II

THE MISLEADING EXPERIMENT

WE have seen that most of the important scientific discoveries are made by the guessers and not by the accumulators, by the men whose slogan is "First get your working hypotheses" and not by the men whose slogan is "First get your facts." This is purely empirical, however, and we should like to know why the Baconian method does not work out well. It is not an unreasonable line of attack and why should it be unworkable? The answer is because of the danger inherent in an experiment. Many people think that the appeal to experiment is the last resort, and of course there is some truth in that. On the other hand, all who do research know how difficult it is to make an experiment come out right when we know how it ought to go; and consequently we put very little trust in an experiment which we do for the sake of getting information.

Meldola[1] has put the case very well. "It is only the active worker—the original investigator—who, by personal appeal to Nature through artificially imposed conditions, *i.e.* experiment, or through observation, *i.e.* ready-made phenomena, has come to understand what a *fact* really means in the scientific sense; to realize how laborious is the process of wooing truth and how ambiguous are the answers often given by Nature to his cross-examinations. I have elsewhere recorded a humorous rejoinder by Darwin on one of the very few occasions when it was my never-forgotten privilege to

[1]Gregory: "Discovery," 40 (1923).

have met him; as this reply bears so closely upon the present topic I will venture to repeat it. I had been dwelling upon this very point of the difficulty of getting Nature to give a definite answer to a simple question, when, with one of those mirthful flashes that occasionally lighted up his features, he retorted: She will tell you a direct lie if she can."

According to Sir Francis Darwin,[1] his father carried this point of view so far that "I think he personified each seed as a small demon trying to elude him by getting into the wrong heap, or jumping away altogether; and this gave to the work the excitement of a game."

I am defending the thesis tonight that an experiment should never be trusted until it has been checked by a good theory. Many people take the opposite view; but I intend to show that they are wrong.

The most extreme people that I know about are Wrinch and Jeffreys.[2] "We notice that where a simple law exists it is obtained from the observations; then it is found that the observations do not fit the law exactly. The discrepancies are called errors and are usually ignored afterwards. This is so far conventional, but nevertheless the convention is an extremely important one. The use of the word 'error' has led to the idea that there is something wrong with such observations, which is not the case. The observation is always right, in consequence of the mere fact that it is an observation. All errors of observations seem to be reducible to this conventional form: a physical law is chosen to fit the observations as closely as possible, giving, in other words, a first approximation; then another law is discovered to be relevant, and the two together give a closer approximation, and so on, the error at each stage being merely the unex-

[1] Henshaw Ward: "Charles Darwin," 380 (1927).
[2] Phil. Mag. (6) 42, 377 (1921).

plained balance. Thus an error is just the difference between an observed quantity and its value predicted by the combination of all the physical laws so far known to be relevant. The 'theory of errors' appears to be an extraneous hypothesis, based on a particular plausible assumption about the nature of errors; its utility is chiefly in giving a unique solution in particular cases where the solutions that fit the facts almost equally well differ considerably among themselves. This advantage is, however, liable to be exaggerated."

I doubt whether many scientific people would admit that all errors of observation are reducible to this conventional form, because then there would be no errors of observation until one had a theory. I am certain that practically no scientific people would accept the bald statement that "the observation is always right in consequence of the mere fact that it is an observation." I doubt whether even Wrinch and Jeffreys would stand for this statement when detached from the context.

The authors have also overlooked one important distinction between the orthodox physical chemist and the followers of Mother Eddy. The Christian Science people deny the existence of sickness but recognize error. The orthodox physical chemist of today recognizes sickness but denies the existence of error. His universal panacea, the activity concept, enables him to fit a set of bad experiments absolutely to a bad theory or to any number of bad theories, though not simultaneously.

Some of the psychologists push Wrinch and Jeffreys pretty hard. Everybody knows, as an abstract proposition, that making one thousand observations instead of one may cut down the probable error due to accidental errors; but that it has no effect on systematic errors. When you come to any particular case, many psychologists believe that they

will get the right answer if they make enough experiments. At one time Cattell was interested in determining, among other things, what colors scientific men liked best. When I took the test I found that all his colors except the yellow were bad. It was like trying to find out which one of six meats a man liked best and smearing five of them with garlic. There might be enough people from the south of France to keep the test from being unanimous, in which case one could calculate a probable error. Cattell was not interested at all in the question whether his test was a good one or not. If he could get enough data, he felt sure that the answer would be right. Anybody but a professional psychologist would have been a bit worried over a method of comparison[1] which does not put either the Department of Chemistry of the University of California or the Department of Physics of Princeton University among the first ten in its respective field. I should class that as a striking case of the misleading experiment.

The phenomenological psychologists seem to be pure Baconians. They pride themselves on not having a working hypothesis and on making statistical studies of what they observe, believing that in that way they will acquire merit— which may be true—and will attain to truth—which they certainly will not do. I am picking out a paper by Bixby,[2] entitled "A Phenomenological Study of Luster," because I once had to study the theory of metallic luster in its bearing on the colors of colloids. When considering metallic luster, no experiments were made with dyes showing selec tive reflection or with oil films on a dark background. Silver, copper, lead, galena, exfoliated mica, and an Indian pheasant's head showed metallic luster. "The characteristic fea-

[1] Cattell: "American Men of Science," 1128 (1927).
[2] J. Gen. Psychology, *1*, 136 (1928).

ture here is large, smooth, almost glass-like reflection."
Here the author is confusing specular reflection and luster.
The metallic colors on the grackle are differentiated from
those on the Impeyan pheasant, the first being called sub-
metallic. Since both are thin-film colors, they must be alike
unless the thin films are farther down beneath the surface in
the case of the grackle; but there is nothing to show that.
The exfoliated mica is called metallic and the colored gela-
tine films not. They are two cases of the same thing and
must be classified together, unless the difference in the sur-
face has an effect. As against that, Bixby has ruled out the
effect of surface. Bixby admits that the synthetic pie plate
"looks like an aluminum pie plate;"[1] but he is sure that there
is no metallic luster. It does not appear whether this is
because aluminum does not have metallic luster; and no
experiments were made with a rotating disc which should
look like copper, which he does consider to have a metallic
luster.

What it comes down to is that the phenomenological psy-
chologist makes a non-critical and superficial series of obser-
vations, and is quite indifferent whether he separates cases
which should belong together or not. For this reason it is
impossible for him to get at basic principles except by
accident.

There is one case of a misleading experiment which has
been tried by inconceivable millions of people, each many
thousands of times. It always comes out wrong and no
amount of knowledge ever makes it come out right. No
matter how hard we try, we always see the sun go round the
earth instead of seeing the earth revolving with the sun
relatively stationary.

Newton was once the victim of the misleading experi-

[1] Bancroft and Allen: J. Phys. Chem., 29, 581 (1925).

ment.[1] "Taking the value accepted in 1666 [for the radius of the earth], Newton calculated that the moon would fall towards the earth by 44 thousandths of an inch in a second; in other words, this is the amount by which the path of the moon should deviate from a straight line in a second in order to describe its curved path around the earth in a month. The amount by which the moon actually swerves from a rectilinear path in a second is 53 thousandths of an inch, so Newton saw that the calculated result did not agree with what was then considered to be a fact. The discrepancy between theory and observation "induced him to abandon the subject and pursue other studies with which he had been previously occupied."

"Not until 1684 did he 'resume his thoughts concerning the moon.' A few years before that time an accurate determination of the size of the earth had been made by Picard, and this gave a more correct value of the length of the earth's radius than had previously been accepted. Using the new value, Newton again took up the calculation of the moon's deflection from a straight path, on the assumption of the force controlling it being the same as that which causes bodies to fall on the earth, but diminished in strength on account of the distance of the moon from the earth. The result now obtained showed that the central force should cause the moon to swerve from a straight-line path by 53 thousandths of an inch in a second, which is exactly the amount that will produce the curved path described by the moon around the earth."

Most of us would have considered 44 and 53 as of the same order of magnitude. If Newton had had the courage to say that his reasoning was right and that the experiment must be wrong, he would have saved nearly twenty years.

[1] Whewell: "Novum Organum Renovatum," *81* (1858); Gregory: "Discovery," 171 (1923).

About the middle of the eighteenth century Needham[1] sent a paper to the Royal Society in which he described heating mutton gravy, putting it in a bottle which he closed with a cork to prevent anything coming in from outside, heating the bottle again, and then putting it away. At the end of a few days the liquid was swarming with animalcules.[2] The same result could be obtained with a soup made from seeds or almonds. This looks like a clear-cut proof of spontaneous generation; but the Abbé Spallanzani was not convinced. He had an innate fear of the misleading experiment. He trusted his general theory against the experimental evidence and he started in to find the flaw in Needham's work. He thought of two possible sources of error. Needham might not have stoppered his bottles well enough or he might not have heated them long enough to destroy all life. The first possibility could be eliminated by sealing the glass necks in a flame. The second could be tested by heating the sealed flasks for different lengths of time. The tests were conclusive. The bottles which had been boiled for a few minutes showed animalcules; those which had been boiled for an hour did not. This proved that there were organisms which were killed by long boiling and not by short boiling. When once killed, there was no spontaneous generation of life. Spallanzani was a good experimenter, so he repeated Needham's experiments, using corks but heating the flasks for different lengths of time. All the flasks contained animalcules, which showed that closing with corks was not adequate.

Galvani assumed that the twitching of a frog's legs when the muscles and nerves were touched simultaneously by wires was because the frog's legs acted like a Leyden jar, the muscles corresponding to one coating and the nerves to the

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[1] Phil. Trans., *45*, 615.

[2] DeKruif: "The Microbe Hunters," 31 (1926).

other. If this were true, the twitching should be greater if one coated the muscles and the nerves with tin-foil, just as one puts tin-foil on the inside and the outside of a Leyden jar. The experiment confirmed this prediction; but was misleading because Volta showed that the same effect could be obtained by touching the nerve at two points. The frog proved to be an electroscope and not a Leyden jar.

In 1802 it was already known that water was composed of hydrogen and oxygen. It therefore occurred to Simon, in Berlin, that the weight of the hydrogen and oxygen obtained by electrolysis of water should be exactly equal to the weight of water during the electrolysis.[1] The first experiment showed a weight of 1.56 grains of oxyhydrogen gas and a loss of water equal in weight to 2.2 grains. The grain is equal to 0.0648 grams. Instead of drawing the conclusion that water is equal to hydrogen and oxygen plus about forty per cent by weight of electricity, Simon said to himself that the theory is right and the experiment is wrong. On thinking over the possible sources of error, it seemed probable that water vapor had been carried off with the oxyhydrogen gas. A second run, made with all precautions, lasted seventy-two days, at the end of which time he had collected 4.61 grains of oxyhydrogen gas and had lost 4.60 grains of water, equivalent to about 0.3 grams. The two results were now equal within the limits of experimental error. Purely as a side issue, it is interesting to note that it took Simon seventy-two days of continuous electrolysis to decompose three-tenths of a gram of water.

The work of Sir Humphry Davy[2] on the electrolysis of water is one of the classical cases of the struggles between a skillful experimenter and recalcitrant experiments. In

[1] Ostwald: "Elektrochemie," 164 (1896).
[2] "Works of Sir Humphry Davy," 5, 2 (1840).

1800 Nicholson and Carlisle had electrolyzed the so-called
pure water of the day, getting hydrogen at one pole and
oxygen at the other, which was as it should be. In addition
there was a base formed at the hydrogen pole and an acid at
the oxygen pole. Davy felt certain that the formation of a
base and an acid in addition to the evolution of hydrogen
and oxygen was the result of experimental error.

The first experiments were made with platinum electrodes
and distilled water in agate cups connected by fibrous asbes-
tos. Both asbestos and the agate cups had been boiled for
some hours in distilled water. Some hydrochloric acid was
found at the oxygen pole and some soda at the hydrogen
pole. "This result was unexpected, but it was far from con-
vincing me that the substances which I had obtained were
generated."

Thinking that the agate might contain traces of salt, the
electrolysis was repeated again and again with fresh sam-
ples of water. The hydrochloric acid disappeared in time
and most of the soda; but there was nitrous acid at the oxy-
gen pole and traces of fixed alkali at the hydrogen pole. The
electrolysis was repeated with vessels of pure gold instead
of agate ones. The amount of fixed alkali was decreased;
but there was quite a good deal of nitrous acid, relatively
speaking, at the oxygen pole.

"It was now impossible to doubt that the water contained
some substance in very minute quantities, capable of causing
the appearance of fixed alkali, but which was soon ex-
hausted; and the question that immediately presented itself
was, Is this substance saline matter carried over in distilla-
tion? Or is it nitrogen gas which exists in minute portions
in all water that has been exposed to air, and which, if an
element of the fixed alkali, would under the circumstances of
the experiment have been soon exhausted, whilst its absorp-

tion from the atmosphere would be impeded by the saturation of the water with hydrogen?

"I was much more inclined to the former than to the latter supposition. I evaporated a quart of the distilled water that I had used, very slowly at a heat below 140° Fahrenheit, in a silver still; a solid matter remained equal to 7/10 of a grain [about 45 mg]; this matter had a saline but metallic taste, and was deliquescent when exposed to air: I could not obtain from it regular crystals; it did not affect turmeric or litmus, but a part of it, after being heated red in a silver crucible, exhibited strong alkaline properties. It was not possible to make a minute analysis of so small a quantity, but it appeared to me to be principally a mixture of nitrate of soda and nitrate of lead; and the metallic substance, it is most likely, was furnished by the condensing tube of the common still.

"The existence of saline matter in the distilled water being thus distinct, it was easy to determine its operation in the experiment. I filled the two gold cones with water in the usual manner; that negatively electrified, soon attained the maximum of its effect upon turmeric paper. I then introduced into it a very minute portion of the substance obtained by the process of evaporation that has been just described; in less than two minutes its effects were evident; and in five minutes the tint of the paper was changed to a bright brown.

"I now conceived that by collecting the water obtained in the second process of slow distillation I should be able to carry on the experiment without *any* appearance of fixed alkali, and the trial proved that I was not mistaken."

"I had never made any experiments in which acid matter having the properties of nitrous acid was not produced, and the longer the operation the greater was the quantity that appeared.

"Volatile alkali likewise seemed to be always formed in very minute portions, during the first few minutes in the purified water in the gold cones, but the limit to its quantity was soon attained.

"It was natural to account for both these appearances, from the combination of nascent oxygen and hydrogen respectively with the nitrogen of the common air dissolved in water: and Dr. Priestley's experiments on the absorption of gases by water (on this idea) would furnish an easy explanation of the causes of the constant production of the acid, and the limited production of the alkali: for hydrogen, during its solution in water, seems to expel nitrogen; whilst nitrogen and oxygen are capable of co-existing dissolved in that fluid.

"To render the investigation more complete, I introduced the two cones of gold with purified water under the receiver of an air-pump; the receiver was exhausted till it contained only 1/64 of the original quantity of air; and then, by means of a convenient apparatus, the tubes were connected with an active Voltaic pile of 50 pairs of plates of 4 inches square. The process was carried on for 18 hours, when the result was examined. The water in the negative tube produced no effect upon prepared litmus, but that in the positive tube gave it a barely perceptible tinge of red.

"An incomparably greater quantity of acid would have been formed in a similar time in the atmosphere, and the small portion of nitrogen gas remaining in contact with the water, seemed adequate to the effect.

"I repeated the experiment under more conclusive circumstances. I arranged the apparatus as before; I exhausted the receiver, and filled it with hydrogen gas from a convenient airholder; I made a second exhaustion, and again introduced hydrogen that had been carefully prepared. The

process was conducted for 24 hours, and at the end of this time neither of the portions of the water altered in the slightest degree the tint of litmus.

"It seems evident then that water, chemically pure, is decomposed by electricity into a gaseous matter alone, into oxygen and hydrogen."

These experiments are usually cited to show Davy's ingenuity in detecting the flaws in what seemed like perfect experiments, and they do illustrate this admirably. Even more important is that Davy was always convinced of the accuracy of his working hypothesis and that he never wavered from the belief that every discrepancy between theory and experiment was due to experimental error.

Wedgewood and Davy studied the action of light on paper or white leather impregnated with silver nitrate and were able to obtain photographs which seemed good to them. The matter was dropped because they could find no way of removing the unreduced silver salt. Since silver nitrate is very soluble in water, they thought that it should be easy to wash it out of paper; but they did not know about adsorption and consequently they drew the false conclusion that there could be no silver nitrate in the paper.

In December 1824 Faraday attempted to obtain an electric current by means of a magnet, and on three occasions he had made elaborate but unsuccessful attempts to produce a current in one wire by means of a current in another wire or by a magnet. It was not until August 1831, nearly seven years later, that he succeeded in making the experiment fit the theory. He had even more trouble with the electromagnetic rotation of the plane of polarized light, for it took him more than twenty years to get a positive result. People say that this long series of researches is an instance of his perseverance; but there would have been no sense in perse-

vering if he had been wrong. In that case he would have been called pig-headed. The important thing was that he knew all the time that the negative results were misleading and that the theory was better than the experiments.

In 1851 William Thomson[1] (afterwards Lord Kelvin) published a paper in which he calculated the electromotive force of a voltaic cell from the thermochemical data, on the assumption that the cell could be so arranged that the only heat evolved was the Joule heat and therefore proportional to the square of the current. He tested the equation on the Daniell cell, which consists of $Zn|ZnSO_4|CuSO_4|Cu$, and found a perfect agreement. The equation, $I = \theta$, or $E = Q$ in modern units—has been known since then as Thomson's law. It was the most natural thing in the world to take the Daniell cell. It was practically the only constant cell in use at the time and it came pretty near to being a completely reversible cell. There was no reason to suppose that there was anything abnormal about it. As it happens, however, Thomson's law holds only when the temperature coefficient of the electromotive force is zero; and the Daniell cell is one of a very few which has practically a zero coefficient. Thomson was fooled by the misleading experiment, and Helmholtz was the man who deduced the exact formula about thirty years later.

When Cailletet and Pictet first liquefied hydrogen by releasing the pressure, they reported that the escaping jet of liquid had a steel blue color.[2] This did not seem surprising in 1878 because people rather expected that solid hydrogen would be a metal. We know now that liquid hydrogen is colorless and that the jet cannot have shown a pigment blue. It is another case of the misleading experiment. The liquid

[1] Phil. Mag., (4) *2*, 429 (1851).

[2] "Collected Papers of Sir James Dewar," *1*, 169 (1927).

drops in the hydrogen mist were of such a size and the light was in such a place, that the observer saw a Tyndall blue, a structural color. It cannot have been anything else and yet the statement about the blue hydrogen appears in many books to this day.

In 1873 Dewar[1] was caught for some years by the misleading experiment. He determined the vapor density of potassium in a cylindrical iron bottle of at least 200 cc capacity. "In the experiments we have hitherto carried out, we have satisfied ourselves that the amount of mercury vapour *not* swept out by the potassium is quite inappreciable; and as our object has been in the meantime merely to arrive at approximate results and to perfect our methods of manipulation, we have neglected the minute correction, which, on account of that small remnant of mercury, ought, strictly speaking, to have been applied to the volume of the vapour as calculated from the capacity of the bottle in the cold, the coefficient of expansion of iron, and the temperature (1040° Deville) at which the vapour was measured. The results of our observations show conclusively that the density of potassium-vapour, as produced in the process described, cannot exceed 45 times that of hydrogen, and that therefore the molecule of potassium consists of *two atoms* (K_2)."

In 1879 another run[2] was made by the recently-discovered Victor Meyer method, using wrought iron bottles. The molecular weights thus found for potassium varied from 74.4 to 90.5, with a mean value of 81.6, which corresponds closely enough to a diatomic vapor. The authors say that "the above experiments show that no great accuracy in the determination of the vapour-density of sodium and potas-

[1] Proc. Roy. Soc., *21*, 203 (1873).
[2] Dewar and Scott: Proc. Roy Soc., *29*, 206 (1879).

sium can be obtained by this method of working when vessels of wrought iron are employed. The results are, however, conclusive as regards the *normal character* of *their respective vapour-densities.*"

Only a little later these conclusions went by the board completely. Experiments were made[1] in a platinum vessel packed in magnesia instead of sand. "The new determinations of the molecular weights of potassium and sodium are just about half the former values, and would seem to support the inference that the atom of each of these metals resembles mercury and cadmium in the gaseous state, as regards molecular volume. Such a remarkable result cannot be accepted without a very thorough investigation of the secondary reactions which may be induced at high temperatures. It is certain that in the platinum vessels there is much less absorption of vapour than in the case of iron, and that the action of the furnace gases is all but eliminated. The following suggestions might be made to explain the results. In the first place, the metals may contain a large amount of occluded hydrogen. With reference to this assumption, we have examined the sodium used in our experiments and find, on careful exhaustion and boiling in a Sprengel vacuum, that one volume of sodium only contains one-third of its volume of occluded hydrogen, so that this will not account "for the double volume of the atom of the metals." The alkali metals may form volatile compounds with platinum, although, judging from analogy, such compounds are not likely to exist. If so, the vapour blown out of the bottle ought to contain platinum. The use of platinum tubes to blow out the vapours prevented the test being applied. The metals may be changed into oxides from occluded oxygen in the platinum. If so, no free metal ought to remain in

[1] Ibid., 490 (1879).

the bottle after this rapid evaporation. This however is not the case; so that, unless some other explanation can be given, it will be necessary to admit some anomaly in the behaviour of potassium and sodium, as regards their vapour-densities at high temperatures. In future the variation of the density with the temperature must be determined, but this is very difficult at temperatures about 1500° C. The chief drawback to the prosecution of the experiments is the terrible waste of platinum vessels, which never stand the combined action of potassium, sodium, and hydrogen temperatures beyond two or three operations."

Von Babo[1] and Wüllner[2] studied the change of the vapor pressures of aqueous salt solutions with temperature and concentration. Von Babo found that, for a given concentration, the percentage lowering of the vapor pressure was pretty nearly independent of the temperature. Wüllner found that, at constant temperature, the percentage lowering of the vapor pressure was pretty nearly proportional to the concentration. It was perfectly natural that they should have worked with aqueous salt solutions. Water is the cheapest of all solvents and can be obtained more nearly pure than any other solvent. Salts are the cheapest of all solutes and are more easy to purify than any other solute. By the irony of fate, the most natural combination to have studied was the worst possible. As we know now, organic solutes in organic solvents are normal as a rule. Organic solutes in water are normal and salts in alcohol are usually normal. It is only when we come to salts in aqueous solution that we meet the difficulties of electrolytic dissociation. By avoiding this pitfall Raoult carried off all the honors.

One wonders whether Debye and Hückel may not have

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[1] Ostwald: "Lehrbuch allgem. Chem.," *1*, 706 (1891).
[2] Pogg. Ann., *103*, 529; *105*, 85 (1858); *110*, 564 (1860).

made a similar mistake by starting with salts in aqueous solution. They make the explicit assumption that all the variations are due to the interaction of the ions and they adjust their ionic diameters to fit their assumption. They have not proved that there are no other disturbing factors and the presumption is strongly against them. It might have been wiser to have cleaned up the case of organic solutes in organic solvents before tackling the job that really interested them. Some day people will point to the work of Debye and Hückel as an extraordinarily interesting case of the misleading experiment.

Pfeffer found osmotic pressures of about 52 cm for a one per cent solution of cane sugar with a copper ferrocyanide membrane and pressures of about 36-39 cm when membranes of calcium phosphate and Prussian blue were used. From this he concluded that the osmotic pressure was a function of the nature of the membrane. Since there is always an apparent effect of the nature of the membrane when one measures osmotic pressures experimentally, it is not surprising that the people who believe in the trustworthiness of an experiment, should continue to hold this belief.[1] On the other hand the use of the chemical potential by Gibbs[2] or the method of van't Hoff is absolutely convincing that the magnitude of the osmotic pressure cannot be a function of the nature of the membrane. In a letter to me, written years ago, Raoult expressed his doubts whether there was, experimentally, such a thing as a semipermeable membrane. In this work with ether and methyl alcohol using diaphragms of rubber and of pig's bladder, Raoult[3] had satisfied himself that he was only measuring the difference between two flows in opposite direction.

[1] Cf. Kahlenberg: J. Phys. Chem., *10*, 141 (1906).
[2] "The Scientific Papers of J. Willard Gibbs," *1*, 83 (1906).
[3] Z. physik. Chem., *17*, 737 (1895).

Raoult was probably right in this. If we have a non-porous membrane, like rubber, through which one liquid passes because it is soluble in the membrane, the presence of that liquid in the membrane will cause the second liquid to dissolve to some extent in the membrane. Consequently, the membrane is no longer theoretically semipermeable even though it may have been theoretically impermeable to the second liquid in the absence of the first. If we have a porous membrane, like copper ferrocyanide, which owes its semipermeability to strong negative adsorption, we can hardly say that the concentration of the solute in the pores will be absolutely zero for any concentration of the solution, and it will certainly not be zero for high concentrations of the solute in the solution. We can calculate osmotic pressures more accurately than we can measure them. If Pfeffer, Kahlenberg, and others had said that the maximum osmotic pressure actually will practically always depend on the nature of the membrane, nobody could have disputed that. They did not know about the misleading experiment and they made the entirely warranted assumption that measurements had been made with membranes which were theoretically semipermeable under the conditions of the experiment.

If we start with the law of the conservation of energy and Ohm's law, we can deduce Joule's law that the heat developed in a metallic conductor is proportional to the first power of the resistance and to the second power of the current. Experiment failed at first to confirm this relation, especially for higher currents. The cause of the misleading result was the heating of the wire, which changed the resistance.

Raoult's first work[1] on the vapor pressures of solutions established a relation between the lowering of the freezing-

[1] Compt. rend., *87*, 167 (1878).

point and the lowering of the vapor pressure at $100°$ for the same aqueous solutions. He found the beautifully simple relation $7.6\Delta = p_0 - p_1$, where Δ is the lowering of the freezing-point and $p_0 - p_1$ the lowering of the vapor pressure. There was no reason to suppose that there was anything abnormal about water and consequently no reason to suppose that the relation was not general. As a matter of fact, Raoult had started, quite unconsciously, with the only liquid, so far as we now know, which would have given him this relation. On the theory of probability this is practically impossible; but it is just what one would expect from the misleading experiment.

The real formula for the relation between the lowering of the freezing-point and the lowering of the vapor pressure at $100°$, if we assume von Babo's law, is

$$\Delta = 18.5 \frac{100}{M_2} \cdot \frac{p_0 - p_1}{p_0}$$

where Δ is the freezing-point lowering, M_2 is the molecular weight of the solvent as vapor, and 18.5 is the freezing-point constant. For water M_2 is 18 and $p_0 = 760$ at $100°$. The equation therefore becomes[1] $7.6\Delta = \frac{18.5}{18} (p_0 - p_1)$, which is Raoult's relation within his limits of experimental error. It was pure coincidence that the freezing-point constant for water has very nearly the same numerical value as the gram molecular weight of water vapor. For benzene the corresponding ratio is a little over 0.6 instead of being practically unity as in the case of water.

Raoult[2] had other difficulties with the misleading experiment. He found experimentally that the molecular lowering

[1] Through an oversight p_0 has been left in the denominator in the paper by Bancroft and Davis: J. Phys. Chem. 32, 30 (1928).

[2] Compt. rend., 101, 1056 (1885).

of the freezing-point for one gram-molecular weight of the solute in 100 gram-molecular weights of the solvent came out approximately as follows: formic acid, 0.63°; acetic acid, 0.65°; benzene, 0.64°; nitrobenzene, 0.59°; ethylene dibromide, 0.63°; water, 2.61°. With the exception of water, the values of all the solvents tested (five) varied between 0.59° and 0.64° with a mean value of 0.63°. "Water is the only exception; but that is not surprising for a liquid which shows many other peculiarities and it is permissible to explain the anomaly by assuming that each of the physical molecules, of which it is formed, consists of several chemical molecules united together. At a time when I had only obtained a small number of molecular lowerings higher than the mean lowering of 37 [maximum molecular lowering for one mol per hundred grams of solvent] in aqueous solutions, I believed that the physical molecules of water were composed of three chemical ones. In fact, if we divide 37 by 18×3, we get as quotient 0.685, which is not very far from the mean quotient of 0.63 obtained with the other solvents. I have called attention to this in an earlier paper.[1] But new determinations make it no longer possible to consider the molecular lowerings distinctly higher than 37 as doubtful. I am, therefore, compelled to recognize that molecular lowerings in water may really rise to 47, a maximum value in many cases where the dissolved substances do not decompose. To explain such a lowering, *it is sufficient to assume that the molecules of water are united in fours,* at least near zero. The quotient of 47 by 18×4, is 0.65, a number remarkably close to the mean value of 0.63 obtained with the other solvents."

It must have given Raoult a real thrill to have brought all six solvents together like this. We know now that it is

[1] Compt. rend., *95,* 1030 (1882).

not justifiable to take 47 for the molecular lowering, and we know now that the molecular weight of liquid water has nothing to do directly with the lowering of the freezing-point; but Raoult did not know this. Leaving water out of account, it seems perfectly impossible that all the other five solvents should have come together as they did purely by coincidence, and yet they did. We know now that this particular relation does not hold and that the heat of fusion is the important factor in determining the lowering of the freezing-points. I do not criticize Raoult at all for making this mistake. I feel that he was the victim of fate. His two big generalizations were correct, and he slipped up on two minor ones, which nobody in the world except van't Hoff could have avoided. Raoult's experience should put each of us on his guard against the danger of the misleading experiment. As Darwin said: "Nature will tell you a direct lie if she can."

Roux's work on the diphtheria bacillus[1] is a striking case of the triumph of conviction—one can hardly say theory— over recalcitrant experiments.

"Roux and Yersin went to the Hospital for Sick Children —diphtheria was playing hell with Paris—and here they ran on to the same bacillus Loeffler had found. They grew this microbe in flasks of broth, and did the regular accepted thing first, shooting great quantities of this soup into an assorted menagerie of unfortunate birds and quadrupeds who had to die without the satisfaction of knowing they were martyrs. It wasn't particularly enlightened searching, this, but almost from the tap of the gong, they stumbled on one of the proofs Loeffler had failed to find. Their diphtheria soup paralyzed rabbits! The stuff went into their veins; in a few days the delighted experimenters watched

[1] DeKruif: "The Microbe Hunters," 188-192 (1926).

these beasts drag their hind legs limply after them; the palsy crept up their bodies to their front legs and shoulders —they died in a clammy, dreadful paralysis. . . ."

It seemed certain to Roux that this bacillus was the cause of diphtheria in human beings; but he could not find any trace of the bacilli in the tissues of the dead rabbits. Then Loeffler's prediction flashed over Roux. "It must be that the germs make a poison in this broth to paralyze and kill the beasts . . ." he pondered.

"He took big glass bottles and put pure microbeless soup into them, and sowed pure cultivations of the diphtheria bacillus in this broth; into the incubating ovens went the large-bellied bottles. At the end of four days they filtered the soup through a bougie. The filtrate was injected into rabbits and guinea-pigs with no result. The animals did not die."

In spite of all the evidence to the contrary, Roux said: "There must be a poison in this soup where the diphtheria germs have grown—else why should those rabbits have died?"

"Then—I have told scientific searchers about this and they have held their noses at such an experiment—Roux nearly drowned a guinea-pig. For weeks he had been inject-ing more and more of his filtered soup, but now (it was like facing a night on a park bench with your last dime on the two dice) he injected thirty times as much! Not even Pas-teur would have risked such an outlandish dose—thirty-five cubic centimetera Roux shot under the guinea-pig's skin and you would expect that much water would kill such a little beast. If he died it would mean nothing. . . . But into the belly of a guinea-pig and into the ear-vein of a rabbit went this ocean of filtered juice—it was as if he had put a bucket-ful of it into the veins of a middle-sized man.

"But that was the way Roux carved his name on those tablets which men while they are on earth must never allow to crumble; for, though the rabbit and the guinea-pig stood the mere bulk of the microbe-less broth very well, and appeared perfectly chipper for a day or so afterwards, in forty-eight hours their hair was on end, their breath began to come in little hiccups. In five days they were dead, with exactly those symptoms their brothers had, after injections of the living diphtheria bacilli. So it was Emile Roux discovered the diphtheria poison. . . .

"By itself this weird experiment of the gigantic dose of feebly poisonous soup would only have made microbe hunters laugh. It was scandalous. 'What!—if a great flask of diphtheria microbes can make so little poison that it takes a good part of a bottle of it to kill a small guinea-pig—how can a few microbes in a child's throat make enough to do that child to death? It is idiotic!'

"But Roux had got his start. With this silly experiment as an uncertain flashlight, he went tripping and stumbling through the thickets, he bent his sallow bearded face (sometimes it was like the face of some unearthly bird of prey) over a precise long series of tests. Then suddenly he was out in the open. Presently, it was not more than two months later, he hit on the reason his poison had been so weak before—he simply hadn't left his germ-filled bottles in the incubator for long enough; there hadn't been time enough for them really to get down to work to make their deadly stuff. So, instead of four days, he left the microbes stewing at body temperature in their soup for forty-two days, and when he ran that brew through the filter—presto! With bright eyes he watched unbelievably tiny amounts of it do dreadful things to his animals—he couldn't seem to cut down the dose to an amount small enough to keep it from doing

sad damage to his guinea-pigs. Exultant he watched feeble drops of it do away with rabbits, murder sheep, lay large dogs low. He played with this fatal fluid; he dried it; he tried to get at the chemistry of it (but failed) ; he got out a very concentrated essence of it though, and weighed it and made long calculations.

"One ounce of that purified stuff was enough to kill six hundred thousand guinea-pigs—or seventy-five thousand large dogs! And the bodies of those guinea-pigs who had got a six hundred thousandth of an ounce of this pure toxin— the tissues of those bodies looked like the sad tissues of a baby dead with diphtheria. . . ."

In 1817 Bunsen tried to determine the rate of explosion of an ignited gas mixture[1] and he went about it in what seemed like a very ingenious way. "An explosive mixture of gases was sent through a small orifice in the end of a tube, and the jet was ignited. In the Bunsen burner, it will be remembered, the flame is only steady when the mixture of gases travels along the tube faster than the flame can travel through the combustible gases. If otherwise, the flame 'strikes back.' Now, Bunsen measured the least speed which would prevent the flame striking back into the reservoir. In this way Bunsen found that a mixture of two volumes of hydrogen and one volume of oxygen burns at the rate of about 34 metres per second, while most other gases burn at the rate of about a metre per second."

It seemed reasonable to suppose, as Bunsen did, that, subject to minor corrections, "when the velocity of efflux of the gas is equal to the velocity of propagation of explosion the flame will not run back." Bunsen's results stood for fourteen years; but the misleading experiment had fooled him after all. Berthelot and Vieille and Dixon measured the

[1] Mellor: "Chemical Statics and Dynamics," 450 (1904).

actual detonation wave in tubes and found a velocity of about 2800 meters per second for oxyhydrogen gas as against the thirty-four meters found by Bunsen. The two rates are not of the same order of magnitude.

In Cohen's doctor dissertation[1] on the electrical determination of inversion points, the temperature coefficient for a cell with hydrated and anhydrous sodium sulphate was calculated to be about 1.1 millivolt per degree between 28.3° and 32.6°. The experimentally found values were about 8-9 millivolts, a hopeless disagreement. Cohen had the courage of his convictions for he said: "I believe that these differences are due to overlooking some factor, whose nature is for the moment a complete mystery."

A little later he had his reward[2], for it was found that some of the samples of sodium sulphate were alkaline to phenolphthalein while others were acid to methyl orange. Working with carefully neutralized sodium sulphate the calculated temperature coefficient was 1.2 millivolts as against an experimentally observed value of 1.5 millivolts.

Nichols and Franklin[3] thought they had proved that a strong magnetic field destroyed the passivity of iron in nitric acid, sp. g. 1.40 "When finely divided iron is placed in a magnetic field of considerable intensity and exposed to the action of an acid, the chemical reaction differs in several respects from that which occurs under ordinary circumstances. The cause of one such difference may be found in the fact that the solution of iron in the magnetic field is in a sense equivalent to its withdrawal by mechanical means to an infinite distance. Mechanical removal requires the expenditure of work and the same thing is doubtless true of

[1] Z. physik. Chem., *14*, 91 (1894).

[2] Cohen and Bredig: Z. physik. Chem., *14*, 545 (1894).

[3] Am. J. Sci., (3) *31*, 272 (1886); *34*, 419 (1887); *35*, 296 (1888).

what might be called its chemical removal. In other words
the number of units of heat produced by the chemical reac-
tion should differ, within and without the field, by an amount
equivalent to the work necessary to withdraw the iron to a
position of zero potential. Experiments upon this point
which have been briefly described in a note already published
in abstract,[1] brought out other and unlooked-for modifica-
tions of the reactions."

"Nitric acid was mixed in various proportions with water
for the purpose of finding the degree of dilution at which
the most rapid, uniform, and complete solution of the pow-
dered iron could be obtained. During the search for the
most desirable mixture, a new and very interesting effect
of the magnet was accidentally discovered. Five grams of
powdered iron lay in the beaker close above the poles of
the electro magnet, which was in circuit. Some cold nitric
acid was poured upon the iron but the latter remained
passive. Wishing to note the character of the reaction, we
warmed the beaker slightly, then placed it upon the poles of
the magnet and put a thermometer into the solution to get
its temperature. The bulb of the thermometer touched the
iron in process of stirring the acid, when the hitherto pas-
sive mixture burst, almost explosively, into effervescence,
and a cloud of red nitrous fumes was given off. The removal
of the solution from the field of the magnet restored the
passivity of the iron, and the action ceased entirely in a few
seconds. All attempts to destroy the passivity by further
stirring failed until the beaker was brought back into the
neighborhood of the magnet, when, at the merest touch with
the thermometer, or any glass rod, the reaction would begin
again and continue until the beaker was removed from the

[1] A Preliminary Note on the Action of Acids on Iron in the Magnetic Field:
Proceedings Am. Association for the Advancement of Science, 1884.

field. It was found possible to render the iron passive and to destroy that passivity at will by the above process; and after the solution had become warm the reaction was found to begin spontaneously whenever the beaker was brought into the field."

"It appears from these experiments that the action of the magnet is to lower the temperature of transition to the active state, and that the intensity of the magnetic field necessary to convert passive into active iron at a given temperature increases rapidly with the concentration of the acid."

One can hardly believe that this is not a real phenomenon. Everything happens just as Nichols and Franklin say and yet none of it is really so. These results stood for nearly thirty years, until Bennett and Burnham[1] repeated them and found the hidden flaw. "Nichols and Franklin used iron filings, and we have shown that if filings are made passive and placed between the poles of an electro-magnet, and the current turned on, the filings become active. This is due to one piece scratching another, caused during orientation of the particles of iron when magnetized. When a solid piece of iron is passivated in 1.40 nitric acid, and placed in the field, it does not become active."

Since nitric oxide is formed when copper or mercury corrodes chemically in nitric acid and since the electrolytic reduction of nitric acid gives ammonia at a copper cathode and hydroxylamine at a mercury cathode, Tafel[2] denied absolutely any identity between chemical and electrolytic reactions. His reasoning seemed absolutely conclusive; but he was dealing with the misleading experiment, as was shown by Turrentine.[3] When copper reacts chemically with nitric

[1] J. Phys. Chem., *21*, 140 (1917).

[2] Z. anorg. Chem., *31*, 291 (1902).

[3] J. Phys. Chem. *10*, 715 (1906).

acid, the anode product, copper nitrate, is formed at the same spot where the reduction takes place. In the electrolytic reduction of nitric acid with a copper cathode, the reduction takes place in a solution practically free from copper salt. The conditions are therefore not the same in the two cases. This is the point that was overlooked by Tafel and which vitiates all his conclusions with regard to copper. To show that this difference in conditions was the cause of the difference in the products, Turrentine electrolyzed a solution of copper nitrate and nitric acid, using a copper cathode. A gas was evolved at the cathode, which proved on analysis to be chiefly nitric oxide. This experiment can be done in another way which is more striking. If dilute nitric acid be electrolyzed between copper electrodes, there will be at first no evolution of gas at the cathode; but gas will begin to appear as soon as the blue solution formed at the anode comes in contact with the cathode.

Another case of apparent contradiction between the chemical and the electrolytic reactions—which was cleared up by Joss[1]—is in the quantitative, electrolytic determination of nitric acid as ammonia. "Luckow,[2] Vortmann,[3] Ulsch,[4] and Easton[5] all developed methods for the estimate of nitrates by electrolytic reduction to ammonia. A feature of all of the methods is the presence of copper sulphate and sulphuric acid in their solutions. This is obviously the condition under which we should expect to get nitric oxide, and yet the methods give quantitative yields of ammonia. The reason why nitric oxide was not evolved must be merely a question

[1] J. Phys. Chem., *30*, 1234 (1926).
[2] Z. anal. Chem., *19*, 11 (1880).
[3] Ber., *23*, 2798 (1890).
[4] Z. Elektrochemie, *3*, 546 (1897).
[5] J. Am. Chem. Soc., *25*, 1042 (1903).

of reaction velocity; that is, the velocity of the direct reduction (dependent only on the current density) must be so great, compared to the velocity of decomposition of the intermediate compound giving nitric oxide, that this latter reaction is unappreciable. This was tested by repeating Easton's experiments using a current density approximately one hundredth of the lowest value he recommends. Under these conditions no ammonia was formed, even after two weeks of continuous electrolysis."

Copper does not corrode in a bichromate solution and therefore should not be attacked when made anode in such a solution. Actually, it was corroded practically quantitatively, and it was only when Miss Souders[1] made the current density very small that the chemical and electrolytic reactions became identical. The film making copper passive breaks down under a very small drop in voltage while the corresponding film on iron is quite stable.

Ignoring the significance of the current density got Dennis and Lemon[2] into trouble. They electrolyzed solutions of lanthanum and other rare earth nitrates—in one case nearly pure praseodymium nitrate—at constant voltage and actually obtained a fractional separation. They apparently think that the separation has something to do with the decomposition voltage, because they speak of keeping the voltage "sufficiently constant to permit of fractional decomposition of the different nitrates in solution." Since the voltage drop across the terminals was nine volts, this explanation is quite impossible, because the current density was too high. It is impossible to give the real explanation without repeating the work; but the most probable guess is that they were reducing the nitrates to ammonia. If this is true, the method

[1] J. Phys. Chem., *28*, 831 (1924).

[2] J. Am. Chem. Soc., *37*, 131 (1915).

is slow and crude in comparison with a suitable method of running in ammonia gas.

One case of corrosion puzzled Bengough and Stuart[1]—and others before them—very much. "A very formidable difficulty in the way of the electrochemical theory of corrosion is found in the effect of ions of the corroded metal on the rate of corrosion in a liquid containing them. The presence of these ions, in the case of such metals as magnesium, zinc, aluminum, iron, nickel, and tin, should decrease the rate of corrosion according to the theory, by increasing the osmotic pressure which opposes the solution tension. It has, however, long been known that magnesium chloride is an extremely powerful corrosive agent for magnesium,[2] far more so than distilled water or the chlorides of the alkaline earths or heavy metals, and hydrogen is freely evolved from the metal and does not protect it at all."

Since magnesium cannot be precipitated from an aqueous solution, a magnesium electrode in an aqueous solution of a magnesium salt is not a reversible equilibrium and one cannot apply the Nernst theory to it. This is the same sort of mistake that Carhart[3] made over twenty-five years ago when he wished to consider nickel in a nickel sulphate solution as a reversible electrode. This is, however, a minor matter and the really important thing is why magnesium corrodes more rapidly in a magnesium chloride solution than in distilled water, which everybody admits that it does. It is again a case of the misleading experiment. The different investigators reported accurately on the analytical results

[1] "Sixth Report to the Corrosion Research Committee of the Institute of Metals," J. Inst. Metals, 28, 61 (1922).

[2] Tommasi: Bull., (3) 21, 885 (1899); Kahlenberg: J. Am. Chem. Soc., 25, 380; Roberts and Brown: 841 (1903); Getman: 38, 2596 (1916); 39, 596 (1927).

[3] Trans. Am. Electrochem. Soc., 1, 105; 2, 122 (1902).

and on nothing else. It was, therefore, their sad fate to overlook the really significant phenomena.

The explanation was suggested by Bryant[1] the same year that Tommasi published his experiments. Bryant studied the action of alcohol, water, and sodium sulphate upon magnesium and found that the rate of reaction increased from alcohol to sodium sulphate. "Magnesium has itself, I submit, the power to decompose water at all temperatures above $0°$ C., and the action is stopped by an insoluble coating of oxide forming on the metal. This would explain the change of colour seen after the action has ceased, the renewal of action when the surface is cleaned, and the abundant evolution of gas from a solution of sodium sulphate, since magnesium oxide is more soluble in that than in pure water." If Bryant had only known the magic word, peptization, he could have explained everything.

Miss Souders[2] immersed "two rods of magnesium, each 10 cm long and 1 cm in diameter, in pure water and in one per cent magnesium chloride solution respectively. The rod in the magnesium chloride solution became covered with white flakes[3] which were easily removed; the solution was milky, and a considerable precipitate settled to the bottom. The rod which had been in the water acquired a dull, lusterless surface which was moderately smooth; the liquid was clear. The rods were then transposed, the one that had been in the water being placed in the magnesium chloride solution, and the one that had been in the magnesium solution being placed in the water. The rod which was now in the magnesium chloride solution began to flake and become rougher, the film originally produced by the water being obliterated

[1] Chem. News, 80, 211 (1899).

[2] J. Phys. Chem., 28, 834 (1924).

[3] Cf. Evans: J. Inst. Metals, 28, 117 (1922).

entirely. The rod, which had been transferred to the water became more like the one which had started in the water, the surface seeming smoother and the coating more adherent. It never got really back, because the original pitting had been too severe. There is no question, however, but that the two films are quite characteristic and that the film in water retards corrosion. For this discussion it is immaterial whether one says that magnesium peptizes zinc oxide or not. That is the simplest explanation, because we know that zinc chloride peptizes zinc oxide, ferric chloride peptizes ferric oxide, and chromic chloride peptizes zinc oxide. The essential thing is that there is nothing mysterious about the corrosion of magnesium in a magnesium chloride solution. Any sceptic can repeat the experiments and satisfy himself." This would have been cleared up much sooner if the previous experimenters, with the exception of Bryant, had realized the dangerous possibilities for error in the misleading experiment.

Twenty-odd years ago Falk[1] devised a very ingenious method for determining the ignition temperatures for gaseous mixtures. "The ignition temperature was defined as the temperature at which a gaseous mass would ignite if left entirely to itself for some time, the catalytic action of the walls of the vessel in which the gas was enclosed being eliminated. The new method for determining these temperatures consisted of compressing instantaneously the mixtures enclosed in a suitable vessel. This compression raises the temperature of the gas and, if carried out with sufficient rapidity is adiabatic, no heat being lost by radiation or conduction. The rise in temperature of the mixture may then be calculated from the initial and final volumes of the gas, its initial temperature, and the ratio of the specific heats

[1] J. Am. Chem. Soc., *28*, 1517 (1906) ; *29*, 1536 (1907).

of the gas at constant pressure and constant volume. In compressing the mixtures, as soon as the temperature of ignition is reached there is a sudden reaction (explosion), enough force being developed by the reaction to make the determination of the final volume of the mixture a comparatively simple matter."

For hydrogen and oxygen Falk obtained a smooth curve, with ignition temperatures of about 890° for 80% H_2 and 20% O_2, of less than 800° for 56% H_2 and 50% O_2, and of about 850° for 20° H_2 and 80% O_2. The ignition temperature for the mixture, H_2+O_2, lies lower than that of any of the other mixtures studied. "The most evident explanation for this is that, in the combination of hydrogen and oxygen, the first product formed is hydrogen peroxide which may or may not then be decomposed, the conditions determining how complete the second reaction is."

To anybody who has not worked with explosive gas mixtures, Falk's experiments seem conclusive. They did not seem so to H. B. Dixon.[1] He quotes Falk's statement that the fact that the maximum affinity is shown by the mixture, H_2+O_2, proves that H_2O_2 must be the first product of the reaction between hydrogen and oxygen.

"Falk gives as his reasons for the assumption that the gas detonates instantaneously throughout its whole mass, once the ignition temperature is reached, the fact that the explosions are of great violence, and that the compression was very nearly the same in the case of electrolytic gas whether the weight fell from a lower or a higher altitude. What he found to be nearly true of the rapidly-firing mixtures, $2H_2+O_2$ and H_2+O_2, he has assumed to be also true of the less rapidly-firing mixtures with excess of oxygen, and of mixtures of hydrogen and air.

[1] J. Chem. Soc., *97*, 661 (1910) ; *105*, 1091, 2027, 2036 (1914).

"When I read Falk's first paper, it occurred to me that the descending piston must send in front of it sound-waves, which would be reflected from the bottom of the cylinder back to the piston again, and so on, producing by their collisions zones of higher temperature, at one of which the flame would eventually start. Falk states in his second paper that Professor Jouguet has made the same criticism. By photographing the explosion produced by the adiabatic compression on a rapidly moving film, I have shown that the flame *does* start from a point, and in the more slowly burning mixtures the spread of the flame throughout the gas takes an appreciable time. Moreover, the point of ignition can be made to vary by altering the velocity of the piston. With electrolytic gas the photographs show that the explosion wave is very quickly set up, but the flame always starts *from one point*. The mass of the gas *is not fired instantaneously*, although the time required in this case for the flame to reach the piston is negligible. With such a mixture as H_2+2O_2, the time required to set up the explosion-wave is *not* negligible.

"If we accept the Nernst definition of the ignition point of a mixture of gases as that temperature at which a mass of the gas *rapidly* self-heats itself by combination until it bursts into flame, and if this flame starts *at some point* in the mixture and spreads from that point, there will be two periods during which the piston may continue to move after the "ignition point" has been reached: (i) the period from the beginning of rapid self-heating until the flame appears; and (ii) the period required for the flame to spread through the gas and stop the descent of the moving piston.

"Just as the time required for the flame to set up the explosion-wave differs in different mixtures, so does the

time required for the self-heating from Nernst's 'ignition point' to the actual appearance of the flame.

"When a mixture of air and hydrogen (5 vols. to 2) was compressed in the cylinder, and the descent of the piston was arrested by means of a steel collar, I found the ignition temperature a few degrees only above that of electrolytic gas. This was in agreement with our previous determinations at atmospheric pressure. But when the piston was allowed to descend until it was stopped by the explosion of gases, as in Falk's experiments, I could obtain ignition points, not only as high as Falk's (649°), but, by increasing the velocity of the piston, I got temperatures of 700°, 800°, or 900° at pleasure. A similar variation was found for the mixture $H_2 + 4O_2$.

"It was evident that the error due to the movement of the piston during the 'pre-flame' period of self-heating might be far greater than the error due to the movement of the piston *after* the flame had started.

"In determining the temperature of ignition of mixtures of hydrogen and oxygen, it was necessary, therefore, to stop the descent of the piston artificially the moment the gases were brought to the self-heating temperature. This was effected by having on the end of the piston a steel head, which was caught by a steel collar at a certain point in its descent. By varying the thickness of the collar, the piston could be stopped at any point. By a series of trials a compression was found which fired the mixture, and a slightly less compression, which did not. The mean between the two was taken as the ignition point. On repeating each experiment several times, nearly concordant ignition points were obtained."

"My ignition point for electrolytic gas [$2H_2 + O_2$] agrees closely with that found by Falk, an agreement which shows

that this mixture must have a very short period of flame-less combustion, and the speed of the flame must be very rapid. I find the mixture in equal volumes has a lower ignition point than electrolytic gas, but it is not the mixture of 'maximum affinity.' The further addition of oxygen regularly lowers the ignition point. I would submit, there-fore, that the ignition points of hydrogen and oxygen mix-tures do not prove that hydrogen peroxide is the first product of the reaction."

Spoehr[1] seems to have been the victim of the misleading experiment in his work on sodium ferropyrophosphate. "The pyrophosphates of iron are soluble in a solution of sodium pyrophosphate. There are thus formed salts in which the iron is present as a complex ion. These salts have been investigated by Pascal[2] who gave to the sodium ferropyro-phosphate the formula $Na_8Fe_2(P_2O_7)_3$. This substance is a strong reducing agent, liberating the free metal from salts of gold, silver, mercury, and copper. When ferrous sulphate is added to sodium pyrophosphate, there is first formed a precipitate of ferrous pyrophosphate which, on the addition of more sodium pyrophosphate, dissolves to form a clear, light green solution. Such a solution gives none of the ordinary tests for iron [ferrous] ion, nor does it give a precipitate with alkalies."

Of course Spoehr does not mean that there is a zero concentration of ferrous ion because it would not then be a powerful reducing agent and because iron would dissolve readily in the solution with evolution of hydrogen. As a matter of fact Spoehr calculates in the third paper that the ratio of ferrous to ferric ion may be about 2.4:1. What Spoehr does believe, however, is that the concentration of

[1] J. Am. Chem. Soc., *46*, 1496 (1924) ; *48*, 107, 236 (1926).
[2] Ann. Chim. Phys., (8) *116*, 386 (1909).

ferrous ion is below that which can be detected by the ordinary tests for ferrous ion. While this may be true, it does not follow from Spoehr's experiments. Since the usual test for ferrous ion is the addition of potassium ferricyanide, this is undoubtedly one of the tests which Spoehr applied, though he does not say so specifically. As a matter of fact potassium ferricyanide does not give any blue color with a sodium ferropyrophosphate solution; but this does not prove anything in regard to the concentration of ferrous ions. Since the solution has a strong reducing power, it would reduce potassium ferricyanide to potassium ferrocyanide, which would give no test with ferrous ion. We took a dilute ferrous sulphate solution and added potassium ferricyanide to it, getting a deep-blue precipitate. On adding this to the sodium ferropyrophosphate solution, the color bleached at once. Spoehr was using an ordinary test under extraordinary conditions where it means nothing. The test with alkali is positive and shows that the concentration of ferrous ions is below that for a saturated solution of hydrous ferrous oxide.

If we add a potassium fluoride solution to a ferrous sulphate solution, there is no precipitation and no visible change. It has been shown by Peters[1] that potassium fluoride takes out ferric ions, forming a ferric fluoride; but has little or no effect on the ferrous ions. If we add a sufficient amount of potassium fluoride, we can then add a potassium ferricyanide solution without getting a blue color.[2] If the local concentration of ferricyanide is too high, a blue color is formed, which disappears on shaking the test-tube. Addition of alkali to solution of ferrous sulphate and potassium fluoride causes a precipitation of hydrous ferrous oxide.

[1] Z. physik. Chem., 26, 219 (1898).
[2] This has since been confirmed independently by Szebellèdy: Z. anal. Chem., 75, 165 (1928).

Sometimes the gods are good to the research man, though not often. The world knew that Sabatier had obtained cyclohexane by the hydrogenation of benzene; but the world did not know until Sabatier[1] told us in 1926 how easily he might have failed.

"This special power of reduced nickel [of hydrogenating acetylene and ethylene] seemed to us so perfect that we thought of generalizing it, and we attacked a case of hydrogenation, which up to that time had not been realized by any method, that of benzene. Berthelot had attempted to effect it with his universal agent of hydrogenation, a concentrated solution of hydriodic acid at 250°. But instead of cyclohexane, which boils at 81° he had prepared only its isomer, methylcyclopentane, which boils at 69°. Under the influence of the hydriodic acid the hexagonal nucleus was transformed into a substituted pentagonal nucleus.

"It was with real emotion that we proceeded to this decisive test. The benzene vapors, carried along by a current of hydrogen in excess, were directed over a bundle of reduced nickel maintained at 200°; the gases issuing from the tube were sent to a U-tube surrounded by ice, within which the vapors of cyclohexane should be expected to condense in a liquid state. The operation seemed to proceed well from the beginning, the velocity of hydrogen issuing from the condenser tube seeming very little less than that at the entrance. But after boiling for a rather short time, the gas ceased to pass, the U-tube was stopped up by the condensation of a solid product, which it seemed could only be benzene, solidifiable at 4°—that is to say, within the ice— whereas we had seen in the literature that cyclohexane, extracted from Caucasian petroleum by Markounikov by means of 110° fractional distillations, was condensed to a

[1] Ind. Eng. Chem., _18_, 1007 (1926).

solid which melted at −11°. But our despair was of short duration and was changed to a very lively joy, when on opening the U-tube we perceived, instead of the odor of the original benzene, the special intermediate odor between that of chloroform and that of the rose, which belongs to cyclohexane. The condensed product was cyclohexane, entirely pure, melting, not at −11°, but above 6°, absolutely unattacked by the sulfonitric mixture. The transformation of benzene had been complete. . . .

"Either with M. Senderens or with two others of my pupils, M. Mailhe and Murat, I have been able to accomplish with success more than two hundred different hydrogenations. These direct fixations of hydrogen in the presence of reduced nickel in the neighborhood of 180° are usually very easy and frequently give very high efficiencies without any difficulty. But this is accomplished only by using carefully prepared nickel and pure hydrogen, and avoiding the presence of any substance capable of forming with the nickel a combination irreducible by hydrogen, thus diminishing the active surface of the catalyst. The rôle of such a substance is analogous to that of microöganisms in fermentations. A poison introduced into the liquid kills the ferments and suppresses their useful action. In the same way the metallic ferment, which is the nickel catalyst, is killed by traces of chlorine, bromine, sulfur; and thus neglect of sufficient precautions explains the failure that so many chemists experience in certain hydrogenations such as those of benzene and phenol.

"I should acknowledge that in this respect M. Senderens and I have had very good fortune. Naturally we were ignorant at the beginning of our labor, of the extreme susceptibilities of the metal catalyst and from the first, instead of ourselves preparing the oxide destined for the reduction,

we made use of an oxide bought on the market, which fortunately was found good. By good fortune also, our benzene and our phenol, bought it is true as pure, were so in reality. But if there had been in the benzene a small portion of thiophene or chlorobenzene, we would not have obtained any hydrogenation and, discouraged by this accidental failure, we would perhaps have attributed it to the direct impotence of nickel in this particularly difficult case of hydrogenation."

It was his previous experience which enabled Langmuir[1] to recognize and rise superior to the misleading experiment. "By this time I was familiar with all the harmful effects which gas can produce in contact with filaments and knew under what conditions these bad effects could be avoided. In particular, I realized the importance of avoiding even almost infinitesimal traces of water vapor. Thus, when I found a marked effect of mercury vapor and nitrogen in reducing the rate of evaporation, it occurred to me that it might be possible to operate a tungsten filament in gas at atmospheric pressure and obtain a long useful life. Of course, it would be necessary to raise the temperature far above that at which the filament could be operated in vacuum in order to compensate for the serious loss in efficiency due to convection by the improved efficiency resulting from the rise in filament temperature. Whether or not the increased rate of evaporation, due to this increase in temperature, would more than offset the decrease in the rate due to the gas was a matter that could only be tested by experiment. . . .

"Calculations showed that it was hopeless to get practical lamps with filaments in nitrogen, if these filaments were of very small diameter. . . . With filaments of much larger diameter, however, the effect of the gas in decreasing the

[1] Ind. Eng. Chem., 20, 334 (1928).

efficiency was not nearly so marked. We therefore con-
structed lamps having filaments of large diameter in the
form of a single loop and filled these lamps with nitrogen
at atmospheric pressure. We ran these lamps with a fila-
ment temperature so high that, in spite of the gas, the
efficiency corresponded to about 0.8 watt per candle instead
of the usual one watt per candle at which we tested our
vacuum lamps. We were disappointed to find that these
lamps blackened much more rapidly than vacuum lamps of
similar efficiency so that the total useful life of the lamp
was short.

"This result, which is what most lamp engineers would
have expected, seemed to indicate that the rise in tempera-
ture necessary to offset the heat losses by the gas increased
the evaporation by more than the amount of the reduction
in evaporation due to the gas. If I had not previously be-
come so familiar with the behavior of various gases, this
discouraging result might easily have stopped further experi-
menting in this direction. However, I noticed that the bulb
had blackened during the short life of the lamp, whereas
from my knowledge of the interaction of tungsten and
nitrogen I had expected a deposit of a clear brown color. I
felt that the black deposit could mean only one thing, water
vapor, notwithstanding the fact that, to avoid this water
vapor, we had taken precautions which were greater, I
believe, than had ever been used before for the preparation
of moisture-free gases and glass surfaces. We were thus
led to take still greater precautions and use still larger bulbs,
so that the glass should not become overheated by the con-
vection currents in the gas that rose from the filament. We
were then soon able to make lamps having a life of over
1,000 hours with an efficiency about 30 to 40 per cent better
than could have been obtained with filaments in vacuum.

"As I look back upon these experiments, I think that we were very fortunate at that time in not having had at our disposal a supply of argon gas. From theoretical reasons I had concluded that argon should be better than nitrogen, and if I had had argon I should have tried it first. If these lamps had blackened because of traces of water vapor, I would naturally have attributed this to the increase in evaporation caused by the high temperature, and would have had no reason for suspecting that water vapor was the cause of the trouble, for, of course, in argon a brown deposit would not be expected in any case."

The attempted transformations of the elements[1] have given rise to a good many misleading experiments. "A brief statement will be given of a number of experiments made by Cameron and Ramsay[2] in order to test whether ordinary matter can be transformed by the radiations. The question is a difficult one on account of the smallness of the effects to be expected. Several positive results have been published; but these have not stood the test of more rigorous and careful examination. Ramsay and Cameron first investigated the action of the radium emanation on water. For this purpose, a large quantity of the emanation was added to a small bulb partly filled with water. In this case part of the emanation was absorbed in the water and part remained in the gases formed above it. They concluded that not only did the emanation produce helium but also neon and a small trace of argon. The experiment was repeated by Rutherford and Royds[3] who found evidence only of helium. The neon and argon observed in the experiment of Cameron and Ramsay were undoubtedly derived from the small quan-

[1] Rutherford: "Radioactive Substances and their Radiations," 321 (1913).
[2] J. Chem. Soc., *91*, 1593 (1907) *93*, 966, 992 (1908).
[3] Phil. Mag., (6) *16*, 812 (1908).

tity of air which admittedly leaked into the apparatus. Neon is so sensitive spectroscopically that by suitable methods its presence in 1/10 c.c. of air can be easily observed. Cameron and Ramsay also observed that the radium emanation added to a solution of salts of copper gave rise to small quantities of sodium, potassium, and lithium, and concluded that lithium was produced by the transformation of copper. The experiments were carefully repeated by Mme. Curie and Mlle. Gleditsch,[1] who were unable to confirm the results. The experiments are difficult, since traces of lithium are ordinarily present in many substances. They found, for example, that, when pure water had rested for some time in a glass vessel and then evaporated, a small residue was obtained consisting chiefly of sodium, but also containing a small quantity of lithium. Similar results were observed with quartz. To avoid these difficulties, experiments were made with platinum vessels, and in this case the presence of lithium could not be observed.

"The question was attacked in another way by Mlle. Gleditsch[2] and by McCoy[3] by determining the amount of lithium in radioactive minerals containing copper. If copper was transformed into lithium by the radiation, it would be expected that there would be some relation between the proportions of copper, radium, and lithium in the various minerals of about the same age, but no evidence was obtained of any such relation. Ramsay and Usher[4] stated, later, that carbon dioxide was produced by the radium emanation in solutions of thorium and zirconium. It is well known that the emanation gives rise to the carbon dioxide when any

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[1] Compt. rend., *147*, 345 (1908).

[2] Ibid., *145*, 1148 (1907); *146*, 331 (1908).

[3] Nature, *77*, 79 (1907).

[4] Chem. News, *100*, 209 (1909); see also Ramsay: Compt. rend., *153*, 373 (1911).

organic matter is present, and it is very difficult to prove that carbon dioxide is derived from the atomic transformation of thorium and zirconium."

Paneth[1] calls attention to other cases in his introductory address as the George Fisher Baker Non-resident Lecturer at Cornell University. "You may have heard that just before the war, Collie and Patterson announced, from the laboratory of Ramsay, that helium and neon were formed when an electric discharge was sent through hydrogen that was in a closed vessel. But shortly afterwards, Strutt, the present Lord Rayleigh, showed that this experiment could not be repeated if air, which always contains both helium and neon, was perfectly excluded. Nevertheless, the assertion that they are thus formed was repeated a few months ago in the Proceedings of the Royal Society of London, but this experiment fails to convince one that Strutt's criticism is incorrect. In experiments, as yet unpublished, which were carried out by Dr. Peters and myself at the University of Berlin, the entire apparatus was submerged in water which served so to cool the glass walls as to render them impermeable to atmospheric helium. After hours of continuous electric discharge, we found no trace of helium.

"Many of you are doubtless familiar with the fact that last year a German chemist Miethe, and a Japanese physicist, Nagaoka, independently asserted that gold may be formed from mercury by electric discharge. It is a special irony of fate that in this case alchemy reappeared in the old-known vestment of the artificial production of gold. Gold is particularly apt to cause this error, because it may be present in various materials but so finely distributed as to escape detection by ordinary methods of analysis. But in various ways the gold may be concentrated to such an extent that

[1] "Radio-Elements as Indicators," 16 (1928).

it can then be detected without difficulty. Concentration was, therefore, in all the ages very often misunderstood as production. In the experiments of Miethe and Nagaoka quite the same happened. Today extremely small quantities of gold can be recognized and the scarcely visible beads of gold which Miethe could identify under the microscope would have entirely escaped the observation of the alchemists of the seventeenth century. But if in the final product we are satisfied with such small quantities of gold, this necessitates the employment of much more delicate methods of ascertaining that the original material is perfectly free from gold. Hence the difficulties and the danger of error have been about the same in all centuries. That this modern 'transmutation,' like that of old, amounted only to a concentration of gold and not to its genesis, has been proved by Tiede, Riesenfeld, Haber, and their co-workers in Germany and by Sheldon, Estey and Harkins in this country."

In spite of his knowledge of what had happened to many of his predecessors in the same field Paneth[1] believed that he had converted hydrogen to some extent into helium by means of finely-divided palladium, only to find that, like the others, he had been the victim of the misleading experiment.

Although people have taken great pains to determine physico-chemical constants, the tests for purity have been so inadequate in the past that Cohen[2] stated, not long ago, that "most, if not all, hitherto determined physico-chemical constants of solid substances are in need of a revision, since it is very probable that the present values refer not to the physically and chemically pure modifications, but to physically impure and metastable mixtures which contain the

[1] Naturwissenschaften, *14, 956*; Ber., *59* B, 2039 (1926) ; *60* B, 808 (1927).
[2] "Physico-chemical Metamorphosis and Some Problems in Piezochemistry," 94 (1926).

respective forms in unknown proportions. This state of affairs opens up an immense field of research to scientists and investigators, and one which may yet have many a surprise in store for us."

We are always told that pectin will not form a jelly with sugar and water, and that acid is necessary. Consequently, people have started with that as a fundamental in working out the theory of jelly-making. The statement is true, but entirely misleading. It is true if one works with about one-half per cent of pectin. It is not true if one works with one per cent of pectin.

In 1877 Downes and Blunt[1] showed that ultraviolet light destroys many bacteria.[2] "They thought that they had established the necessity for the presence of free oxygen. In this they were undoubtedly in error. This error persisted for a long time, being repeated and emphasized by Roux in 1887, until it was corrected by Marshall Ward in 1892. It is instructive to consider the causes for this mistake. The early experimenters used the whole radiation of the sun, or of the arc lamp. When attempting to test whether the exclusion of oxygen would prevent the sterilizing action, they adopted one of two methods. Usually, they enclosed the test culture in an exhaustive glass tube and exposed this to the rays. Now we know that glass absorbs all but the longest of the ultraviolet rays: and that although the investigator had eliminated oxygen, they had simultaneously shut out the active rays. Occasionally they caused the rays to fall normally to the surface of a culture on a solid medium. Observing that in this case only the upper layers were sterilized, they concluded that the deeper strata were protected by the absence of free oxygen. We know that the active

[1] Proc. Roy. Soc., 26, 488 (1877).
[2] Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 237 (1925).

rays have scarcely any power of penetrating organic films, and that this is the true explanation of the limitation of the sterilizing effect to the surface layers of the culture. . . .

"The germicidal action[1] is concentrated in the ultraviolet, somewhere between $\mu\mu$340 and $\mu\mu$185.   Ward discovered that the action was just as vigorous in the absence of free oxygen as in the air. This has, since, received ample confirmation. Oxygen, in the free state, is, therefore, not necessary for the sterilization action of ultraviolet rays."

Wheeler and Wells[2] considered that they had proved definitely the existence of solid KI_3, stable at $25°$. The substance had a different crystalline form from potassium iodide, columns instead of cubes, and analyzed for potassium tri-iodide. If one puts cubes together, one on top of another, one gets a column. The crystals were not of a different form but only seemed to be. When the crystals were dried between filter paper, the latter adsorbed potassium iodide in preference to iodine and did not remove the mother-liquor as a whole. The crystals were really potassium iodide stained by iodine; but a faulty crystallographical identification and a faulty analysis seemed to prove conclusively that they were potassium tri-iodide. The probabilities are all against two errors giving such results; but the thing did happen.

Posnjak[3] points out that "among the large number of substances which have at one time or another been X-rayed, the record for potassium is, in a way, a singular one. According to the record no regular diffraction of X-rays, but only a so-called general scattering, is obtained at room temperature by the usual powder method. The first to

[1] Ward: Proc. Roy. Soc., *52*, 393 (1892).

[2] Am. J. Sci., (4) *43*, 476 (1892); Johnson: J. Chem. Soc., *31*, 249 (1877).

[3] J. Phys. Chem., *32*, 354 (1928).

investigate the crystal structure of the alkali metals was
A. W. Hull.[1] He reports encountering considerable difficul-
ties in obtaining X-ray diffractions from sodium and lithium
and the failure to obtain any from potassium. The obser-
vation that no diffraction was obtained from samples made
from freshly melted sodium and lithium and that even sam-
ples made from old stock produced a large amount of con-
tinuous scattering led him to believe that sodium and lithium
were only partly crystalline and that potassium must be
completely amorphous. Later McKeehan[2] re-investigated
potassium. He found that, if the potassium is cooled to
−150°, weak reflections are obtained, as from large crys-
tals; however he says that this crystalline structure does not
persist when the temperature is allowed to rise to about 20°.

"The conclusion derived from X-ray experiments, that
potassium must be amorphous at room temperature, is very
surprising, as the fractured surface of potassium shows
brilliant facets; and well-defined crystals have been grown
even from the molten metal;[3] and further, of course, because
potassium has a definite and sharp melting and freezing
point. It is not quite conceivable that an amorphous sub-
stance could possess such properties, and R. W. G. Wyckoff,[4]
in discussing this case in his book on 'The Structure of
Crystals,' tries to explain these conflicting facts by the
assumption, not that potassium is an amorphous substance,
but that the amplitudes of the thermal vibrations of potas-
sium atoms at room temperature are so great as to 'oblite-
rate the crystalline diffraction maxima.' We do not need,
however, to go into the details of this discussion, as it will

[1] Phys. Rev., (2) *10*, 661 (1917).

[2] Proc. Nat. Acad. Sci., *8*, 254 (1922).

[3] Long: J. Chem. Soc., *13*, 122 (1860); Schroedler: Ann., *20*, 2 (1836);
Pleischl: J. prakt. Chem., *31*, 45 (1844).

[4] "The Structure of Crystals," 372–373 (1924).

be shown that the assumption is unnecessary. The reason for mentioning this is chiefly to call attention to the danger of drawing definite conclusions and of putting too much reliance on a few negative results of X-ray experimentation.

"The present investigation grew out of experiments on non-crystalline substances of which potassium was supposed to be one. Contrary to earlier statements, every sample of potassium that was X-rayed in this investigation showed normal diffraction effects. In view of this, and for comparison results, a few preparations of sodium and one of lithium were made and X-rayed. These substances also in each case gave definite diffraction effects, which were in good agreement with previous determinations of their crystal structure. . . . The reason for obtaining only a general scattering and no definite diffraction in former experiments is thought to be the formation of films on the sample of potassium by moisture, by oxidation, or by interaction of the potassium with the glass."

It seemed perfectly natural that the converting of milk into a powder would destroy vitamin C and this belief was considered to be proved when a sample of milk powder was found on analysis to be low in vitamin C. This is a case of the misleading experiment. The observation was right; but the obvious conclusion to be drawn from it was wrong. The catch in the case is that the amount of vitamin C in the milk varies with the time of year because of the difference in feed. Milk powder made from milk low in vitamin C will itself be low in that vitamin. This has been brought out clearly in an investigation carried out at Cornell by Professor Cavanaugh.[1]

"On account of the conflicting statements in the litera-

[1] Cavanaugh, Dutcher and Hall: J. Children's Diseases, *25*, 498 (1923); Ind. Eng. Chem., *16*, 1070 (1924).

ture regarding vitamin C content of dried milk products, and especially in view of definite statements regarding the effect of the spray process on vitamin C, a special investigation of this problem has been conducted.

"This investigation was started in February, 1922. The method consisted in feeding young guinea-pigs a standard basal diet free from vitamin C. To this was added raw liquid milk or spray-process powdered milk in varying amounts, these milk products being the only source of vitamin C in the diet.

"The milk, both liquid and powdered, was shipped by express daily from the Merrell-Soule Powdered Milk Factory at Perry, N. Y. The milk, both raw and powdered, which was used in this experiment was taken from the mixed milk of 175 dairies representing 1,276 cows. The raw milk for feeding was drawn each day from a large vat. In order to prevent souring of the raw milk, it was cooled and shipped in sterilizing bottles. The milk in the vat was pasteurized under conditions known to be favorable to the preservation of vitamin C and then reduced to powder. The powdered milk for feeding was drawn each day from this powder so that the raw milk and powdered milk came from the same lot of fresh milk. Unless this precaution is taken, a fair comparison between raw and powdered milk cannot be made, as the vitamin C content of different lots of fresh liquid milk has been found to vary considerably. The experiments on winter milk were kept separate from those on summer milk on account of a similar variation.

"This difference between summer and winter milk was confirmed by the present experiment. The fact indicates that no reliable conclusions regarding the effect of drying processes on the vitamin C content of milk can be drawn unless comparison is made between dried milk and fresh raw milk

taken from the *same* lot. Failure to take this precaution may probably account for some of the contradictory reports previously published."

"A study of the groups at the end of sixty-one days shows that the control group developed scurvy more quickly than the groups fed raw or powdered milk. Each group fed powdered milk did at least as well as the group receiving an equivalent amount of raw milk. So far as we can judge from data obtained from these experiments with guinea-pigs, there appears to be no destruction of the antiscorbutic properties of milk when it is thus powdered. This confirms the conclusions drawn from our first experiment; i.e., that milk powdered by this form of spray process possesses as great antiscorbutic properties as the raw milk from which it was made."

Since winter milk is notably deficient in vitamin C, the use in the winter of milk powder made from summer milk would give the child more vitamin C than would the use of raw winter milk—always supposing that there is no serious loss of vitamin C in milk powder which has been kept nearly a year.

I am indebted to Dr. J. E. Mills of Edgewood Arsenal for a striking case of the misleading experiment. The Chemical Warfare Service was trying the effect of toxic gases on the boll weevil. Naturally they began with a relatively high concentration of gas so as to be sure of killing the weevil. Thirty minutes exposure to a fairly concentrated hydrocyanic acid gas produced very few casualties among the boll weevils and the obvious conclusion was that the boll weevil is extraordinarily insensitive to hydrocyanic acid gas. The more Dr. Mills thought this over, the less probable it seemed. Dr. Mills and his staff decided that the boll weevil recognized in some way the unpleasant possibilities of con-

centrated hydrocyanic acid gas, and that he shut up like a clam, refusing to breathe while the experiment lasted. Of course if the weevil did not breathe the gas, it would not hurt him. It was decided to try a relatively low concentration of hydrocyanic acid gas in the hope that the boll weevil would not recognize its danger until it was too late. The experiment was successful and the boll weevils were killed by the low concentration of hydrocyanic acid gas, though unharmed by the high concentration. The boll weevil is quite sensitive to hydrocyanic acid gas provided the gas gets to it.

Dr. M. J. Brown of the Roessler and Hasslacher Chemical Company has cited the reverse case with some scale insects on citrus trees. A relatively high concentration of hydrocyanic acid gas killed the eggs of the scale; but a low concentration stimulated the eggs so much that a larger percentage hatched than in the control groups. People had not considered this possibility in the case of scale insects; but it is not very surprising when we stop to think about it. Many of us have taken small doses of strychnine at one time or other to stimulate digestion. Over seventy-five years ago certain English brewers were accused of taking an unfair advantage of their competitors by adding strychnine to their pale ales. The fact that the charge was not true is of no importance now, though it was then. While small doses of strychnine may be and often are beneficial, larger doses are invariably painful and fatal.

In the non-resident lectures at Cornell University under the George Fisher Baker Foundation, Professor Barger, of the University of Edinburgh, stated that Zuetzer called an insulin preparation toxic because he gave an over-dose to a dog, and that was toxic.

When I lectured on "The Misleading Experiment" at the

University of Indiana, Professor Weatherwax[1] called my attention to experiments running over many years which are certainly cases of misleading biological experiments.

"An unusually fascinating problem met in a botanical study of the Indian corn plant is that pertaining to its origin and relationships. Since this cereal has been known to the white man, no plant that seemed to be its wild ancestor has ever been seen. Either the centuries of aboriginal domestication have so changed the cereal that we do not now recognize its wild progenitors, or the latter has disappeared or become extremely rare. It is appropriate, then, that the chasm be bridged in theory, and the theories and hypotheses that we have in this connection are many. The merits of some of these have been discussed elsewhere.[2] It is my intention to deal critically here with only one, which has, unfortunately I believe, gained wide popular publicity. This theory is all the more interesting because it was arrived at independently by two widely separated workers, one of whom is adapted to give it publicity and the other to give it the stamp of scientific approval.

"When we look over the list of species that the taxonomist has grouped with Indian corn we soon eliminate from close relationship all but one. This is teosinte (*Euchlaena mexicana* Schrad.), which still grows wild in some parts of Mexico. This plant resembles corn so closely in vegetative characteristics and in staminate inflorescence that most persons pass it by as merely a peculiar kind of corn. In the pistillate inflorescence, however, the difference between it and corn is readily seen. When teosinte first became generally known to the scientific world, it was thought that it might be wild corn. In many respects, however, teosinte is

[1] Proc. Indiana Acad. Sci., *34*, 225 (1925).
[2] Weatherwax: Bull. Torrey Bot. Club, *45*, 309 (1918).

too highly specialized to stand in such relationship, and most investigators have looked in other directions for the answer to the question."

Luther Burbank believed that, after eighteen years of selection, he had changed teosinte to corn. Bento de Toledo believed that he had done the same thing after only five years of work in Brazil. "Neither Burbank nor Toledo has anything definite to say about the exact nature of the material with which he started the series of selections. It was merely 'teosinte,' and beyond this their figures are allowed to speak for themselves. But it must be remembered that teosinte hybridizes freely with corn, and hybrids of all degrees are fertile among themselves and with either parent. Neither is there any mention of precautions to prevent contamination of the stock by wind-blown pollen of corn during the experiment."

A comparison of the drawings with that of what is believed to be pure teosinte seems to Weatherwax to be conclusive. "There seems to be little room for doubt that the breeding stock used by both Burbank and Toledo was already as much corn as teosinte and that both have simply selected out the characteristics of corn possessed by the hybrid. That both did change the nature of the stock used is not to be doubted. But, on the basis of the figures cited, it is the writer's opinion that the probable impurity of the original stock and its possible contamination with corn during the experiment are sufficient to invalidate any conclusions that may be drawn as to the ancestry of Indian corn."

Physical chemists have been calculating hydrogen ion concentrations for years on the assumption that the solution pressure of hydrogen was the same in all aqueous solutions. We now know that it is possible to make up solutions in which this method of calculation will give a five hundred

per cent error owing to the displacement of the water equilibrium.[1] This is not so serious in itself because nobody is especially interested in solutions containing a little hydrochloric acid and a great deal of sodium chloride. What hurts is that we do not know the magnitude of the possible error in any case.

Luther and Forbes[2] studied the effect of light on the reaction between quinine and chromatic acid, finding that the photo-chemical activation of chromate must be negligible compared with that of quinine. In a later paper Forbes and Leighton[3] have failed to find any effect of light from a mercury lamp on the electrolysis of a chromatic acid solution. Plotnikow[4] objected to findings which belittled the photoactivity of chromates, and I wish to join in the protest. While Luther and Forbes undoubtedly found what they said they did, that does not make their experiments any less misleading. There can hardly be any question of where Forbes stands, because Forbes and Leighton speak of testing further "the alleged activation of chromates by light." This is quite unintelligible in view of the fact that there are technical processes depending on this very thing.[5]

"When mixed with organic substances, potassium dichromate is reduced on exposure to light; gelatine under such circumstances is rendered insoluble. This reaction is taken advantage of in the 'Carbon' process of photography. The gelatine is mixed with a pigment of any colour and the paper carrying this film is sensitised by floating on a solution of potassium dichromate. On exposure under a negative, the

[1] Bancroft: J. Phys. Chem., *30*, 1194 (1926).

[2] J. Am. Chem. Soc., *31*, 770 (1909); Forbes, Woodhouse and Dean: *45*, 1891 (1923).

[3] J. Phys. Chem., *30*, 1628 (1926).

[4] "Allgemeine Photochemie," 215, 416, 583 (1920).

[5] Thorpe: "Dictionary of Applied Chemistry," *2*, 241 (1921).

gelatine becomes insoluble in those portions exposed to the light, and retains the pigment, while the portions protected by the darker parts of the negative are almost unacted upon, and may be dissolved in warm water. In this manner photographs of any desired colour, and of great beauty and permanence, may be produced. . . . The insoluble gelatine does not absorb water, but will take oil, which may be mixed with any desired pigment and this forms the basis of the oil and bromoil processes. Gum, mixed with dichromate, is also made insoluble by exposure to light, and this is made use of in photography in the gum dichromate process."

Plotnikow has shown that ammonium bichromate oxidizes alcohol in the light. In the Cornell laboratory, Mr. Morton[1] has found that a solution of potassium dichromate in aqueous alcohol is decomposed—as of course it must be—by light which has passed through a filter made of copper sulphate solution. It seems probable that Forbes obtained his misleading results by working with solutions which were so strongly acid that no marked increase in oxidizing power could be detected. In his electrolysis experiments his solutions contained normal and three-normal sulphuric acid—which was certainly riding for a fall. In the experiments with quinine and chromic acid the sulphuric acid was 5.4 normal.

In Fittig's laboratory at Strassburg, Pagenstecher[2] found that addition of bromine to tiglic acid and to angelic acid gave the same dibromvalerianic acid. In Wislicenus' laboratory at Leipzig, Puckert[3] obtained two isomers, which he called tiglic acid dibromide and angelic acid dibromide, the latter being new. This started a long dispute, because Fittig[4]

[1] J. Phys. Chem., *33*, 1135 (1929).
[2] Ann., *195*, 123 (1879).
[3] Ann., *250*, 240 (1889).
[4] Ann., *259*, 1 (1890); *273*, 127 (1893); *283*, 65, 107 (1894).

claimed that it was impossible that such an error could have been made in his laboratory. The matter was cleared up by Wislicenus,[1] who showed that the nature of the addition product varied with the illumination.

"That Pückert obtained this isomer [angelic acid dibromide] of the tiglic acid dibromide, which latter had been prepared pure in several ways by Fittig and his pupils, and that this compound was not discovered years before in Fittig's laboratory, was due to an unnoticed detail. In the upper rooms of the Leipzig laboratory, almost all the hoods were in the outer walls *between* the windows, and were therefore dark. In the Strassburg laboratory, the hoods were *in* the windows, and were therefore filled with the brightest light. Without thinking about it, Pückert had therefore done his addition of bromine to angelic acid in the absence of bright light and obtained a product consisting chiefly of angelic acid dibromide, while Fittig and his pupils obtained chiefly tiglic dibromide because they worked—also without recognizing it consciously—in bright sunlight, the other conditions being practically the same. If the internal arrangements of the Leipzig laboratory had been like those of the Strassburg laboratory, the repetition of Pagenstecher's work in the Leipzig laboratory would have confirmed his results at least temporarily. The true angelic acid dibromide would have been discovered before now in any case. In some still unpublished work done four years earlier but interrupted by the present paper, I had noticed the great effect of varying illumination on the yield of the geometrically isomeric dibromides in the case of the bromine addition products of tolane. It was therefore intended to repeat Pückert's work with this in mind."

A tragic case of the misleading experiment, or of the

[1] Ann., *272*, 7; *274*, 99 (1893).

failure to work out cause and effect, has been cited by Jarvis, Clough and Clark.[1] "Goiter is a disease of world-wide distribution, but most especially of the temperate zone. It is most prevalent in districts far removed from the sea and in high mountain ranges, such as the Himalayas, Alps, Pyrenees, Andes, Cascade and Rocky Mountains. A very graphic report is given by Keith[2] whose account of the incidence of goiter in the Pemberton Valley of British Columbia furnishes a striking illustration of this point. This valley, some 40 to 50 miles long, lies in the mountains of the Coast Range, about 90 miles north of Vancouver, B. C. It is watered directly from the Lillioet river, which rises from a glacier near by. In former years every white baby born in this valley had a goiter, and women developed goiter within a few months after arrival. It was especially severe on livestock. There was a mortality of 90 per cent of all calves born, 85 per cent of the colts, and no pig survived more than one day after birth. Abandonment of the valley was seriously considered at one time. It will thus be seen that this question is not only one of public health but of economic importance."

"As regards chickens, ducks, and, I believe, turkeys as well, all brought into the valley appeared to thrive; but their eggs, though producing embryos, failed to hatch out, the apparent cause being the thickening of the white envelope inside the shell which was so thick and rubbery that apparently the young chick could not break its way through. Occasionally, too, a full-grown hen would suddenly drop dead, or a rooster lose his voice."

"A village of Indians is located at the lower end of the

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[1] "University of Washington Publications in Fisheries" (1926). Iodine Content of the Pacific Coast Salmon.
[2] Canadian Med. Ass. J., *14*, 284 (1924).

valley at the junction of the Lilloet and Birkenhead Rivers, situated in this same spot as far as the memory of man goes. None of the Indians have goiter, and they have no knowledge of any of their tribe ever having had goiter. . . . If insanitary conditions have a connection with goiter, as is contended by McCarrison, then one would expect a high incidence of goiter among these Indians, who have not the faintest conception of sanitation. That the freedom from goiter of this particular group is not a question of race is shown by Clark and Pierce, who state that Indians living in Minnesota, Michigan and Wisconsin had as high an incidence of goiter as white inhabitants in the same district."

While one might wish to make the improbable assumption that this tribe of Indians had perhaps, after many generations, become immune to goiter in some mysterious way, that seems to be barred out by the fact that "only rarely have their pigs been found to suffer from myxœdema, though the pig is susceptible to diseases of the thyroid." If the Indian can raise pigs and the white man can raise none, there must be a local reason.

Keith's explanation sounds plausible. "Whilst considering the lack of goiter among these Indians, I would like to draw attention to the fact that they eat a great deal of salmon. The fish come up the Birkenhead to spawn, and many millions of eggs are secured at the Government Hatchery a mile above the village. The Indians are allowed to use the spent salmon, and annually cure thousands for winter use. Their pigs also eat the dead salmon washed ashore on the gravel banks of the stream. It is quite probable that the Indians and their pigs get enough iodine from the salmon to give their thyroids the necessary quantum of this element."

It is almost like a fairy story; but it happens to be true.

The white inhabitants of the valley then took up eating
iodized food and lived happily ever afterwards, they and
their animals.

"Confronted then with this grave economic problem,
Ronayne [an Irishman of good old yeomanry who, with his
two brothers have farms about fourteen miles up the valley]
applied for advice to the Bureau of Animal Industry at
Washington and was referred to Dr. Marine of Cleveland,
as the best known authority on the subject. Marine in-
formed him that the cure was very simple, namely the admin-
istration of tincture of iodine or potassium iodide to the ani-
mals. He suggested five drops a week for horses and cows,
three drops for sows, and a few drops for chickens. The
iodine acted in a miraculous way. All the goiters disap-
peared from his animals and no further trouble in rearing
stock or fowl has occurred, and in October, 1922, when the
writer visited the valley he could not find a goiter in an ani-
mal or human being. . . .

"Acting on Dr. Marine's suggestion, Ronayne gave a cow
that had previously had four goitrous calves (this cow was
born in the valley, and had shown no goiter herself) five
drops of tincture of iodine twice a week, beginning the treat-
ment one month before the calf was due. The result was
a perfectly healthy calf. After some experience with giving
iodine, Ronayne found that very little was necessary in sum-
mer and that the most necessary time to give iodine was in
winter and early spring. He mixes fifty drops with salt,
giving this occasionally to the whole herd during the winter
months. This entails very little labour, but he found that
a weak member of the herd would sometimes get pushed
aside and not get its required quota. Mares in foal get five
drops of the tincture a week, beginning two months before
foaling time. Pigs require the least, and no iodine is neces-

sary if they are getting skimmed milk from cows receiving iodine. Ronayne gives iodine to the chickens only in spring when eggs are being gathered for hatching and then a few times is sufficient, mixed with mash or in the milk. It is only given as a preventive measure as his hens often get skimmed milk. It costs Ronayne for iodine to keep 100 cattle, 12 horses, 30 pigs, and 200 chickens free from goiter, and their progeny free also, $2.00 worth of tincture annually.

"Any resident of the valley exhibiting a goiter takes a little iodine till it disappears. If the cows are getting iodine and the children and grown-ups are drinking from these cows, it is not necessary for them to take iodine direct."

A practical test extending over more than a quarter of a century seemed to indicate conclusively that the Pemberton Valley was uninhabitable for white people and their animals. This result was entirely misleading, as it has now been proved that the whole trouble was due to a deficiency of iodides. On the other hand we must not let this new set of facts mislead us as to what has actually been proved. It has been proved that administering a suitable amount of iodine is of tremendous value in a goitrous district. A natural corollary of this would seem to be that small doses of iodine might be good for everybody as a precautionary measure. Acting on this assumption many people in New York City are using iodized salt. While this may be desirable, Dr. Keith[1] presents some evidence which raises some doubts.

"A number of observers in Europe and on this continent have drawn attention to the harmful effects that may result under some circumstances from continued use of iodine. They have found that when it is employed for the prevention of goiter without due medicinal supervision, used in quack medicines or taken as iodized salt in irregular amounts

[1] Canadian Med. Ass. J., *16*, 1171 (1926).

for a long period, serious toxic symptoms may be provoked.

"Birker, of Aarau, Switzerland, states that the carrying out of systematic iodine treatment has its dangers. Although he favors the use of iodine as a preventive measure, he thinks that it will take almost a lifetime before we know its action completely. He states that the immediate result in Switzerland has been a great increase in the number of toxic goiters; that at least 2,000 Swiss people have consulted physicians for the symptoms provoked by iodized salt; and that, in his own clinic, where operations for goiter formerly showed 2 to 5 per cent of cases with toxic symptoms, now his records show that 20 to 25 per cent are toxic cases; some clinics in that country report as high as 50 per cent of toxic cases."

I do not know whether detective stories are permissible evidence in a scientific discussion; but I read them and I wish to close with a quotation from one.[1] "The evidential value of any fact is an unknown quantity until the fact has been explained."

[1] R. A. Freeman: "The Singing Bone," 254 (1923).