determinations potassium chloride effects an increase, but greater in magnitude. Further, with trichloracetic acid Taylor has shown that addition of 1/4 normal salt to 1/4 normal acid effects a decrease in reaction constant equal to 8 percent. In the present work there is a decrease but not so considerable, *viz.*, about 1.5 percent in half normal acid. For comparison with the results using monochloracetic acid, the work of Dawson and Reiman may be used: addition of 0.2 normal salt to 0.1 normal acid effected a diminution of 66 percent. With half normal acid in the present case a diminution of 20 percent was obtained with the same concentration of salt. These results are not directly comparable since the influence of a given concentration of salt will necessarily be greater on a weaker concentration of acid, but they serve to show comparability between the phenomena now under discussion and those of acid catalysis. Finally, for acetic acid, comparison may be made with the results of Arrhenius on sugar inversion. Salt of 1/4 normal concentration practically suppresses the catalytic activity of quarter normal acetic acid; the actual diminution of the reaction constant is nearly 99 percent. In the present work a similar concentration of salt diminishes the solubility by about 40 percent.

The comparison between the results of the present investigation and those of acid catalysis may thus be generalized. The influence exerted by neutral salts on the solubility of calcium oxalate and tartrate in acids having an ion in common with the neutral salt is in the same general direction as that exerted by neutral salts in acid catalysis. In degree the influence differs. Where increase is effected in solubility this increase is greater than in acid catalysis. Where decrease is caused this decrease is less pronounced than the decrease produced in catalytic reactions.

If it be assumed that the same factors operate in both cases it is obvious from the above generalization that the assumptions necessary to account for the phenomena in acid catalysis would be inadequate for the interpretation of the solubility phenomena. For, it is plain that, superimposed on the assumed operating factors, there would be a further influence tending to increase the solubility of the calcium salts which gives rise to the greater increase and the lesser decrease of solubility than is found in increase or decrease of reaction constant in acid catalysis. This conclusion has been tested by applying to the solubility determinations the assumption of activity of the undissociated molecule. Taylor, and Dawson and his co-workers have shown that a dual theory of hydrogen ion and undissociated molecule activity is adequate for the interpretation of the results of acid catalysis. Test has shown, however, in the present case that no mathematically concordant results can be obtained by applying to them a similar method of calculation. The presence of the superimposed factor prevents this. This factor is not such as was noted by Kendall[1] in his work on the ionic solubility product in which distinction was drawn between two

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[1] Proc. Roy. Soc., 85A, 200 (1911).

influences—the one the ionic, the other a definite solvent effect of the components in each other. For the solubility of calcium oxalate in potassium chloride solutions is not measurably greater than in water, certainly not to the extent which would produce the variations recorded in this communication.

Nor does it seem that the results could be interpreted on the assumption of the influence of the added salt on the ionized products of the solution process. For if it be possible to explain, say, the increased solubility in hydrochloric acid in presence of potassium chloride it is difficult to see, without calling into play some other factor than influence on the end products, why in an almost equally strong acid like trichloroacetic acid a diminution in solubility occurs.

Consideration has been given to the influence which hydration of the added salt would have on the solubilities determined, whereby by withdrawing water from the solution increase of solubility would be obtained. To obtain an explanation of both increase and decrease observed with varying acids it is apparent that such a theory would have to be combined with the influence of the salt in repressing the hydrogen-ion concentration of the acid. This would lead to the conclusion that the hydrating action of potassium chloride was sufficiently great to counteract the repressive influence exerted on the hydrogen-ion concentration. With potassium acetate, on the other hand, concentrating influence would appear to be small compared with the initial depression of hydrogen ion. Only at higher concentrations of salt would this latter become small so that a change of sign of the solubility variation would become evident. This would explain the minimum in the curve. As suggested in the introduction, however, this hydration theory does not appear plausible when compared with the facts concerning these salts in hydrate formation in the solid state.

It will be seen, therefore, that the phenomena are complex and that as yet no completely satisfactory theory seems to be present to explain the observed relations. It is possible that the results obtained represent an integration of many of the influences which have been considered and possibly others.

The results bear some resemblance to those obtained in a study of the electromotive forces of hydrogen electrodes in mixtures of acids and neutral salts. A recent paper of Harned[1] has demonstrated that the influence of potassium chloride on the potentials of hydrogen in hydrochloric acid solutions seems to indicate that the concentration of the hydrogen ion is increased by addition of salt. This would mean that the law of mass action or in other words the theory of isohydric solutions, was not directly applicable to the case in question. On the other hand, the earlier work of Walpole[2] along the same lines with mixtures of acetic acid and sodium acetate indicates that in this case the law of mass action is obeyed within the limits of the error of the experiment. If some explanation were forthcoming as to why the hydrogen-ion concentration in hydrochloric acid is apparently increased by potassium chloride an explanation of the present phenomena might be made possible.

One experiment in the present series is explainable from the standpoint of the results of Harned. Reference to Table II will show that the influence of potassium nitrate on solubility in hydrochloric acid is of the same order of magnitude as that of potassium chloride. This is in accord with the result of Harned that sodium bromide had a similar influence on the electromotive force measurements to that of sodium chloride. As was shown also by Harned, this result is in full theoretical accord with the law of mass action as usually applied if the equilibrium constants of the several substances concerned in the equilibrium are equal. That this is substantially true a recent paper of Arrhenius[3] demonstrates.

Summary

A series of solubility determinations with hydrochloric,

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[1] Jour. Am. Chem. Soc., 37, 2460 (1915).

[2] Journ. Chem. Soc., 105, 2501 (1914).

[3] Medd. fr. K. Vet. Akad. Nobel Inst., Vol. 2, No. 42 (1913)

trichloracetic, monochloracetic, and acetic acids in presence of varying concentrations of their respective potassium salts has been made for calcium oxalate and calcium tartrate as substrate. From the experimental figures it has been shown that the influence of the neutral salt on solubility is a progressive function of the acid strength, causing greatest decrease for weakest acids and greatest increase for the strongest. The phenomena in question have been duly considered with regard to the several theories of mass action and intermediate product formation, hydration of salts, and activity of both hydrogen ion and undissociated molecule, yet no strict mathematical formulation has been obtained to elucidate the phenomena.

Neutral salts of uncommon ions have been shown to have effects similar to those possessing common ions under certain circumstances.

A NEW METHOD FOR THE STUDY OF SILVER PEROXYNITRATE

BY MORTIMER J. BROWN

When an aqueous solution of silver nitrate is electrolyzed between insoluble electrodes under certain conditions, a black compound of silver is formed at the anode. This compound was first described by Ritter in 1804, and many people since then have tried to establish its composition. Margrete Bose[1] and Baborovsky and Kuzma[2] have given literature references to the more important papers which are here repeated with additions.[3] Some of the formulas which have been suggested for this silver salt are as follows:

Ag_2O_2	Wallquist
$Ag_2O.Ag_2O_3$	Brauner and Kuzma (1907)
Ag_2O_3	Luther and Pokorny (1908)
Ag_3O_4	Baborovsky and Kuzma (1909)
$Ag_4O_6.AgNO_3$	Fischer
$2Ag_2O_2.AgNO_3.H_2O$	Fischer
$5Ag_2O_2.2AgNO_3.H_2O$	Mahla
$4Ag_2O_3.2AgNO_3.H_2O$	Berthelot (1881)
$Ag_2O_3.2AgNO_3$	Hampe (1890)
$3Ag_2O_2.O_2.AgNO_3$	Mulder and Heringa (1896)
$2Ag_3O_4.AgNO_3$	Tanatar (1901)
$3Ag_4O_5.2AgNO_3$	Sulc (1896)
$3Ag_2O_2.O_2.AgNO_3$	Sulc (1900)

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[1] Zeit. anorg. Chem., **44**, 262 (1907); cf. also Gmelin Kraut's Handbuch der anorg. Chem., **5**, II, 69 (1908).

[2] Zeit. phys. Chem., **67**, 48 (1909).

[3] Ritter: Gehlens neues Jour., **3**, 561 (1804); Wallquist: Jour. prakt. Chem., **31**, 179 (1842); Fischer: Ibid., **33**, 237 (1844); Grotthuss: Jahresber Chem., **1852**, 423; Mahla: Liebig's Ann., **82**, 289 (1852); Berthelot: Comptes rendus, **90**, 653 (1880); Hampe: Chem. Zeitung, **14**, 1777 (1890); Novák: Rozpravy Ceské Akad., **5**, No. 6 (1896); Sulc: Zeit. anorg. Chem., **12**, 89, 180 (1896); Mulder and Heringa: Rec. Trav. chim. Pays.-Bas., **15**, 1, 236 (1896); Mulder: Ibid., **16**, 57 (1897); **17**, 57 (1898); **18**, 91 (1899); **19**, 115, 165 (1900); **22**, 385, 405 (1903); Sulc: Zeit. anorg. Chem., **24**, 305 (1900); Tanatar: Ibid., **28**, 331 (1901); Kuzma: Rozpravy Ceské Akad., **19**, No. 11 (1905); Watson: Jour. Chem. Soc., **89**, 578 (1906); M. Bose: Zeit. anorg. Chem., **44**, 237 (1907); Wilkinson and Gillett: Jour. Phys. Chem., **11**, 382 (1907); Brauner and Kuzma: Ber. deutsch. chem. Ges., **40**, 3371 (1907); Luther and Pokorny: Zeit. anorg. Chem., **57**, 290 (1908); Baborovsky and Kuzma: Zeit. phys. Chem., **67**, 48 (1909); M. Bose: Ibid., **68**, 383 (1909); Barbieri: Gazz. chim. ital., **42**, II, 7 (1912).

Margrete Bose[1] determined the decomposition point for silver nitrate solution and silver sulphate solution. Only one break was found in each solution and consequently she concludes that only one compound is formed at the anode in each case. A platinum wire anode was used and the other pole was a $N/10$ KCl calomel electrode, the potential difference of which was called 0.33 volt against the hydrogen electrode taken as zero. The anode decomposition voltage for silver nitrate solution was found to be 1.573 volts and that for silver sulphate solution 1.53 volts. Although the decomposition voltage is higher in the more concentrated nitrate solution, the author considers that these two values are the same and that the difference is due to a difference in potential between the two solutions. On that basis the conclusion is drawn that the precipitate is the same from the two solutions and consequently cannot contain either silver nitrate or silver sulphate.[2]

"The precipitated silver oxide is unquestionably the same in the two cases. Regardless of the solution the oxide precipitates in exactly the same form as beautiful, sepia-colored crystals with metallic luster. There seems no reason for assuming that we are dealing with two different substances, such as compounds of a silver oxide with silver nitrate or silver sulphate. When one remembers how many chemically prepared compounds can only be washed free from adhering mother liquor with great difficulty, and how often crystals contain enclosed mother liquor, it is not surprising that these crystals, formed by electrolysis and precipitated very rapidly, should contain some of the solution in which they grew."

The difference between 1.573 volts and 1.53 volts is nothing like as large as the changes in the decomposition voltage of silver nitrate solutions with varying concentration and varying amounts of nitric acid,[3] which may be taken as an argument in favor of or against the assumption that the same compound is precipitated from silver nitrate and silver

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[1] Zeit. anorg. Chem., 44, 237 (1907).

[2] M. Bose: Ibid., 44, 263 (1907).

[3] Wilkinson and Gillett: Jour. Phys. Chem., 11, 382 (1907).

sulphate solutions. Margrete Bose[1] made no analyses because she considered it impossible to get accurate results.

Luther and Pokorny[2] determined the voltage-current curve for a silver anode in caustic soda solution. They obtained one break corresponding to Ag_2O and one corresponding to Ag_2O_2. Silver is oxidized quantitatively to silver oxide and then quantitatively to silver peroxide. The peroxide is reduced quantitatively to oxide and then to metal. The following equilibrium potentials were observed:

$$\mathrm{Pt(H_2)} \mid N.\mathrm{NaOH} \mid N.\mathrm{NaOH},\ \mathrm{Ag_2O} \mid \mathrm{Ag} = 1.170\ \mathrm{V}$$
$$\mathrm{Pt(H_2)}N.\mathrm{NaOH} \mid N.\mathrm{NaOH,Ag_2O_2,Ag_2O} \mid \mathrm{Pt} = 1.40\ \mathrm{V}$$

from which follows[3]

$$\mathrm{Pt(H_2)} \mid N.\mathrm{NaOH} \mid N.\mathrm{NaOH,Ag_2O_2} \mid \mathrm{Ag} = 1.285\ \mathrm{V}$$
$$\mathrm{Ag} \mid \mathrm{Ag_2O},N.\mathrm{NaOH} \mid N.\mathrm{NaOH,Ag_2O,Ag_2O_2} \mid \mathrm{Pt} = 0.23\ \mathrm{V}$$

It was shown that these values were practically independent of the concentration of the hydroxyl ions, as required by theory.

Luther and Pokorny then prepared Mulder's so-called peroxynitrates and peroxysulphates, washed them repeatedly with water and caustic soda[4] and reduced them at constant current in normal caustic soda. Three definite potentials were observed against hydrogen in normal caustic soda, one at 1.57 volts, a second at 1.41 volts, and a third at 1.17 volts. The second and third evidently correspond to the Ag_2O_2, Ag_2O and Ag_2O, Ag stages respectively. The value of 1.57 volts must correspond to a higher oxide, to which Luther and Pokorny assign tentatively the formula Ag_2O_3. Since the same curves were obtained with Mulder's so-called peroxynitrate and peroxysulphate, the authors conclude, as M. Bose had done, that neither silver sulphate nor silver nitrate is an integral part of the compound, which is therefore an impure oxide of silver.

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[1] Zeit. phys. Chem., 68, 383 (1909).

[2] Zeit. anorg. Chem., 57, 290 (1908).

[3] Calculated according to Luther and Wilson: Zeit. phys. Chem., 34, 488 (1900).

[4] [This would decompose them to some extent.—M. J. B.]

In flat contradiction with this are the conclusions of Sulc[1] and of Watson.[2] Sulc says: "I believe that I have shown that the crystalline substance formed at the anode, when aqueous silver nitrate solutions are electrolyzed between platinum electrodes, has a composition corresponding to the formula Ag_7NO_{11} and that it loses five atoms of oxygen gradually when heated, leaving behind a complex, Ag_7NO_6, which is to be considered as $3Ag_2O.AgNO_3$. Three out of the five atoms of oxygen are to be considered as different from the other two, because only these three take part in the reaction with ammonia and probably with oxalic acid (unfinished experiments). It is probably these three atoms of oxygen which give the substance the properties of a peroxide, as shown in its energetic oxidizing action.[3] These properties can be represented provisionally by the formula $AgNO_3.3Ag_2O_2.2O$".

Marshall[4] says: "I have varied the conditions of electrolysis of silver nitrate by altering the current-concentration and density and also the strength of solution, and have found the product to be the same in all cases and identical with the compound described by Sulc. This disposes of the possibility of this definitely crystallized product being a mixture. Sulc has satisfactorily investigated the effect of heat on this peroxynitrate. I have not been able to confirm Sulc's analytical data for the reaction of the peroxynitrate with ammonia.

"I have examined the decomposition of the peroxynitrate by water. Even at the ordinary temperature of the laboratory (27°–32°), reaction occurs slowly with the evolution of oxygen. This change occurs more readily on boiling, and is complete in less than an hour. Oxygen is evolved, part of the silver goes into solution, and there remains a black substance

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[1] Zeit. anorg. Chem., **24**, 312 (1900).

[2] Jour. Chem. Soc., **89**, 578 (1906).

[3] The "silver peroxide" inflames dry hydrogen gas at ordinary temperature just as other metallic peroxides do, lead peroxide (Vanino and Hausner: Ber. deutsch. chem. Ges., **33**, 625 (1900)) or thallium peroxide (Carstanjen: Jour. prakt. Chem., **102**, 77 (1867)) for instance.

[4] Jour. Chem. Soc., **89**, 579 (1906).

which I have found to be silver dioxide, Ag_2O_2, probably obtained pure for the first time. The course of the reaction is represented by the equation,

$$Ag_7NO_{11} = AgNO_3 + 3Ag_2O_2 + O_2.$$

"I have determined quantitatively the correctness of this expression for the decomposition of the peroxynitrate by boiling, and also the composition of the insoluble substance as being that of silver dioxide. It is a grayish black powder of sp. gr. 7.44, approximately, which may be heated to 100° without change. At a higher temperature, it evolves oxygen and leaves a residue of silver.

"The behavior of the dioxide with ammonia is remarkable; it dissolves with the evolution of nitrogen, but in the amount required by the equation:

$$6Ag_2O_2 + 2NH_3 = N_2 + 3H_2O + 3Ag_4O_3$$

and not, as would have been expected, in accordance with the equation:

$$3Ag_2O_2 + 2NH_3 = N_2 + 3H_2O + 3Ag_2O$$

"Both the peroxynitrate and the dioxide of silver, also the peroxysulphate produced by the electrolysis of aqueous silver sulphate solution, dissolve in cold strong nitric acid with the production of an intensely brown solution, and in cold strong sulphuric acid with an olive-green color. These colors are due to the formation of silver peroxy-salts. It can hardly be doubted that the same colored salt is formed from the peroxynitrate as from the dioxide, because the colors and absorption spectra of the solutions obtained from the three substances are identical. These colored salts gradually decompose at the ordinary temperature, and more quickly on heating or on adding water, silver sulphate or nitrate remaining in solution. Up to the present, attempts to isolate these peroxy-salts have been unsuccessful. During the decomposition of these solutions, some evolution occurs of what appears to be oxygen, but no hydrogen peroxide is formed."

Working in pyridine solution Barbieri[1] has prepared silver

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[1] Gazz. chim. ital., 42 II, 7 (1912).

persulphate with pyridine of crystallization, $Ag_2S_2O_8.4Pyr$; but this really has no bearing on our problem because Luther and Pokorny have proved that silver peroxide, Ag_2O_2, can exist and that it is not identical with the so-called peroxynitrate.

Since the composition of the so-called silver peroxynitrate has not been determined with a satisfactory degree of accuracy, it seemed desirable to make another attempt to get a satisfactory analysis of the compound. This investigation was undertaken at Prof. Bancroft's suggestion and was carried out under his direction. The experimental work was suddenly and reluctantly abandoned in 1911 and is published at this time because there is no hope that the author will be able to take it up again.

When silver nitrate solution is electrolyzed between insoluble electrodes, silver is deposited at the cathode and silver peroxynitrate at the anode, there being presumably a simultaneous formation of nitric acid at the anode. Both solid deposits are crystalline, and they grow rapidly one toward the other in arborescent crystals. Because of this fact, there is no doubt that the anode product is a good electrical conductor. However, almost as soon as the electrolysis begins, the black crystals break away from the anode, are attacked by the nitric acid in solution and they eventually go entirely into solution with liberation of gas.

After studying this electrolysis carefully and at considerable length in a variety of types of apparatus, transparent and opaque, the author became strongly of the opinion that so long as the peroxynitrate remained in electrical contact with the anode it was not attacked by the nitric acid simultaneously formed. It therefore seemed possible to develop a type of apparatus which would permit of the quantitative electrolytic precipitation of the peroxynitrate and the checking of its weight against the gain in copper coulometers in the same electric circuit. Previous investigators had used no apparatus specially adapted to the problem in hand, and it is highly probable that none of them had for purposes of analysis more than a part of the material originally deposited, much of it having been lost by being dissolved in the electrolyte. This one supposition held the possible explanation for discrepancies between the analyses and conclusions of different men. Special apparatus was therefore developed.

The Apparatus

In Fig. 1, A is a capsule of glass. The edges at the top are well fired so that the one-hole rubber stopper can be inserted tightly and smoothly with no cutting of the rubber. The shoulder is square as shown, and the small glass tube constituting the lower part of the capsule is also well rounded on its edges so that it can be easily inserted into the tightly fitting rubber tube which serves, with the rubber stopper mentioned above, to connect the capsule into the apparatus. The capsule measures 3 8 cm × 2.3 cm over all, and above the shoulder it measures 2 cm × 1.6 cm inside. Upon the shoulder rests the filter and anode which will be described later.

B is a composite piece of glass. The cathode chamber b_1 is closed by the stopcock 11 at the bottom, and by a one-hole rubber stopper at the top. The chamber b_2 serves to maintain a good head of electrolyte and also to hold a filter on the square shoulder as shown. This filter consists of a layer of hardened filter paper between two perforated porcelain plates.

C serves, first, as a holder for the cathode; second, as an exit for air when the apparatus is being filled with solution; third, as an inlet for air and also for wash water when the solution is being removed from the apparatus. The cathode c_1 is a silver wire sealed into the small glass tube c_2 which is in turn filled with mercury in the well known manner. The rubber tube c_3 provides an air tight yet non-rigid connector between c_2 and the larger tube around it.

Electrical contact with the anode in capsule A is provided by means of the small glass tube b_3 which has a very fine platinum point sealed through its end, and is also filled with mercury. The tube is very small throughout most of its length, so that the cross section of the column of electrolyte from anode to cathode may be as large as possible, to provide good conductivity The upper end of this tube is made large so that a good surface may be presented to the rubber tube around it. When setting up the apparatus, this rubber tube is wired into position in such a manner that a slight tension holds the platinum point firmly on the anode, thus securing a good electrical contact.

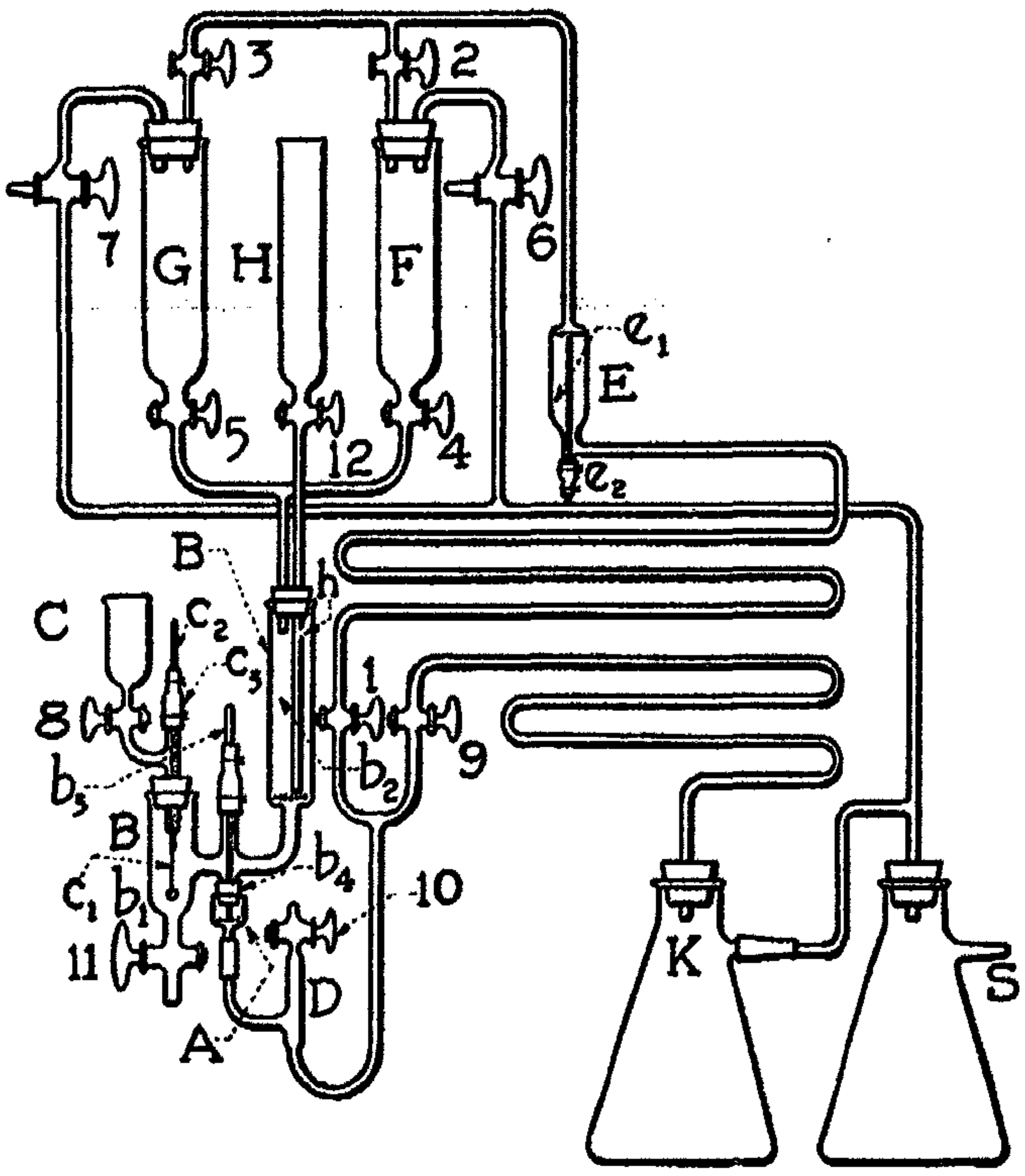

Fig. 1

E is a container for suspended silver carbonate. There is a square shoulder at the upper end, against which a filter is held, the filter consisting of one layer of hardened filter paper between two perforated porcelain plates. This filter is held in position by means of the small glass rod e_1 which is held firmly by the tension of rubber tube e_2.

H is a special form of tube extending down into B. The lower end rests firmly against the filter, holding the latter in place. There is a small opening in one side of the tube, h_1 well below the rubber stopper.

With the exception of the seven rubber stoppers and five pieces of rubber tubing represented in the drawing, the containing apparatus is entirely of glass, hardened filter paper, porcelain, platinum and gold.

The function of other parts of the apparatus will be apparent from what follows.

Manipulation

Let it be assumed that the apparatus is clean and ready for use. An unweighed capsule A is fitted into place. All stopcocks but 12 are closed. Suction is applied to the system at S. Silver nitrate solution is poured into H. Stopcock 6 (or 7) and 2 (or 3) are opened, followed by a cautious opening of 1. Solution passes through B, A, D, and E into F with a speed dependent upon the manipulation of 1. Before all of the electrolyte is introduced, A is replaced by a funnel through which suspended silver carbonate can be introduced into the system. This carbonate is not able to pass E. A is replaced; the addition of electrolyte proceeds until F or G is full and also both compartments of B. It will be noticed that the details of construction prevent the solution from touching either of the two rubber stoppers in the compartments of B. Compartment G being empty, continuous circulation of electrolyte is begun and maintained as follows: (Stopcock 1 is always used for final control) close 2; connect F to air by means of 6; open 4; (electrolyte rises to same height in H as in F) connect G to S by 7; open 3; cautiously open 1. Electrolyte passes from F to H into B which remains full up to h_1; thence through A, D, E and into G. As soon as F is empty, close 4; connect F to S by 6; open 2; close 3; connect G to air by 7; open 5; as soon as G becomes empty, the cycle is completed, regular repetition of which gives continuous circulation. As soon as the apparatus is working smoothly and the electrolyte is clear of silver carbonate (excepting of course in E), quantitative electrolysis is begun by emptying B and A and exchanging for the latter a new, weighed capsule and filter. After electrical connections are made ready circulation is started, after which the circuit is closed.

After the electrolysis has proceeded far enough, 4 and 5 are closed; the solution level is allowed to run down toward the lower end of b_2; distilled water is then quickly poured into H and C; 8 is opened; 9 is opened and 1 immediately closed; distilled water is added to H and C until the milliammeter shows that no more current is passing, whereupon the capsule is sucked dry and removed from the apparatus.

This manipulation requires practice, but great skill is not required for successful operation. The complexity of the apparatus is a result of the satisfaction of several very exacting needs:

1. A continuous, well-controlled circulation can be maintained as explained above.

2. The nitric acid formed at the anode is removed immediately from the zone of formation and is continuously and very thoroughly neutralized by reaction with suspended silver carbonate. On any ordinary filter, silver carbonate packs so badly that a solution cannot be pulled with any practical speed through it. In this apparatus a relatively large amount of silver carbonate can be used in E, without the inconvenience of a packed filter. Practically none of the carbonate escapes this filter, and what does is caught on the filter in B. The gas which is formed by the neutralization of the nitric acid escapes from the system by way of S.

3. In such work as this it is desirable and almost essential that the solutions be limited in volume. This apparatus used about 100 cc. of solution.

4. The construction of the apparatus ensures freedom from contamination. The materials used are glass, hardened filter paper, porcelain, platinum, gold and rubber. Rubber touches

the solution only at A and E, and it is seemingly not acted upon during the course of many electrolyses.

5. At times the solution becomes heated during electrolysis. By bringing a large beaker of ice water up around A and B, satisfactory refrigeration can be maintained.

Specific Details of Construction and Manipulation

The capsule A is made with a square shoulder to give stability to the anode and filter. The combination is made as small as possible so that the total weight is such as to permit of analytical accuracy. In the early experiments made by the author, asbestos filters were tried and abandoned; the lack of success attending their use was due to the fugitive character of fine asbestos fibers in such a circulating solution. However, after perfecting the apparatus and acquiring skill at manipulation, asbestos filters were used with surprising success in Experiments 28 and 29. Unfortunately, alundum or similar porous plates were not tried. Paper filters were used for Experiments 1 to 27 inclusive. There were used, in order from top to bottom, a perforated platinum plate, a perforated porcelain plate under and around the edges of which were a sufficient number of hardened filters (generally three) to make a tight fit. All but one of these hardened papers were used with their centers cut out, so that too great an obstruction was not offered to the moving liquid. For Experiments 28 and 29, the capsules were made up so that there were in order from top to bottom, a gold-plated perforated platinum plate, an asbestos filter, a perforated porcelain plate and three hardened paper filters, two of which had their centers removed. While asbestos filters can be made to work well their use is not advisable because of the desirability of using the same capsule and filter repeatedly, a constant weight of which greatly enhances the reliability of data obtained. Were the author ever to resume this investigation he would endeavor to have the apparatus specially constructed to take accurately fitting porous plates which should render unnecessary the use of paper.

The cathode c_1 is a platinum or silver wire of small surface, so that the silver crystals can be broken off by a gentle tapping of the glass tube c_2. This is very important for the silver crystals grow with such surprising rapidity that a tongue of silver can easily bridge the gap between the cathode and the horizontal tube leading to A. If this once happens during an electrolysis, the crystal grows within a very few seconds of time over into the region above A and continuously drops minute crystals of silver upon the anode deposit. These thin crystals are sometimes detected with great difficulty even in good light, and since a horizontal layer of silver, though detached from the cathode, acts bipolar with the resultant production of such crystals, great care must always be taken. In the earlier forms of this apparatus, data from which are not reported in this paper, the cathode was placed above the filter in B. Such construction was abandoned because silver always grew through the filter. During electrolysis it is necessary to tap the tube c_2 occasionally in order to break off the long needle crystals from the cathode. They settle quickly to the bottom of b_1.

The tubes from D to E and K must be of the zigzag form commonly used in glass apparatus of this type; the capsules can be changed freely with no danger of breakage.

D is a gas trap. At the beginning of an electrolysis it is entirely filled with solution. If at any time an appreciable amount of gas is formed at the anode and is drawn through the filter, it is caught in D. Although gas did form during these experiments as will be recorded below, at no time was there enough to make a small-sized bubble in D; in other words, this gas trap only served to demonstrate that no measurable amount of gas was being drawn through the filter in such a manner as to escape detection.

Two copper coulometers were used in all work, the one serving as a check upon the other. The solution was as follows: 150 g copper sulphate, 50 g conc. sulphuric acid, 50 g alcohol and one liter of distilled water. Two anodes were used in each coulometer. The cathodes were of copper foil to give lightness of weight, and each cathode below the solution measured 2.5 cm × 10 cm on each face. They never weighed more than 5 g each.

The silver nitrate used was obtained by recrystallizing the C. P. salt found in the laboratory stock. The solutions were carefully preserved and were never used if any turbidity was apparent.

Methods of Washing, Weighing and Analyzing the Peroxynitrate

It was presumed from the beginning of the investigation that the peroxynitrate was more or less instable, and that therefore the methods of washing and weighing were of fundamental importance. It was found that capsules made up with complete filters could be washed freely with water, silver nitrate solution, dilute nitric acid, ammonium hydroxide and alcohol with losses so small that errors of weighing generally masked any losses of weight. The reason for using ammonium hydroxide was that it dissolves peroxynitrate; but since a good white filter could not be thus obtained dilute nitric acid was always used as a supplementary cleansing agent. Water was used to remove all soluble materials, and absolute alcohol, to remove water which because of the slowness of evaporation tended to decompose the peroxynitrate on a wet filter.

Washing and drying operations were not standardized until after the 10th experiment. Beginning with the eleventh experiment, the capsules with fresh precipitate were washed quickly with distilled water until all silver nitrate was removed, then with absolute alcohol to remove water, after which air (dried with conc. H_2SO_4) was forced through the capsules for a few minutes until the alcohol was all removed. After weighing, this treatment could be repeated with no appreciable loss of weight; hence the conclusion that alcohol did not react upon the peroxynitrate. The use of alcohol was considered to be warranted by reason of the rapid desiccation thus secured. The undesirable effect of slow drying was demonstrated by the following tests:

A fresh lot of peroxynitrate was made and divided into three parts. The first sample was left on the filter in the capsule and washed with successive 10 cc portions of distilled water. These portions of wash water were examined for silver by adding HCl. Before making the tests the product was hurriedly washed to remove the last traces of silver nitrate. The first five tests were made within fifteen minutes after the above mentioned washing. Thirty minutes elapsed between the fifth and sixth washings, one hour between the sixth and seventh, and fifteen minutes between the seventh and eighth. The addition of HCl resulted as follows: 1. Very perceptibly turbid. 2. Slightly turbid. 3. Very slightly turbid. 4. Presence of silver questionable. 5. Very slightly turbid. 6. Slightly more than in 5. 7. Turbid. 8. More silver than in any other except 1. Hence the conclusion that the peroxynitrate decomposes to an appreciable extent in water at ordinary temperature and pressure.

The second part of the peroxynitrate was placed in a small weighing bottle in previously boiled and cooled distilled water. It was then placed under low pressure in a vacuum desiccator. Within five minutes from the time the pressure was reduced, there was an easily observable evolution of gas from the peroxynitrate, and it continued for several hours.

The third part of the peroxynitrate, in a capsule, was connected between a Hempel mercury gas burette and a Hempel mercury gas pipette, both miniature in size for working with small amounts of gas. As in other tests, the sample was wet, and within five hours there was an unmistakable evolution of 0.25 cc of gas, against a slight positive pressure maintained in the apparatus.

Accurate weighing was rendered difficult because of the fact that the filters contained filter paper. Beginning with the 8th experiment, all capsules were allowed to come to constant weight in the balance before final weighing. The most satisfactory agreements were obtained by leaving them in the balance case over night, the case being desiccated by means of conc. H_2SO_4. Agreement between re-weighings was sometimes exact, and lack of agreement was seldom more than 0.0005 g. Exposure in the balance case did not always, if ever, result in a significant loss of weight, for the product from Experiments 12 and 13 were made on July 3rd, and were re-weighed on July 22nd, the weights checking exactly in each case. During the intervening time the samples were in colorless glass containers, exposed to diffused light during the day time.

The only analyses made were for the percent of silver in the product, simple heating of which causes a decomposition to form metallic silver. For this decomposition a small porcelain crucible was used. After introduction of the peroxynitrate, two disks of ashless filter paper were pressed into the crucible, the lower disk being about equidistant from the upper disk and from the peroxynitrate. These disks were cut out and pressed into position with cork borers. After placing the porcelain cover, the crucible was gradually heated in a hot air bath to the charring temperature of paper, and then it was carefully ignited in a blast flame. The papers were used because of the fact that the peroxynitrate decomposes with slight explosions if heated suddenly. They prevented any possible losses from such source.

The Anodes

Up to and including the 25th experiment, the anodes were made of perforated platinum plates. One of the anodes used in earlier work was discarded because of the fact that the peroxynitrate formed less readily on some portions than others; from those portions where the deposit of peroxide was not normal, there was an excessive evolution of gas during the electrolysis. (The word "excessive" is here used in a purely relative sense, for at no time in any of the experiments was gas evolved in more than minute quantities.) Beginning with the 26th experiment, the platinum anodes were gold plated and burnished, the purpose being tb avoid possible catalytic decomposition.

Acidity of Solution

Beginning with the 7th experiment, a large excess of silver carbonate was always used in all work, and there can be no doubt that the solution was continuously well neutralized.

Temperature of Solution

Experiments 11, 12, and 13 were made with artificial cooling, but no significant changes were noticed, and subsequent work was done at ordinary temperatures.

Light Conditions

A part of the work was done by artificial light, and some by diffused daylight. No effort was made to carry on any of the work by non-actinic light.

The results of the experiments are given in Table I.

Whenever possible, the weight of a capsule and filter was obtained after the completion of each experiment. It will be noted that positive evidence was thus secured that at least some of the capsules did not change weight appreciably during use.

In this work the greatest emphasis was placed upon the ratio of the weight of peroxynitrate deposited to the weight of copper gained in the coulometer. Since the coulometers did not always check, and there was in some instances a loss of weight of the capsule and filter, two calculations were made, showing the highest and lowest possible ratios deducible from the data in hand.

Because of the sudden interruption of the investigation, analyses were not made of the samples from Experiments 28 and 29.

In the study of this whole problem, there are two details which can not receive too much emphasis and attention. Any apparatus which contains a diaphragm or filter for the separation of metallic silver from the anode product is open to suspicion and should not be used unless the apparatus is so transparent and the light conditions so good that all doubt concerning the bipolar action of isolated particles of metal is entirely removed. In earlier work the author obtained

TABLE I—DATA

	Weight of capsule and filter before Grams	Weight of capsule and filter after Grams	Weight of capsule with product Grams	Weight of product Gram	Coulometer gain in gram of copper No. 1	Coulometer gain in gram of copper No. 2	Weight ratio, peroxynitrate to copper. High	Weight ratio, peroxynitrate to copper. Low	Solution strength, percent silver nitrate	Current, ampere	Time, minutes	Percent Ag in the peroxynitrate
2	7.6707	—	7.8983	0.2276	0.0874	0.0887	2.60	—	5	0.18	30	—
3	—	—	7.8479	—	0.1023	0.1022	—	—	5	0.18	30	—
4	7.1989	—	7.5062	—	0.1400	0.1405	—	—	5	0.25	30	—
5	7.6513	—	8.0430	0.3917	0.1449	0.1451	2.70	—	5	0.30	25	—
6	8.1048	—	8.3658	0.2610	0.1066	0.1067	2.45	—	5	0.25	25	—
7	7.5899	7.5886	7.7634	0.1748	0.0620	0.0621	2.82	2.80	5	0.075	45	79.39
8	7.1824	7.1819	7.3569	0.1750	0.0623	0.0623	2.81	2.80	5	0.075	45	79.07
9	7.5492	7.5463	7.6777	0.1314	0.0481	0.0479	2.74	2.67	5	0.075	30	79.47
10	7.4255	7.4259	7.6013	0.1758	0.0604	0.0606	2.91	2.90	5	0.075	45	79.03
11	7.5886	7.5881	7.6963	0.1082	0.0396	0.0396	2.73	2.72	5	0.065	30	79.82
12	7.1819	7.1812	7.3585	0.1773	0.0644	0.0643	2.76	2.74	5	0.075	45	79.36
13	7.5463	7.5444	7.7072	0.1628	0.0609	0.0604	2.69	2.64	5	0.075	45	79.35
14	—	—	—	—	—	—	—	—	—	—	—	—
15	7.2682	7.2685	7.4482	0.1800	0.0656	0.0659	2.75	2.73	5	0.060	45	—
16	6.8293	6.8290	7.0903	0.2613	0.0892	0.0891	2.94	2.93	20	0.10	45	79.04
17	—	—	—	—	—	—	—	—	—	—	—	—
18	7.1812	7.1816	7.4174	0.2362	0.0800	0.0800	2.96	2.95	20	0.25	15	79.03
19	7.5444	7.5439	7.3333	0.1894	0.0690	0.0639	2.97	2.96	20	0.25	13	79.32
20	6.9311	6.9314	7.1090	0.1779	0.0598	0.0597	2.98	2.97	20	0.20	12	79.17
21	6.8291	6.8290	7.0374	0.2084	0.0708	0.0706	2.95	2.95	20	0.25	12	79.46
22	7.1086	7.1088	7.3164	0.2078	0.0701	0.0701	2.96	2.96	20	0.25	11	79.49
23	—	—	—	—	—	—	—	—	—	—	—	—
24	7.5439	—	7.6926	0.1487	0.0521	0.0521	2.86	2.86	5	0.20	12	79.71
25	7.4249	—	7.5442	0.1193	0.0419	0.0419	2.85	2.85	5	0.26	10	79.44
26	6.5785	6.5754	6.7126	0.1372	0.0499	0.0500	2.75	2.69	5	0.22	10	79.66
27	—	—	—	—	—	—	—	—	—	—	—	—
28	6.5754	—	6.7326	0.1572	0.0564	0.0561	2.80	2.79	5	0.05	52	—
29	7.2118	—	7.3630	0.1512	0.0520	0.0518	2.91	2.90	5	0.05	50	—

anode deposits with silver content up to and in some cases above the theory for Ag_7NO_{11}. After the subtle character of this source of error was recognized, and the apparatus properly modified, no anode deposits contained the theoretical amount of silver for this compound. Also, the evolution of gas from the anode during electrolysis was very slight in all of this work, and had the capsules not been of glass, the gas bubbles could not have been seen. It is very probable that accurate observations of such small bubbles can not be made in opaque vessels such as porcelain evaporators, crucibles and platinum dishes. In these experiments, the total volume of gas evolved during the course of any single electrolysis could not have been more than (estimated) 0.10 cc; but there was a positive evolution of gas in all experiments excepting as noted below.

Experiment 28 was the first one during the course of which no gas evolution from the anode could be detected. The anode was gold plated.

The percentage of silver in the deposit is fairly constant, varying only from 79.03 to 79.82, the mean being about 79.37. The coulometer ratio of compound to copper varies from 2.98 to 2.69 if we take the "high" ratios[1] and from 2.96 to 2.64 if we take the "low" ratios. There is apparently no relation between the fluctuations of the coulometer ratios and those of the silver content. Silver values of 79.44, 79.46, 79.47 and 79.49, correspond to coulometer ratios of 2.85, 2.95, 2.74 and 2.96, respectively. It is a simple matter to eliminate some of the formulas proposed for the peroxynitrate. In Table II are given the percentages of silver, the theoretical number of Faradays (96,600 coulombs) necessary to precipitate silver and the theoretical coulometer ratio.

Discussion of Results

The anode precipitate cannot be a pure oxide because the oxides up to Ag_2O_3 have too high a silver content, and Ag_2O_3 has much too low a coulometer ratio. It cannot be a pure

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[1] Omitting Expts. 2–6 because conditions were not yet standardized.

hydrated oxide of definite composition because the coulometer ratios are too low for $Ag_3O_4.H_2O$ and $(Ag_2O_3)_2.H_2O$, for which the silver content is fairly close. We must, therefore, admit the presence of silver nitrate in the crystals, with or without water. The compound $(Ag_3O_4)_2AgNO_3$, comes very close to meeting the requirements. In Expts. 18–22 in a 20% $AgNO_3$ solution with a current of 0.20–0.25 ampere, we get a mean silver content of 79.3% instead of 79.9%, about 1% low, and a mean coulometer ratio of 2.96 instead of the theoretical value of 2.97, which is well inside the limits of error. If we are to consider this as Ag_3O_4 with adsorbed silver nitrate, we must assume an adsorption of well over twenty percent which seems absurd. That hypothesis may, therefore, be eliminated.

TABLE II

	Percent Ag	F	Coulometer ratio
Ag_2O_2	87.9	2	3.90
Ag_3O_4	83.5	5	2.44
Ag_2O_3	81.8	4	2.07
$Ag_2O_2.2H_2O$	77.1	2	4.4
$Ag_3O_4.H_2O$	79.7	5	2.55
$(Ag_2O_3)_2.H_2O$	79.1	8	2.14
$(Ag_3O_4)_2.AgNO_3$	79.9	10	2.97
$(Ag_2O_3)_2.AgNO_3$	77.3	8	2.74
$(Ag_2O_3)_3.AgNO_3$	78.8	12	2.52
$Ag_3O_4.Ag_2O_3.AgNO_3$	77.3	11	2.87

It is difficult to account for the variations satisfactorily however. Traces of mother liquor in the deposit would cut down the percentage of silver; but it would raise the coulometer ratio. With the five percent silver nitrate solution the values for the coulometer ratio are uniformly low without any marked change in the percentage of silver. There seem to be only two ways of accounting for this. We may have an admixture of some substance like $(Ag_3O_4)_2.H_2O$ or $(Ag_2O_3)_2.AgNO_3$ with a low coulometer ratio, or the precipitation at the anode may not be quantitative owing to the solvent action of the nitric acid formed during the run. These experiments do not warrant a final decision between the two hypotheses. Special experiments with this in view ought to clear the matter up however. In any case, it seems probable that the deposit is essentially $(Ag_3O_4)_2.AgNO_3$, which is the composition assigned to it by Mulder, Tanatar, Sulc, and Watson.

Baborovsky and Kuzma[1] actually obtained a substance having a composition $(Ag_3O_4)_2AgNO_3$; but they decided that the silver nitrate was not essential and so they dropped it from the formula. Luther and Pokorny preferred the formula Ag_2O_3; but they say[2] that their experiments are not accurate enough to enable them to distinguish between the formulas Ag_4O_5, Ag_3O_4 and Ag_2O_3. They made no direct analyses and admit that their method does not show whether the oxide is hydrated or not.[3] Their method also does not show whether the oxide contains silver nitrate or not. Their reason for assuming that the oxide contains no silver nitrate is that practically identical values for the electromotive forces are obtained whether one starts with silver nitrate solution or silver sulphate solution. There is no necessary reason, however, why silver nitrate and silver sulphate should have noticeably different effects upon the electromotive forces. Even if the reasoning of Margrete Bose and of Luther and Pokorny were apparently sound, which it is not, it could not stand for a moment against the silver determinations which show that the compound can not possibly be a pure oxide.

The general results of this paper are as follows:

1. An apparatus has been devised which makes it possible to prepare and to collect for analysis silver peroxynitrate with greater accuracy than ever before.

2. Solutions containing 5% and 20% silver nitrate were electrolyzed with various current strengths. The silver content of the anode deposit averaged 79.37% Ag, the limits being 79.03 and 78.2.

3. The ratio of the anode deposit to copper precipitated in the coulometer varied from 2.98 to 2.69.

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[1] Zeit. phys. Chem., 67, 68 (1909).

[2] Luther and Pokorny: Zeit. anorg. Chem., 57, 301, 308 (1908).

[3] Loc. cit., 297.

4. No pure oxide and no hydrated oxide can give both the observed silver content and the observed coulometer ratio.

5. The calculated values for $(Ag_3O_4)_2AgNO_3$ are 79.9% and 2.97, while the values found for electrolysis of 20% $AgNO_3$ and a current of 0.20–0.25 ampere are 79.3% and 2.96; with 5% $AgNO_3$ the corresponding values are 79.4% and 2.75.

6. The anode deposit is, therefore, impure $(Ag_3O_4)_2.AgNO_3$.

7. The low value for the silver content may be due in part to occluded mother liquor or adsorbed silver nitrate; but this would raise the coulometer ratio and, therefore, cannot be the sole factor.

8. The low coulometer ratio may be due to the presence of some substance like $(Ag_3O_4)_2.H_2O$ or $Ag_2O_3.AgNO_3$. There is nothing in the experiments to show what the admixture is or in what form it is present.

9. The low coulometer ratio may also be due to the anode deposit being dissolved by the solution. Special experiments are needed to determine this point.

10. It requires ten Faradays to precipitate one gram molecular weight of $(Ag_3O_4)_2.AgNO_3$.

11. These experiments confirm the conclusions of Mulder, Tanatar, Sulc, and Watson; they are in agreement with the experimental data of Baborovsky and Kuzma, though not with their conclusions. There is no real contradiction with the data of Luther and Pokorny, because these latter are admittedly not accurate enough to warrant any conclusion beyond the one that the peroxynitrate contains a higher oxide than Ag_2O_2.

12. Experiments should be made to determine under what conditions silver nitrate splits off from the peroxynitrate.

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PLASTER OF PARIS

BY L. A. KEANE

The literature in regard to plaster of Paris is in a very confused state. It was shown by van't Hoff, Armstrong, Hinrichsen and Just[1] that there is an inversion point for gypsum, $CaSO_4.2H_2O$, and the hemihydrate or plaster, $2(CaSO_4)_2.H_2O$, at 107° and 971 mm. Plaster is really a metastable phase, for van't Hoff found an inversion point for gypsum and the insoluble anhydrite at 63.5° and 175 mm. Following the lead of others, van't Hoff recognized a so-called soluble anhydrite and he estimated the inversion temperature for gypsum and the soluble anhydrite at about 93° and 588 mm. The temperature at which plaster and the soluble anhydrite should coexist was estimated at 36° while the hypothetical inversion point for plaster and the insoluble anhydrite is below zero.

Since gypsum should break down to insoluble anhydrite at 63.5°, we have 40° superheating. This is not all however. Kremann[2] says that "107° is the only temperature at which dihydrate and hemihydrate can coexist in equilibrium; this temperature is, therefore, of practical importance, since the gypsum burner uses this transformation to obtain burnt gypsum, *i. e.*, plaster of Paris; in this case, however, he is working under atmospheric pressure and obtains the water as steam. Theoretically a temperature only slightly above 107° would be sufficient; but in practice a higher temperature is employed, over 130°, mainly because the reaction velocity just above the transition point would be too small. Apart from the influence of rise in temperature, which increases the reaction velocity of every reaction and transformation, the reaction velocity of the transformation of the instable into the stable phase is in itself greater the higher the temperature

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[1] Zeit. phys. Chem., 45, 257 (1903).

[2] "The Application of Physical Chemical Theory to Technical Processes and Manufacturing Methods," 153 (1913).

is above the transition point. On further heating there is another transition point at 130°, that of the transformation of the hemihydrate, plaster of Paris, into anhydrous gypsum. ... When the dihydrate is heated to 130°, water and an anhydrous form should be produced in stable equilibrium. However, we observed that the hemihydrate, $2CaSO_4.H_2O$, is produced first, which, theoretically though instable, nevertheless has a certain degree of stability. It only evolves[?] water after rather a long time, giving a mixture of $CaSO_4.2H_2O$ and $CaSO_4$.

"The instability of the hemihydrate explains the fact that the dihydrate often occurs in nature in direct contact with anhydrite, while the hemihydrate does not occur naturally; we will use this fact in considering the hydration and hardening of different kinds of gypsum. The anhydrous modification formed above 130°, which Rohland calls α-$CaSO_4$, is dead-burnt gypsum, which possesses the power of taking up water, but not of hardening without further treatment. It appears to be an instable polymolecular modification of $CaSO_4$. On heating α-$CaSO_4$ to a rather high temperature, 525°, it appears to dissociate into simpler molecules with a measurable velocity, giving, according to Rohland, β-$CaSO_4$, which differs from the α modification, dead-burnt gypsum, in possessing not only the power of hydration, but also that of subsequent hardening. These properties make this modification, like the hemihydrate, plaster of Paris, practically important as Estrich gypsum (flooring plaster). It is only capable of existence up to about 600°, and on heating above this temperature it turns into a third anhydrous modification, γ-$CaSO_4$. This modification has lost all capacity for hydration and hardening, and is, therefore, a dead-burnt form which, however, differs from the dead-burnt form α-$CaSO_4$, which is in instable equilibrium from 130 to 525°, by the fact that the latter, α-$CaSO_4$, can be given the capacity for hydration and hardening, while the former, γ-$CaSO_4$, cannot.

"We have mentioned that when preparing the hemihydrate, plaster of Paris, in practice by burning the dihydrate, a temperature is chosen which is fairly high above the transition point of the hemihydrate to the anhydrous form, mainly in order to attain sufficient velocity for the transformation, which theoretically should occur even at 107°. This temperature shows that at all events part of the hemihydrate must have been transformed into the anhydrous form. It is not completely transformed on calcining at a temperature not far from 130°, firstly, because the reaction velocity for the transformation of the hemihydrate into the anhydrous form α-$CaSO_4$ is too small just above the transition point. The second reason is the particular construction of the calcining apparatus. Köster[1] states that in the rotating drum of the Petri-Hecking gypsum calcining apparatus the temperature is 220°, but owing to an ingenious mechanical contrivance the heat is rapidly removed from the gypsum above the transition temperature of 130°, and thus complete transformation into the anhydrous modification is hindered. The gypsum which is thus made in practice only consists to a small extent of the hemihydrate (plaster of Paris), the greater part being the first anhydrous modification. Such gypsum can be employed technically, since the active mass need only be small; yet it must be in the finest possible state of division to possess the greatest possible reaction velocity with water, so that in practice great stress is laid upon fineness of grinding."

Kremann's account is based on Rohland's work.[2] According to Rohland we must postulate three anhydrous forms of calcium sulphate in addition to anhydrite; α-$CaSO_4$, which is formed between 130° and 525° and which takes up water but does not set by itself; β-$CaSO_4$, which is formed at 525°, which takes up water and hardens; and γ-$CaSO_4$ which is formed above 600°, and which does not hydrate or harden. There is no satisfactory experimental evidence for the inversion points at 130° and 525°. While four different modi-

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[1] Tonindustrie-Zeitung, 32 (1901).

[2] Rohland: Zeit. anorg. Chem., 31, 437 (1902); 35, 194; 36, 332 (1903).

fications of the same substance may exist, definite proof of their existence should be given, and this has not been done.

There are other difficulties. Rohland claims that the α-$CaSO_4$ is formed when the temperature is raised above 130°, whereas Eckel[1] states that no anhydrous calcium sulphate is formed under technical conditions until the temperature reaches 204°. He also states that it is found most economical of fuel and time to burn the gypsum at the highest possible temperature, and that the usual limiting temperatures for making plaster are 175°–200°. This is in accordance with what Desch[2] says, that "care must be taken in the preparation of ordinary plaster that the temperature of calcination does not exceed 200°; for if heated more strongly gypsum becomes dead-burnt and loses its property of setting with water." On the other hand, Blake[3] says that when gypsum "is heated to 100°–120°, it give up three-fourths of its water rather quickly; but it requires a temperature of 200°–250° to expel the remainder.......If the gypsum has been heated to a little over 200°, thus being deprived of all its water, it becomes dead-burnt, and takes up water very slowly and without hardening. Plaster of Paris is prepared very extensively on the large scale by burning gypsum. Its good qualities depend mainly upon the choice of raw material—heavier and denser varieties yielding the best commercial results—and upon the mode of burning. The lowest temperature at which gypsum can be burnt advantageously is 80°; but a temperature of 110°–120° gives the best technical results. As a rule also, the smaller the pieces, the more homogeneous the product."

From these statements one may conclude that the American practice is to burn gypsum to plaster at 175°–200°, because complete dehydration takes place only above 200°, whereas the Germans burn at about 130° to prevent the formation of anhydrous calcium sulphate above 130°. The English apparently burn at 110°–120°, though admitting that the

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[1] "Cements, Limes, and Plasters," 31 (1905).

[2] "The Chemistry and Testing of Cement," 48 (1911).

[3] Thorpe's Dictionary of Applied Chemistry, 1, 611 (1912).

temperature may be raised to about 200° before anhydrous calcium sulphate was formed. It was pointed out by Professor Bancroft in his lectures during the winter of 1914-15 that these discrepant statements could be reconciled if we took the time factor into account. If we assume that gypsum loses water slowly at 110° and more rapidly at 200°, it would then be possible to burn it to plaster at 110° if one took time enough, whereas one could burn it to the same end point in less time at 200°. This is in accord with the statement by Hursch[1] that "commercially, temperatures up to 200° or above are used, but for short periods of time." Whether the saving in time would balance the cost of heating to a higher temperature is a matter which would vary with varying conditions. One might be quite justified in adopting one procedure in America and another in Germany. Since plaster is a theoretically instable form, it might easily happen that much of the plaster would change to anhydrous calcium sulphate during a long heating at 130° while this change might be negligible during rapid heating to 200°. At the suggestion of Professor Bancroft I made some experiments on the burning of gypsum as part of my senior research work.

A sample of very pure commercial gypsum containing 20.9% H_2O was crushed to a coarse powder and about 80 g were placed in a porcelain crucible. A thermometer was suspended so that its bulb was approximately in the center of the powdered mass. The crucible was heated by means of a Bunsen burner; readings of the temperature were taken every half minute up to 200°; and the gypsum was stirred constantly throughout the run. The data for the first run are given in Table I.

Since the plan was merely to get a general knowledge of what happens, no special precautions were taken and consequently no special accuracy is claimed for these results. There is apparently a break at about 99° and another at about 139°. The thermometer shot up so suddenly after

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[1] Trans. Am. Ceram. Soc., 17, 549 (1915).

TABLE I

Temp.	Rise per minute	Temp.	Rise per minute	Temp.	Rise per minute
75°	—	108°	8°	139.5°	1.6°
85	20°	112.5	9	165	51
95	20	116	7	170	10
98	6	119	6	174.5	9
99	2	122.5	7	177	5
99	0	125	5	179	4
99	0	127	4	183	8
99.2	0.4	128	2	186	6
99.2	0	130.5	5	189	6
99.5	0.6	132	3	192	6
100	1	135	6	194	4
100.6	1.2	137	4	196	4
102	2.8	139	4	201	10
102.5	1.0	139	0	—	—
104	3.0	139.2	0.4	—	—

passing 140° that the reading at 165° has no significance. A more accurate statement would be that the thermometer rose only half a degree in two minutes at 139° and then rose about 38° in the next two minutes. The loss in weight during the heating was 11.7 g or 14.6%. This means that the gypsum had gone down nearly but not quite to plaster, which would have been a loss of 15.7%. In other words, there is some unchanged gypsum left when eighty grams of gypsum are heated in a porcelain crucible from 75° to 200° in just under the hour and a half.

This experiment shows the total amount of water lost; but does not show how the loss was distributed. Another run was made with about 66 g gypsum; but the crucible was removed when the temperature reached 156°. The crucible was allowed to cool, was weighed, was heated to 200°, and was weighed again after it had cooled a second time. The data are given in Table II, the temperature readings being taken every half minute as before.

TABLE II

Temp.	Rise per minute	Temp.	Rate per minute	Temp.	Rise per minute
89°	—	103.1°	6.2°	153°+	5.6°
97.5	17°	106	5.8	156	6
98.5	2	108.1	2.2	—	—
98.6	0.2	111	5.8	120	—
98.9	0.6	113	4	128	16
98.9	0	117.6	9.2	137	18
98.9	0	121.5	7.8	145	16
98.9	0	124	5	149	8
98.9	0	129.6	11.2	159.5	21
99.0	0.2	135.5	11.8	167.5	16
99.0	0	138	5	177	19
99.5	1	141	6	184.5	15
100	1	142.2	2.4	192.7	16.4
101	2	144	1.8	198	10.6
103	4	146	4	200	4
98.5	—9	147.5	3	—	—
100	3	150.2	5.4	—	—

Since less gypsum was taken, the heating was somewhat more intense. There is a very marked halt at about 99° and no halt at all at 139°, thus bringing out clearly the differences due to slight changes in the conditions. The results of the weighing were quite unexpected. In the first heating up to 156° only 7.6% water was lost. In the second heating to 200°, 11.4% water was lost, making a total for the two heatings of 19%. In other words the gypsum was brought down nearly to the anhydrous state. Since the crucible was cooled down from 156° and then heated to 200°, the time of heating was much longer than in the first run. This shows in the different amounts of water lost, 14.6% in one case and 19% in the other.

The halt at 99° was supposed at first to be due to loss of moisture; but this was apparently not the case. A 30 g sample of gypsum lost only about 0.2 mg on standing in a desiccator over sulphuric acid for twenty-four hours. There was practically no loss when a sample was heated in an air oven at a temperature of 103°. Under these circumstances the gypsum was not stirred. The total water content of 20.9% was determined by heating a sample of gypsum in a blast lamp for several hours.

Instead of heating with a free flame, a sample of gypsum was heated in an oil bath kept at about 150°. The temperature of the gypsum rose steadily to about 107° and then the thermometer reading remained nearly constant at that temperature for about an hour. After the 120° point was reached, the temperature rose more rapidly. This made it probable that most of the water is lost below 120° if the heating is not done too rapidly. In order to prove this, a sample of gypsum was kept in a constant temperature bath at 120°. The data given in Table III show that the gypsum is completely dehydrated at this temperature.

Table III
Temperature = 120°

Time in hours	Percent loss	Time in hours	Percent loss	Time in hours	Percent loss
1	9.9	4	15.7	5.5	17.2
2	13.6	4.5	16.8	12	20.6
3	14.9	—	—	—	—

The same experiment was repeated at 110°, the gypsum being held at that temperature for 24 hours,[1] at the end of which time it was found to have lost 20.1% water. Gypsum and plaster are both substances which develop their true vapor pressures very slowly, so that it is possible to superheat them enormously. While gypsum can be heated rapidly to 200° in an open vessel, the theoretical vapor pressure must be at least fifteen atmospheres at that temperature. It would be distinctly an interesting experiment for somebody, who was equipped to make pressure measurements, to determine the maximum pressure which gypsum would develop if heated to 200° in a closed vessel and also the time necessary to reach equilibrium.

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[1] Cf. Rohland: Zeit. angew. Chem., 21, 2115 (1908).

The experiments of Precht and Kraut[1] show nothing as to the dissociation pressure of gypsum because they worked with such small amounts of substance in most cases that the equilibrium pressure could not be reached. Their experiments are valuable as showing the slow rate at which equilibrium is reached. They worked at 100° and allowed the hydrated salt to dissociate into an evacuated tube. The data are given in Table IV.

TABLE IV

$CaSO_4.2H_2O$ at 100°

Gypsum Milligrams	Time hours	Pressure Mm Hg	Volume vapor cc	Water loss in percent
4.2	2.25	13.4	78.2	19.36
13.6	3.5	35.6	84.3	17.14
21.0	2.75	50.8	85.2	16.02
29.5	5.17	67.7	89.4	15.56
50.4	4.33	94.2	98.4	14.28
74.9	6.04	140.0	104.2	13.85
103.6	5.83	170.8	106.2	13.59
133.2	6	205.8	111.9	13.42
184.7	9	251.2	126.4	13.35
342.4	9.17	351.2	141.2	11.23
534.7	10	417.2	153.8	9.14
776.5	10	474.0	164.4	8.66
921.3	11	570.2	170.9	7.29
1000	14	519.1	172.2	6.94

According to van't Hoff[2] the dissociation pressure of gypsum is 564.8 mm at 95° and 710.8 mm at 100°. If 342.4 mg $CaSO_4.2H_2O$ give a pressure of 351.2 mm when 11.23% water has been vaporized, they would give a pressure of only about 654 mm if totally dehydrated by a loss of about 20.9% water. Consequently, it is only in the last four experiments that the equilibrium pressure could be reached. It is interesting to note that with 1000 mg gypsum equilibrium had nowhere near been reached after fourteen hours heating. Precht and Kraut also report that a fragment of a gypsum crystal weigh-

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[1] Liebig's Ann., 178, 138 (1875).

[2] Zeit. phys. Chem., 45, 267 (1903).

ing 0.85 g gave 57.1 mm pressure after being heated for eight hours, whereas a pressure of 400 mm was reached when the same amount of gypsum was first ground to a powder. For the case of gypsum it seems impossible to assume with Nernst that equilibrium exists at the surface of the crystal and that the delay in reaching equilibrium is due solely to slow diffusion of water vapor.

Since gypsum can be burned to plaster without any difficulty at any temperature between 110 and 200°, the best temperature for commercial work will vary with cost of fuel, size of plant, overhead charges, etc. Another factor, for which there are no data, is the quality of the product, which undoubtedly varies with the temperature of formation.

We can now consider the behavior of anhydrous calcium sulphate in hopes of eliminating some of the hypothetical modifications. Desch[1] says that "it is well known that if the temperature is allowed to rise too high in the burning of plaster, the gypsum becomes dead-burnt, and no longer hardens with water. In this case the whole of the water of crystallization is expelled, and the anhydrous calcium sulphate thus obtained, like the native mineral anhydrite, $CaSO_4$, is not capable of forming a supersaturated solution, owing to the extreme slowness with which it dissolves in water, and, therefore, cannot set. Very slow dehydration of gypsum at a moderate temperature also yields an anhydrous product, differing from anhydrite in dissolving in water and in hardening, although more slowly than plaster of Paris. This soluble anhydrous calcium sulphate is a constituent of the hard plasters used for flooring, of the so-called 'Estrich gypsum,' and of most of the medieval plaster cements, all of which are characterized by comparative slowness of setting, and by attaining considerable hardness if kept moist during the process of setting. The details of hardening of such plasters have been comparatively little studied. An account of some experiments in this direction is given by Gary.[2] It is known that the hydration

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[1] "The Chemistry and Testing of Cement," 107 (1911).

[2] Mitt. k. Material. Prüf. Amt., 22, 50 (1904).

of flooring plaster may require months for its completion. The addition of Estrich gypsum to ordinary plaster retards the setting of the latter, and this device may be employed[1] to prepare a plaster having any desired rate of setting."

Under flooring plaster and hard-finish plasters Eckel[2] classifies two groups of plasters which are prepared by burning gypsum at a higher temperature than is employed in the manufacture of plaster of Paris and "cement" plasters, and which set rather slowly for plasters but finally take on great hardness. "Because of these last properties, the flooring plasters and hard-finish plasters are available for certain uses to which ordinary plasters are ill adapted. Their points of difference are, that the flooring plasters are prepared by simple burning at high temperatures, while the hard-finish plasters are produced by a *double* burning, with the additional uses of chemicals. Neither product is made to any extent in the United States, though a considerable quantity of hard-finish plasters are imported every year. The data obtainable as to processes of manufacture are scanty, and the descriptions published are often contradictory, so that it has been difficult to prepare a satisfactory account of these products. It is believed, however, that the descriptions given below contain no errors of importance.

"The flooring plasters ('Estrichgips' of German reports) include those plasters made by calcination of a relatively pure gypsum at temperatures of 200° C or higher. In the literature of gypsum and plaster it is often stated that gypsum, burned at temperatures exceeding 200° C yields a completely dehydrated product—an artificial anhydrite—which is entirely valueless as a structural material, because it has completely lost its property of recombining with water. This statement is erroneous, however, for plasters burned at such temperatures are regularly made and used. They set with extreme slowness, however, and require very fine grinding....

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[1] Frey: Tonindustrie-Zeitung, 34, 242 (1910).

[2] "Cements, Limes, and Plasters," 68, 75 (1905).

"Flooring plaster is a pure plaster, entirely free from water. It is manufactured by burning pure gypsum, broken into lumps but not finely crushed, in a vertical kiln. The fuel, usually coal, is burned on a grate set at one side of the kiln, and the hot gases pass directly through the mass of gypsum, though neither fuel nor ashes come into direct contact with it. The temperature reached is about 500° C according to Wilder.[1] The gypsum must not be exposed to this temperature for more than four hours, for a longer heating would deprive it entirely of its setting properties, as noted by van't Hoff.[2]

"As its name denotes, flooring gypsum (Estrichgips) is used extensively in Germany for floors, giving a very hard and durable surface. As the material attains this hardness only when it is protected from moisture during setting, care must be taken to give it a suitable foundation. If the material dries unevenly or very rapidly, cracks will appear on its surface. In this case the floor should be covered with water until the surface is soft and the cracks closed, after which it is allowed to dry again. After standing about twelve hours and becoming fairly hard the floor is pounded with wooden mallets and smoothed with trowels."

All this is comparatively simple; but everything is apparently changed in a paper by Hursh.[3] "When heated above 200° C for some time, gypsum becomes completely dehydrated, and the time required for its re-hydration is very much increased. However, heating for short periods of time at temperatures even in excess of this does not seriously reduce the setting properties. The anhydrous calcium sulphate formed above 200° is generally termed the No. 1 anhydride. When heated for long periods of time at 200°–300° or for short periods of time at somewhat higher temperatures, the product becomes dead-burned. It will hydrate very slowly but gives

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[1] Iowa Geological Survey, 12, 139.

[2] Sitzungsber. Akad. Wiss. Berlin, 1903, 249.

[3] Trans. Am. Ceram. Soc., 17, 549 (1905).

no real hardening reaction and is, therefore, of no technical value.

"At a somewhat higher temperature of heating, there is developed a further modification of the anhydrous sulphate termed variously the β-form, the No. 2 anhydride, or Estrich. Its properties are very different from those of the preceding modifications. Unlike the dead-burned anhydride, it has the ability to hydrate and harden, forming an extremely dense hard cement. Its rate of hydration and setting are very much slower than that of the hemihydrate, several hours being required, and full strength is developed only after weeks. The strength developed by Estrich is exceedingly high, comparing well with that of Portland cement. The temperature at which Estrich is formed is somewhat in dispute. It is too often confused with the alum plasters, the Scott or Keene's cements. Commercially, Estrich plaster is burned at 900°–1000° C and possibly higher. In laboratory study it may, without doubt, be formed at considerably lower temperatures, since the duration of heat treatment is an extremely important factor in such cases. . . .

"At 600°, Rohland finds the formation of a dead-burned $CaSO_4$ without hydraulic properties. Müller gives the temperature for formation of Estrich as 800°–900°. In his experiments, partial reduction of the sulphate took place, and he suggests the influence of the products of reduction as being a factor in the increased rate of hydration. An attempt to obtain an Estrich by heating together natural anhydrite and CaO did not prove successful.

"Glasenapp[1] has made a study of the properties of gypsum heated at different temperatures up to 1400° C. Up to 400°, the burned material would hydrate to form crystalline hemihydrate, the rate of the reaction decreasing with increasing burning temperature. From 400°–800° there was practically no ability to hydrate and harden. Up to this temperature, it shows a retention by the particles of the crystalline

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[1] Cf. Zeit. angew. Chem., 27, 308 (1914).

form of the hemihydrate. From 800° up, there is a change in the appearance, the particles becoming more or less rounded and granular. Coincident with this change in the microscopic appearance of the particles, there appears the property of hydrating and hardening with the development of great strength. In other words, he finds that Estrich is only formed at burning temperatures above 800°. The granular structure is taken as a criterion for true Estrich, all products at lower temperatures being similar in appearance to the gypsum burned at 300° which is very slow to hydrate and shows little ability to harden.

"At 800°, with four hour heating periods, the $CaSO_4$ began to dissociate showing about 3 percent CaS. At still higher temperatures, more CaO is found in the product. A sample to Cone 12 [1370°] in a porcelain kiln contained 83 percent CaO but still hardened as well as Estrich. Glasenapp concludes that Estrich formation depends upon the production of a basic sulphate which appears at the higher temperatures as a glassy matrix surrounding particles of $CaSO_4$ which show the granular structure of Estrich. The hydration he finds to take place without change in form or volume, water being taken up in an amount equivalent to that of dihydrate, but little or no crystallization occurring.

"Glasenapp concludes that Estrich is formed only above 800°, temperatures of 900° and upwards being the best in practice, and that over-burning is practically impossible. The granular appearance under the microscope is taken as a positive means of distinguishing true Estrich.

"Cramer notes that in burning gypsum the specific gravity increases as the water is driven off up to 500° C, where the specific gravity falls but again rises with higher burning temperatures. Gypsum was burned at Cones 015, 010 and 07 [800°, 950° and 1010°], then mixed with water and the amounts of combined water determined at the end of ten days. The results showed for Cone 015 none, Cone 010 10.6 percent, Cone 07 5.4 percent. It was concluded that dead-burned gypsum was produced by underburning and that overburning was possible."

Blake[1] is non-committal in regard to theory and practice. "If gypsum is heated to a higher temperature, *e. g.*, above 130°, it becomes completely dehydrated and yields $CaSO_4$. It appears that $CaSO_4$ can exist in two or more modifications, which behave differently with water. As all eventually become hydrated, but not all will set as plaster of Paris, it is probable that only those which will set possess the characteristic property of forming a supersaturated solution, and allowing the mass to crystallize in stages in the manner described above. Keene's cement and Estrichgips (flooring plaster) are examples of cements consisting substantially of anhydrous calcium sulphate. Their setting is influenced both by the temperature at which they have been burnt and by the presence in them of small quantities of substances other than $CaSO_4$, the *modus operandi* of which is exceedingly obscure. In whatever way they are prepared, the final product of setting is $CaSO_4.2H_2O$."

The non-setting variety of calcium sulphate, insoluble anhydrite, was prepared by van't Hoff[2] at 30°. It can also be obtained at any other temperature up to 1000°. The soluble anhydrite, or variety of calcium sulphate which sets with water, can apparently be obtained at any temperature between 60° and 1000°. Since no inversion point has been found by anybody and since it is possible to obtain all variations from an anhydrous salt which sets more rapidly than plaster of Paris to an anhydrous salt which does not take up water at all in any reasonable time, the simplest explanation is to postulate that there is only one modification of anhydrous calcium sulphate, which, however, differs markedly in its properties depending on the conditions of formation. This is not an improbable or far-fetched hypothesis.

Lime becomes relatively inert if heated hot enough.[3]

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[1] Thorpe's Dictionary of Applied Chemistry, 1, 612 (1912).

[2] Zeit. phys. Chem., 45, 282 (1903).

[3] Desch: "The Chemistry and Testing of Cement," 53 (1911).

"The chemical reactivity of lime, like its specific gravity, depends on the temperature at which it is prepared. Lime which has not been heated above 1000° slakes instantly on the addition of water, while a more strongly ignited product requires a considerable time for hydration. If heated strongly in an electric furnace, lime may be fused....A lump of such lime, placed in water, is dissolved very slowly at the surface, the hydration being so gradual that no appreciable rise of temperature is observed. On the other hand, the finely powdered crystals, mixed with water, appear to be inert, but after a few minutes the reaction sets in with explosive violence.[1] It appears, therefore, that the increase in the reactivity of lime with increasing temperature of ignition is due less to a molecular change than to shrinkage and consequent reduction of surface. It is found that loose powdered lime, if kept for any length of time at 1400°, agglomerates to form crystals, which increase continually in size. Lime prepared at a low temperature is loose and porous, so that a large surface is presented to the action of the water, and hydration takes place very rapidly. The more strongly burnt lime is denser, and offers a smaller surface in proportion to its mass; the action is, therefore, confined to a smaller area and proceeds more slowly. Crystalline lime, being dense and nonporous, is naturally the least reactive."

On the assumption that there is only one anhydrous calcium sulphate and that the question of setting or not setting is primarily one of size of grain, the two important factors are temperature and time of heating. The anhydrous calcium sulphate which I obtained by heating at 120° set very well when mixed with water. If the Germans find that gypsum dehydrated above 130° does not set, it must be because they have heated the material so slowly that it has had time to sinter. It is extremely probable that the material would set if it were ground finely. As Eckel points out, the material obtained at 200°-300° sets admirably if finely ground. In-

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[1] Day, Shepherd and Wright: Am. Jour. Sci. (4) **22**, 265 (1906).

stead of doing experiments at all sorts of temperatures, it seemed simpler to test the theory by a crucial experiment. Since everybody admits that dead-burned plaster is obtained at 600°, a sample of gypsum was heated for quite a while at a temperature above 600°. When a portion of this was mixed with water it did not set and was evidently dead-burned plaster. Another portion was ground very fine in a McKenna grinder. When this very fine powder was mixed with water, it set rather rapidly to a hard, resistant mass.

A microscopic examination of this dead-burned plaster showed that the average particle was about 0.05 mm in diameter before grinding. After grinding, the largest particles rarely exceeded 0.005 mm. Owing to the burning of Morse Hall, it was not possible to try the experiment of grinding natural anhydrite; but there can be no question that the material would set if this were done, though it is possible that it might be necessary to grind the mineral more finely than the anhydrous calcium sulphate obtained by dehydrating gypsum.

It is apparently primarily a question of size of grain whether anhydrous calcium sulphate sets faster or slower than plaster of Paris, whether it hydrates without setting, or whether it does not hydrate appreciably.

While the effect of different substances on the rate of setting of plaster is not properly a part of this paper, it seemed that a statement of the facts might be of interest since many of the books are obscure on this point. Desch[1] gives a good account of the facts in regard to setting and I quote from him. "The hemihydrate dissolves readily in water, forming an instable supersaturated solution, which tends to deposit crystals of the dihydrate; and such a deposition having begun at some point the series of changes continually repeats itself, the hemihydrate dissolving, becoming further hydrated, and then depositing crystals of the dihydrate. It is characteristic of crystals separating from such a supersaturated solution

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[1] "The Chemistry and Testing of Cement," 105, 108 (1911).

that they tend to group themselves in radiating bundles, each of which starts from some point as a center. When ordinary plaster sets, the quantity of water used in mixing is so small that the particles are in close contact, and the resulting crystals form a confused and dense mass, the strength of which is due to the interlocking of the bundles of radiating prisms. It is impossible to obtain a clear photograph of such a mass, but by employing dilute alcohol instead of water, we may cause the hydration to take place so slowly that the crystals have time for development, and aggregates of an appreciable size are obtained....The quantity of liquid is so large in proportion to that of solid that the centers of crystallization are rather widely separated, and the prisms formed do not become interlocked. Under such conditions, the gypsum formed is not coherent. The presence of a strictly limited quantity of water is necessary to hardening, in order that crystallization may take place from a strongly supersaturated solution. If plaster is mixed with a large excess of water, hydration takes place quite readily; but the crystals separate from comparatively dilute solution, and the resulting mass, consisting of entirely isolated prisms, is loose and incoherent. The quantity of water generally used in mixing is not capable of dissolving more than one-thousandth of the calcium sulphate with which it is in contact; but, by this process of dissolving the hemihydrate and precipitating the dihydrate, it suffices for the conversion of the whole.

"The existence of the supersaturated solution on which the above explanation depends is not a mere inference, but may be proved by an experiment originally due to C. Marignac.[1] A quantity of plaster is shaken with water for five minutes and is then filtered rapidly. The filtrate is five times more concentrated than a saturated solution of gypsum; but it soon becomes turbid, deposits crystals, and ultimately attains the normal concentration.[2]

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[1] Arch. Sci. phys. nat., **48**, 120 (1873).

[2] [The change is from about 1.2 percent $CaSO_4$ in solution to about 0.2 percent at 18°.]

"As the specific gravity of the hemihydrate is 2.75 and that of the dihydrate is 2.32 the setting is accompanied by a contraction of about 7 percent.[1] This appears at first sight to be contrary to experience, as the utility of plaster in the preparation of casts is known to depend on its power of filling the mould by its expansion and so taking a sharp impression of its surface. It appears probable that the setting really involves two distinct processes. The crystals of the dihydrate which at first separate are not identical with gypsum, which is monoclinic; but consist of a second, rhombic modification, which subsequently passes into the stable form.[2] It was found by van't Hoff that the process was actually accompanied by a large contraction, followed by a smaller expansion. Microscopical examination also proves that such a change from a rhombic to a monoclinic modification of gypsum really occurs.

"The above account fairly represents the course of events in the setting of ordinary plaster of Paris. . . . The setting of plaster may be modified considerably by the presence of soluble salts in the water used for mixing it. Some salts, such as potassium sulphate accelerate the conversion of the hemihydrate into gypsum, while others, such as borax, retard it. It has been found[3] that the substances which accelerate the change are those which increase the solubility of gypsum, and conversely, that those which retard the change lessen the solubility. This action of catalytic agents is of great importance in the setting of cements. The same catalyst may affect different cements in very different ways. For example, potassium sulphate, which greatly accelerates the setting of plaster, retards that of lime and Portland cement.

"The rapidity of setting is also influenced to a very marked

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[1] $2(CaSO_4)_2H_2O$ = 290; H_2O = 18; $CaSO_4.2H_2O$ = 172; volume before setting $= \frac{290}{2.75} + \frac{3 \times 18}{1} = 159.5$; volume after setting $= \frac{2 \times 172}{2.32} = 148.1$, a contraction of 7 percent.

[2] Davis: Jour. Soc. Chem. Ind., 26, 727 (1907).

[3] Rohland: Zeit. Elektrochemie, 14, 421 (1908).

degree by the addition of substances which interfere with the formation of crystals, that is, substances of a colloidal character. The addition of a sufficient quantity of such a colloid as gelatine to ordinary plaster completely inhibits the formation of crystals, while the addition of a much smaller quantity merely retards the setting. The 'retarders' added in the manufacture of wall-plaster, for the purpose of prolonging the time during which the plaster may be manipulated without injury, are of a gelatinous character.

"This mode of setting by crystallization from supersaturated solution is not peculiar to calcium sulphate. Many other salts capable of existing in an anhydrous and in a hydrated form behave in the same way. The experiment is readily performed with sodium sulphate or with the double sulphate of potassium and calcium. The ready solubility of these salts in water renders them useless as cements; but anhydrous barium metasilicate sets by a process of simple hydration, forming a cement of exactly the same character as plaster:

$$BaSiO_3 + 6H_2O = BaSiO_3.6H_2O$$

Although the existence of a solution of the anhydrous modification supersaturated with respect to the hydrate, has not been directly proved, there can be no reasonable doubt that the mechanism of the process is identical with that of the setting of plaster."

While the ratio of the solubilities of plaster of Paris and of gypsum are large, the absolute solubilities themselves are small, 1.2% and 0.2%. The case of thorium sulphate is, therefore, a more striking one.[1] When finely powdered thorium sulphate was shaken with water at 25° a solubility of 27 parts $Th(SO_4)_2$ per 100 parts water was obtained in five minutes whereas this dropped to 2.26 parts at the end of forty-eight hours owing to the crystallization of the hydrated salt $Th(SO_4)_2.9H_2O$. By taking suitable amounts of the anhydrous salt it was sometimes possible to get it to dissolve completely, the stable hydrate only precipitating after long standing.

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[1] Roozeboom: Zeit. phys. Chem., 5, 206 (1890).

While there is no reason to doubt the existence of an instable rhombic and stable monoclinic modification of gypsum, the change from the less stable to the more stable one may be accompanied by an increase in volume without this being much help in explaining why plaster has the power of filling the mould by its expansion. The specific gravity of 2.32 given by Desch is the value for the stable form of gypsum and consequently gypsum does have a greater true density than the corresponding mixture of plaster and water. Desch has pointed out that we get radiating groups of interlocking crystals; but he has apparently overlooked the fact that such an arrangement leaves spaces between the crystals and that a plaster cast is porous as a matter of fact. The apparent density of a plaster cast is less than that of the plaster and water constituting it. When casting aluminum bronze it is very difficult to keep the metal from being porous; with plaster of Paris the only precaution taken is to avoid an excess of water. If Desch had paraffined a plaster cast and then determined its volume instead of calculating it, he would have worded the passage differently.

While it is true that colloids are added to retard the setting of plaster, it does not necessarily follow that every colloid will act in this way. The essential thing is that the colloid shall act as a protective colloid; in other words it must be adsorbed markedly by gypsum. There are apparently no experiments to show that those colloids have the least retarding action which are the least effective in keeping gypsum in colloidal solution.[1] It is practically certain, however, that such a relation exists.

The general results of this paper are as follows:

1. The setting free of water vapor from gypsum or from plaster of Paris is a slow reaction.
2. Though there is an inversion point for gypsum and plaster at 107° and 971 mm, gypsum can be heated to 200°

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[1] There is an interesting experimental study by Troxell: Am. Jour. Sci., (4) 41, 198 (1916).

without being changed completely to plaster, provided the heating is done sufficiently rapidly.

3. By prolonged heating at 110° gypsum can be converted quantitatively into anhydrous calcium sulphate.

4. The German practice in making plaster of Paris is not to heat the gypsum above 130° whereas the American practice appears to be to heat to 200°. The heating must be more rapid in the second case than in the first, provided the kilns are otherwise the same.

5. There seem to be no data as to the difference in quality of the plaster obtained by calcining at 130° or up to 200°.

6. There is no inversion temperature at 128° and none at 194°. The work of van't Hoff appears to be final so far as inversion points go.

7. There is only one modification of anhydrous calcium sulphate; but its properties vary considerably with the conditions of formation.

8. Anhydrous calcium sulphate may set more rapidly than plaster or very much more slowly. All intermediate values could probably be realized and some few of them have been.

9. Anhydrous calcium sulphate may hydrate without setting or it may not hydrate to any appreciable extent.

10. The properties depend on the degree of agglomeration and these are determined both by the temperature and the time of heating.

11. The rate of setting can be increased by grinding the anhydrous calcium sulphate.

12. When people report that an anhydrous calcium sulphate, obtained in a given way, will or will not set, they are often referring to the behavior without grinding.

13. It is commercial practice in America to convert an apparently dead-burned plaster, obtained by heating at 200°–300°, into a slow-setting plaster by grinding.

14. It is possible in the laboratory to change a dead-burned plaster, obtained by heating at about 600°, into a slow-setting plaster by grinding.

15. If a dead-burned plaster is ground to a diameter of 0.005 mm or less, it will set fairly rapidly with water. A similar result could probably be obtained by starting with anhydrite; but the experiment has not been tried.

16. When the diameter of the particles in a dead-burned plaster is about 0.05 mm the plaster will not set. This statement does not necessarily apply to a particle of that apparent size which is a porous mass really made up of very much smaller particles.

17. It seems desirable to follow the American practice and to call all anhydrous calcium sulphates flooring plasters if they set with water but less rapidly than plaster of Paris.

18. The German equivalent for flooring plaster should be Estrichgips; but some Germans seem to wish to limit the term Estrichgips to certain flooring plasters.

19. The volume occupied by crystallized gypsum is less than the sum of the volumes of the plaster and the water corresponding to it.

20. Since a plaster cast is porous, its volume may be, and apparently is, greater than the sum of the volumes of the plaster and water from which it was made.

21. Though gypsum apparently sets first to an instable rhombic modification and then to a stable monoclinic form, this cannot be the important factor in determining that one gets sharp casts with plaster.

22. The precipitation of the gypsum in radiating interlocking crystals is what fills the mould; but the change to the more stable and less dense form may then give an added thrust and produce still sharper impressions.

23. The setting of plaster may be retarded by adding flooring plaster, by adding protecting colloids to the water, or by adding dissolved substances which decrease the solubility of gypsum.

24. The setting of plaster of Paris can be accelerated by adding to the water dissolved substances—usually electrolytes—which increase the solubility of gypsum.

Cornell University

NEW BOOKS

A System of Physical Chemistry. *By William C. McC. Lewis. 19 × 13 cm; 2 vols. pp. xiv + 523; vii + 552. New York: Longmans, Green & Co., 1916. Price: $2.50 net each volume.*—In the preface the author says: "The title which has been employed requires, perhaps, a word of explanation. The 'System' consists in regarding all physico-chemical phenomena as being capable of separation into two classes: first, phenomena exhibited by material systems when in a state of equilibrium; and, secondly, phenomena exhibited by material systems which have *not* reached a state of equilibrium. It is clear that this is not only a perfectly natural division but likewise a perfectly general one, since any conceivable material system must belong to one class or the other. By emphasizing this idea I hope to have impressed upon the reader's mind the fundamental co-relations which exist between what might at first sight appear very widely different phenomena. It has been my endeavor to get as far away as possible from the 'selected chapter' method of treatment, which, however necessary and suitable in a preliminary accumulation of facts, is very liable to cause the student to lose sight altogether of the essential unity of his subject."

Evidently Gilbert knew his countrymen when he commented on the singular fact that every boy that is born into this world alive is either a little Liberal or else a little Conservative. The reviewer had supposed that the important distinction between systems in equilibrium and not in equilibrium had been hinted at in Mellor's title "Chemical Statics and Dynamics." The fundamental classification is not adhered to in all its simplicity because the author has "divided the book into three parts, in which the phenomena exhibited by systems in equilibrium and not in equilibrium are treated, first, from the 'classical' kinetic standpoint only; then independently from the thermodynamic; and finally from the standpoint of thermodynamics and the new or 'modified' principles of statistical mechanics." As a matter of fact things are not as bad as one might assume from this quotation. No subjects are presented more than twice because the author takes up only radiation phenomena and the quantum theory in the third part, under considerations based upon thermodynamics and statistical mechanics.

The author's evidently extensive knowledge is apparently of the acquisitive and not of the critical type. He accepts all work at its face value like Tomlinson. "This I have read in a book," he said, "and that was told to me, and this I have thought that another man thought of a Prince in Muscovy." All the regular mistakes are here. The special limitations of the van't Hoff formula are not emphasized. Methyl orange is treated as a strong acid. The distribution of acetic acid between benzene and water is discussed without a word as to the increased miscibility caused by the acetic acid. The limitations are not emphasized in the theory of isohydric solutions, and consequently the discussion of the solubility product is unsatisfactory. The author speaks of the Gibbs-Helmholtz formula when he means the Helmholtz formula and he uses the Gibbs deduction in regard to dissolved substances to prove that suspended substances will tend to concentrate in the surface film. On the other hand he does write the formula of calomel as Hg_2Cl_2 when discussing concentration cells, p. 193, though he does not point out that the calculation comes out exactly the same whether one postulates the formula Hg_2Cl_2 or HgCl and he therefore does not show why we take the double value. The book is neither so interesting nor so good as Mellor's "Chemical Statics and Dynamics," but it covers a great deal more ground. *Wilder D. Bancroft*

Outlines of Industrial Chemistry. *By Frank Hall Thorp. Third revised and enlarged edition. 22 × 15 cm; pp. xxii + 665. The Macmillan Company, 1916. Price: $3.25.*—The book is divided into three parts: inorganic chemistry; organic chemistry; metallurgy. Under inorganic chemistry the author takes up: sulphur; sulphuric acid; salt; hydrochloric acid and sodium sulphate; chlorine industry; nitric acid; ammonia; potash industry; fertilizers; lime, cement, and plaster of Paris; glass; ceramic industries; pigments; bromine; iodine; phosphorus; boric acid; electric furnace products; arsenic compounds; water glass; peroxide; oxygen; sulphates; cyanides; carbon bisulphide; carbon tetrachloride; manganates and permanganates. Under organic industries are listed: destructive distillation of wood; destructive distillation of bones; illuminating gas; coal tar; mineral oils; vegetable and animal oils, fats, and waxes; soap; candles; glycerine; essential oils; resins and gums; starch, dextrin, and glucose; cane sugar; fermentation industries; explosives; textile industries; paper; glue; leather; plastics. The subdivisions under metallurgy are: metallurgical processes; roasting; iron and steel; copper; lead; zinc; cadmium; tin; silver; gold; platinum; mercury; aluminum; nickel; sodium; arsenic; antimony; bismuth; magnesium; alloys.

Since the book deals primarily with industrial chemistry the author is interested only in what is done and not in why it is done. It is only every now and then that he gives anything in the way of theory. When he does, pp. 51, 583, 535, the results are not always absolutely satisfactory.

"Saline or alkaline waters, or those whose content of alkali sulphates and chlorides has been artificially raised by purification methods, as above, may give trouble in steam boilers by causing 'priming,' *i. e.*, the passage of water particles, mixed with the steam, from the boiler. Priming is associated with foaming, resulting from much dissolved matter, or due to finely-divided suspended particles. When water contains a great number of suspended fine solid particles, each serves to release steam bubbles in its immediate vicinity, and this increases the space occupied by the water in the boiler, *i. e.*, foaming is caused."

"The exact nature of tanning was for long not understood, two theories being maintained. The physical theory held that the hide fiber is merely coated with a layer of the tan-stuff, which prevents adhesion of the fibers on drying; the chemical theory assumed a true chemical combination between tan-stuff and hide substance. At the present time it is generally thought that the tanning agent is adsorbed on the surface of the fiber. Only substances of high molecular weight, colloidal in their nature, are capable of such adsorption; these are the vegetable tannins, chromium and aluminum hydrates produced by hydrolysis of their salts, and aldehydic condensation products in the case of oil and formaldehyde tannages."

"Wool is dyed with acid colors by boiling in baths containing free sulphuric acid and 10 to 20 percent Glauber's salt. The former sets free the color acid and reduces its solubility by driving back its dissociation in accordance with the law of mass action, while the latter acts as a restraining assistant, and promotes level dyeing by driving back the dissociation of the sulphuric acid, thus decreasing both the amount of the color acid set free, and the lowering of its solubility.

There are a few technical slips. The calcium carbide furnace, p. 266, is not the one used at Niagara Falls. The reviewer had supposed that the making of barium hydroxide in the electric furnace, p. 268, was given up when the company failed which patented the process. The details in regard to the manufacture of carborundum, p. 265, are some of them unexpected.

The book is a remarkably good one as a whole and will be of value as a reference book. It is of course a question whether we need most a condensed book like this, or a more elaborate one in many volumes. The reviewer would like to see the latter but it is probable that the author knows his audience or his publisher better. *Wilder D. Bancroft*

The Utilization of Waste Products. *By Theodor Koller. Second revised and enlarged English edition. 22 × 16 cm; pp. viii + 327. London: Scott, Greenwood & Son, 1915. New York: D. Van Nostrand Company. Price: $3.00 net.*—The subject is taken up under the following headings: the waste of towns; blood and slaughter-house refuse; fat from waste; tannery waste; leather waste; fur and feather waste; waste horn; fish waste; mother-of-pearl waste; vegetable ivory waste; waste wood; cork waste; waste paper and book-binders' waste; the by-products of paper and paper-pulp works; the waste produced in the manufacture of parchment paper; wool waste; silk waste; the waste waters of cloth factories; cotton spinners' waste; jute waste; utilization of rags; coloring matter from waste; residues in the manufacture of aniline dyes; dyers' waste waters; waste produced in butter making; molasses; the waste liquids from sugar works; fruit; waste products of the manufacture of starch; brewers' waste; wine residues; India rubber and caoutchouc waste; amber waste; utilization of turf or peat; manufactured fuels; illuminating gas from waste and the by-products of the manufacture of coal-gas; by-products in the treatment of coal-tar oils; ammonia recovery; petroleum residues; by-products in the manufacture of rosin oil; soap-makers' waste; alkali waste and the recovery of soda; sulphur; salt waste; gold and silver waste; platinum residues; iridium from goldsmith's sweepings; metal waste; tin plate waste; calamine slimes; waste iron; by-products of the manufacture of mineral waters, infusorial earth; meerschaum; mica waste; slate waste; broken porcelain, earthenware, and glass; utilization of waste glass.

This is an ambitious programme and it has been carried out in an interesting way, though the chapter on scrap tin and the omission of the Chance-Claus process under sulphur will scarcely increase one's confidence as regards details. There is an interesting paragraph on mother-of-pearl waste, p. 69: "A substance, which formerly could not be utilized, is the lining cut out by button-makers from the shells, the innermost layer of which is the so-called mother-of-pearl. The suggestion was made to convert this waste into a fine powder, when a soft bronze powder, of a silky, metallic luster, was obtained, which could be employed in many ways, especially since it can be colored to any shade. The pulverization of the mother-of-pearl waste is accomplished in the same manner as that of wood which is to be worked up into wood-pulp; *i. e.*, the waste is ground by a suitable rotating grindstone, in such a manner that it is first beaten to pieces, and then brought into a cylinder, in which it is pressed on the grindstone by means of a piston. The powdered mother-of-pearl obtained in this manner is then levigated, and, after drying, brought on the market with or without previous dyeing. In order to convert mother-of-pearl into a glittering powder, suitable for makers of artificial flowers, the shells are first treated with high-pressure steam, after which they can readily be powdered."

The author treats the formation of sulphur colors as a special case under the utilization of the waste from dye-wood extracts, p. 133. "Croissant and Bretonière of Lavalle gave a detailed account of their work in this direction in 1875. In the first place, this concerns the solid dye-wood extracts, each of which contains its own peculiar tannin. Now gallic acid, a product of the decomposition of tannic acid, on heating to about 250° C, gives metagallic acid. The chemists named therefore treated logwood extract by the same reaction, when they obtained an evolution of carbon dioxide and a black voluminous substance, insoluble in water but readily soluble in alkalies, and readily precipitated from these solutions in the form of brown flocks. With solutions of different metallic salts it gave variously colored precipitates. This decomposition of logwood extract, accompanied by the evolution of carbonic acid gas, also takes place at 200° C in the presence of caustic alkalies. In the latter case there is obtained the soluble alkali salt of an acid analogous to metagallic acid, which is precipitated from its solutions on the addition of other acids or of metallic salts. One important point is that the alkaline solution of this compound has a very strong direct dyeing power for vegetable fibers. If, instead of the natural coloring matters, the process is applied to other organic substances, there is known to result by the action of the alkalies a salt of oxalic acid, *e. g.*, from sawdust. The reaction, however, takes quite a different course if sulphur be at the same time introduced into the compounds. Either the sulphur enters into direct combination with the substance without the elimination of any element, as in the case of the aloe, or, as more frequently happens, the sulphur unites with a portion of the hydrogen of the organic substance to form sulphuretted hydrogen, which is volatilized, the organic substance thus becoming reduced. In both cases, however, and from many organic materials, there are produced in this manner new substances, which act as substantive dye-stuffs for animal and vegetable fibers, and produce intense and fast shades without the assistance of a mordant." *Wilder D. Bancroft*

The Flotation Process. *Compiled by T. A. Rickard. 23 × 16 cm; pp. 364. San Francisco: Mining and Scientific Press, 1916. Price: $2.00.*—In the preface Mr. Rickard, who is the editor of the *Mining and Scientific Press*, says: "This book has been prepared to meet the need of the hour. Flotation is engaging the attention of a rapidly increasing number of metallurgists, mill-men, and mine-owners. Information on the subject is lacking. The only book heretofore issued was written four years ago and is now out of date. In 1912 the flotation process had hardly won a foothold in the United States; today fully 50000 tons of ore are being treated daily by the frothing or bubble levitation method. In

July, 1915, the *Mining and Scientific Press* began to publish a series of articles describing current progress in this new branch of metallurgy. These were followed by a number of interesting contributions on the theory of the subject. All of them are reproduced in this volume. They claim no finality. The physics of flotation is still a riddle unsolved; but the beginnings of investigation have been made. In the pages that follow will be found the rudiments of a connected theory explaining the phenomena underlying the life and activity of the metallurgic bubble."

The volume consists of thirty-seven papers by different people. It is interesting to note that the amount of oil has decreased from one ton or more of oil per ton of ore in the Elmore bulk-oil process to about one-third of a pound of oil per ton of ore in the modern froth flotation. It is also interesting to note, p. 56, that at Mount Morgan a mixture of 95 percent of eucalyptus oil with only 5 percent of oleic acid gave a concentrate containing 47 percent silica, thus showing the power of oleic acid to float silica.

On p. 112 James Hebbard reports that any material below a certain size is floated owing to the density of the solution, regardless whether the material is gangue or mineral. For this reason if the finer particles of gangue were not eliminated before treatment they would be floated with the mineral and would lower the value in metals to such an extent as to make the flotation product unmarketable.

This is a very useful book though perhaps the less said about the theoretical side the better. The various authors pay no especial attention to facts when they start discussing the theory. It is quite immaterial to them whether they say that lowering the surface tension of a liquid promotes or retards the formation of bubbles, and the things they do with surface tension are almost unbelievable. *Wilder D. Bancroft*

Laboratory Manual. *By William McPherson and W. E. Henderson. 21 × 15 cm; pp. v + 141. Boston: Ginn and Company, 1915. Price: 60 cents.*—As the authors say in the preface, the problem in making a manual for use in introductory chemistry is one of selection. Consequently, it is always interesting to see what new experiments have worked back from the advanced courses to the introductory course. We have passed through the stage in which experiments illustrating ionization were novelties and now we find experiments in colloids putting in their appearance. There are experiments with colloidal antimony sulphide, and colloidal ferric oxide (wrongly called FeO_3H_3). There is an experiment on coagulation, one on the protective action of gelatine, and one on the precipitation of one colloid by another. There is even an experiment on the emulsification of kerosene in water, and, in the next edition, we shall probably find one on the emulsification of water in kerosene. This is as it should be. The reviewer has an indistinct vision of a time when there will be a course coming after the present introductory course in physics and before the present introductory course in chemistry, which will consist almost entirely of colloid chemistry because that is so pre-eminently the chemistry of every-day life. *Wilder D. Bancroft*

EMULSIONS AND SUSPENSIONS WITH MOLTEN METALS

BY H. W. GILLETT[1]

The object of this paper, which is written at Prof. Bancroft's request, is not to present any new information, but to suggest a line of thought.

In the refining of aluminum chips to ingot a loss of 30 percent of the metallic content is common, and a 15 percent loss represents very good practice. In a study[2] of these losses it was found that the cause for the high loss is not primarily the ease of oxidation of aluminum, but the failure of the globules to coalesce. That is, the loss is not due to oxidation in the furnace unless abnormally oxidizing conditions obtain there, and is not preventable by retorting, vacuum furnaces, electric furnaces, etc. Commercial aluminum chips from the machine shops of the automobile manufactures contain about 20 or 30 percent of the total weight that will pass a 20 mesh sieve and are about 0.005" thick. There is usually not less than 3 percent and sometimes 15 percent of cutting oil or compound and usually not less than 5 percent and sometimes 15 percent of very fine dirt, such as floor sweepings mixed with the chips.

If one tries to melt down aluminum chips in the way brass chips would be melted, the larger and thicker chips melt down to fairly large globules that succeed in breaking through the skin of dross, getting into true metallic contact with each other and coalescing into a pool of metal that can be poured satisfactorily. But the tiny droplets formed by the melting of the smaller chips are so microscopic in size and so very light in weight that they cannot break through the honeycomb of oxide and dross about them. So, instead of going down where they are wanted, they remain in the dross.

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[1] Published by the permission of the Director of the Bureau of Mines.

[2] H. W. Gillett and G. M. James: "Melting Aluminum Chips," Bureau of Mines, Bull. 108 (1916).

In order that as many of the medium sized drops as possible may not be too viscous to flow down, the temperature is raised far above the melting point. When the very hot dross, which is dry and powdery, is skimmed off and reaches the air, the tiny entangled globules burn up at once, with a thermit-like behavior. The pool of coalesced metal even in the open air takes on a thin coat of oxide which then protects it from further oxidation.

So while oxidation (and nitridation as well) is the ultimate cause of the loss, this oxidation would not take place save for the very finely divided physical state of the metal.

Two methods serve to reduce the loss by promoting coalescence, and both are in commercial use, though the details of the methods appear to be known only by a few refiners. One is the "puddling" process where the chips are melted in an open iron pot, small amounts being added at a time, and each addition being thoroughly stirred and pushed into the main mass, the temperature being very carefully kept only just above the melting point, so that the mass is pasty, but not truly fluid.

By the constant working over of the mass, the tiny globules are squeezed together with enough force to break the entangling film and bring them into metallic content. Finally, after the mass of metal surrounds the particles of dirt and oxide instead of the honeycomb of dirt surrounding the globules, *i. e.*, the disperse phase of the emulsion—using this term loosely to include suspensions also—has been reversed, the mass is heated up so that the dross will rise. The other method is to mix large amounts of NaCl with the chips, as a menstruum to dilute or soak up the envelope phase of dirt, preferably using with the NaCl a small amount, say 15 parts to 85 parts of NaCl, of some fluoride, such as CaF_2, to dissolve the little Al_2O_3 present, and heating without much stirring. This method also breaks up the emulsion and the tiny globules settle satisfactorily. Of course the best method is one of prevention, that is, collecting the chips without contamination by dirt. Removing the dirt by washing and screening is possible, but troublesome and expensive.

There are many other cases where a molten metal or alloy forms an emulsion or supension with a solid, a liquid or a gas.

"Floured" or "sickened" mercury, where globules of mercury refuse to coalesce when coated with talc, graphite, grease, etc., is one, and dirty molten sodium, another example of a liquid and a solid. Blue powder is an interesting example, and the problem of melting it is quite analogous to that of aluminum chips. Roeber[1] distinguishes between "physical" blue powder, or "zinc snow," which consists of particles of zinc uncoated by foreign materials, and which coalesces on melting, and "chemical" blue powder, in which each particle is coated with a skin of ZnO and probably a little SiO_2. The methods of separating the phases in this case are, distilling the volatile zinc away from the non-volatile impurities, heating under pressure, to break up the enveloping skin, as in the old Montefiore system, or dissolving off the skin by the process of Bleecker,[2] who adds the blue powder to an electrolytic bath of fused $ZnCl_2$, kept above the melting point of zinc. The $ZnCl_2$ has some solvent action on the coating and the particles migrate to the cathode and coalesce.

Another case where a small amount of a solid phase is distributed through, or emulsified with a molten metal, is in defective fusible boiler plugs, where Burgess and Merica[3] find that a network of oxides may prevent the plug from blowing out although the metal of the plug is fully molten.

Entangled oxides, the bane of the foundryman in steel, brass, bronze, and aluminum, are in a sense at least, emulsions of a solid phase with the liquid metal which are not broken up, but freeze into place and result in unsound castings. Here

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[1] E. F. Roeber: Editorial, Met. Chem. Eng., 10, 451 (1912).

[2] W. F. Bleecker: "The Electrolytic Method for the Reduction of Blue Powder," Trans. Am. Electrochem. Soc., 21, 359 (1912).

[3] G. K. Burgess and F. D. Merica: "An Investigation of Fusible Tin Boiler Plugs," Trans. Am. Inst. Metals, 9 (advance copy), 3 pp. (1915).

one either reduces the oxide chemically or attempts to collect it in a slag by means of some flux.

The retention of metal by slag in reduction and refining processes is a case of an emulsion of two liquids. In the Pattinson process we have another case where the breaking of the emulsion is essential. Metal fog in the electrolysis of fused salts is still another example. Richards[1] has recently brought this out in the cases of strontium and cerium.

The emulsion of a gas in a metal gives rise to a problem no less serious to the foundryman than that of a solid or a liquid with the molten metal, for if the emulsion is not broken, we have blowholes and porous castings.

Sometimes it is desirable to maintain an emulsion or suspension of a metal with another phase. Examples of a suspension of some solid with a liquid metal (or, more strictly of a solid with a plastic mixture of solid eutectic and liquid metal) are the "near alloys" of Friedrich[2] where such materials as cobalt silicate are mixed with an alloy of 90 Sn, 10 Cu, kept within the eutectic range.

Here the cobalt silicate is probably the disperse phase. But there are useful cases where the metal is the disperse phase within a solid.

In sherardizing, zinc dust coated with enough oxide to prevent coalescence is a necessity. In calorizing, aluminum oxide is mixed with the aluminum powder for the same purpose. Here an "emulsion" of solid metal and solid oxide, if the process is run below the melting point of the metal, is required to prevent the welding together of clean metal surfaces below the fusion point of the metal, or one of liquid metal and solid oxide to prevent coalescence of the globules, if run above the fusion point.

Emulsions of two liquid metals find a notable example in the mixture of half copper and half lead used for packing, bearings, brake bands, etc. Molten copper and lead, in equi-

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[1] J. W. Richards: "The Metallurgy of the Rarer Metals," Met. Chem. Eng., **15**, 26 (1916).

[2] See K. Friedrich: "Near Alloys," Met. Chem. Eng., **8**, 191 (1910).

librium, form a two liquid layer system, being immiscible. Yet it is possible, by the use of S or Ni as an emulsifying agent, to produce a quite uniform mixture of the two metals, though it is as ticklish a job as the foundryman often tackles. To a lesser degree, the liquation of lead or of some other low melting, immiscible phase in brass and bronze casting, offers the same problem.

Could we obtain stable emulsions of metals normally immiscible in the liquid state surely some of them, after solidification, would be industrially useful.

Useful emulsions of gases with metals are hard to find. Yet uniformly porous metals or alloys might be useful. Hannover[1] has shown that lead, made porous by an indirect method, makes a storage battery of four times the capacity for the same weight as one with solid lead plates.

The chemistry of colloids is proving of immense use to industry. It is right that the colloid chemist should deal with the system water, benzene, soap, at room temperatures at the start, for seldom is much gained by attacking the more complicated problems before the simple ones are solved.

Yet when he has flocculated and peptized, frothed and floated, long enough to bring some semblance of order out of chaos and to get some working hypotheses on the mechanism and causes of emulsions and suspensions, he may find it of use for the clarification of the present somewhat emulsified theories, as well as of practical value, if he will remember that there are other systems than water and oil and other temperatures than 0° to 100°. Molten metals and alloys, from mercury to tungsten, also offer their problems of colloid chemistry. And when the colloid chemist shall have solved only a few of the problems waiting for him in that field, the foundrymen and metallurgists at least, will rise up and call him blessed.

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[1] H. I. Nannover: "The Production of Porous Metals," Met. Chem. Eng., 10, 509 (1912).

YELLOW BRICKS

BY L. A. KEANE

In the chapter on the chemical properties of clays, Ries[1] says: "Many clays show a yellow or brown coloration due to the presence of limonite and a red coloration due to hematite; magnetite is rarely present in sufficient quantity to color the clay; siderite or pyrite may color it gray, and it is probable that the green color of many clays is caused by the presence of silicate of iron, this being specially true of glauconitic ones. The intensity of color is not always an indication of the amount of iron present, since the same quantity of iron may, for example, color a sandy clay more intensely than a fine-grained one, provided both are nearly free from carbonaceous matter; the latter, if present in sufficient quantity, may even mask the iron coloration completely. The coloring action will, moreover, be effective only when the iron is evenly distributed through a clay in an extremely fine form. It is probable that the limonite coloring clay is present in an amorphous or non-crystalline form, and forms a coating on the surface of the grains.

"All of the iron ores will in burning change to the red or ferric oxide, provided a sufficient supply of oxygen is able to enter the pores of the clay before it is vitrified; if vitrification occurs, the iron oxide enters into the formation of silicates of complex composition. The color and depth of shade produced by the iron will, however, depend on: first, the amount of iron in the clay; second, the temperature of burning; third, condition of the iron oxide; and fourth, the condition of the kiln atmosphere.

"Clay free from iron oxide burns white. If a small quantity, say 1 percent, is present, a slightly yellowish tinge may be imparted to the burned material; but an increase in the iron contents to 2 or 3 percent often produces a buff product, while 4 or 5 percent of iron oxide in many cases makes the clay

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[1] Clays, 81, 194 (1908).

burn red. There seems, however, to be not a few exceptions to the above statements. Thus we find that the white-burning clays carry from a few hundredths percent to over 1 percent of iron oxide, the more ferruginous containing more iron than the purer grades of buff-burning clays. Again, among buff-burning clays we find some with an iron oxide content of 4 or 5 percent, an amount equal to that contained in some red-burning ones. The facts, therefore, seem to indicate that the color of the burned clay is not influenced solely by the quantity of iron present.

"Seger has divided the buff-burning clays into two groups, namely: (1) those of such high iron contents as to burn red normally, but which are sufficiently calcareous to enable the lime to destroy the red iron color and form a yellow compound of iron and lime; and (2) those low in iron and high in alumina, which would normally burn pale red, but develop a yellow color due to the alumina-iron compound. He thus believes that the red coloration of the iron is destroyed by similar causes; but, on account of the lime being a stronger and more active base than the alumina, it is able to take care of a greater quantity of iron.

"Orton[1] has argued against the effect of alumina, claiming that, if this were true, synthetic mixtures should easily give the buff color, which, in his experience, it is not possible to produce. As he states, there is a great uniformity in the color of buff-burning clays, while their iron-alumina ratios fluctuate greatly; some fire-clays containing 40 percent of alumina and 0.5 percent iron, and yielding a good buff product, while others with 15 to 20 percent alumina and 2.5 percent iron burn to almost exactly the same tint. On the other hand, some clays with about the same alumina and iron content burn red. If Orton is correct, it would seem, therefore, as if the cause of this buff-burning quality must be sought for in some other direction.

"The evenness of color is apparently closely connected with the physical condition of the iron oxide, that in colloidal

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[1] Trans. Am. Ceram. Soc., 5, 389 (1903).

form giving a uniformity of shade not obtainable by the admixture of very finely ground material.

"If a clay is heated at successively higher temperatures, it is found that, other things being equal, the color usually deepens as the temperature rises. Thus if a clay containing 4 percent of iron oxide is burned at a low temperature, it will be pale red, and harder firing will be necessary to develop a good brick-red, which will pass into the deep red and then reddish purple. Seger explained the successive shades of red by assuming that the iron oxide increased its density with rising temperature.

"The brilliancy of the color appears to be influenced by the texture, as the more sandy clays can be heated to a higher temperature, without destruction of the red color, than the more aluminous ones. Alkalies also appear to diminish the brightness of the iron coloration."

"Burned clays may be of many different colors. Although the majority of clays contain sufficient iron oxide to burn red, nevertheless it is not safe to predict, from the color of the raw clay, the shade that it will burn, since some bright red or yellow clays may yield a buff brick. If considerable iron oxide is present, 4 to 5 percent, the brick usually burns red, unless much lime or alumina is also present. An excess of lime in the clay will, however, counteract the effect of the iron oxide and yield a buff brick, but a brick owing its buff color to this cause will not stand as much fire as one which owes its buff color simply to a low percentage of iron oxide."

Burton[1] says: "The clays of earths from which burnt bricks are made may be divided into two principal types, according to chemical composition: (1) clays or shales containing only a small percentage of carbonate of lime and consisting chiefly of hydrated aluminum silicates (the true clay substance) with more or less sand, undecomposed grains of feldspar, and oxide or carbonate of iron; these colors usually burn to a buff, salmon or red color; (2) clays containing a considerable percentage of carbonate of lime in addition to

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[1] Encyclopaedia Britannica, 4, 518 (1910).

the substances above mentioned. These latter clay deposits are known as marls,[1] and may contain as much as 40 percent of chalk. They burn to a sulphur-yellow color which is quite distinctive....

"All clays contain more or less free silica in the form of sand, and usually a small percentage of undecomposed feldspar. The most important ingredient, after the clay-substance and the sand, is oxide of iron; for the color, and, to a less extent, the hardness and durability of the burnt brick depend on its presence. The amount of iron oxide in these clays varies from about 2 to 10 percent, and the color of the bricks varies accordingly from light buff to chocolate; although the color developed by a given percentage of oxide of iron is influenced also by the other substances present and also by the method of firing. A clay containing from 5 to 8 percent of oxide of iron will, under ordinary conditions of firing, produce a red brick; but if the clay contains 3 to 4 percent of alkalies, or if the brick is fired too hard, the color will be darker and more purple. The action of the alkalies and of increased temperature are probably closely related, for in either case the clay is brought nearer to its fusion point, and ferruginous clays generally become darker in color as they approach to fusion. Alumina acts in the opposite direction, an excess of this compound tending to make the color lighter and brighter...

"As before stated, the marls (which usually contain from 15 to 50 percent of calcium carbonate) burn to a yellow color which is quite distinctive, although in some cases, where the percentage of limestone is very high, over 40 percent, the color is gray or a very pale buff. The action of lime in bleaching the ferric oxide and producing a yellow instead of a red brick, has not been thoroughly investigated, but it seems probable that some compound is produced between the lime and the oxide of iron, or between these two oxides

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[1] The term "marl" has been wrongly applied to many fire-clays. It should be restricted to natural mixtures of clay and chalk such as those of the Paris and London basins.

and the free silica, entirely different from that produced by oxide of iron in the absence of lime."

Burton[1] repeats much the same facts without any explanation. "In ordinary clays, and with an oxidizing atmosphere, 1–2 percent of iron oxide produces a buff color, 2–4 percent a salmon color, and above 4 percent a red color, which becomes darker as the percentage of iron increases. The presence of other impurities, however, modifies the color produced by iron oxide considerably, and this is especially the case when a large percentage of lime or magnesia is present. Some clays (commonly called marls) contain from 15 to 30 percent of lime, and although they may also contain as much as 6–8 percent of iron oxide, they fire to a light yellow or buff color. Such clays are largely used for making the well-known yellow facing bricks, which were at first made chiefly from the marls of the Thames basin, the Paris basin, etc., and are now made from artificially prepared mixtures of clay and chalk or limestone."

Since there seemed to be no plausible explanation of the action of lime in causing bricks to burn yellow, Professor Bancroft suggested that I make a preliminary study of the problem as part of my senior research. The red color of bricks is admittedly due to the red ferric oxide or haematite. It is equally clear that the yellow color is due to an anhydrous yellow form analogous to limonite; but that does not get us ahead much because we do not know what limonite is or why lime should cause the formation of, or stabilize, an anhydrous limonite. It is customary among mineralogists[2] to classify the hydrates of ferric oxide as follows:

Haematite	Fe_2O_3	Limonite	$2Fe_2O_3.3H_2O$
Turgite	$2Fe_2O_3.H_2O$	Xanthosiderite	$F_2O_3.2H_2O$
Goethite	$Fe_2O_3.H_2O$	Limnite	$Fe_2O_3.3H_2O$

Haematite occurs frequently in well-characterized crystals though often as an amorphous red mass or powder.

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[1] Thorpe's Dictionary of Applied Chemistry, 2, 76 (1912).

[2] Robinson and McCaughey: Bureau of Soils, Bull. 79, 16 (1911).

Goethite occurs in nature as a definite crystallized hydrate; but van Bemmelen[1] has shown that a definite hydrate can be obtained in the laboratory only under special conditions, the decomposition of sodium ferrite by water at 15°. A definite hydrate is not obtained by the decomposition of potassium ferrite, for instance. No other hydrate of ferric oxide is known, so the formulas usually mean nothing more than that a hydrous iron oxide of varying water content happened to be analyzed under conditions such that the percentage composition could be represented approximately by the desired formula. Haematite is black when crystalline, though red by transmitted light, and its powder is red. Turgite is deep brown; limonite is a light brown or yellow,[2] while xanthosiderite,[3] which is probably to be classed as limonite,[4] is a golden yellow-brown to brownish red. Limonite is a full yellow.[5] While it is generally true that the more hydrous the ferric oxide the yellower it is, this is not an absolute rule. Robinson and McCaughey[6] say: "By heating limonite or any hydrate of ferric oxide, it loses water, changes color, and becomes, in fact, red haematite. There is, however, no satisfactory measurement of a temperature of inversion of limonite to haematite, and it is doubtful if such an inversion point exists. At ordinary pressures limonite does not lose water appreciably at any temperature which may be realized under field conditions.

"The literature on ferric hydrates is voluminous and contradictory. It appears, however, from laboratory investigations that ferric hydroxide, when first precipitated, is dark red. On standing it apparently becomes more compact,[7]

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[1] Die Absorption, 145 (1910).

[2] A golden yellow oxide having the formula of limonite has been patented by Ramage and Sperry, U. S. Pat. 691,324 (1902).

[3] Schmid: Pogg. Ann., 84, 495 (1851).

[4] Fischer: Zeit. anorg. Chem., 66, 43 (1910).

[5] Dammer's Handbuch der anorganischen Chemie, 3, 304 (1893).

[6] Bureau of Soils, Bull. 79, 18 (1911).

[7] [This statement must not be interpreted as meaning that the precipitate becomes coarser.]

and the color changes toward the characteristic yellow of limonite. Tommasi,[1] who has done much work on this subject, divides ferric hydrates into two series, *a* and *b*. The red or *a* series is obtained by precipitation with alkalies from solution. This series is easily soluble in dilute acids and is dehydrated by boiling. The yellow or *b* series is realized by the oxidation of ferrous hydroxide, ferrosoferric hydroxide, or ferrous carbonate. The *b* series is sparingly soluble in dilute acids and retains the water of hydration on boiling. The red or *a* series represents the condition of the freshly precipitated hydroxide. On standing it becomes yellow and occupies less bulk. Freezing and thawing and boiling hastens the process."

From this summary it is clear that the yellow color of certain hydrous ferric oxides depends on other factors than the percentage composition. With that settled for the moment we can now consider the effect of lime on the color of bricks. The yellow color cannot be due to calcium ferrite because Percy reports that this is black.[2] "I found that a mixture of sesquioxide of iron and lime in certain proportions yields a well-melted product. A mixture consisting of 160 grains of pure sesquioxide of iron and 100 of white marble (= 56 grains of lime)—that is in the ratio of Fe_2O_3 : CaO—was exposed in a covered clay crucible to a high temperature. It was perfectly melted, and when broken across resembled a black opaque, vitreous slag: the crucible had one large perforation. In a second experiment a mixture according to the same formula, of 40 grains of sesquioxide of iron and 25 of carbonate of lime, was heated in a clay crucible lined with platinum foil. It was perfectly melted and escaped through the crucible. Recently this reaction has again been investigated with the following results: An intimate mixture of 190 grains of sesquioxide of iron and 6.5 grains of lime was kept heated to whiteness in a platinum vessel during several

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[1] Bull. Soc. chim. Paris, (2) 38, 152 (1882).

[2] Percy's Metallurgy: Fuel, 78 (1875).

hours in a muffle, the atmosphere of which is oxidizing, and left to cool in the furnace. The product appears to have been perfectly melted, and consisted of a mass of interlacing acicular crystals, exceeding an inch in length: lustre, dark bright metallic; fracture, uneven and lustrous; very brittle; when in powder resembled brown iron ore in color; sp. gr. 4.693; it was magnetic.

"Its percentage composition was found by analysis to be as follows:

Sesquioxide of iron	73.39
Protoxide of iron	0.72
Lime	24.50
Silica	1.35
Alumina	0.10
	100.06

This compound may, in respect of composition, be regarded as *magnetite*, in which the protoxide of iron has been replaced by lime; or as a *spinel*, in which alumina has been replaced by sesquioxide of iron. It is analogous to the mineral termed magnoferrite, of which the formula is $MgO.Fe_2O_3$."

I have tried heating various mixtures of rouge and lime and of rouge, lime, and alumina to different temperatures below those at which the mixtures fused. In no case was a yellow color obtained. This statement applies only to cases in which an appreciable amount of solid rouge is taken. It does not hold when an oxide is precipitated on or with the alumina.

The yellow color cannot be due to an iron silicate because ferrous silicate is a deep, olive-gray and ferric silicate appears to be instable.[1] "It is now known that when sesquioxide of iron is exposed to a high temperature, it is reduced to magnetic oxide without the intervention of any reducing agent; and that when a mixture of sesquioxide of iron and silica is strongly heated, even in the presence of atmospheric air, silicate of protoxide of iron is formed with evolution of oxygen."

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[1] Percy's Metallurgy: Fuel, 71 (1875).

If the yellow color is not due to a calcium-iron or to an iron-silicate salt, the next hypothesis is the rather despairing one of Burton[1] that "some compound is produced between the lime and the oxide of iron or between these two oxides and the free silica, entirely different from that produced by oxide of iron in the absence of lime."

Percy reports upon a number of slags containing varying amounts of lime, iron oxide, alumina and silica.[2] No one of them showed any trace of yellow. Both red and yellow bricks fuse to slags like those recorded by Percy, thus showing that the hypothetical compound, if formed, must be stable at a lower temperature and, therefore, should be easy to isolate. If we were dealing with a definite compound of lime and iron, or lime, iron and silica, we ought to be able to get the color by heating a synthetic mixture of the ingredients. Orton[3] has pointed out that other factors come in.

"The powerful influence of the physical factor is well realized by all who have tried to stain clays artificially to some particular tint. Iron oxide in masses of appreciable size becomes red on calcination at a low temperature, changing gradually to a bluish black as the temperature increases. When added to a clay, it appears as dark-colored grains in the matrix of the clay, which is itself changed little or none by this addition. Even when we grind ferric oxide to an impalpable powder, and distribute it into a clay most perfectly, it merely causes a darkening of the color, nothing like the buff or red colorations of natural clays.

"The failure of these simple synthetic attempts to produce iron colors in clays leads us to a study of the condition of the iron in natural clays. We find two states easily distinguished. First, the precipitated or colloid form, whose fineness exceeds all method of measurement and which we may fairly assume to be almost molecular. Second, the concretionary or granular form, in which its grains or crystals are of appreciable size.

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[1] Encyclopaedia Britannica, 4, 519 (1910).

[2] Percy's Metallurgy: Fuel, 72 (1875).

[3] Trans. Am. Ceram. Soc., 5, 382 (1903).

"The precipitated form is necessary to the development of either a buff or red color. We may easily verify this by precipitating artificially some ferric hydroxide into a fluid slip of clay. It is possible to produce colors as uniform and as free from specks as natural clays but it is not possible to get some of the tints of natural clay or to get as much color for the amount of iron used as is developed by Nature's methods. As shown in discussing the origin of the shale clays, the iron has been associated with the clay minerals from the very time of formation. The primary clay was usually deeply stained by the solution of iron which formed with it. The soft gelatinous hydroxide has enveloped its grains from their very origin, and left each tiny particle covered by its coloring film. Every succeeding process tends to increase this uniformity, grinding, transportation, erosion, and deposition in swamps, all tend to increase the iron and to reduce its blend to perfection.

"Thus in the ordinary red-burning shale-clay, for instance, it becomes impossible to distinguish the hydroxide from the clay minerals. The sand, and the mica, and concretionary minerals of all sorts, can readily be separated by screens or by sedimentary processes; but the pulp which remains inseparable to the end, contains the bulk of the iron, and is red-burning, while the coarser matters which have been separated out, may burn light or dark or speckled, but hardly red. In fact, the question has been raised as to whether iron is not chemically combined as a part of the clay substance. No proof of this view has ever been attempted, and all the evidence obtainable points the other way."

Since there is no evidence of any binary or ternary compound of iron with lime and silica which is yellow, and since hydrous ferric oxide may be yellow, the most reasonable thing to do is to attempt to account for the yellow color in bricks as being due to ferric oxide in some way and not as being due to any compound with lime or silica. There is nothing impossible about this. In addition to ordinary silver we have blue, yellow and red silver, the color being a function of the size of the particles. These forms of colloidal silver are not very stable as a rule; but this is largely a question of conditions. Baker[1] reports one case where colloidal silver was apparently stable enough to cause trouble in a technical process. Since this paper seems to have been overlooked by writers on colloid chemistry, I quote it in full.

"In some contributions to the metallurgy of lead, published in the Philosophical Magazine in 1862, I attributed a certain pink tint, occasionally seen in white-lead corrosions, to the presence of small quantities of copper. As the results of any experiments upon the corrosion of lead by the combined action of fermenting bark, acetic acid vapor, and atmospheric oxygen can only be arrived at after the expiration of ten weeks or three months, the progress of further investigation in this matter has necessarily been slow. I have been unable to isolate the coloring matter; but I wish to correct the statement that the pink color is due to copper, and to detail some conclusive proofs that it is caused by finely divided silver.

"Having obtained many tons of lead which contained only traces of copper, I found in several instances the pink color still quite evident in the corrosions. By the method which had been employed for refining the metal, there could be only silver left as an impurity in any perceptible amount. I, therefore, sought for evidence that this substance could produce such a result. Upon analyzing 5000 grains of a perfectly white corrosion, and of one which was distinctly and uniformly pink, the result showed that the two samples differed mainly in the amount of silver.

	CuO	FeO	NiO	Ag
White corrosion	0.0050	0.0022	trace	0.0005%
Pink corrosion	0.0060	0.0022	0.0013	0.0058%

"A small quantity of silver was then added to a portion of the lead which had produced the white corrosions, and this was again submitted to the corroding action. The result

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[1] Phil. Mag., (4) 37, 344 (1869).

was a decided pink carbonate. This synthetical experiment was repeated many times with a like result upon various samples of lead which had before produced a white carbonate; and I found that the pink color begins to show at the edge of the metallic portion left uncorroded when the silver amounts to more than 0.5 oz. per ton of lead. A decided color, which is uniform throughout the mass of the corrosion, is obtained when the silver amounts to about 1.5 oz. per ton. A fracture of a dense corrosion often shows the crystalline character of the metallic lead, which is defined to some extent by the pink color as if the silver had segregated out at certain faces of the lead crystals. By the addition of a small quantity of arsenic or antimony the pink color was replaced by a dull purple; and a clear tint was only obtained when all the oxidizable metals had been removed.

"I come to the discussion of the state in which the silver exists to cause a pink or reddish reflection of light. Silver does not oxidize under the conditions of exposure to acetic acid vapor and oxygen of the air. Moreover oxide of silver and silver carbonate are themselves decomposed and reduced to a metallic state by a heat below that attained in the stacks of fermenting tan. The silver must consequently be in the metallic state. As confirming this statement I made the following experiments: Silver carbonate was triturated with white lead and water and then dried. Upon increasing the temperature, a delicate pink tint became visible upon the reduction of the oxide of silver. If a small quantity of silver carbonate be precipitated along with lead carbonate, the color upon drying and heating is more uniform, and it may be obtained exactly resembling the tint seen on white-lead corrosions.

"The color of the photographs obtained by means of silver salts is also evidence in favor of the metallic state of the silver, and I may also adduce the fact that a ray of light, when reflected ten times from a polished silver surface, is distinctly of a reddish[1] color."

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[1] [According to Percy's Metallurgy: Fuel, 33 (1875), the color is golden yellow.]

We will start with the working hypothesis that the yellow color of ferric oxide is due to the very fine subdivision, in which case we should expect to get a yellow if we precipitated the hydrous oxide under conditions such that agglomeration would be kept down to a minimum, in other words in presence of another colloid. The production of a yellow by precipitating hydrous ferric oxide in presence of hydrous aluminum oxide appears to be used technically in the production of the so-called Mars pigments. Hurst[1] says: "Under the generic name of Mars colors the late George Field, a noted color manufacturer, introduced a series of yellows, oranges, reds, and violets, owing their color to ferric oxide. Field did not publish any account of the method by which he produced these colors; but descriptions of similar products have been given by various French and German writers on pigments. These colors present no advantage over ochres and iron-reds as regards permanency or brightness of tone, but have disadvantages as regards cost. Mars yellow is made by taking equal weights of ferrous sulphate and alum, and adding a solution of carbonate of soda, thereby precipitating the iron and alumina; the precipitate is collected, washed well with water, and dried slowly. Mars orange is made by slightly calcining the yellow; Mars red is made by calcining the yellow at a red heat; Mars violet is made by calcining the yellow at a white heat. By using milk of lime instead of the soda salt the colors could be made cheaper, a plan which is in use in making some forms of iron-reds. Mars brown was made in a similar manner from a mixture of ferrous sulphate, alum, and manganese chloride. Mars colors can be distinguished from the ochres and ochre-reds by being soluble in strong hydrochloric acid, and by containing a large proportion of alumina but no silica."

Church[2] says that Mars yellow "is a kind of yellow ochre prepared artificially. It may be made by precipitating a salt of iron mixed with alum by means of caustic soda, or

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[1] Painters' Colors, Oils and Varnishes, 151 (1901).

[2] "The Chemistry of Paints and Painting," 157 (1901).

potash, or lime. The salts of iron used are either green vitriol (ferrous sulphate) or the ferric chloride. If green vitriol be employed, the precipitate gradually becomes yellow on exposure to the air. Upon the proportion of alum mixed with the iron salt depends the depth of the yellow color in the product, for the alumina precipitated with the iron hydrate acts as a diluent of the color. When lime is used as a precipitant for the iron compound (if this be green vitriol or ferric sulphate), calcium sulphate, that is, gypsum, comes down also with the ferric hydrate and basic ferric sulphate, and serves to lighten the color.

"By submitting the different varieties of Mars yellow to various degrees of heat, with or without a little nitre, a number of products of different hues are obtained, including Mars orange, Mars brown, and Mars violet. All these preparations require very thorough washing to fit them for use on the palette of the artist.

"The Mars colors are permanent when carefully prepared and thoroughly purified from soluble salts. They seem sometimes to have a slightly injurious effect upon a few of the best semi-permanent pigments of organic origin, such as the madder colors. This action may be due to the ferric hydrate in them combining with the coloring matter, and displacing some of the alumina previously united with it. In this direction it is probable that Mars yellow will be more active than the deeper-colored pigments produced by calcining it at various temperatures."

Bersch[1] recognizes the possibility of obtaining the color without using alumina. "Mars yellow, which is generally reckoned among the best artists' colors, is usually a mixture of ferric oxide and calcium sulphate or alumina. The pigment is prepared by mixing a solution of ferrous sulphate with milk of lime, when ferrous oxide is precipitated, which becomes yellowish brown on exposure to air, in consequence of the oxidation of the ferrous oxide. By heating the precipitate,

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[1] "Manufacture of Mineral and Lake Pigments," 155 (1901).

according to the temperature, different shades are obtained varying between yellow and red. In addition to Mars yellow, Mars orange and Mars red are found in commerce.

"The manufacture of this pigment is very simple: 1 part of ferrous sulphate is dissolved in 10 parts of water, and the solution mixed with milk of lime made from 1 part of quicklime and 40 parts of water. If it is desired to produce a darker shade, and especially a product to be afterwards converted into Mars orange, the amount of ferrous sulphate is increased to 2 parts. When the mixture had been made, it must be stirred for a long time, in order that the reacting substances may come thoroughly into contact. The precipitate, which at first is greenish gray, soon acquires by the action of the air the color of ferric hydroxide, which becomes deeper on drying.

"When dried and finely ground Mars yellow is heated in thin layers, it changes to dark yellow, and finally to orange-red, a similar alteration taking place to that occurring when ferric hydroxide itself is heated.

"A Mars yellow of a deeper shade, consisting of a mixture of ferric hydroxide and alumina, is obtained by precipitating with caustic soda a solution of ferrous sulphate and alum. The sodium sulphate, which is formed at the same time, must be removed as completely as possible by washing with boiling water.

"By calcining Mars yellow for a long time at a high temperature, Mars brown is produced, a fine brown pigment. The value of Mars yellow and the pigments obtained from it lies not only in their fine shade, but in their permanence, which distinguishes the majority of the iron colors."

Toch[1] mentions the Mars colors but gives no information in regard to the way they are made and ignores the alumina content. In regard to Mars orange he says that "this has sometimes been called extract of burnt sienna, because it is composed entirely of hydrate oxide of iron which has been properly precipitated and washed. It is very uniform in

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[1] "Materials for Permanent Paintings," 140 (1911).

composition, and identical with ordinary iron rust. It has generally been regarded as a perfectly safe and permanent pigment, but this is not a fact. It attacks not only every lake with which it may be mixed, but is such a hard drier that it has a tendency to crack. It makes most beautiful clear yellowish tints when mixed with zinc white, and when diluted with constant white, it has every characteristic of a lake; but, owing to its chemical composition, it darkens upon extreme exposure, and the beautiful clear tones which it produces when mixed with white have a tendency to sadden upon exposure.

"Mars red is similar in all respects to Mars orange with the exception that it has been heated until the water of combination is driven off, and while it is identical with light red, it is much more transparent. It is a soft, permanent color, and although it is supposed to affect a number of lakes, it is very doubtful whether it does; but, in order to practice precaution, it may be wise not to mix it with several of the lakes but to use the lakes over it as a glazing color. It dries well and is permanent.

"Mars violet is a very dark form of crocus martis, or Indian red. It is similar to the color known as caput mortuum, and is nothing more or less than a purple oxide of iron. It has a distinctly bluish shade, is very durable, dries well and is permanent to light.

"Mars yellow has also been called extract of ochre, or extract of raw sienna, because it is composed of the coloring matter of these two pigments. It frequently cannot be distinguished from a good quality of raw sienna, is permanent, dries well, and is translucent. It has been suggested frequently that Mars yellow, or a good form of raw sienna, should be used as a substitute for the yellow lakes; and this can easily be done when these colors are mixed with constant white. As a glazing color it is permanent; but, like all of the oxides of iron which contain water in combination, it must not be mixed with an organic color such as one of the lakes."

Nobody seems to have bothered himself with the question why a yellow is possible under these circumstances. The existence of yellow ochre in nature has convinced the painter that hydrous iron oxide does occur in a yellow form and he has naturally let it go at that. From the published accounts it is quite clear that we are dealing with an irreversible reaction, the yellow hydrous oxide agglomerating on heating to an orange, brown or red form on heating, the change being also accompanied by a loss of water. It is not a question, strictly speaking, of Tommasi's two series because it is possible to obtain a yellow either by oxidizing hydrous ferrous oxide or by precipitating hydrous ferric oxide, whereas Tommasi's theory called for a yellow color in the first case and a red one in the second. On the assumption that the yellow form is the one with the finest particles, it is easy to see that the simultaneous precipitation of hydrous alumina would tend to make the color yellow. It is not exactly obvious why one should get the same result when lime water is added to a ferrous sulphate solution containing no aluminium sulphate. The only explanation to be offered for this at present is that the simultaneous precipitation of calcium sulphate prevents the agglomeration of the yellow pigments to the red pigment.

In order to have some first-hand knowledge in regard to the Mars colors a few qualitative experiments were made. Two parts of ferrous sulphate and two of aluminum sulphate were dissolved in forty parts of water. To this was added a solution of one part of lime in eighty of water. A dirty green precipitate was formed which gradually oxidized and became yellowish brown. When air-dried the color was a light ochre. When heated slightly it darkened somewhat, the color becoming a raw sienna. Increasing the amount of ferrous sulphate in the first solution gave a darker shade while increasing the amount of lime gave a lighter shade. One part of ferrous sulphate plus three parts aluminum sulphate plus caustic soda gave a bright yellow precipitate. When washed and air-dried the color was a yellow ochre. When heated this sample darkened considerably, while further heating changed it to an iron oxide red.

In another run the aluminum sulphate was omitted. One part of ferrous sulphate was dissolved in ten parts of water. To this was added one part of lime dissolved in forty of water. The precipitate was green at first and then oxidized to a brownish yellow which was a shade darker than in the preceding runs. On heating, this behaved quite differently from the others, changing to an olive-gray.

When a fairly concentrated solution of ferric chloride was boiled, a bright yellow precipitate was obtained which turned the characteristic red on heating, the one heated to the higher temperature being more of a purple-red.

Instead of using lime or caustic soda as a precipitating agent, we may use sodium carbonate. Equal parts of ferrous sulphate and aluminum sulphate in the dry state were mixed thoroughly and then a solution of sodium carbonate added. This gave a yellow ochre verging on the orange. Increasing the amount of ferrous sulphate darkened the color. Increasing the amount of aluminum sulphate seemed only to make the color lighter. When heated these went over into a reddish brown, changing at the highest temperatures (in the blast lamp) to a brownish black. A good deal more work on these colors had been planned; but the loss of time due to the fire in Morse Hall cut down the time available. The experiments show the same general results as those given in the books. One would like, of course, to know why the presence of lime and the absence of alumina caused the precipitate to turn an olive-gray when heated. It looks as though this would not be difficult to work out but it would need time. One thing is clear, however, and that is that the alumina tends to keep the iron oxide from turning red, which is exactly what should happen if the yellow color is due to the iron oxide being in a very finely divided state. The analogy between the Mars colors and the yellow bricks is not a close one because the yellow in the pigments is due to hydrous iron oxide while this is undoubtedly not the case with the bricks. The Mars colors are cited as being technical products in which the fine division of the iron oxide is maintained by alumina.

According to the theory as outlined, the alumina seems to be the prime factor in determining the yellow color of bricks. With clay high in alumina we get yellow or buff bricks for a suitable percentage of iron. If we keep the iron constant and reduce the percentage of alumina, we get a clay which burns red. If we add lime to our clay, the lime will combine with the silica when the clay is heated, setting free alumina and the brick will burn yellow or buff. It is therefore the free alumina which counts and not the total alumina. The general conclusion may, therefore, be formulated that a clay containing three to four percent of iron oxide will burn red if the free alumina is low and yellow or buff if the free alumina is high. The question of how to determine the amount of free alumina can fortunately be left to somebody else. This explanation can be checked very simply. If the importance of lime consists in its setting free alumina, the addition of an acid like sulphuric acid should cause the appearance of the red color, quite regardless of whether we assume that calcium sulphate and aluminum silicate are formed or calcium silicate and aluminum sulphate. This has actually been observed by Biedermann and Gabriel.[1] There had been trouble owing to the formation of red patches on yellow tiles. Analysis showed that the red spots contained considerably more sulphate than the yellow portions, the sulphate being present apparently as calcium sulphate. The trouble was, therefore, due to sulphuric acid in the kiln gases.

Since the alumina in the Mars colors does not prevent the agglomeration of the ferric oxide, when it dehydrates, it was hoped that perhaps a yellow brick would turn red if heated to a higher temperature. Unfortunately the brick tends to vitrify before it turns red. The experiment was an interesting one because it brought out several points which had not been foreseen by us though perfectly familiar to ceramists as we learned later. A piece of a commercial yellow brick was heated in an electric furnace. Although

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[1] Ber. deutsch. chem. Ges., 10, 1548 (1877); Kerl: Handbuch der gesammten Thonwaarenindustrie, 512 (1907).

the brick was exposed to the air, an apparent reduction took place and the resulting slag was of a dark green color. The brick was next heated in an oxyacetylene flame, but again reduction took place. Much better results were obtained on using a blast lamp. The brick assumed a decidedly red shade which was most marked at the surface. It is not surprising that the effect is less striking than with the Mars pigments because these latter contain a great deal more iron. When Mars yellow was mixed with a large excess of $BaSO_4$, SiO_2, etc., and heated, it turned red much less rapidly. The apparent reduction of the iron oxide is really a dissociation into a lower oxide. At high temperatures ferric oxide breaks down into ferrous oxide and oxygen.[1] When the brick vitrifies, ferrous silicate is formed. If the brick cools in an oxidizing atmosphere, the ferrous silicate breaks down to ferric oxide and silica. It is, therefore, not surprising that the red color should be more marked at the outside. This matter of reoxidation has been discussed by Hull.[2] "When a dark or 'flashed' burn is finished, top, middle and bottom trials are all nearly black and their predominant color is green or bluish green. If the brick could be taken out of the kiln at that stage and chilled quickly, as is done with the trials, the brick would be as dark as these finishing trials. In practice the reverse is true. The cooling, in ordinary practice, takes place under more or less strongly oxidizing conditions. The tendency is for oxidation to take place rapidly while the brick are still at high temperature and at a gradually lessening ratio during the progress of the cooling, down almost to atmospheric temperature. This reoxidation, following the reduction, brings the color back through various combinations towards the red, and the result is a kiln of brick of a variety of colors in all of which red, yellow, blue and green are intimately intermingled in various proportions. The colors of the finished product are dependent to so great an extent upon the chemical

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[1] Percy's Metallurgy: Fuel, 50, 71 (1875); Orton: Trans. Am. Ceram. Soc., 5, 425, 429 (1903); Kinnison: *Ibid.*, 16, 136 (1914).

[2] Trans. Am. Ceram. Soc., 16, 185 (1914).

changes which take place during the cooling, that this process lays special claim to the burner's study. The problems of the control of reoxidation are fully as important as those of the reduction period. If there were no reoxidation, strongly reduced kilns would turn out, as is indicated above, nearly black bricks in which the colors would be a combination of green and blue, with the green predominating."

It is now possible to discuss the very careful and interesting work of Binns and Makely.[1] They started with an English plastic ball clay to which they added iron in different forms and various mixtures of ground quartz and pure alumina. The resulting masses were burned at 1200° C and at 1270° C. They recognize that adding quartz and alumina in this particular way is not quite fair. Of course, the adsorption is quite different from what it would be with hydrous alumina. Even under these unfavorable conditions the alumina tends to change the color to buff, the effect being most marked the higher the alumina content, the higher the temperature and the lower the iron content. They themselves say that alumina is undoubtedly responsible for the production of buff colors and in this the opinion of Seger is confirmed. In one series the iron was added "as commercial ferric oxide, the whole mixture being ground together in water in a porcelain ball mill. An inspection of the results shows that no red color can be expected from this source. The prevailing tone is a pinkish gray, the color being somewhat lightened as the content of alumina increases. At the lower fire the alumina produces no change in hue but simply a lighter tint. This is probably due to the fact that the alumina is more bulky than the quartz and consequently the whitening effect is greater. At the greater heat, however, the tone of the color is changed, as the alumina increases to buffs of varying strength. This is especially the case at the 5 percent iron content though it is apparent in every instance......It is not possible to produce red colors in burned clay by the use of pulverized iron-bearing minerals, however finely they may be ground;

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[1] Eighth Int. Cong. Applied Chem. New York, 5, 7 (1912).

but buff tones are produced under the influence of alumina and at a temperature at which the clay approached vitrification. These buff colors are apparently due to the blending of a multitude of minute brown specks."

It is not surprising that iron oxide powder does not color the bricks red. To produce a maximum color the iron would have to be distributed as nearly uniformly as possible over the grains constituting the body of the brick. This is obtained to a certain extent by addition of ferrous sulphate solution and subsequent precipitation of the hydrous oxide. Binns and Makely say that "red colors are the result of the precipitation of a colloidal iron compound in the clay mass." This precipitation apparently results from a solution of ferrous sulphate, which is itself the result of the oxidation of pyrite, either becoming oxidized with the separation of limonite or meeting with carbon dioxide in some form with the resulting precipitation of ferrous carbonate. This is the only way of explaining the statement of Prof. Orton, quoted above, that "as good a red color may be developed from a clay containing its iron as ferrous carbonate as from ferric hydroxide." Siderite does not decompose under ordinary conditions and in the finely ground form no red is produced.

"Pyrite is responsible for several phenomena. As already stated it is the parent of other forms of iron, and, while it is true as stated by Orton that the granules of pyrite 'are never small enough to produce a red color,' it is also true that pyrite is extremely susceptible of oxidation. Unless the clay containing this mineral is dried very rapidly, ferrous sulphate and ultimately ferric hydroxide will be found. There are examples of this in the specimens shown; in fact, in these there is the actual birth of a red clay."

At the high temperatures the alumina evidently peptized the iron oxide in spite of the former being present in granular form.

While the analogy of the yellow bricks with Mars yellow is striking and helpful, it has been pointed out that the iron oxide in the Mars colors is hydrated, while this is probably not the case in a yellow brick. In fact a yellow-burning clay becomes red before it turns yellow.[1] It is, therefore, necessary to consider whether an anhydrous yellow iron oxide is possible. No such substance seems to have been produced in a pure state. Tommasi[2] claims that the anhydrous oxide of the "red" series is brown and that of the "yellow" series is red or reddish yellow. The yellow oxide might easily be stabilized by other substances and, as a matter of fact, we find that iron may produce a yellow color in glass,[3] where there can certainly be no water. "It is generally admitted that oxide of iron gives a greenish color to glass to the mixture of which it has been added; but the truth is, that this color is produced *only* in peculiar circumstances. The manufacturers of china, porcelain and earthenware, are well aware that oxide of iron is the coloring material of a fine *purplish red* enamel fired in their muffle (and it is quite clear that *enamels* are real *glass*); if the temperature were raised too high, this enamel would lose its purplish tinge and tend towards *orange;* so that three colors of the spectrum are produced by oxide of iron, even at the degrees of heat which I should call *low*, compared with the temperature of furnaces for glass melting, which we shall now consider.

"If into a pot containing white melted glass or flint glass we introduce during the blowing a small fragment of iron, it will, from its gravity, fall to the bottom; now, if after the blowing this pot is taken out of the furnace, we shall see close to the fragment of iron partly oxidized, a portion of the glass colored from *orange* to *yellow*. We have also an illustration of the *yellow* color produced by oxide of iron in the manufacture of artificial *aventurine*. It is known that this aventurine is produced by the exposure of soft glass containing a large proportion of the oxides of copper and iron, to a temperature below its fusion: during this exposure the

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[1] Orton: Trans. Am. Ceram. Soc., 5, 402 (1903).

[2] Bull. Soc. chim. Paris., (2) 38, 152 (1882).

[3] Bontemps: Phil. Mag., (3) 35, 440 (1849); cf. Shaw: Trans. Am. Ceram. Soc., 16, 142 (1914).

copper is produced in the form of metallic crystals, and the glass being colored only by the oxide of iron, takes a *brownish yellow* color; and the greater the reduction of the copper the yellower is the glass."

Mène[1] writes formulas for the iron colors: Fe_2O_3 gives purplish red; $FeO.3Fe_2O_3$ gives orange-red; $2FeO.Fe_2O_3$ gives yellow; $FeO_3.Fe_2O_3$ gives green; $3FeO.2Fe_2O_3$ gives blue and $6FeO.Fe_2O_3$ black; but there is no proof for any of this.

If the theory as outlined here is correct, it should be possible to obtain a buff product which would stand heating by precipitating a relatively small amount of ferrous hydroxide along a relatively large amount of alumina. This experiment has been carried out successfully by Mr. Scheetz in the Cornell laboratory. It is, therefore, evident that an anhydrous yellow ferric oxide can be obtained provided agglomeration is prevented. While alumina is probably the most important agent in preventing the iron in bricks from changing from yellow to red, it is not claimed for a moment that other factors may not come in. Thorp[2] says that quicklime, when pure, is white and amorphous; but iron gives it a yellow tint. In this case we evidently have anhydrous ferric oxide in a finely divided state. Desch[3] states that Roman cements have a dark brown color, owing to the presence of considerable quantities of ferric oxide.

Orton[4] has brought out an interesting point in regard to carbonaceous matter. "It seems as if some other influence than the amount of iron, its distribution, or its masking by other oxide must be brought in to explain the buff-burning fire-clays. The significant fact is that fire-clays occur so very generally in connection with coal veins or other accumulations of organic matter; wherever carbon has been accumulated in bygone ages, there we find buff-burning clay imme-

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[1] Kerl: Handbuch der gesammten Thonwaarenindustrie, 513 (1907).

[2] "Outlines of Industrial Chemistry," 177 (1916).

[3] "The Chemistry and Testing of Cement," 41 (1911); cf. Köhl and Knothe: "Die Chemie der hydraulischen Bindemittel," 67 (1915).

[4] Trans. Am. Ceram. Soc., 5, 389 (1903).

diately underneath. Often the coal has been washed away while still soft, and disseminated; but the fact that it had been there is proven by the fire-clay vein which is left behind. In fact, the fire-clay more uniformly marks the coal swamp than the coal itself.

"This connection, so constantly shown, all over the world, in strata of all ages where coal has grown, certainly seems significant. Whether the swamp growth has formed certain organic salts of iron which influence the color, or whether it is by the removal of other substances than iron, or whether it is by stimulating the growth of concretionary forms of iron and thus preventing the distribution of the color, cannot be stated.

"On the other hand, in support of Seger's theory that alumina masks the iron and produces the buff color, the fire-clay beds of New Jersey, the flint clays of Missouri, and many of the Cretaceous fire-clays of Germany, may be cited. They do not occur in connection with coal veins, nor is it reasonable to suppose that they are composed by the erosion of other carboniferous fire-clay beds, and deposited without sensible blending or intermixture with red burning sediments. In fact, their occurrence, alternating with beds of sand, gravel, and red clays, gives the lie to any such assumption.

"The most we can say at present on the cause of buff color of the fire-clay groups, is that they generally contain less iron than is needed to produce a red color; that this iron is distributed in the most perfect manner possible. Seger's alumina theory does not seem to wholly fit the case, and the geological history of fire-clays and their production by swamp growth and carbon accumulation is after all not a cause. There must be a difference in compound, or amount, or distribution, or their geological history could hardly avail to produce a difference. The settlement of this most interesting point is one which invites the attention of the ceramic investigator."

The matter seems rather simple as stated. In presence of decaying organic matter, the iron oxide will come down in an extremely finely divided form and may easily retain enough adsorbed organic matter to cut down very greatly the agglomeration of the iron oxide on heating. The whole argument of this paper is that the yellow color caused by iron is due to sufficiently finely divided ferric oxide. The medium plays no part directly though it may play a very important one indirectly because some media will be much more effective than others in preventing agglomeration.

While it does not come properly within the scope of this paper, there is one interesting point to which reference may be made. Red bricks are apt to turn pink or even buff when heated[1] to a temperature just short of vitrification. This is undoubtedly connected with the dissociation of ferric oxide, but the details seem to be somewhat uncertain. Michaelis[2] believes that an olive-green calcium ferrite is first formed and that the green and the pink are complementary colors forming white. Kinnison gives no very clear explanation; but he seems to favor the view that ferric oxide breaks down to ferrous oxide which then reacts to form ferrous silicate. A peptizing action by the alumina may also be a factor. In any case it is quite clear that a great deal more work needs to be done on the colors of colloidal ferrous and ferric oxides.

Some experiments were made on grinding the red oxide of iron with water and with gelatine solution in the hope of obtaining a yellow oxide; but the experiments were unsuccessful and had to be given up when the laboratory burned. It is planned to repeat them at some future time under more favorable circumstances.

The general conclusions to be drawn from this preliminary paper are:

1. The yellow color of bricks is due to iron oxide and not to a compound of iron oxide with lime or silica or both.
2. The yellow color is due to ferric oxide in a very finely divided form; when the particles are larger the color is red.
3. Alumina seems to be the important peptizing agent in the bricks and the color is yellow when the ratio of free alumina to iron is high.

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[1] Kinnison: Trans. Am. Ceram. Soc., 16, 136 (1914).

[2] Kerl: Handbuch der gesammten Thonwaarenindustrie, 513 (1907).

4. The effect of lime is chiefly an indirect one in setting free alumina.

5. In Mars yellow the color is due to a hydrous iron oxide; but this can hardly be the case in bricks and cannot be the case in glass.

6. The dyeing of cotton an iron buff or khaki is apparently analogous to the formation of Mars yellow.

7. While no anhydrous yellow ferric oxide has ever been prepared pure, it may be and evidently is stabilized by other substances.

8. When a small percentage of ferrous hydroxide is precipitated along with a large percentage of aluminum hydroxide, the buff color of the heated product is undoubtedly due to anhydrous ferric oxide.

9. The yellow color of slightly impure quicklime is due to anhydrous ferric oxide.

10. When clay is deposited in presence of organic matter, the iron oxide is likely to be precipitated in a very finely divided state. Such clays may burn buff without the lime or the alumina content necessarily being high.

11. There is enough alumina in the Mars pigments to prevent the formation of a red color until the iron oxide becomes anhydrous; but not enough to keep the anhydrous ferric oxide yellow. With less iron oxide a buff color is obtained which will stand heating. It is probable, though not proved, that such a color would be more stable than the usual type.

12. In so far as agglomeration is more marked at high temperatures, yellow bricks should turn red if heated hot enough. On the other hand, the peptizing action of the alumina increases with rising temperature. With bricks this latter seems to be the predominating factor, because red bricks become paler or even buff when heated.

13. The changes of color, when yellow bricks are heated, are complicated by the dissociation of the ferric oxide. Heating in oxygen should be tried.

14. A great deal more work must be done before we can account satisfactorily for all the colors produced by iron in soils, pottery and glass.

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STUDIES IN DYEING AND CLEANING

BY D. B. LAKE

Studies on the displacement of adsorbed substances have been made quite recently by Freundlich,[1] and by C. G. Schmidt.[2] Freundlich studied the adsorption, by charcoal, from a solution containing two dissolved substances. The solutions studied contained the following pairs of acids: oxalic acid and acetic acid; oxalic acid and succinic acid; and oxalic acid and benzoic acid. They found that each acid diminished the adsorption of the other; in other words that a given amount of one acid in the presence of another acid was adsorbed less by charcoal than it was from its own solution. From this it was concluded that each acid of the pairs studied displaced the other from the charcoal. By the same method, Schmidt studied the adsorption by charcoal of iodine and acetic acid dissolved in chloroform and obtained results similar to those of Freundlich. He states in general that if a dissolved substance, A, is adsorbed by charcoal, the addition of a substance, B, soluble in the solvent, will bring about a displacement of A; and *vice versa*. He found that the amount of the two dissolved substances adsorbed was less than the sum of the amounts adsorbed separately.

These experiments seem strongly to confirm the idea of the displacement of one adsorbed substance by another. This displacement, it is evident, is by no means confined to the above examples. Among the many interesting cases where it would seem to apply is that one relating to the adsorption of two dyes, under certain conditions, by a fiber as wool. Thus if a dyed fiber such as wool is treated with another dye of the same class under the same conditions, the second dye seems partially or completely to displace the

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[1] Van Bemmelen's Gedenkboek, 88 (1910).

[2] Zeit. phys. Chem., 74, 731 (1910).

first dye as indicated by the change of color of the dyed fiber, and the mixed color of the final bath.

Preliminary experiments to verify this matter were carried out in the spring of 1915 by Miss R. R. Murray. Miss Murray used a silk-wool flannel cloth, the warp of which is wool, the woof silk. Briefly, the method of procedure was to put a piece of cloth into a cold, dilute solution of the first dye, bring to a boil and keep at that temperature for one-half hour; remove; wash; set aside a piece for comparison, and place the remaining piece in the fresh bath of the second dye, in which the cloth received the same relative treatment as in the first case. The reverse treatment was also carried on at the same time. "Thus a succession of displacements of dyes by each other under similar conditions was obtained." Acid and basic dyes were used. Among the acid dyes used were: acid green BBN, acid violet 3R, crocein orange R, alkali blue, lanafuchsine, cyanole green, and brilliant scarlet; among the basic dyes: safranine, thioflavine T, brilliant green and emerald-green.

Concerning the displacement of one color by another on wool, the work seemed to show that crocein orange could be displaced by acid green and acid violet; acid green by alkali blue; thioflavine T by safranine and brilliant green; and safranine by brilliant green and emerald-green. On silk, also, a color displacement was shown. On it, acid green and crocein orange, acid violet and crocein orange, brilliant scarlet and cyanole green displaced each other in the order named, and in the reverse order. In one direction only, thioflavine T was replaced by safranine; and brilliant green and safranine by emerald-green. The color changes indicated above were clear and sharp. With both the wool and the silk there were, in addition to the above, several cases of a partial displacement of one color by another. On wool, there was the case of the partial displacement of acid violet by crocein orange; on silk that of safranine by thioflavine T.

From the evidence of the fiber, it is seen that in many cases we have complete displacement of one color by another.

From the point of view of the final bath also the work seemed to show that there was a more or less complete displacement of one dye by another. Thus in the final bath from the fiber dyed either in crocein orange or acid violet, and then followed by acid violet or crocein orange, both dyes were present as indicated by the color of the final bath which was a wine-red. As with acid violet and crocein orange, so with the other dyes studied, the final baths always contained some unadsorbed dye and some "apparently displaced dye."

Thus it is seen that Miss Murray's work brought out the interesting question: Does one dye, under the experimental conditions described, displace another as indicated (1) by the change of color of the fiber, (2) by the presence in the second final bath of the two dyes?

In the fall of 1915 additional experiments were carried out along the lines indicated above. The fiber chosen was pure hank wool, and was used as bought. At room temperature, one gram of the wool was placed in the dye bath of definite volume (50 cc) and concentration, brought to the temperature of a boiling water-bath, and kept there for one-half hour. The dyed fiber was then removed, thoroughly washed in distilled water, and placed in a bath (50 cc) of the second dye of definite concentration, and the same treatment repeated.

First, an account will be given of the attempts to bring about color changes on the wool fiber, and then an account of the apparent displacement of one dye by another dye. The dyes used in the greater part of the experiments here recorded were those sent to the Physical Chemical Department through the courtesy of the Schoellkopf, Hartford and Hanna Company of Buffalo, N. Y.

On the wool in the silk-wool flannel acid violet was not displaced completely by crocein orange, the color obtained being a "mixed brown;" accordingly, experiments were first carried out with these two dyes. It was thought that by dyeing the fiber in a comparatively small amount of acid violet and then treating this dyed fiber by varying amounts of crocein orange, *viz.*, 10, 20, 30, 40 and 50 mg, respectively, a concentration of crocein orange, within reasonable limits, could be found that would completely displace the color of the acid violet. Negative results were obtained; that is, in no case was the final color of the fiber that of pure crocein orange. At the concentrations of 40 mg and 50 mg of crocein orange, however, its color tended to predominate, that is, the color of the acid violet was more or less completely masked. The final color of the fiber at these higher concentrations of crocein orange was on the whole of a light brick-red.

A few experiments were made to ascertain the minimum amount of acid violet with which the fiber could be dyed in order that the color imparted to the fiber would just influence the succeeding crocein-orange color. The concentration of acid violet varied from 5 mg to 0.2 mg per 50 cc, while that of the crocein orange was kept at 25 mg per 50 cc. The minimum concentration of acid violet was found to be 0.25 mg. This experiment brings out strikingly the comparative intensity of the color of the two dyes when adsorbed by the wool.

Results for the wool dyed in a bath of crocein orange followed by acid violet were somewhat different than for the above experiments. In these cases, the crocein-orange color was practically although not completely displaced by acid violet. The concentration of both dyes in 50 cc was 25 mg, respectively. To learn whether by prolonged treatment of the dyed fiber by the second dye, a complete displacement of the first dye could be brought about, the dyed fiber from the crocein orange was left in the acid violet bath at the temperature of the dyeing for four hours. Twenty-five milligrams of each dye per 50 cc were used. On the whole the result was negative; that is, even after this prolonged treatment of the dyed fiber in acid violet, the acid violet did not entirely mask the color of the crocein orange. However, these results are in harmony with those of the preceding experiments where acid violet was followed by crocein orange, since they show that acid violet is by far the stronger of the two colors on wool.

A few other combinations of colors were then tried out according to the same general method. The combinations were: crocein orange and acid green, alkali blue and acid green, acid violet and acid green, brilliant green and safranine. The concentration of each dye with the exception of brilliant green and safranine was 50 mg in 50 cc of water. In the case of the brilliant green and safranine, 25 mg of dye in 50 cc were used. For the above combination for dyes, as for the acid violet and crocein orange, in no instance was the first color replaced by the second color. The resulting color for the first two combinations was practically the same, namely, a brownish black; for the acid violet followed by acid green a greenish black. When the safranine was followed by the brilliant green, the color resulting was a greenish black; when the fiber was dyed in the reverse order, the color resulting was a bluish black, thus showing that the brilliant green tended to displace the safranine more readily than the safranine the brilliant green, that is, the brilliant green is the stronger color on wool. This is analogous to the behavior of acid violet and crocein orange. The acid violet displaced the crocein orange more than the crocein orange did the acid violet.

It is evident from the above data that on wool alone, one color cannot be completely replaced by another in one treatment unless, as in the case of acid violet, the amount of the first dye used is very small in comparison to the amount of the second dye used.

To ascertain whether the color on a fiber could be displaced by successive treatments of the second dye, wool was dyed in the usual manner and then further treated to fresh successive baths of the second dye. As a typical case, the fiber dyed in acid green followed by crocein orange was studied. The concentration of the acid green was 50 mg in 50 cc. Two samples were dyed first in acid green and then each of these in fresh baths of crocein orange (40 mg). The first treatments of the dyed fiber resulted in a brownish black color which color remained after the second treatment. In the third treatment an orange tint of the fiber was noticeable. In the fifth treatment practically all of the acid-green color had been displaced. Similar experiments were carried out with alkali blue and crocein orange, and acid violet and crocein orange. With respect to alkali blue and crocein orange the fiber was dyed first in 50 mg of alkali blue. This dyed fiber was then treated with four successive amounts of crocein orange, namely, 50, 25, 25 and 25 mg, respectively. The resulting color of the fiber at the end of the fourth treatment was only slightly different from that at the end of the first treatment. However, a slight orange tinge of the fiber was noticeable. Concerning the acid violet and crocein orange two sets of fibers were dyed in 30 mg and 40 mg of acid violet, respectively. These dyed fibers were then treated with five successive amounts of crocein orange, namely, 50, 25, 25, 25 and 25 mg respectively. At the end of the last treatment the color of the fibers did not seem markedly different from that at the end of the first treatment.

From the above experiments the conclusion may be drawn that it is very difficult to mask completely, that is, displace, by a second dye the color of the dye adsorbed by wool fiber. This would seem to show that the influence of the dye in the bath in displacing the adsorbed dye is small, if not negligible. Furthermore, it would seem that where the final color of the dyed fiber tended to become more like that of the second dye it was due, in part at least, to the more or less partial masking of the color of the original, adsorbed dye by the second dye.

From this we should conclude that if it is desired to bring about a rapid complete change of color of a fiber, dyed for example with acid violet, it would first be necessary to remove the dye from the fiber by means of a solution of either Na_2CO_3 or $NH_4C_2H_3O_2$ before treating the fiber with the dye for the desired color.[1] There are cases where this method would not be necessary as shown in the experiment with acid green and crocein orange. There it was seen that the acid green was not held so tenaciously as was acid violet or alkali

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[1] Knecht, Rawson and Lowenthal: A Manual of Dyeing, 1, 217 (1910).

blue; hence by successive treatments of the dyed fiber in fresh baths of crocein orange, the acid-green color should eventually be completely displaced by the crocein-orange color. From preceding experiments we should expect this color displacement to be accompanied by a fairly rapid displacement of the dye, acid green. This displacement of the acid green may be explained as due to the fact that it was either dissolved or peptized by the water, or peptized by the crocein orange. There is no doubt that in the case of alkali blue and acid violet their complete displacement could be brought about eventually and for the same reason.

The idea that the displacement of a dye from a fiber may be accounted for by assuming that the first dye is either dissolved or peptized by the solvent or is peptized by the second dye, leads us to the second point in the investigation, namely, to account for the apparent displacement of one dye by another.

If we go back to the experiments described, we can consider this evidence of the displacement of a dye from a fiber by the appearance of the final baths in each case. In the case of the first experiments with acid violet and crocein orange, where only a small amount of acid violet was used for the first color, it was rather difficult to detect any acid violet in the second final bath. Up to a concentration of 20 mg of crocein orange the final bath was of a dark lemon color. To the naked eye there was no evidence of acid violet present. Beyond a concentration of 20 mg of crocein orange the color of the final bath was that of the original color of the crocein-orange bath. In none of these experiments was there any visible evidence of the displacement of acid violet. This was especially noticeable as the crocein orange was adsorbed to a considerable extent by the dyed fiber.

However, seemingly more positive evidence of the displacement of acid violet by crocein orange was obtained when the wool was dyed in more concentrated solutions of the acid violet. For example, in the case where two sets of the fiber were dyed in 30 and 40 mg, respectively, and then treated to successive, fresh baths of crocein orange the final baths in every case, even in the last treatment, were of a wine-red color, thus showing that in each final bath there was present unadsorbed crocein orange and some apparently displaced acid violet. As in the case of the acid violet and crocein orange, so in the case of acid green and crocein orange, alkali blue and acid green, and acid violet and acid green where the fiber was dyed in a rather concentrated solution of the first dye, the final baths in all cases showed the presence of the unadsorbed dye and the apparently displaced dye. This was particularly striking in the case of acid green followed by crocein orange. In every treatment of the dyed fiber, even to the last one, the color of the final bath was of a "dirty" green showing that both dyes were present. In all cases, the apparently displaced dye seemed to be present in considerable amounts.

Doubt as to the correctness of the idea of the actual displacement of one dye by another arose when the fact of the bleeding of a fiber dyed at the temperature of a boiling water-bath was taken into consideration. Thus wool dyed with acid violet, crocein orange, alkali blue and acid green, respectively, was practically stripped of each dye by putting the dyed fiber in successive fresh baths of boiling water. The removal of the dye in each case was brought about by either the solvent or peptizing action of the water. In accordance with the law of "reverse adsorption"[1] more dye was removed during the first two or three treatments than during the succeeding treatments. In fact when the amount of dye on the fiber was rather small its removal was very slow and difficult.

Now at the temperature of the water-bath, at which the experiments described were carried out, bleeding of the dyed fiber likewise readily occurred. This was shown for fibers dyed in acid violet, crocein orange, alkali blue, and acid green. Therefore, from these data it is seen that the question to settle was

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[1] Hatschek: "An Introduction to the Physics and Chemistry of Colloids," 82 (1916).

whether a dyed fiber would bleed more in the presence of a second dye solution than in pure water at the temperature at which the experiments had been carried out.

Briefly the method used to answer the question was first to treat four samples of the wool in a dye bath of known concentration at the temperature of the boiling water-bath at about 97° for forty-five minutes; remove; wash; test two of the samples for bleeding at the same temperature for twenty-five minutes in the same volume of water and dye the other two dyed samples in a fresh bath of the second dye of the same concentration as the first dye and under the same conditions. Since the idea was to obtain relative information concerning the bleeding of the dye in its relation to displacement, a volume of 250 cc was used instead of 50 cc as in the previous experiments. The final solutions were analyzed colorimetrically by means of a Duboscq colorimeter.

The following data were obtained for wool, silk, and poplin (a cloth made of silk and wool, and used in place of the silk-wool flannel):

TABLE I

I—*Undyed Wool*

1 gram wool, 5 mg dye per 250 cc H_2O

Temperature—about 97° C

Dye	A	B	C
	Dye adsorbed Milligrams	Dye unadsorbed Milligrams	Bleeding test. Am't dye from dyed fiber given up to 250 cc H_2O at about 97° after 25 minutes Milligrams
Crocein orange	4.26	0.74	0.53
	4.30	0.70	0.58
Acid green	4.20	0.80	0.45
	4.30	0.70	0.35

II—*Dyed Wool* from A, not tested for bleeding; 5 mg dye per 250 cc H_2O; temp. about 97° C

Dye	D Dye adsorbed by dyed fiber Milligrams	E Dye unadsorbed by dyed fiber Milligrams	F Dye given up to 250 cc H_2O at about 97° by dyed fiber from D during dyeing Milligrams
Crocein	4.35	0.65	(Acid 0.40
orange	4.50	0.50	green) 0.30
Acid	4.25	0.75	(Crocein 0.50
green	4.35	0.65	orange) 0.50

I—*Undyed Silk*
1 gram, 20 mg dye per 250 cc H_2O
Temperature about 97° C

Dye	A Dye adsorbed Milligrams	B Dye unadsorbed Milligrams	C Bleeding test. Am't dye from dyed fiber given up to 250 cc H_2O at about 97° after 25 minutes Milligrams
Crocein	1.8	18.2	0.46
orange	1.8	18.2	0.23
Acid	9.3	10.7	0.88
green	8.7	11.3	0.79

II—*Dyed silk* from A, not treated for bleeding; 20 mg dye per 250 cc H_2O; temp. about 97° C

Dye	D Dye adsorbed by dyed fiber Milligrams	E Dye unadsorbed by dyed fiber Milligrams	F Dye given up to 25 cc H_2O at about 97° by dyed fiber from D during dyeing Milligrams
Crocein	1.8	18.2	(Acid 0.70
orange	2.0	18.0	green) 0.65
Acid	9.0	11.0	(Crocein orange)
green	9.0	11.0	Presence not indicated by method of analysis

I—*Undyed Poplin*

1 gram poplin; 20 mg dye per 250 cc H_2O
Temperature—about 97° C

Dye	A	B	C
	Dye adsorbed	Dye unadsorbed	Bleeding test. Am't dye from dyed fiber given up to 250 cc H_2O at about 97° after 25 minutes
Crocein orange	3.1	16.9	1.1
	2.9	17.1	1.1
Acid green	5.5	14.5	2.0
	5.6	14.4	2.0

II—*Dyed Poplin* from A, not treated for bleeding; 20 mg dye per 250 cc H_2O; temperature about 97° C

Dye	D	E	F
	Dye adsorbed by dyed fiber Milligrams	Dye unadsorbed by dyed fiber Milligrams	Dye given up to 250 cc H_2O at about 97° C by dyed fiber from D during dyeing Milligrams
Crocein orange	3.0	17.0	(Acid green) 2.0
	3.0	17.0	2.1
Acid green	5.0	15.0	(Crocein orange) 1.0
	5.0	15.0	0.9

Other data for crocein orange and acid violet were obtained with respect to wool but were lost when Morse Hall burned. Since acid violet could not be obtained in the market, experiments with these two dyes were not repeated. The data in all respects, however, agreed with the above for acid green and crocein orange.

The data seem to account for the apparent displacement of one dye by another. In all of the experiments in which the final bath indicated the presence of the two dyes, it is evident that the presence of one dye is due to bleeding, and the presence of the other dye to incomplete adsorption. It is evident also that the bleeding of the first dye is not increased as a result of the adsorption of the second dye, or is independent of the presence of the second dye. In other words these data seem to bring out the fact that the removal of the dye on the dyed fiber is brought about through peptization by the liquid rather than peptization by the dissolved dye. This is indicated by comparing Columns C and F of the above tables for any fiber. Thus in the case of wool:

Dye	C	F	
	Bleeding test. Amount dye given up by dyed fiber to 250 cc H_2O at about 97° C after 25 minutes Milligrams	Dye given up by dyed fiber to 250 cc H_2O at about 97° C during dyeing Milligrams	
Crocein orange	0.53	Crocein orange	0.50
	0.58		0.50
Acid green	0.80	Acid green	0.40
	0.70		0.30

This apparent inactivity of the dissolved dye is probably due to the fact that the set adsorbed dye is "extremely difficult" to peptize even by boiling water. This is shown, for example, in the case of acid violet 3R which on wool bleeds but slightly in boiling water, that is, is peptized only slightly by it. Hence the conclusion that a dye in solution (true or colloidal) possesses apparently far less ability to peptize an adsorbed dye than does water and, therefore, the dye in solution plays little part in the removal of the adsorbed dye.

Concerning the final color of a fiber, especially with regard to wool, complete change takes place only when the amount of the dye adsorbed is rather small and the amount of second dye adsorbed is relatively large; in other words, when the amount of the first dye adsorbed is so small that the color of the second dye is able to mask it completely. This is illustrated in the case where only 0.25 mg of acid violet, adsorbed as the first dye, was completely masked by crocein orange. In any case where a large amount of the first dye has been adsorbed, the color replacement goes hand in hand with its actual displacement from the fiber, which displacement seems to be entirely independent of the presence of the second dye.

With regard to silk we have a complete replacement of one color by another as for wool. This is illustrated in the displacement of crocein-orange color by acid-green color. The amount of crocein orange adsorbed was comparatively small; and hence when this dyed fiber was treated to a fresh bath of acid green at the temperature of the boiling water-bath, with the result that considerable bleeding of the crocein orange took place, the amount of crocein orange left on the fiber was so small that its color was easily masked by that of the acid green. Thioflavine T on silk followed by safranine affords an instance in which the color of one dye is displaced by another, and yet in which large amounts of the first dye are taken up. A one-gram sample of silk dyed in 25 mg of each dye per 250 cc H_2O at about 97° C adsorbed about 80 percent of each, respectively. Notwithstanding that relatively large amounts of thioflavine T were adsorbed its color was easily masked by the safranine. It is obvious that the amount of thioflavine T given up to the safranine solution was not sufficient to account for the displacement of the thioflavine T color by the safranine color, as in the case of crocein orange followed by acid green. The probable reason for the masking of the thioflavine color is due to the fact that it is of very light shade, thus making its displacement or masking comparatively easy by a darker one as safranine. It should be pointed out that safranine color was not replaced by the thioflavine T color in one treatment.

Summing up then the results of the experiments, we conclude that we may speak of the displacement, or preferably the masking, of one color by another under suitable conditions.

This masking of one color by another is accompanied by a partial displacement of the dye from the fiber. But this displacement does not seem to be brought about by the presence of the second dye but by the solvent or peptizing action of the solvent.

The above experiments were carried on at the temperature of the boiling water-bath. Since, at this temperature under ordinary conditions, there was no complete replacement of one color by another on wool, a few experiments were carried out at room temperature to ascertain whether dyes behaved similarly at that temperature. In all of these experiments the wool, used as bought, was entered in the first dye bath containing 25 mg of dye per 50 cc H_2O for 36 hours; after which it was removed, washed in distilled water, and then entered in the second dye bath of the same concentration, for the same length of time. The following pairs of dyes were studied: acid violet 3R and crocein orange R, cyanol green and brilliant scarlet, safranine and brilliant green, thioflavine T and safranine, cyanol green and lanafuchsine, brilliant green and thioflavine T.

Acid violet at room temperature is adsorbed very slightly by wool. Crocein orange, on the other hand, is adsorbed strongly, hence it readily displaced the acid violet color from the fiber. Crocein orange color, on the other hand, was in no way displaced by acid violet. The color of cyanol green was completely displaced by brilliant scarlet, although brilliant scarlet followed by cyanol green was not so completely displaced. The second final baths in each case contained both dyes. Safranine, followed by brilliant green, gave a dark-colored fiber, the color of the safranine predominating. Brilliant green, followed by safranine, likewise gave a dark-colored fiber, the brilliant green predominating. The fiber dyed in emerald-green followed by safranine took on a slightly greenish tinge, while in the reverse procedure the safranine color predominated on the fiber. In all of these cases the second final baths showed both dyes to be present. Thioflavine T followed by safranine was completely replaced by the safranine. Thioflavine T was present in the second final bath. Safranine was not replaced at all, so far as the color of the fiber was concerned, by thioflavine T, although in the final bath safranine was present. Cyanol green followed by lanafuchsine gave a slate-blue color to the fiber, as well as did lanafuchsine followed by cyanol green. The final baths in both cases contained the two colors. Brilliant green followed by thioflavine T retained its color on the fiber, while thioflavine T was completely replaced by brilliant green. In this latter case, I could see no evidence of thioflavine T in the final bath.

The results of these experiments at room temperature are similar to those carried on at the higher temperature. They are purely qualitative, although there is no reason for assuming that quantitative data as to the principles involved would not agree with the data obtained for the higher temperature. At the lower temperature there seemed to be, on the whole, a more complete replacement of one color by another, and a more complete apparent removal of the first dye by the second. This latter phenomenon may be accounted for by postulating that at the higher temperature the dye is more completely "set" on the fiber and hence does not bleed so readily even at that temperature. It was very noticeable that the bleeding of fibers dyed at room temperature was far greater at that temperature than fibers dyed at about 100° and tested for bleeding at that temperature. At the lower temperature two cases were brought out where one color practically replaced the other completely; namely, thioflavine T by safranine and thioflavine T by brilliant green. With respect to thioflavine T followed by safranine, both dyes were present in the second final bath. In the case of thioflavine T followed by brilliant green it was rather difficult to detect the presence of thioflavine T in the second final bath. In fact, with the naked eye, no evidence of thioflavine T could be seen.

An interesting experiment showing how one color will predominate at one temperature, and the other at a higher temperature was brought out in the case of acid violet and crocein orange. A one-gram sample of wool in 5 mg of crocein orange and 45 mg of acid violet per 50 cc H_2O was dyed at room temperature for 72 hours; another sample in a bath of the same concentration of the dyes at the temperature of the boiling water-bath. At room temperature the fiber was dyed a pure crocein-orange color, while at the higher temperature it was dyed largely the color of the acid violet. This experiment illustrated selective adsorption very finely, especially at the lower temperature. As showing more strikingly this selective adsorption at room temperature in the case of these two dyes a one-gram sample of wool was entered in a volume of 50 cc containing 10 mg orange and 1000 mg acid violet and left in this bath 24 hours. At the end of that time the fiber was dyed a fairly pure color of crocein orange. There was no evidence of the adsorption of any acid violet.

In the experiments described there is one fact that stands out quite prominently, namely, that a dyed fiber, under suitable conditions, will bleed; that is, if placed in water under suitable conditions it will lose some of its dye to the water. This bleeding will continue until, for the particular volume of water, equilibrium is reached between the dye in the solution and the dye on the fiber. As has already been pointed out, if one set of fibers is dyed at room temperature, and another set at a higher temperature, for example, the temperature of a boiling water-bath, the fiber dyed at the higher temperature will bleed less, even when tested for bleeding at the higher temperature, than the fiber dyed at room temperature and tested for bleeding at the lower temperature. In fact a fiber dyed at a high temperature as mentioned above will not bleed at all at room temperature. This difference in bleeding, depending on the temperature of dyeing, is probably due to the fact that the dye adsorbed at the higer temperature is coagulated on the fiber, or, as is popularly known "set" on the fiber, with the result that bleeding is more or less prevented. These general observations concerning bleeding led to a study of the conditions involving the dyeing of a fiber, or the treatment of a dyed fiber, that would lead to a minimum of bleeding when the dyed fiber is exposed to practically boiling water.

The first experiment was concerned with the relation between the length of time of dyeing at high temperature and bleeding. "The real object of heating is to coagulate or agglomerate the dye, thus making it less soluble."[1] Hence the conclusion that prolonged dyeing at a high temperature should practically prevent bleeding. The dyeing was carried on at the temperature of the boiling water-bath. Samples of wool, one gram each, were entered in a dye bath of 40 mg per 250 cc H_2O. The time of dyeing varied from one to three hours. The dye used was acid violet.

The test for bleeding was carried out as follows: The washed dyed fiber was put in a beaker containing 250 cc of water and the whole heated to the temperature of the water-bath for one-half hour.

The dye unadsorbed and bled was determined colorimetrically. The data following are the average of duplicate experiments:

TABLE II

Time	Dye adsorbed	Dye unadsorbed	Bleeding test. Am't dye given up to 250 cc H_2O at about 97° C after 30 minutes
1 hour	37 mg	3 mg	about 0.30 mg
1 1/2 hours	39 mg	1 mg	about 0.80 mg
3 hours	38.5 mg	1.5 mg	about 0.60 mg

These data indicate that prolonged dyeing at practically the temperature of boiling water does not cut down the amount of dye that will bleed from a fiber. This may be accounted for by assuming that equilibrium between the adsorbed and unadsorbed dye was reached at the end of one and one-half hours, hence the dyeing beyond that time was of no avail.

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[1] Bancroft: Jour. Phys. Chem., 19, 145 (1915).

In practical work, especially with acid dyes, dyeing is carried on in so-called acid baths, that is, baths to which a certain amount of hydrochloric acid or, preferably, sulphuric acid is added. It is generally accepted that the presence of these acids brings about a better "setting" of the dye and hence makes it faster to washing or bleeding. With this idea in mind, experiments were carried out with acid violet in the presence of hydrochloric acid and sulphuric acid. The conditions of dyeing were the same as in the preceding experiment. Forty milligrams of dye were used and the amount of acids 3 percent by weight of the wool.

The data, the average of duplicate experiments, follow:

TABLE III

Time	Acid used 3% by weight of wool	Dye adsorbed Milligrams	Dye unadsorbed Milligrams	Dye bled. Am't dye given up by dyed fiber to 250 cc H_2O at about 97° after 30 minutes Milligrams
1 hour	H_2SO_4	39.83	0.17	0.10
1½ hours	H_2SO_4	39.70	0.30	0.20
3 hours	H_2SO_4	39.70	0.30	0.20
3 hours	HCl	39.70	0.30	0.20

Thus, as indicated above, these data bring out the fact that a fiber such as wool dyed with an acid dye in an acid bath gives up less dye to practically boiling water than it does when dyed with the same dye in a neutral bath. (See immediately preceding table.) The most probable reason for this is that the acid aids in coagulating or setting the dye on the fiber, thus making it less soluble; hence less dye is extracted by hot water, or the dye bleeds less readily.

It was observed in the above experiments that the fiber adsorbed the dye much faster in the acid bath than in the neutral bath. This was to be expected as postulated by Bancroft.[1]

Experiments were next carried out in which wool was

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[1] Jour. Phys. Chem., 18, 4 (1914).

dyed in neutral and acid baths as usual, but before testing for bleeding it was subjected to heating in a hot-air oven at a temperature of 105°–110° C for one hour. The acids used were hydrochloric and sulphuric. Negative results were obtained in all cases; that is, after this heating the dyed fiber bled as much as the fiber which had not been subjected to this extra heating.

In the above experiments the temperature of dyeing was about 96°–97° C.

It was hoped that by dyeing in an atmosphere of "live" steam the dye would be fixed more firmly on the fiber, so that it would be faster to washing. Accordingly, an apparatus was arranged by which live steam was allowed to bubble through a solution of dye contained in an Erlenmeyer flask. The Erlenmeyer flask was partially immersed in boiling water. Before the passage of the steam the fiber was thoroughly wet with the dye solution. The dye used was acid violet and the amount 40 mg per 50 cc of water. The dyeing was carried on for one hour. Duplicate experiments were performed in neutral and acid (HCl) baths.

In the first set of experiments after the dyeing in live steam the fibers were put at once into distilled water and tested for bleeding as usual at 97°. The bleeding was no less than in the case carried on at 96° to 97°. The fibers dyed in the neutral baths bled slightly more than those dyed in the acid bath. An experiment in which the fibers, dyed as above, were subjected to live steam for one-half hour before testing for bleeding in the usual manner likewise gave negative results; that is, the bleeding by this treatment was not cut down any. The fibers dyed in the acid bath bled considerably less than those dyed in the neutral bath. Another set of fibers was subjected to the live steam for 1/2 hour, and tested for bleeding by immersing in water through which live steam bubbled for one hour. Here profuse bleeding took place. The fibers dyed in the neutral and acid baths bled about equally. The container in both experiments was immersed in boiling water.

At first thought it seems strange that at the temperature of the live steam the dye was not fixed more firmly on the fiber, as shown when tested for bleeding at the temperature of the boiling water-bath. However, the explanation is similar to that advanced to account for the greater bleeding of the fiber dyed in a neutral bath as compared to its bleeding when dyed in an acid bath. At the temperature of the "live" steam the dye was fixed no more firmly on the fiber than at the lower temperature. Hence the fiber gave up as much color to the hot water as to the one dyed at the lower temperature.

With reference to the bleeding of the dyed fiber at the temperature of "live" steam the data brought out the fact that it was profuse. This profuse bleeding can be explained, however, by assuming that at this high temperature the dye on the fiber was quite readily peptized.[1] Hence a larger amount of color was given up to the water than would ordinarily have been the case.

In dyeing at the temperature of live steam it was found that in all cases not so much dye was taken up by the fiber at this temperature, as was taken up at 96°–97° C, which was from 3 to 5 percent less. This is in harmony with data published by Mills and Rennie,[2] and Brown.[3] Mills and Rennie found that wool dyed with rosaniline acetate adsorbed a maximum amount at 31° and practically none at 81°. The experiments were run for one hour at the temperature —1.46° + 1.50, 6.25°, and at successive ten degree intervals to 80.25°, respectively. The amount of dye left in the bath at the end of one hour was determined colorimetrically. Brown's method of experimentation was similar to that of Mills and Rennie. He studied the adsorption of acid and basic dyes by the wool. The figures in the subjoined table are from his data, and are the percentages of the dye left in the solution. The first three dyes are acid dyes, the last three basic dyes.

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[1] Bancroft: Jour. Phys. Chem., 20, 85 (1916).

[2] Jour. Soc. Chem. Ind., 3, 215 (1884).

[3] Jour. Soc. Dyers and Colourists, 17, 92 (1901).

Dye	20° C	40° C	60° C	80° C	100° C
Acid magenta	79	14	4	4.3	5.6
Acid green	79	28	4	4.6	5.2
Acid violet 4 B W	44	26	20.8	20.8	28.7
Chrysoidine FF	28.2	32	36	46.5	46.0
Methylene blue	29.2	24.4	28.6	33.1	57.1
Methyl violet B	37.0	7.0	5.3	4.7	6.2

With the exception of the data of the methylene blue these data bring out the fact that from 60° onward the amount of dye adsorbed per unit of time decreased with rise of temperature. This can be accounted for by assuming that with the rise in temperature the peptizing action of the water toward the adsorbed dye increased, thus cutting down the amount of dye adsorbed. With the exception of chrysoidine FF it is seen that up to the temperature of 60° with the rise in temperature there is an increase in the amount of dye adsorbed. This increase, however, is more apparent than real for notably under the conditions of Brown's experiments time was not allowed for a complete adsorption of the dye, especially at 20°, that is, time was not allowed for the adsorption equilibrium to be reached. At 60° and higher one hour's time was, to all intents and purposes, sufficient to bring about a practically complete adsorption of the dye; but at the lower temperatures this was not true. Hence it would seem that if at the lower temperatures the wool had been left in the bath till equilibrium had been reached the amount of dye adsorbed probably would have equalled the amount adsorbed at 60°, and even might have exceeded it. This assumption seems to hold for chrysoidine FF where it is seen that the amount of dye adsorbed up to 80° decreased with the rise in temperature. At 20° it is assumed that the adsorption equilibrium was reached at the end of one hour. Experiments carried on in the latter part of October, but with an entirely different object in view, further confirm the idea that at room temperature the amount of dye adsorbed is rather large in many cases. One-gram samples of wool were left in their respective dye baths for 48 hours. The baths contained 25 mg dye per 50 cc water. The dye left in the bath was determined colorimetrically. The figures in the subjoined table refer to the percentage of dye left in the bath.

Dye	Percentage dye left in bath
Thioflavine T	18
Acid green	36
Brilliant green	20
Emerald-green	20
Lanafuchsine	54
Brilliant scarlet	60

Without doubt had the fibers been allowed to remain in their respective baths for a longer period of time a greater adsorption of dye would have resulted in each case. Especially would this be expected of lanafuchsine and brilliant scarlet.

At this point it was thought advisable to test a few more acid dyes to see how far the general results obtained for acid violet would hold. The other dyes used were: acid green BBN, crocein orange R, and crystal ponceau. The acids used were HCl, H_2SO_4 and H_3PO_4. Two points were kept in view in these experiments; first to show the relation of "bleeding" to the kind of treatment, that is, to ascertain whether in neutral or acid dyeing bleeding was greater or less; and secondly, to study the adsorption of these acid dyes on wool in the presence of these acids. From the point of view of the adsorption of the dye, the data given above for acid violet in which dyeing was done in hydrochloric acid and sulphuric acid baths, when equivalent amounts of the two acids were used, show that the fiber immersed in a sulphuric acid bath adsorbed as much dye as did the fiber immersed in the hydrochloric acid bath. This is not in accordance with the theory of dyeing as postulated by Bancroft, for according to that theory any acid dye in the presence of a readily adsorbed anion, either from an acid or neutral salt, should be less readily adsorbed than in the presence of an anion not so readily adsorbed by the fiber.[1] In the case of HCl and H_2SO_4, the sulphate ion is much more readily adsorbed by wool than the chloride ion, hence a fiber dyed in the presence of H_2SO_4 should take up less acid dye than a fiber dyed in the presence of an equivalent amount of HCl. The data above do not confirm this.

In this new series of experiments acid violet was included, for the concentration of the dye used and the method of heating were changed, and it was thought desirable to get comparable data for all dyes. The fiber, one gram of wool, was entered in 250 cc of dye solution containing 40 mg of the respective dye. The dyeing was carried on at the boiling temperature for a period of one hour. Preliminary experiments had shown that at the temperature of boiling water practically complete adsorption of the dyes was brought about at the end of 45 minutes. The fibers were then tested for bleeding in a volume of 250 cc H_2O at the same temperature for 20 minutes. The amount of each acid used was 10 cc of $N/10$ strength. The data, the average of duplicate experiments, follow:

These data bring out facts similar to those obtained above for the wool dyed in neutral and acid baths of acid violet. Here as there in the bleeding test fibers dyed in acid baths gave up less color to the water than those dyed in neutral baths. This is as should be expected as pointed out above. The data show also that the fibers dyed in acid baths adsorbed more dye than those dyed in neutral baths. Furthermore, if we compare the data of the acid violet and crystal ponceau as a whole, it is seen that both dyes gave up about the same amount of color to the water in the test for bleeding. This can be accounted for by assuming that during the dyeing both dyes were about equally set. In general this comparison of crystal ponceau and acid violet holds also for crocein orange and acid green where for each dye under the same conditions there was

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[1] Bancroft: Jour. Phys. Chem., 18, 4 (1914).

TABLE IV

Temperature—100° C
40 mg dye per 250 cc H_2O
Time—1 hour

Dye	Acid used 10 cc of each N/10 acid	Dye adsorbed Milligrams	Dye unadsorbed Milligrams	Bleeding test. Amount dye given up by dyed fiber to 250 cc H_2O at boiling temperature for 20 minutes Milligrams
Acid violet	No acid	38.0	2.0	1.0
	HCl	39.2	0.8	0.4
	H_2SO_4	39.2	0.8	0.4
	H_3PO_4	39.1	0.9	0.6
Crocein orange	No acid	32.5	7.5	5.0
	HCl	38.0	2.0	4.4
	H_2SO_4	35.5	4.5	3.1
	H_3PO_4	35.5	4.5	3.7
Acid green	No acid	30.1	9.9	3.9
	HCl	37.5	2.5	2.7
	H_2SO_4	36.3	3.7	2.7
	H_3PO_4	36.0	4.0	3.3
Crystal ponceau	No acid	37.7	2.3	1.3
	HCl	39.8	0.2	0.5
	H_2SO_4	39.4	0.6	0.6
	H_2PO_4	39.4	0.6	0.6

the same amount of bleeding. A comparison of the data of the acid violet with crocein orange or acid green brings out strikingly the relation between the setting and the subsequent bleeding of. the dye. According to the theory postulated the acid violet was more firmly set on the wool than the crocein orange as the data show in all cases the amount of acid violet given up to the water during the bleeding test was much less than the amount of crocein orange. Finally a comparison of the effect of the acids, among themselves, on the adsorbed dyes does not seem to bring out any of the above general relationships. There were apparently disturbing factors that entered in that offset the effect of each acid. However, if we turn to Table VI which contains the data for experiments carried on exactly like those whose data are recorded in Table

IV, except that a larger amount of dye was used, it is seen that on the whole an acid dye adsorbed in a hydrochloric acid bath seemed to be more firmly coagulated on the fiber, or made less soluble in water, than a dye adsorbed in a sulphuric acid bath; and that a dye adsorbed in a sulphuric acid bath was more firmly coagulated on the fiber than one adsorbed in a phosphoric acid bath.

Another interesting point concerning these data in addition to those above is that the sulphuric and phosphoric acids are equally efficient in bringing about the adsorption of the dyes. This seems strange for in the case of crystal ponceau data have been published showing[1] that when fibers were dyed in baths containing equivalent amounts of hydrochloric, phosphoric, and sulphuric acids, respectively, the greatest adsorption of dye occurred in the hydrochloric acid bath, a less adsorption in the sulphuric acid bath, and the least adsorption in the phosphoric acid bath. Since, according to the theory of dyeing,[1] a readily adsorbed anion will decrease the amount of acid dye taken up it can be seen why wool dyed in a sulphuric acid bath should adsorb more dye than when dyed in a phosphoric acid bath. In the case of these acids the anions of each are readily adsorbed by the wool, but the phosphate anion is more readily adsorbed than the sulphate anion, hence the wool dyed in a phosphoric acid bath will take up less dye than when dyed in a sulphuric acid bath of equivalent strength. Now it is to be observed from the above data that the concentration of dye used was nearly equal to the amount which in practical language the fiber would "about clean up" even in neutral baths. This fact then leads to the conclusion that when a fiber as wool is dyed, as described above, the "cutting down effect" of the adsorbed anion is practically overcome for probably the capacity of the fiber to adsorb more dye or sulphate and phosphate ions is still very high. Hence under such conditions wool takes up as much acid dye from a phosphoric acid bath as from a sulphuric acid bath.

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[1] Bancroft: Jour. Phys. Chem., 18, 4 (1914).

In order to show that the amount of phosphoric acid used is not so efficient as an equivalent amount of sulphuric acid in bringing about adsorption of acid dyes, or what is the same thing, that in the presence of practically equivalent amounts of adsorbed hydrogen ion the adsorbed phosphate ion cuts down the amount of dye adsorbed more than the adsorbed sulphate ion two methods of experimentation are open: (1) to the same concentration of dye and acid as in the previous experiments add a neutral salt with a common anion; (2) to the same amount of acids as above add a larger amount of dye per 250 cc H_2O.

In the first method as mentioned, the same concentration of dye and acid were used as in the above experiments. The method of dyeing also was the same. To the hydrochloric acid bath 10 cc of *N*/1 NaCl were added; to the sulphuric acid bath 10 cc *N*/1 Na_2SO_4; to the phosphoric acid bath 10 cc *N*/1 Na_2HPO_4. The dyes acid violet and crocein orange only were studied. The data are the average of duplicate experiments.

Table V

Temperature—100° C
40 mg dye per 250 cc H_2O
Time—1 hour

Acid dye used	Acid used 10 cc. *N*/10 acid	Salt used 10 cc *N*/1 neutral salt	Dye adsorbed Milligrams	Dye unadsorbed Milligrams
Acid violet	HCl	NaCl	39.5	0.5
	H_2SO_4	Na_2SO_4	36.8	3.2
	H_3PO_4	Na_2HPO_4	1.0	39.0
Crocein orange	HCl	NaCl	33.4	6.6
	H_2SO_4	Na_2SO_4	20.0	20.0
	H_3PO_4	Na_2HPO_4	0.1	39.9

These data bring out rather strikingly the fact that the chloride, sulphate, and phosphate ions cut down the adsorption of an acid dye, even when the concentration of dye used is about what the fiber will "easily clean up." The order in which the salts cut down the adsorption of the dye the least, namely, Na_2HPO_4, $NaSO_4$ and NaCl is exactly what one would expect on the basis that the phosphate ion is adsorbed the most, and the chloride ion the least. These readily adsorbed anions not only offset the effect of the hydrogen ion, but also counterbalanced the still very great saturation capacity of the fiber for the dye.

In the second method the concentration of dye used was 75 mg; the kind and amount of acid used in each case was the same, namely, 10 cc of *N*/10 HCl, H_2SO_4 and H_3PO_4, respectively. The method and other conditions of dyeing were the same. Acid green, crocein orange, and crystal ponceau were studied. The data, the average of duplicate experiments, follow:

TABLE VI

Temperature—100° C
75 mg dye per 25 cc H_2O
Time—1 hour

Dye	Acid used 10 cc of each *N*/10 acid	Dye adsorbed Milligrams	Dye unadsorbed Milligrams	Bleeding test. Amount dye given up by dyed fiber to 250 cc H_2O at boiling temperature for 20 minutes Milligrams
Acid green	No acid	57.9	17.1	5.7
	HCl	72.2	2.8	4.5
	H_2SO_4	67.4	7.6	4.9
	H_3PO_4	65.2	9.8	5.3
Crystal ponceau	No acid	59.8	15.2	5.8
	HCl	74.5	0.5	1.8
	H_2SO_4	73.2	1.8	1.6
	H_3PO_4	72.3	2.7	4.1
Crocein orange	No acid	61.8	13.2	7.8
	HCl	72.7	2.3	3.9
	H_2SO_4	69.4	5.6	4.3
	H_3PO_4	69.4	5.6	5.3

In discussing Table V it was suggested that when the capacity of a fiber for an acid dye is as yet high the effect of an adsorbed ion in cutting down the adsorption of the dye is largely overcome. On the other hand, a low capacity of the fiber for a dye should indicate that adsorbed anions as the above could bring about a decrease in the amount of acid dye adsorbed. To denote this varying adsorbing capacity of a fiber under the conditions indicated above the use of the term saturation capacity is suggested. By the term saturation capacity of the wool then is meant the capacity of the fiber to adsorb a given amount of dye under definite conditions. In other words as suggested by Professor Bancroft: "If the amount of dye that will be taken up from a concentrated solution is 100 and if x is taken up from any given concentration, then 100 — x is the saturation capacity of the latter solution." It is evident that when the fiber has adsorbed a large amount of dye its capacity to adsorb more dye (its saturation capacity) is considerably less than when it has adsorbed a much smaller amount of dye. Thus if we consider the two points A and B in Fig. 1 on an adsorption isotherm as representing the amounts, respectively, of a dye adsorbed by wool, it is seen that the fiber which had adsorbed an amount corresponding to A has a much larger capacity to adsorb more dye, and its saturation capacity is much greater than the same fiber which has adsorbed an amount corresponding to B.

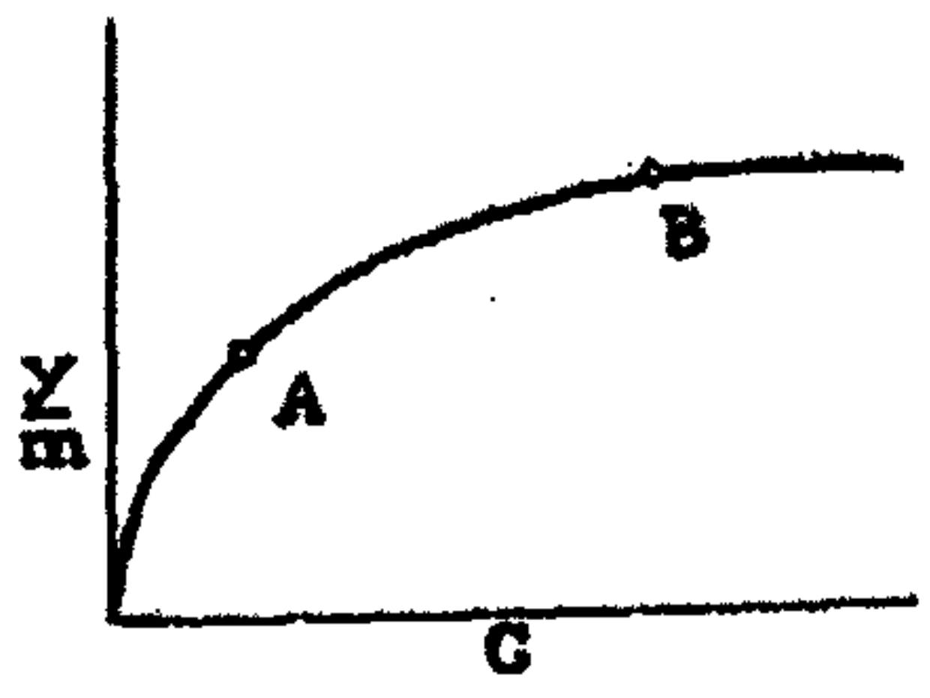

Fig. 1

If now we compare the data for the adsorbed dye in Table IV (40 mg dye per 250 cc H_2O) with the corresponding data in Table VI, we see strikingly illustrated in the first data as compared with the latter data the marked force of the fiber manifested in cutting down the repelling effect of the adsorbed anion on the adsorption of the dye. In the data of Table VI we see that the cutting down effect of the phosphate ion over the sulphate ion is considerable, with the exception of the crocein orange. It is to be observed that 22.1 mg and 27.8 mg more of crystal ponceau and acid green, respectively, in neutral solutions, were adsorbed by the wool dyed in 75 mg dye per 250 cc H_2O, than were adsorbed in 40 mg of the respective dyes per 25 cc H_2O. This indicates that the saturation capacity of the fiber for these dyes in the former case has been so nearly reached as to allow the cutting down effect of the adsorbed phosphate ion over the sulphate ion to be manifested.

The table of comparison follows:

TABLE VII

Dye	Acid used	Dye adsorbed from solution 40 mg per 250 cc H_2O Milligrams	Dye adsorbed from solution 75 mg per 250 cc H_2O Milligrams
Acid green	H_2SO_4	36.3	67.4
	H_3PO_4	36.0	65.2
Crystal ponceau	H_2SO_4	39.4	73.2
	H_3PO_4	39.4	72.3
Crocein orange	H_2SO_4	35.5	69.4
	H_3PO_4	35.5	69.4

As seen in the data, H_2SO_4 and H_3PO_4 are equally efficient in bringing about an adsorption of crocein orange. Experiments with a higher concentration of the dye, 100 mg per 250 cc H_2O, show, however, that the laws of adsorption of an acid dye in an acid solution as postulated by Bancroft hold. The data showing the effects of H_2SO_4 and H_3PO_4 on the adsorption of the dye follow:

TABLE VIII

Temperature—100° C
100 mg dye per 250 cc H_2O
Time—1 hour

Dye	Acid used 10 cc $N/10$ of each acid	Dye adsorbed Milligrams	Dye unadsorbed Milligrams
Crocein orange	H_2SO_4	92.5	7.5
	H_3PO_4	90.7	9.3

After one of the bleeding tests carried on for wool dyed in a neutral bath of acid violet the dyed fiber was left in the hot solution of the dye that had bled from the fiber, and the whole allowed to cool. As the beaker and contents cooled it was observed that the dye was quite rapidly readsorbed. In an hour practically all of the dye had been readsorbed. This experiment was repeated for acid violet with similar results. Experiments with fibers dyed in crocein orange and acid green and treated as those dyed in acid violet gave similar results, the slight differences being (1) that not quite all of the dye that bled was readsorbed, (2) that the readsorption was slower than in the case of acid violet. The results of these experiments seemed to indicate an irreversible adsorption of dyes. That there is also this irreversible adsorption between the adsorbed and unadsorbed dye in direct dyeing was shown in experiments carried out with acid violet, crocein orange, and acid green. One-gram samples of wool were dyed in 60 mg acid violet, crocein orange, and acid green per 250 cc H_2O, respectively, for one hour at the temperature of the boiling water-bath, after which time the beaker and contents (the dyed fiber was left in the solution of unadsorbed dye) were allowed to cool. At the end of ten hours all of the acid violet unadsorbed (about 10 mg) in this direct dyeing was completely adsorbed. The adsorption of the unadsorbed crocein orange and acid green was much slower. To insure complete adsorption of these dyes the dyed fibers were left in the cold dye bath (room temperature) for eight days. At the end of that time about 7 mg of the unadsorbed crocein orange in the direct dyeing and 10 mg of the unadsorbed acid green were adsorbed; or in terms of percentage of the respective unadsorbed dyes 91 percent of the crocein orange was adsorbed, and 90 percent of the acid green.

Various experiments were made to account for this irreversible adsorption of the dye. It was thought, although improbable, that the wool, when heated, was in some way changed so that its specific adsorbing power had increased. Hence an experiment was carried out in which the wool was placed in water heated to the temperature of the boiling water-bath for one hour and then entered while hot in 10 mg of acid violet (room temperature) in 250 cc H_2O. After 24 hours there was no appreciable adsorption of the dye. An experiment in which the acid violet (10 mg per 250 cc H_2O) was heated at the same temperature for one hour and then the cold wool entered the hot dye bath and the whole allowed to cool, gave scarcely better results although slightly more dye was adsorbed than in the previous case. An experiment in which the wool and dye were heated separately, as in the above, for one hour and then the fiber entered the hot dye bath, gave similar results. A final experiment in which the fiber was dyed in 60 mg of acid violet and then the dyed fiber removed from the bath and entered again when both were cooled to room temperature resulted in an appreciable adsorption of acid violet at the end of six weeks. Experiments of a similar nature with acid green, 11.2 mg dye per 250 cc water, gave negative results in indicating a reason for this irreversibility. The dye, however, in contrast to that of the acid violet, was almost completely adsorbed in all cases at the end of one week.

Although these experiments do not seem to point to any reason for the irreversible adsorption of a dye they do seem to bring out the interesting fact that the more irreversible a dye the less completely and readily that dye is adsorbed at low temperatures. From methods described below it is brought out that of the dyes acid violet and acid green, acid violet is far more irreversible than acid green. From the experiments just described above we see that acid violet, even after a long period of time, is adsorbed very slightly at room (low) temperature. Niagara violet 3R, like acid violet, is a highly irreversible dye. An experiment in which a one-gram sample of wool was left in a bath of 60 mg of the dye per 250 cc water for three weeks at room temperature brought out the fact that the dye was very slightly adsorbed. Acid green in contrast to the above dyes is much more reversible, and hence was much more largely adsorbed at room (low) temperature.

That this apparent irreversible adsorption of dyes is quite general is indicated by the work of Freundlich and Losev.[1] In four cases of the six studied this phenomenon

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[1] Zeit. phys. Chem., 59, 284 (1907).

was exhibited. They found, for example, that on wool patent blue was irreversibly adsorbed; on silk new fuchsin and patent blue, and on cotton new fuchsin. Crystal violet was adsorbed reversibly by wool and silk.

The question now arises: is there any relation between this apparent irreversible adsorption of a dye and its tendency to bleed? If we consider this irreversible adsorption as indicative of the force with which the dye is held by a fiber it would seem that the more irreversible a dye is the less that dye will bleed. Thus, if we consider the experiments described above for acid violet, crocein orange and acid green we see that the irreversibility of the acid violet was complete: the irreversibility of the crocein orange and acid green nearly equal to each other. Therefore, under like conditions of dyeing and testing for bleeding we should expect acid violet to bleed less from a fiber than acid green or crocein orange; and that the two last-named dyes should bleed approximately the same.

To show the relationship between the irreversible adsorption of a dye and its bleeding, two methods of experimentation were carried out: (1) a method suggested by Freundlich, (2) a method suggested by Professor Bancroft. Freundlich's method will be taken up first.[1] One gram of pure wool, used as bought, was entered in 250 cc of water containing 60 mg of dye, and dyed for one hour at the temperature of boiling water-bath. The dye unadsorbed was determined colorimetrically. The dyed fiber was tested for bleeding in a volume of 250 cc H_2O for twenty-five minutes, and the amount of dye bled determined also colorimetrically. Parallel with the above experiment another one was run in which the same weight of wool was entered in just one-half the volume of dye solution containing the same amount of dye, and dyed at the same temperature for one hour. Then the volume of solution was made up to 250 cc and the whole heated at the same temperature for another hour. The amount of unadsorbed dye in

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[1] Zeit. phys. Chem., 57, 385 (1906).

this experiment was likewise determined colorimetrically. Thus by these experiments a relation between the irreversibility of a dye and its bleeding was obtained. The data, the average of triplicate experiments, are given in the table below.

Dye	Amount unadsorbed after 1-hour treatment (direct dyeing) Milligrams I	Amount dye unadsorbed on irreversible experiment Milligrams II	Amount dye irreversibly adsorbed Milligrams III	Amount dye bled Milligrams IV
Crocein orange	11.2	8.6	2.6	5.0
Acid green	7.3	6.3	1.0	4.4
Niagara violet 3R	8.9	1.0	7.9	0.1

These data bring out the fact that the more irreversible the dye the less the bleeding. Column I gives the amount of dye unadsorbed by the fiber in the first experiment as outlined above. Column II gives the amount of dye unadsorbed by the fiber which was first entered in just half the volume of dye of double the strength used in the first experiment. After one hour an amount of water was added making the final volume equal to that used in the first experiment. It is seen that in all cases the end concentration in the second column is less than in the first column. This indicates a certain amount of irreversible adsorption on the part of the dye under the conditions of the experiment, for if there had been a definite equilibrium between the adsorbed quantities and the end concentrations, the final concentration in Column II ought to have been the same as in Column I. Column III gives the difference in end concentrations between Columns I and II. Column IV shows the amount of dye given up by the fibers in the bleeding test. In comparing Columns III and IV we see that for the conditions of the experiment the amount of dye irreversibly adsorbed is greater the faster the dye is to the bleeding test as carried out in the experiment. There does not seem to be any quantitative relationship between the quantities given in Columns III and IV.

The other method of showing the irreversible adsorption, as suggested by Professor Bancroft, was as follows: A one-gram sample of wool was dyed in a bath containing 60 mg of the dye for two hours at 90° C or till equilibrium was reached. The fiber was then removed, washed, and the amount of dye left in the bath determined colorimetrically. The data are given in Column I, of the subjoined table. The dyed fiber was put in a beaker containing 250 cc water and the whole heated to the temperature of the water-bath for about 25 minutes. The beaker and contents were at once cooled to 90° C and the fiber then placed in another beaker which contained in 250 cc H_2O an amount of dye that was not adsorbed by the fiber during the dyeing at 90°. The whole was kept at 90° C till equilibrium was reached, or for about two hours. The fibers were then removed, washed, and the amount of dye left in the solution determined as above. The data are recorded in Column II in the table below. The difference between the amount of unadsorbed dye during the direct dyeing, and the amount of dye in the second final dye bath is taken as a measure of the amount of it irreversibly adsorbed. Column III of the table below contains the data. The data, the average of duplicate experiments, follow:

Dye	Dye unadsorbed on direct dyeing Milligrams I	Dye unadsorbed on irreversible experiment Milligrams II	Amount of dye irreversibly adsorbed Milligrams III
Crocein orange	7.3	6.5	0.8
Acid green	9.5	5.7	3.8
Niagara violet 3R	9.5	1.2	8.3

These data bring out the same general relationship that were brought out in the immediately preceding table. Here as there the most irreversible dye is Niagara violet followed by acid green and crocein orange in the order named.

These two sets of experiments point to the general conclusion that the more a dye is irreversibly adsorbed, other factors being the same, the less it will bleed when subjected to such tests. This is brought out rather strikingly in a comparison of the amounts of dye bled for crocein orange and acid green, in Tables IV and VI. In five out of the eight cases compared crocein orange bled more than acid green. This is what one should expect from a knowledge of the comparative irreversibility of the two dyes. The three exceptions noted may be more apparent than real.

FROM TABLE IV

Treatment	Amount dye bled Milligrams	
	Crocein orange	Acid green
Neutral bath	5.0	3.9
HCl bath	4.4	2.7
H_2SO_4 bath	3.1	2.7
H_3PO_4 bath	3.7	3.3

FROM TABLE VI

Treatment	Crocein orange	Acid green
Neutral bath	7.8	5.7
HCl bath	3.9	4.4
H_2SO_4 bath	4.3	4.8
H_3PO_4 bath	5.3	5.3

To sum up this part of the work:

This irreversible adsorption of a dye, as suggested above (page 792), may be taken as indicative of the force with which a dye is held by a fiber. From this point of view one would conclude that Niagara violet or acid violet is much more firmly held by the wool than is crocein orange or acid green; hence the less bleeding exhibited by the first two named dyes than the last two. This force by which the dye is held by the fiber is of a selective nature; that is, there seems to be no relation between the constitution of a dye, and its irreversibility. It is possible that the more irreversible dyes act as better mordants toward themselves than the less irreversible ones.

Stains and Their Removal

In an experiment in which acid violet was practically, although not completely, removed from the fiber by boiling water we have a case analogous to the partial removal of a fruit stain from cloth by this same means and method. Thus in the experiment with acid violet we can look upon the dye as the stain upon the wool. Its practical removal from the fiber was due to the fact that the boiling water peptized it, that is, made a colloidal solution of it.

Dyes also can be removed from a fiber by reagents other than water, as, for example, by the use of bleaching agents, aqueous solutions of ammonium acetate or sodium carbonate, and solid reagents such as fullers' earth. The above reagents are used also to remove stains from textiles, and in many instances the methods and principles of removal of the stain by a given reagent is the same as for the dye. This very interesting analogy between some stains and dyes with regard to their behavior towards various reagents led to the following classification of the principles underlying the removal of the greater majority of stains from textiles, and to a brief study to confirm each method in this classification.

The following classification has been proposed by Professor Bancroft:

I. Mechanical removal.
    Mud and brush.
II. Dissolving in a liquid.
    Grass in alcohol, benzene.
    Sugar in water; dyes in hot water.
    Iodine in alcohol.
    Syrup in warm water.
III. Peptizing in a liquid.
    Balsam of Peru with kerosene or alcohol.
    Dyes in hot water; chocolate with hot water.
    Machine oil with turpentine.
    Grease with gasolene.

Glue with warm water.
Milk with cold water.
Paraffine with benzine or kerosene.
Pitch with benzine.
Vaseline with turpentine.
Punch with warm water.
Coffee tannin with boiling water.
Iron rust with kerosene.

IV. Peptizing with a solution.
  Dyes with sodium carbonate, ammonium sulphate, borax.
  Blood with ammonia.
  Soot with sodium hydroxide (2 percent solution).
  Glue with acetic acid.
  Paint with sodium carbonate.

V. Peptizing with peptized colloid.
  Blood with soap.
  Soot, iron rust, with soap.
  Cream with soap.
  Perspiration with soap.
  Old black silk clothes with skimmed milk.
  Kerosene with soap.
  Meat juice with soap.

VI. Peptizing in two stages.
  Tar and oil and soap.
  Grease and oil and soap.
  Tea and glycerine and soap.
  Black shoe polish and oil and soap.
  Grass and benzine and soap.
  Rosin and oil and soap.
  Coffee and glycerine and soap.
  Paint and oil and soap.
  Paint and oil and casein and soap.

VII. Adsorption by solid.
  Grease and fullers' earth or blotting paper.
  Wax and French chalk.

Starched white woolen shawls, lace curtains, with rice or potato starch, and treatment with enzymes.
Dyes and freshly prepared alumina.
Charcoal drawings and bread.
Fruit stains and fullers' earth.
Fruit stains and salt.
Wall paper and dough, corn-meal.
Furs and corn-meal.

VIII. Peptizing with a liquid and adsorption by solid.
Grease, alcohol or turpentine, and pipe-clay or fullers' earth.

IX. Change of substance forming the stain.
Fruit stains oxidized by use of "bleaching" agents.
Ink with salt and lemon juice.
Ink with hydrochloric acid, oxalic acid.
Dyes with bleaching agents, as sulphur dioxide.
Dyes with potassium permanganate and oxalic acid.
Iron rust with hydrochloric acid.
Iron rust with citric acid and cream of tartar.
Perspiration with sodium hyposulphite (for silks and wools).
Tobacco with hydrochloric acid and ammonia.

These methods will be taken up in the order given.

Method I involves mechanical manipulation only. The efficiency of the brush depends upon the fact that the material to be removed is generally held loosely by the fiber.

In Method II stains from iodine and the dye safranine were studied.

With respect to iodine a piece of woolen cloth was immersed in an aqueous solution at room temperature for thirty minutes, and another piece at the boiling temperature for ten minutes. The iodine adsorbed by the fiber at room temperature was readily removed by alcohol at the same temperature. The removal of the stain from the boiling solution was not brought about so readily by alcohol at room temperature, a much longer time being required, namely, about twenty-four hours. However, by immersion of a similarly stained piece of cloth in several fresh, hot portions of boiling alcohol the removal of the stain was brought about in a short time. Woolen cloth was stained by the dye safranine in the same manner as by the iodine. The larger part of the dye adsorbed at room temperature was removed by repeated immersion in fresh portions of water at that temperature. The removal was brought about more completely by immersion in water heated to 60°–70° C. Not all of the dye, however, was removed, even by boiling water—there being a small portion which "set" on the fiber.

The larger part of the dye adsorbed by the fiber at the temperature of boiling water was removed slowly, and only by repeated immersion of the dyed fiber in fresh portions of boiling water. The last traces of the dye could not be removed by this treatment.

The other cases listed in this division of the general classification are removed, as safranine and iodine were, with the formation of a true solution of the stain with the solvent. When fresh these stains are quite readily removed by the particular solvent. A stain, as grass stain, may, however, become "set" on the fiber with the result, as in the case of safranine, that it cannot be removed by the solvent, even by repeated applications. Chemicals as listed in IX are then generally the only reagents capable of bringing about its removal. The sugar and syrup stains, as is obvious, can easily be removed by water for they are not strongly adsorbed by fibers, and also are very easily soluble in the liquid.

The cases studied where the liquid peptized the stain were: the dye crocein orange removed by water; grease (lard) removed by gasolene.

In the case of crocein orange the method of experiment was identical with that of safranine. The results obtained were similar; that is, in no case was the dye completely removed from the fiber. In the case of the fiber dyed hot in a solution of 60 mg of dye per 250 cc H_2O for one hour, repeated immersions of the dyed fiber in fresh boiling water removed the greater part of the dye only after $4^1/_2$ hours.

Grease was completely removed by gasolene in a very short time at room temperature.

Peptization of substances by a liquid as in the above cases is a very common phenomenon.[1] In the cases of the fiber stained either by the dye or grease we may look upon the combination as one substance. Thus with the dyed fiber it adsorbs the solvent water, and so part of it, *i. e.*, the colored portion, is peptized. Hence we get a water-soluble colloid of the dye. The same holds for the greased fiber. It readily adsorbed the gasolene and hence part of it was peptized, with a formation of a gasolene-soluble colloid of grease. To quote Professor Bancroft, "If we wash out of cloth a dye which forms a colloidal solution[2] we are peptizing the dye with water. The removal of chocolate by water is another case of the same type because chocolate does not really dissolve in water. The removal of iron rust from iron by means of kerosene is a case of peptization because the iron oxide does not dissolve in kerosene. The removal of grease by benzine, gasolene, naphtha, etc., is another case under this heading because the grease does not form a true solution in these organic liquids. The removal of resin with benzine comes under the same head."

Just as crocein orange was removed from the fiber by water, just as grease was removed from the fiber by gasolene, so the other substances here listed as stains are removed in the same way by the particular peptizing solvent. Colloidal solutions are formed in all cases. Thus with water we have formed the water-soluble colloids of coffee, glue, milk, and punch; with turpentine we have the turpentine-soluble colloids of machine oil and vaseline; with kerosene the kerosene-soluble colloids of paraffine, pitch, and iron.

Many stains can be removed from fibers by means of dissolved substances. This removal is due to the fact that the undissociated dissolved substance, or one of the products of the dissolved substance, is readily adsorbed by the stain

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[1] Bancroft: Jour. Phys. Chem., 20, 85 (1916).

[2] Bancroft: Journal of Home Economics, 8, 356 (1916).

and hence peptizes it, thus giving rise to a colloid solution. In aqueous solutions, in general, peptization by undissociated substances, as for example, inorganic salts, is not so well defined as peptization by an ion.[1] Cases of peptization by an ion, however, are numerous and well known. Thus the removal of the stains as listed in IV can be considered as brought about by their peptization by ions. Thus in the case of the blood stains their removal, from this point of view, is due to the peptization of the haemoglobin of the blood by the adsorbed hydroxyl ions from the aqueous solution of ammonia. Acid dyes can readily be removed from wool by a dilute solution of borax. The borax in solution is hydrolyzed giving rise to the formation, among other substances, of sodium hydroxide, which in turn dissociates into sodium and hydroxyl ions. Now the hydroxyl ions are preferentially and readily adsorbed by the stained fiber,[2] hence they readily peptize the adsorbed acid dye, and its removal in consequence is brought about.

In the laboratory an example studied under this section (IV) was the removal of soot by a dilute solution of sodium hydroxide (2 percent). A piece of cotton cloth was very thoroughly impregnated with soot and then immersed in the slightly warmed alkali solution. In a few minutes the soot was practically removed from the cloth. In this case we have the peptization of the soot by the preferentially adsorbed hydroxyl ions, giving rise to a sodium hydroxide-soluble colloid of soot.

The removal of soot as listed in V was very interesting. Fibers of wool and silk were thoroughly impregnated with soot and then immersed in a dilute "liquid" soap solution which was heated to about 50° C. The removal of the soot from the wool was very rapid and complete. In the case of the silk a longer time was required but the removal was as complete. To quote Professor Bancroft in this connection,[3]

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[1] Bancroft: Jour. Phys. Chem., 20, 102 (1916).

[2] Bancroft: Ibid., 18, 10 (1914).

[3] Bancroft: Journal of Home Economics, 8, 356 (1916).

"Under peptization by a peptized colloid we have all the cases in which soap is used. Soap does not dissolve in water but is readily peptized by it. The theory of washing with soap has been put on a satisfactory basis by Spring.[1] It is to him that we owe a very striking and instructive experiment. If we filter a fine suspension of rouge or soot through filter paper, some of the particles stick to the filter paper or, as we say, are adsorbed by it. If the liquid is filtered several times through the same paper, the water will finally run through clear, the particles of rouge or soot adhering to the previously adsorbed particles and finally clogging the pores of the filter paper. If a soap solution be poured on the filter, a red or a black filtrate is obtained at once, almost as though one had punched a hole in the bottom of the filter with a glass rod. The soap forms a film round the rouge or the soot, removing the particles from the paper and thus allowing them to pass through. All the rest of the particles follow just as a log jam breaks when the key log is started. At first sight it seems as though the soap must have broken up the carbon or the rouge into finer particles which then passed through the filter. There are two reasons for rejecting this hypothesis. In the first place the experiment does not succeed if the rouge or the carbon is too coarse, and there is no apparent reason why the soap should not break up coarse particles if it can break up fine ones. In the second place Spring showed that we are dealing with an adsorption of soot by filter paper. If the black filter paper be reversed and washed with water, only the carbon which is not in immediate contact with the paper is removed.

"Soap acts in a similar way in removing dirt or grease from fabrics or from the hands. The soap forms a film round the dirt or the grease removing it from actual contact with the fiber or the skin, thus simplifying the task of washing it away with water."

Another colloidal solution which acts like soap is ox-gall in water. Owen recommends it for the purpose of cleaning

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[1] Zeit. Kolloidchemie, 4, 161 (1909); 6, 11, 109, 164 (1910).

wool carpets.[1] He says: "Take them and beat and shake them thoroughly in a good breezy place to get out all dust. Have the floor scoured clean and, when dry, replace the carpet, and, if still much soiled and dingy, go all over the carpet with ox-gall and water. The secret of success is to clean and rinse them thoroughly without soaking them through. A pint of fresh ox-gall is put into a pail of clean soft water and another pail of clean water set handy. With a brush rub up a lather upon about a square yard of the carpet by dipping the brush in the ox-gall and scrubbing, not too hard but with just the movement that raises a lather, but does not remove the fiber from the carpet. Now with a soft cloth or large sponge, not too wet, remove the lather, aiming to do this by frequent wringing out of the sponge in clear fresh water. After all is done, open the windows and the carpet will soon dry out."

It is obvious that the other substances listed in this section are removed in the same way as soot was by the soap. In all cases with the exception of the stains on the black silk clothes, the water-soluble colloid, soap, is the effective detergent. Old black silk clothes can be "renovated"[2] by immersing them in scalding hot skim milk and water to which a little glue or gelatine has been added. In this case the dirt and dust are readily removed by the peptized colloid casein in the milk and the peptized gelatine.

It would seem that soluble colloids other than water could be used to remove stains. Thus many aniline dyes that are insoluble in benzene "can be peptized by a benzene-soluble colloid such as zinc or magnesium resinate so-called."[3]

In the method of peptizing in two stages the following cases as listed under VI were studied: grease and oil and soap; rosin and oil and soap; paint and oil and soap; and paint, and oil and casein and soap. The methods suitable for the above cases are practically identical for the other stains listed in this section.

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[1] "The Dyeing and Cleaning of Textile Fabrics," 100 (1909).

[2] Owens: "The Dyeing and Cleaning of Textile Fabrics," 114 (1909).

[3] Bancroft: Jour. Phys. Chem., 20, 108 (1916).

To study the removal of grease and rosin according to the outline suggested white woolen cloth was thoroughly impregnated with automobile grease. These stained pieces of cloth were then very thoroughly rubbed with olive oil till the stains were softened. The whole was finally immersed in a warm soap solution. The removal of both stains was thorough and complete.

With regard to paint stains the following procedure was followed: A large piece of white woolen cloth was thoroughly impregnated with a brown paint, which was allowed to dry thoroughly on the fiber by placing in a hot air oven heated to about 100° C. After the paint had completely dried, the stained cloth was thoroughly rubbed with olive oil till the paint was softened. The cloth was then cut into two parts. One piece of the cloth was immersed in a warm soap solution for about five minutes. It was then removed, washed, rubbed with oil, and again immersed in the soap solution. The removal of the paint was fairly complete. The other piece of cloth before the soap treatment was treated with casein by rubbing into it the finely divided powder. Treatment with a warm soap solution then followed for about five minutes as in the preceding case. The treatment with oil and casein was repeated for this piece of cloth. If anything, the paint in this latter case was more completely removed than it was from the other sample.

It might be well in this connection to quote Owens. He says, p. 90: "Grease spots are of the most common occurrence. To remove these from white fabrics is comparatively easy, but to remove them from colored fabrics without at the same time doing injury to the color is often very difficult and sometimes impossible. Very much depends upon the skill and perseverance of the operator. Good soap and water is the most universal solvent for greasy matters, and where there is no reason for not wetting the goods, soap and water should be tried. Grease spots from carriage wheels, sewing machines, or any source containing iron from wear of bearings, or carbon from any source, red lead, or any insoluble colored substance, should first be rubbed thoroughly with some oil that is itself capable of being washed out with soap and water, such as lard or fresh butter, olive oil, linseed oil, etc.

"Much depends on how this is done. Don't be afraid to use plenty of oil, butter, or lard, and then work with the fingers, bending the cloth back and forth as if you were breaking a wire, until upon holding it up to the light you see that the dark matter of the spot is completely and evenly distributed and worked up with the oil. When sure this result is accomplished, then work in a thick cold, watery, soapy mass obtained by boiling up sliced laundry soap in water and allowing to cool. If on touching the dry soap bar to the tongue, it does not 'bite,' it should have some sal-soda added to it in the boiling. Work the prepared soap into the cloth where the spot is, until the oil in its turn is worked up with the soap as thoroughly as the spot was with the oil. Now, and not before, wash out the spot with soapy water. Only with very old spots will any trace remain after this treatment. Grease spots succumb very well if rubbed up with kerosene, the kerosene rubbed up with new milk, and the whole then worked with soap and water."

In regard to paint, Owens says, p. 103: "Paint, when fresh, washes out as readily as any grease spot. As it ages and oxidizes it becomes more and more difficult to soften and remove it. . . . . . .Oil the spot and rub the oil in patiently, striving to blend the spot with the oil. If the spot is very old, allow to lie with the oil upon it for several days, rubbing occasionally to see if the paint is softening. A few drops of turpentine, kerosene, or any solvent for greasy matters may be added and worked in. Old lead paint is very persistent. Finally, wash out like a fresh grease spot."

In all of these cases we have as a result of the oil treatment a peptization of the particular stain by the oil. The peptized stain was then finally removed by the peptized colloid, namely, the soap as explained in V. In the case where casein was used we have an adsorption by the casein of the peptized paint followed by a peptization of the casein and its adsorbed products by the soap, and their consequent removal.

In Method VII we have an interesting procedure for the removal of stains in that advantage is taken of the greater selective adsorptive power of the solid reagent for the particular stain than the cloth or material to be cleaned. The only case studied was the removal of grease by blotting paper. A piece of cloth, thoroughly stained with automobile grease, was placed between two hot pieces of blotting paper. The grease was removed very rapidly from the cloth. Here, of course, the adsorptive power of blotting paper for the grease was greater than the cloth, hence the removal of the grease.

The use of solid reagents, other than the one studied, for removing stains is quite general as the list in VII indicates. Just before using, these solid reagents should be moistened.[1] They should be thoroughly rubbed into the stained cloth. Repeated applications of the solid reagent will often bring about a complete removal of a stain. Koller[2] states that infusorial earth is especially to be recommended for cleaning glass plates for photographic purposes. Even very greasy plates rapidly become clean when rubbed with infusorial earth moistened with water. A very interesting case to be listed under Method VII is the removal of dirt, etc., from starched curtains. This method was brought to the attention of Professor Bancroft by Mr. C. P. Long of the Globe Soap Company. Starched lace curtains are placed in water with a diastase which converts the starch into soluble starch. When this is peptized by water the dirt comes off with the starch without any rubbing.

In Method VIII we have an example where the stain is first peptized by a liquid and the removal of the whole brought about by selective adsorption. As in Method VII a piece of wool cloth was stained with automobile grease and then thoroughly rubbed with alcohol. Fullers' earth was then rubbed in and the whole washed in cold water. By repeated

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[1] Ray Balderston: "Laundering," 47 (1914).

[2] "The Utilization of Waste Products," 310 (1915).

applications of alcohol and fullers' earth a large percentage of the grease was removed.

Method IX is resorted to among practical cleaners, only with white goods, or where, with dyed goods, it is believed that they can be re-dyed on the spot thus treated. The removal of the stain in this case is brought about by its conversion into other substances which readily can be removed from the goods by washing.

Iodine and safranine stains were studied. In the case of safranine a sample of cloth was taken upon which were traces of the dye which could not be removed by boiling water. The sample was immersed in a dilute solution of bleaching powder. In a short time the cloth was "bleached." Upon washing, no evidence of the dye was visible.

The sample of cloth stained by iodine was immersed in a dilute solution of sodium thiosulphate. The iodine was reduced very rapidly, and on washing the cloth no evidence of the stain was visible.

These two methods are only suggestions of the many cases where "chemicals" may be used for removing stains. In their use proper regard for the kind of cloth, silk, wool, or cotton, the condition of the cloth, as for example whether dyed or not, must be taken into consideration. One of the most frequent uses made of this general method of removal is in the removal of "stubborn" fruit stains as peach, plum, or coffee stains.

Summary

Under the experimental conditions described the color of one dye can be partially or completely masked by another, but one dye cannot be displaced by another. The apparent displacement is brought about by the solvent or peptizing action of the water.

An experiment is described illustrating the selective adsorption by wool of one dye over the other at different temperatures.

With respect to the bleeding of acid dyes, it is shown that the minimum amount of dye is extracted by hot water when the fiber (wool) is dyed in an acid bath. The most probable reason for this is that the acid aids in coagulating or setting the dye on the fiber, thus making it less soluble.

The laws of adsorption of an acid dye in various acid baths as postulated by Bancroft hold when, as suggested, the saturation capacity of the fiber has been so decreased that the cutting-down effect of the respective anions can be manifested.

Of the dyes studied the more the dye was irreversibly adsorbed the less completely and readily was that dye adsorbed at a low (room) temperature.

Of the dyes studied by Brown the decreasing or increasing adsorption with decreasing temperature below 60° may be accounted for, in view of the immediately preceding statement, by postulating that those dyes are irreversibly adsorbed to a greater or less degree, rather than by postulating that those dyes are adsorbed with an adsorption or evolution of heat.

The more a dye is irreversibly adsorbed, other factors being the same, the less it will bleed when subjected to bleeding tests.

A classification of the methods for the removal of stains is suggested. A study was made of each method in the classification. It is suggested that a very interesting field for research in washing and cleaning is by a study of the method belonging under Class VII.

This thesis was carried out under the direction of Professor Wilder D. Bancroft. It is a pleasant duty to me to express to Professor Bancroft my gratitude for his helpful criticism, his unfailing kindness and courtesy during the progress of the work.

Thanks are due to Professor Lewis Knudson, of the New York State College of Agriculture, for his hospitality in sharing with me his laboratory after the loss of Morse Hall; and also to Mr. W. B. White, of the College of Agriculture, for the loan of a Duboscq colorimeter.

Cornell University

NEW BOOKS

Principles of General Physiology. *By William Maddock Bayliss. 25 × 18 cm; pp. xx + 850. New York: Longmans, Green, and Co., 1915. Price: $6.00.* —In the preface the author says, p. ix: "Vital phenomena being essentially dynamic, the study of physiology consists in the investigation of changes. As Jennings says, 'It is of the very greatest importance for the understanding of the behavior of organisms, to look upon them chiefly as something dynamic—as processes rather than as structure.' The velocity of reactions and the conditions affecting it, together with the energy changes involved, are, therefore, more essential than the chemical structure or physical properties of the reacting substances or the resulting products, although the knowledge of certain of these properties is, of course, necessary. To use an illustration, inadequate as that is, of a petrol motor, the problem of the physiologist is analogous to that of the investigation of the amount of fuel consumed in relation to the work done, when the engine is working under various conditions. The greater number of the chemical and physical properties of the materials used in the construction of the engine are of no importance, such as the valency of the iron or the smell of the lubricating oil, while others are fundamental, such as the heat of combustion of the fuel and the insulation of the ignition circuit. Even the exact chemical nature of the fuel is of subsidiary importance, so long as it is sufficiently volatile and capable of giving an explosive mixture with oxygen. Moreover, the precise form of many parts, such as the heads of bolts, is immaterial, just as many structural details of living organisms or the precise chemical composition of connective tissue have, at all events at present, an insignificant physiological interest. In making this statement, it is far from my intention to undervalue in any way the work of the organic chemist or the morphologist. Structure is the indispensable basis of function, and all structures, chemical or morphological, will, no doubt, ultimately have their function assigned. But, in these pages, space cannot be spared for description of such as have no functional importance suggested up to the present.

"The treatment of the subject in the way here attempted undoubtedly has its difficulties. Important points have most probably escaped reference. I shall be very grateful to readers who will inform me of these omissions, and also for criticism in general. I feel that I may, in some places, perhaps, have laid myself open to the charge of neglecting statements which are in opposition to the point of view adopted. I consider myself justified in certain instances in doing this, on account of the disagreement of these statements with a large mass of knowledge otherwise obtained, and in the belief that further investigation will explain the apparent contradiction...... In other cases of omission, my ignorance must serve as an excuse. But, as Bacon has well pointed out, truth is more likely to come out of error, if this is clear and definite, than out of confusion, and my experience teaches me that it is better to hold a well-understood and intelligible opinion, even if it should turn out to be wrong, than to be content with a muddle-headed mixture of conflicting views, sometimes miscalled impartiality, and often no better than no opinion at all......But, at the same time, there must never be the least hesitation in giving up a position the moment it is shown to be untenable. It is not going too far to say that the greatness of a scientific investigator does not rest on the fact of his never having made a mistake, but rather on his readiness to admit that he has done so, whenever the contrary evidence is cogent enough."

"It should be unnecessary to point out that vital processes can only be investigated where they exist, that is, in the living organism, either as a whole or in its separate parts, when these can be prepared in such a way as not to interfere with their function, or, if so, only in a known manner. Such experiments when vertebrate animals are concerned, are known sometimes as 'vivisections,' an objectionable and misleading name. I should not have thought it necessary to refer to this question, were it not that certain people, whom one might reasonably expect to possess better knowledge, appear to hold that the progress of physiological science is possible without such experiments. Vesalius stated that the simplest experiments on the living animal, as a rule, revealed more than a long study of the dead body. With another set of people, who see no value in physiology, and frequently also none in science of any kind, I have naturally no concern except to remind them that a great artist like Leonardo da Vinci, whom they probably hold in some esteem, not only thought differently, but actually performed vivisections."

The headings of the chapters are: protoplasm; energetics; surface action; the colloidal state; the properties of membranes and the properties of the surface of cells; osmotic pressure; electrolytes and their action; water, its properties and functions; nutrition; catalysis and enzymes; secretion; digestion; excitation and inhibition; contractile tissues; nervous systems, peripheral and central; reflex action; receptor organs; tonus; the action of light; oxidation and reduction; respiration; electrical change in tissues; the circulation of the blood; hormones, drugs, and toxins.

There is an interesting passage in the chapter on surface action, p. 65. "Raehlmann has described how the constituents of certain adsorption compounds can be seen to be merely in close apposition. One of his experiments is as follows: The extract of a yellow wood, used in dyeing, and known as fustic, shows itself under the ultra-microscope to be a suspension of minute particles too small to be visible as separate dots. By the addition of alum, these 'amicrons' can be caused to aggregate together to form larger ones, visible as such, and of a greenish color. Serum albumin behaves similarly, and, under the influence of alum, forms yellow particles. The dye, 'Congo fast blue' even without alum, consists of visible particles of a red color by the reflected light of the ultra-microscope. Taking each separately, we have then green, yellow, and red particles. When the three solutions are mixed, an adsorption compound which gives a green solution is formed. This solution, under the ultra-microscope, is seen to consist of compound particles, each containing three of the simpler ones, one each of the red, green, and yellow ones. If albumin, Congo-blue, and fustic are mixed without alum, the particles do not run together. It appears that Congo-blue, and probably also the other colloids, have a negative charge, which must be neutralized by the trivalent aluminum ion before aggregation can occur."

On p. 70, we read that "when rennet is shaken up in solution, it is more or less inactivated by adsorption on the surface of the froth produced. This inactivation is completely absent if a little saponin be added, although the foam is even greater than before. Saponin, in fact, lowers surface energy more than does rennet, hence it obtained possession of the surface. The same fact is seen in the driving out of rennet from its adsorption by charcoal in the experiments of Jahnson-Blohm (1912). Charcoal added to rennet prevents its action on milk (acting as an anti-enzyme), but if saponin be added to such an inactive mixture, it becomes active owing to the driving off by the saponin of the rennet from its 'combination with the antibody.' The fact, that one substance can displace another from adsorption, is of importance with respect to the turning out of oxygen from oxyhaemoglobin by exposure to carbon monoxide."

The visual purple is a substance about which the author records some interesting facts, p. 520. "The color of the pigment is not exactly what most people would call purple; it contains much more red. But, having a trace of violet in it, it is best described as a deep pink or rose color. It is bleached by light; but, in the retina, the colors return in the dark. Whether there is new pigment formed or whether the products of the action of light return to their original state in the dark, a very common phenomenon in photo-chemical reactions, is not altogether certain. It appears, however, that under some conditions, solutions of the pigment recover their color when allowed to stand in the dark after being bleached by light. It has no isolated absorption band in the spectrum, but absorbs light almost equally in all parts, leaving a little red and violet, hence its color. It is to be expected, then, that it would be responsive to light of all wave-lengths, except the extreme red and violet. As indicated above, a series of substances with absorption bands along the course of the spectrum, when mixed together, might give a similar continuous absorption......

"When light falls on the peripheral parts of the retina in man, it is found that, when diminished, so as to be just visible, it is only that part of the spectrum between wave-lengths 600 and 440 $\mu\mu$ (orange to blue) that is visible at all, and the sensation is one of light without color, whatever the wave-length used. Now Victor Henri and Larguier des Bancels (1911) have determined the amount of energy just sufficient to excite (threshold energy), the bleaching effect on the pigment and the amount of light absorbed by it, all at various wave-lengths between the values named. When put into curves these three factors are found to follow the same course. This means that to produce the same sensation, by different wave-lengths, requires such an amount of radiant energy that the amount absorbed by the visual purple is the same in all cases. This is a powerful argument in favor of the participation of the pigment in vision, at all events in that particular form of the sensation investigated. The same investigators find that the absolute quantity of energy required varies with the duration of action according to a complex law, which seems to result from a combination of that of excitation of nerve with that of a photo-chemical reaction. If the energy quantum be worked out by the formula of Nernst, it is 2×10^{-12} erg for the D line, practically the same as the limit of the sensibility of the retina. This sensibility is then the maximum possible."

On p. 524 we read: "The Young-Helmholtz theory assumes that there are only three primary color sensations, red, green, and violet. Now, while it is true that any color may be formed by mixtures of these in appropriate proportions, it is also true that more than three primary sensations would also serve the same purpose; three is, in fact, the minimum. And it is a matter of universal experience that blue and yellow have just as much right to be considered primary as the other three. In fact, Newton's division of the spectrum into red, orange, yellow, green, blue, indigo, and violet is much nearer the truth. Indigo, however, is rarely seen as a distinct color. Edridge-Green divides people into classes according to the number of distinct colors they distinguish and shows that there are various degrees of color blindness according to the number of colors seen in the spectrum. From the point of view of the evolution of the color sense, he points out that it is practically certain that the distinction between different wave-lengths, that is, the recognition of a difference between colors, would first show itself at the extremes of the region which is appreciated as light, the region between the wave-lengths 770 and 396 $\mu\mu$ about. Red and violet would be distinguished first, next green between them would be added, finally yellow and blue. Correspondingly, a common form of color blindness is the tri-chromatic, where red, green, and violet are the only colors perceived. Yellow is called red-green, and blue, green-yellow.

"A further important point established by this investigator is that, contrary to what a casual examination of the spectrum might lead one to suppose, there is not an infinite series of gradations of color along the spectrum, but that it can be divided up into a number of patches, each of these patches being of a uniform color. Thus the eye is not capable of appreciating an indefinite number of spectral colors. The fact can be shown by the use of a spectrometer with adjustable shutters in the ocular. When any part of the spectrum is thus isolated, it is found that a certain breadth can be found which appears to be all of the same color. Thus the whole spectrum is divided up, by normal-sighted people, into some sixteen to twenty monochromatic areas."

On p. 534, the author points out some extraordinary things in regard to the oyster. "The strength with which a bivalve mollusc holds its shells together is known to everyone who has tried to open an oyster by merely pulling the shells apart. On the face of it there is nothing to suggest that this fact may not be due to the reflex action of a powerful muscle. It is found, however, that weights may be arranged to pull continuously, and yet the shells remain firmly closed against a considerable force for many days. To take an example, it requires a tension to be exerted by each square centimeter of the adductor of *Dioxinia exoleta* equivalent to the weight of 2400 g in order to close the shells against the elastic cushion which forces them open. Yet the animal can do this for twenty to thirty days continuously without the evidence of fatigue. Consideration of such facts led Grützner to suggest that the muscle fibers cannot be exerting tensile stress by a continuous excitatory process, but that the fibers must be 'hooked up' in some way, by a kind of arrangement similar to a ratchet, and kept in the position to which the shortening process brought them. If we raise a weight to a certain height and hold it suspended, we have seen that considerable work has to be done all the time, and that fatigue soon results. But if a bolt is shot out under the weight, so as to support it, it remains in the raised position without any further expenditure of energy on our part.

"The next experiment is one on *Pecten* which I will give in the words of von Uexküll (1912). 'If one takes a normal *Pecten* out of the water, it gives two or three flaps with its shells before closing them permanently. While it is open, a piece of wood is pushed between the shells, which then close and bit upon the wood with so powerful a crash that their edges are splintered. The wood is then held as in a vice. One can, however, pull it out by twisting it about backwards and forwards, and then one is surprised to see that the shells remain motionless, just as would the jaws of a vice if an object clamped between them had been forced out. The shell movement shows not the slightest degree of elasticity. The muscular fibers seem to have been suddenly frozen solid.' If one next tries to *open* the shell, no effect can be produced but even the pressure of a finger is sufficient to press them *nearer* together, and in this position they remain fixed again, so that they cannot be brought back. The nearest mechanical illustration that can be given is that of two racks with saw teeth; these will glide over one another if pulled in one direction but resist any pull in the opposite direction. The fact that the animal itself can allow the shells to open, shows that the 'catch' can be removed by some means. This, as we shall see presently, is done by 'inhibition' from the central nervous system."

Special photochemical adaptations are cited on p. 567. "The absorption of light by chlorophyll, as we have seen, is such as to make the best use of the light available. But a green pigment is, of course, transparent to the green rays which preponderate under water, so that it would be inefficient in that situation. Accordingly, as Engelmann has pointed out (1882), we find, in the seaweeds, red and brown pigments corresponding to chlorophyll and having the same function, but able to absorb effectively the green light available. For example, the red seaweeds show a maximum of carbon assimilation in the green and, spectrophotometrically measured, they show the greatest absorption between the lines B and C, where the chief band of chlorophyll lies. The minimum of absorption is in the range between C and D. This fact serves to illustrate the function of chlorophyll as an optical sensitizer; the same effect is produced by light of various wave-lengths, provided that it is absorbed.

"In certain cases, to which Engelmann has given the name '*complementary chromatic adaptation*,' we find that a pigment is actually formed under the action of colored light and that the pigment has a color which is complementary to that of the light to which the organism is exposed, so that this light is then absorbed. The alga, *Oscillaria sancta*, as shown by the work of Gaidukov (1902), occurs in several colors between reddish purple and blue-green. If cultures are made, say, of the purple variety, we find that under red light a green pigment is produced. If we take the green variety, it becomes reddish under green light, brownish yellow under blue light, and so on. The general color of a mixed culture thus tends to become complementary to that of the light under which it is grown. The work was done with great care, and spectrophotometer curves of the various pigments were compared with those of the light under which they made their appearance."

The author has given an admirable exposition of our knowledge up to 1914, which is as far as he goes in his literature references. The book may, therefore, be taken as the summing up of an era. The new period begins with the rational treatment of colloid chemistry as opposed to the empirical development, and with the work of Clowes on emulsions. The author has been singularly fortunate in the time which he has chosen for writing his book. *Wilder D. Bancroft*

Practical Physical Chemistry. *By James Brierley Firth. 18 × 12 cm; pp. xii + 178. New York: D. Van Nostrand Company, 1916. Price: $1.00.*—In the preface the author says: "During recent years it has come to be more widely recognized in the various schools of chemistry that a study of physical chemistry is necessary for all those who wish to study chemistry with any degree of thoroughness. The theoretical significance of physico-chemical constants, and the fact that they find their application in almost every branch of chemistry, renders it essential for all students of the science to become familiar—to some extent, at any rate—with physico-chemical methods."

The headings of the chapters are: thermostats; density of gases, liquids, and vapors; determination of viscosity and surface tension; determination of solubility; determination of molecular weights; determination of transition points; osmotic pressure; refractivity measurements; rotation of the plane of polarization; spectrum analysis; determination of partition coefficients; thermo-chemical measurements; determination of transport numbers; electrical conductivity; electromotive force; velocity of chemical reaction; quantitative electrolytic determinations; electrolytic preparations; preparation of colloids.

There seems to be no reason why the word "practical" should appear in the title. The electrolytic preparations are: aniline, azobenzene, iodoform; ammonium persulphate. Under preparation of colloids we find: colloidal platinum by Bredig's method; antimony sulphide; colloidal gold by Donau's method; colloidal stannic oxide. *Wilder D. Bancroft*

Elementary Qualitative Analysis. *By Benton Dales and Oscar L. Barnebey. 19 × 14 cm; pp. vii + 205. New York: John Wiley and Sons., Inc., 1916. Price: $1.25 net.*—The reasons for writing another book on qualitative analysis are given in the preface. "Our viewpoint has been to give a sufficient number of well-organized characteristic reactions accompanied by appropriate questions to stimulate and encourage analytical thinking. The attempt is made to bring out the value of differential behavior towards reagents early so that the student has at the commencement of his qualitative study an idea of the ultimate application of the reactions.

"We do not deem the study of the reactions used in the schemes followed in the systematic procedure for the analysis of unknowns sufficient to give the student a grasp of qualitative analysis. The use of analytical questions bearing on the reactions studied has an inestimable value in the students' analytical training and greatly broadens his knowledge of the chemistry of the metals."

In regard to the theory of electrolytic dissociation, the authors say: "Several discrepancies between the observed facts and the ionic theory as generally accepted have been made evident during the last few years by physiochemical measurements. It is hoped that the theory will be adjusted to the facts observed and not be thrown out regardless of the good points possessed by it. The difficulty of adjustment and reconciliation of freezing or boiling points with ionization in concentrated and dilute solutions does not seem to be sufficient to cause the theory to be disregarded. Within a few years a more uniform general conception of the exact conditions will be available." *Wilder D. Bancroft*

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