

settling for a proper time the rack is turned to an up-right position, the flasks placed under the outlet cocks as in Fig. 5 and the mixed ethers and fat drained off. If closer drainage is desired the tubes may be held in the hand while the last portion is drained off. Funnels and filter papers may be placed in the flasks if desired.

STATE FOOD COMMISSION
1623 MANHATTAN BUILDING, CHICAGO

MODIFIED APPARATUS FOR THE PUTRESCIBILITY TEST

By A. M. BUSWELL¹

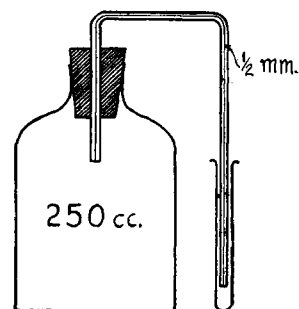
The putrescibility test as described by Jackson and Horton² is made in a 250 cc. bottle provided with a one-hole rubber stopper carrying a medicine dropper with a 5 cc. rubber bulb: 37.5° C. is the temperature of incubation. The bulb is collapsed at the beginning of the test but soon becomes partially filled, due to the expansion of the liquid and the evolution of some of the gases originally in solution. Expansion is thus allowed for without permitting the absorption of air. It has been found, however, that the rubber bulbs deteriorate very rapidly. This not only makes the cost of up-keep of the apparatus high but

occasionally a test is lost, due to the failure of a bulb during incubation.

These facts led the writer to design for the putrescibility bottle the modified form of stopper shown in the figure. The modification consists in replacing the medicine dropper by a J shaped capillary tube of 0.5 mm. bore. The long end of the tube extends to the bottom of a small test tube which catches the overflow. The diffusion of gases through capillary tubing is so slight that the prevention of air absorption is effected. Aside from being more durable the modified stopper can be applied much more easily and rapidly than the old form and the convenience is quite an item when 50 to 100 bottles have to be made up at one time.

The modified stopper has been used in a series of comparative tests made by students in this laboratory and the results obtained so far are entirely satisfactory.

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ADDRESSES

MODERN CHEMICAL INDUSTRY³

By FRITZ HABER

It is a special honor to me to speak here in appreciation of a man who recognized and represented the importance of physical thinking in applied chemistry at a time when almost without exception technical chemists declined to take this view.

Thirty years ago, when Hurter's activity was at its height, the center point of chemical industry was the Leblanc soda process. Here in England a number of technical methods for the manufacture of sulfuric acid and Glauber's salt, bleaching powder, soda, potash and the alkalies had been developed up to a remarkable standard. It is impossible to admire too much the richness of inventive genius and the clearness of judgment which the technical chemists of this period developed in your country. The world has learned of them how to convert chemical laboratory reactions into industrial technical processes and how to build up a system of analytical controls which enables the manager to follow the chemical change in a complicated system of reactions on a large scale.

The picture that technical chemistry exhibits to-day is quite different from that of thirty years ago. There is more brilliancy around the accomplishment of the organic than of the inorganic industries. The replacement of natural dyes by the products of coal tar, the extension of our medical resources by the manufacture of synthetic medicines, has gone far to extend the appreciation of chemical work and to produce the general conviction that chemistry is an inexhaustible field of economic possibilities. Indeed, one natural product after another falls into the domain of chemical synthesis, and chemistry is becoming the important factor in the economy of the tropical products which are used for industrial purposes. As soon as

the price of such a product exceeds a certain limit organic chemistry enters the field and synthesizes it in Western Europe. Thus indigo has succumbed to the onslaught of organic chemistry. Tanning materials at present are in a struggle with the condensation products of formaldehyde and phenolsulfonic acids. Camphor could maintain its position only by large price reduction, and the prospect of synthetic rubber holds down the would-be inflated prices of the natural product. The basis of this marked development in organic chemical industries is the combined working of science and technology. The fact and the success of this intermingling is so obvious that we need not dwell on the point.

In the territory of inorganic technical chemistry things are somewhat different. Here also a great change has taken place. The historical sulfuric acid and soda processes have lost much ground to the ammonia-soda and electrolytic processes, and to the contact process. New branches of industries have taken root and grown up. In this field, however, the connection between scientific and technical progress is neither so obvious nor so well recognized as in the realm of industrial organic chemistry. The reason is that the advance in inorganic science, during the last decade or two, has resulted less in the discovery of new facts which had direct technical applications, than in the unravelling and working out of new theoretical views. In fact, the introduction of physical laws and physical methods into the working sphere of inorganic chemistry has led to the greatest scientific progress. The invasion of physics into chemistry has produced the splendid development of physical chemistry, the basis of which is the second law of thermodynamics, the phase rule, and the theory of electrolytic dissociation. The introduction of the electroscope into chemical analysis has opened up the new chemical world of radioactivity. Now, in my opinion, inorganic chemical industries can gain almost as much by regarding their problems from a physical point of view as organic industries do by the application of structural considerations.

¹ Instructor in Sanitary Chemistry, Columbia University.

² THIS JOURNAL, 1 (1909), 328.

³ The Hurter Memorial Lecture, delivered before the Liverpool Section of the Society of Chemical Industry, November 26, 1913 and printed in the *Jour. Soc. Chem. Ind.*, 33 (1914), 49.

I do not think it will be out of place in this lecture if I speak of one or two inorganic technical questions and lay stress on the physical considerations which bear on them. I may be permitted to pass by many of the current examples of the part played by physical chemistry in technical chemistry, owing to their general recognition and go on to speak of a few industrial cases with which I have come in contact during the last year or two.

ZIRCONIUM OXIDE REPLACES STANNIC OXIDE IN THE ENAMEL INDUSTRY

During the last few years a not very obvious property of stannic acid has become the source of a new inorganic industry. Iron cooking utensils are coated on the inner side with a white enamel¹ which must contain no poisonous material; owing to its relative coefficient of expansion it must be very thin so as not to crack and chip away when the iron expands through rise of temperature. It must have a low melting point so that the iron does not lose its shape when it is coated with the melted enamel. A glass is therefore used which has nearly the following constitution: Borax, 26 per cent; quartz, 17 per cent; feldspar, 34 per cent; sodium silico-fluoride, 13 per cent; soda, 4 per cent; saltpetre, 3 per cent; kaolin, 3 per cent. The constituent parts are melted together; the fused mass is ground with water and some plastic clay to a thin paste of suitable thickness for even coating, then dried on the iron and heated to a temperature of 800° C. for about a minute, whereby fluxing of the enamel is attained. That is roughly the technology of enamelled iron. But such an enamel is too transparent, for the thin coating, which it is necessary to use on the iron, permits the dark color of the background to be seen. It is desirable to add something which, in small quantities, will render the enamel quite opaque, and which will, at the same time, give it a clear white color. The only satisfactory substance up to the present has been stannic acid. The requisite amount for a given surface is small, about one-half gram being required per square decimeter, but the employment of enamelled iron utensils is so great that 3300 metric tons of stannic acid are used yearly for this purpose. In earlier times about double the amount of stannic acid was used per unit area, as it was mixed and melted with the other constituents of the glass, and not, as at present, added to the enamel paste before the baking process.

The substitution of stannic acid by an equally efficient and non-poisonous, but cheaper clouding medium, has long been sought for by the enamel industry. Many and various substances have been tried and now it seems as if the problem has been solved.

The naturally occurring zirconium silicate is treated by alkali and a product of roughly the following composition is obtained: ZrO_2 , 83 per cent; TiO_2 , 4 per cent; SiO_2 , 9 per cent; Na_2O , 2 per cent, the remainder being water. This impure zirconium oxide is replacing stannic acid. It is used in the same quantities and in the same way.

The development of this new industrial process has brought forward the question as to whether the specific property of the product is due to the oxide of zirconium or to some peculiar physical state that it possesses which could be imparted to other substances or perhaps to the impurities contained besides the oxide of zirconium. These questions are solved by some simple considerations.

Zirconium oxide is like tin oxide, namely, when in large crystals, a transparent colorless body. To render a glass opaque by the intermixture of particles of such a body the two substances must have different indices of refraction. The greater the difference, the greater will be the specific power of the particles to render the glass opaque. Now, the easily melting glasses

which are used for enamels have a coefficient of refraction in the neighborhood of 1.5. Natural tin oxide has the refractive index—for yellow light—of 1.9966 or 2.0799, according to the axis chosen. Its refractive power is therefore far greater than that of the glass. This property accounts for its utility in making enamels opaque.¹ Natural zirconium silicate has very similar refractive indices, being only about one unit smaller in the first place of decimals. Calculating from the well known additive properties of molecular refraction we find that the removal of the relatively feebly refracting silica from the zirconium silicate will increase its coefficient so that pure zirconium oxide will have a refractivity about 10 per cent greater than pure tin oxide. Thus we may expect that zirconium oxide with or without the above-mentioned impurities of the technical product acts like tin oxide if it is equally finely divided in the glass. Differences will, however, appear if one of the oxides dissolves in the enamel to a much greater extent than the other. The fact that only half the tin oxide is required when it is not melted with the enamel, but only mixed with it before roasting, shows that it is not so much a question of solubility, but of the rate at which it dissolves. Now the oxide dissolves only after the melting of the glass and the melting is stopped the moment the heat coming from above renders the surface mirror-smooth. Thus there is only time for a limited solvent action of the glass to take place. From this we gather that an equally small quantity of suitably calcined zirconium oxide or of tin oxide will probably render the enamel equally opaque. With voluminous zirconium oxide prepared by heating pure commercial zirconium nitrate to 800°, this conclusion was easily proved by a few experiments. Some minor points about the composition of the enamel would have to be considered if we would go into the subject more fully.² The former difficulty of finding empirically a substitute for tin oxide is now made plain by inspection of a table of refractive indices, because we find that the oxides of tin and zirconium have peculiarly large indices among the substances which are colorless, stable at high temperature and non-poisonous. The oxide of titanium which forms a small part of the technical product would be even better alone, because of its still larger refractive index, but the enamels made opaque by it show a yellowish color.

MESOTHORIUM FROM MONAZITE SAND

I will now pass from the zirconium oxide to its accompanying mineral monazite sand and speak for a moment of a new factor in its industrial treatment. Since the introduction of the Welsbach mantle for lighting purposes, monazite sand has been worked up in large quantities for the production of thorium nitrate. In the last two years a new and very peculiar question has arisen for this industry by the demand of the medical profession for radioactive substances which give penetrating γ -rays. There are in a thousand metric tons of the usual monazite sand containing 5 per cent of thorium oxide, according to the current radioactive figures, 18 milligrams of such a radioactive substance. The value of these few milligrams in a sufficiently concentrated form exceeds the value of any other substance known and covers the original cost of the 1000 tons of monazite sand. Now, the problem was to get these few milligrams out of the thousand tons in the normal thorium extraction process. This extremely valuable substance is the mesothorium I, of Dr. Hahn, which by changing into mesothorium II, becomes a much more powerful source of γ -rays than radium itself in equilibrium with its products.

¹ So far as I am informed, this view is not mentioned in the literature of enamel. But I have recently found that Wilhelm Ostwald, in his "Malerbriefe," Leipzig, 1904, explains the property of white lead of giving the greatest opacity for painting by help of the analogous consideration for oil and carbonate of lead.

² See D. R. P. 189,364; Bela Havas "Ueber Eisenblechemaille." Karlsruhe, 1910 (Doctor-Dissertation); Hartmann, "Zirkonemail." München, 1910 (Doctor-Dissertation); Weiss, *Zeitschrift für anorganische Chemie*, **65** (1910), 218.

¹ See Paul Randau, "Die Fabrikation des Emails und das Emaillieren," Wien und Leipzig, 1909; Julius Grünwald, "Theorie und Praxis der Blech- und Gussemailindustrie," Leipzig, 1908, and "Chemische Technologie der Email-Rohmaterialien," Dresden, 1911; further "Ausgewählte Kapitel aus der Emailiertechnik," herausgegeben von der Redaction des Sprechsaals, Coburg, 1912.

The problem is solved by the addition of 0.1 per cent, of barium to the sand before treating it with sulfuric acid in the usual way. In due course we get a radioactive deposit of barium sulfate rendered impure with SiO_2 , TiO_2 , lead, and rare earths. These impurities must be separated by four distinct chemical processes, resulting finally in the regaining of barium sulfate with radioactive impurities only. This product is then concentrated by the ordinary methods using the chloride, carbonate, and bromide of barium, up to the γ -ray activity of pure radium bromide, or in excess thereof. One might certainly expect from such a complicated process that the largest part of the 18 milligrams would be lost. The real result, however, is found by comparing, using the α -ray method, the amount of mesothorium in the final concentrate and in thorium in equilibrium with its transformation products. Dr. Keetman and Dr. Mayer have done so¹ and obtained the astounding result, that the figures are nearly the same. How is that to be explained? The sand always contains a small amount of uranium (say 0.1 per cent) and in consequence its equivalent of radium, which is saved together with the mesothorium. The amount of radium in the sand and in the final concentrate is determined by using the emanation method of estimation. Keetman and Mayer have also made this comparison and found an equally quantitative agreement. This yield also is almost theoretical. The quantity by weight of the radium is much greater than that of the mesothorium in the sand as well as in the final product. The final radioactive product of the 1000 tons shows a γ -radiation equivalent to 2200 milligrams of RaBr_2 , three-tenths of which come from the bulk of real RaBr_2 , while seven-tenths are due to the small admixture of the much more powerful mesothorium bromide. We have learned from Soddy and Fajans that radioactive elements occurring in the same place of the periodic system are inseparable by any chemical means. Therefore, according to this rule, the quantitative extraction of mesothorium follows from the quantitative extraction of the larger mass of radium. That the latter accompanies the barium fully is usually explained by the greater insolubility of the radium sulfate and their isomorphism.

I wonder whether this explanation will be final. Perhaps adsorption plays an important part, even in case the sulfates should be able to dissolve into each other in the solid state like alcohol and water in the liquid state. Diffusion is so extremely slow with solids that the surface phenomena become more prominent in all rapid changes. The work done by Ritzel² here at Liverpool, in this laboratory on the suggestion of Donnan induces us to regard adsorption as the primary step even in the case that a solid solution can be formed. Now there are certain facts stated quite recently by Fajans and Beer,³ which suggest a near connection between adsorption and chemical affinity. On the other hand we have learned from Bragg's new brilliant investigations, that the ordinary solid crystalline salts are not systems in which one anion and one cation form a molecule which is separated from the next, but that one cation is probably bound to all the surrounding anions and one anion to all the surrounding cations. In consequence of that, we may feel inclined to consider the possibility of chemical forces acting between the atoms or ions in the surface of the solid precipitates and the molecules or ions in the final layer of the surrounding liquid, *i. e.*, in the adsorption layer. We may remember that there are good reasons for the belief that chemical forces are of electrical character and we know from electro-osmosis and similar phenomena that electrical forces are always acting between the surface of the solids and the adjacent layer of fluid. Adsorption phenomena, which are especially instructive with radioactive substances, owing to our being able to detect the presence of minute quantities, may thus perhaps be brought in close connection with chemical affinities.

¹ Private communication.

² *Zeitschrift für physikalische Chemie*, **67**, 724.

³ *Berichte der deutschen chemischen Gesellschaft*, **46**, 3468.

COMPARISON OF BLAST LAMP AND BUNSEN BURNER

The working up of the rare earths presents many physical-chemical points of interest. It is tempting to speak of the electrolytic preparation of the so-called "Mischmetall" containing 80–90 per cent cerium (the rest consisting of didymium and lanthanum) and its use for patent lighters, or about the manufacture of pure fluorides of the rare earths used for the salted arc to make the light white, or of the special properties which a thorium nitrate must show in order to give good Welsbach mantles. I will just consider one point more in detail because it is a good example of how the same simple consideration elucidates problems in very different branches of chemical working. The splendid reasoning of Le Chatelier explained the property of the Welsbach mantle in producing more light when heated by a Bunsen flame than any other radiator, as being due to the fact of the transparency of its substance in the infra-red region. In virtue of this transparency the mantle is unable to give off the heat imparted to it by the burning gas by the emission of heat wave energy. At the same temperature the Welsbach mantle radiates no more light than other substances, but in a given flame it gets hotter and more nearly approaches the temperature of the flame than does any other substance owing to this lack of heat radiation. From this state of things high light economy results, as we get with gas of a heating power of 5000 calories, one Hefner candle-power for an hour with the consumption of 0.8–0.9 l. of coal gas using the inverted type of burner which, as is known, affords a certain amount of previous heating. Now, by using a compressed air burner we can increase the economy to 0.6 liter of gas per Hefner candle-power with the same gas without more previous heating than in the former case. At first sight we may be led to think that the compressed air flame is hotter, but on closer consideration it will be evident that this is wrong. A Bunsen flame consists of two extremely thin reaction zones, the internal cone and the external one, the latter being used for heating the Welsbach mantle. In the internal cone the admixed air burns in an excess of gas, while in the outer cone the burning components undergo complete combustion with the air, forming CO_2 and water. The position of the outer cone is fixed by the fact that in this zone the quantity of oxygen present must be exactly the theoretical amount required for complete combustion. Here, as there is no excess of air, the temperature depends only on the calorific value of the gas and the specific heat of the products of combustion, and is therefore at the maximum attainable with this gas and air. Thus the temperature of a blowpipe, using air, and gas of the same composition cannot exceed this maximum. Nevertheless, the mantle does get hotter in the blowpipe as is proved by the fact of increased economy. We do not even need this special observation of the mantle, as everyone knows from elementary experience that things can be heated to a much higher temperature in a blowpipe than they can in a Bunsen flame. Now, why is this the case? An explanation has been suggested in the fact that as the blowpipe has a smaller flame, the production of heat takes place in a more confined region. But this fact is really no explanation as we do not heat a geometrical space, but a quantity of gas, and we have just proved that it is impossible to get it hotter than it becomes in the outer cone of a Bunsen flame. To find the proper explanation we must consider a phenomenon that has no very obvious connection with this subject, namely, the dissolving of crystals in water. On this subject we have the theory inaugurated by Noyes and Whitney, and developed by Nernst, which states that the layer of liquid in contact with the crystal always consists of saturated solution. This saturated layer is continually losing its dissolved substances to the unsaturated further removed layers and at the same time being resaturated from the surface of the crystal. If the liquid is stirred this surface layer remains without motion, as the external friction is very much greater than the internal, while the neigh-

boring layers have progressively increasing velocities. Now, for the sake of simplicity we may imagine this system of layers of increasing velocities replaced by a stationary layer in contact at one side with the crystal and on the other with the bulk of the solution uniformly moved by the stirrer. Thus, this stationary layer is a region through which diffusion of the dissolved substance takes place and the rate of solution is determined by the amount of substance which diffuses in unit time through this layer. The quicker the stirring is, the thinner is the stationary layer, the shorter is the distance for diffusion and the greater the rate of solution. Bearing in mind that diffusion and conduction of heat are entirely analogous processes, and that both phenomena follow the same differential equations, we at once arrive at the theory of the blowpipe, by introducing this simplifying conception of a stationary layer of gas on the surface of the heated body immersed in the rapidly moving gases of the flame. We see that the temperature of the solid body depends on the gain of heat by conduction through this stationary layer of gas and upon the equally large loss of heat due to radiation. The quicker the flow of the gas, the thinner will be the stationary layer; the thinner the layer, the greater will be the flow of heat and the higher the temperature of the body. Thus the difference in the velocities of the hot gases at equal temperature accounts for the higher efficiency of the blowpipe.¹

The study of flames and the process of combustion and the possible uses of the products of combustion constitute a favorite field for a physical-chemical consideration.

MANUFACTURE OF FORMIC AND OXALIC ACIDS

Among the processes for utilizing the products of combustion in chemical industries, the action of generator gas on alkaline solutions stands out. The old method of making oxalic acid was by the action of fused alkalis on wood, and formic acid was got by splitting off of CO₂ from the oxalic acid. To-day these processes have disappeared. Formic acid is obtained by the action of carbon monoxide, in the form of generator gas, on alkali, and oxalic acid is made from formic acid by heating its salts and decomposing them into hydrogen and salts of oxalic acid. Berthelot discovered this action of CO on alkali as long as 50 years ago and has done much research on this subject. His view was that the caustic alkalis combine with CO best in presence of a little water but always at a very slow rate. In order to quicken up the reaction later on, CO at high pressure was used and Berthelot's concentrated solutions were replaced by solid alkali. This was developed into a technical process in which wet generator gas under pressure acted upon slowly shaken pieces of solid alkali; but finally it was found more expedient to replace the solid alkali by a dilute solution which has the surprising property at high temperature of acting much more quickly than concentrated solutions. This is the most modern form of the technical process.

This reaction has been studied in my laboratory.² The question was first whether the reaction goes on between water vapor and gaseous CO, or between dissolved CO and the constituents of the solution. Experiment proved the latter to be the case. Thus the speed depends upon the concentration of the dissolved CO which is used by the reaction and replaced from the atmosphere above. Under equal conditions of stirring and temperature the speed is strictly proportional to the partial pressure of CO in the gas room. At low temperatures the reaction is extremely slow, and moderate stirring of the gas and

solution is all that is required to keep the solution saturated with CO. Stronger stirring is without influence. Under these circumstances a high concentration of alkali helps to a comparatively rapid chemical change, but the reaction velocity is always far below that required for a technical process. Heating, as usual, increases the reaction velocity very much, and above 100° it becomes difficult to keep the solution saturated with CO by stirring. At 160° to 170° we cannot arrive at a point where stronger stirring would not materially increase the progress of the reaction. In this region of temperature the velocity of reaction meets the technical requirements, provided the absorbing liquid is brought into extremely close contact with the current of generator gas. Concerning the influence of the concentration of the alkali upon the speed of reaction, we find that from 100° upwards solutions containing about 10 per cent of alkali become more and more marked by a high rate compared with stronger as well as weaker solutions under the same conditions of temperature and stirring. At 160°, for instance, the 10 per cent solution works 15 times better than a 43 per cent one. The suggestion that the 10 per cent solution becomes best intermixed with the gas by the stirrer in virtue of an especially small surface tension is not supported by measurements of this constant at high temperature,¹ and this point remains unsettled for the present. The older form of the process which works with solid alkali and the newer using the solution are seen now in very close connection. In the older form the gas used in a wet state produces by virtue of its water vapor a thin coating of concentrated solution of caustic alkali on the surface in which the CO dissolves and reacts as it does in the new process. Perhaps this industrial application illustrates very effectively the influence of temperature and stirring upon reaction velocity. Is it not remarkable that the same alkali which helps us so often to separate CO₂ from CO by the formation of carbonate in gas analysis is able under other conditions to separate perfectly the CO from the nitrogen of the generator gas?

FIXATION OF NITROGEN

Returning to the subject of flames we find that there is to-day much interest connected with the question of the possibilities of developing their power of fixation of nitrogen. Our usual flames give only very small traces of nitrous products by burning in air at ordinary pressure. In the case of the acetylene flame, which is very hot, a distinct yield can be obtained under ordinary pressure by the combustion with an air enriched with oxygen.² With other gas flames the combined application of air enriched with oxygen and of high pressure in the combustion chamber produces the same effect.³ The interest in the utilization of this behavior for the production of nitric acid results from the fact that the question of fixation of nitrogen is a very burning one. It may be interesting to look more closely into this problem. The more the agricultural conditions in the world develop in such a way that the agricultural products are not used in the place of their growth, the greater becomes the necessity for the addition of fixed nitrogen to the soil. Plants take up fixed nitrogen from the soil and animals get it from the plants, both without increasing or decreasing its quantity; but if corn and meat are exported from the place of production, the ground does not regain the nitrogen which it has given up.

It is true that there is a certain natural replacement of nitrogen. In the track of lightning, free nitrogen is fixed to a certain extent and the rain carries it down from the atmosphere into the soil. Besides this there are, in the soil, nitrifying bacteria which transform free nitrogen into the fixed state. But they are very sparsely distributed, and there seems no way of increasing their number. The earlier rational agriculturist made use of the special

¹ See Haber and Le Rossignol, *Zeitschrift für physikalische Chemie*, **66**, 195. The influence of the rate of flow of the flame gases upon the temperature of an immersed body has first been mentioned by Féry, *Compt. rend.*, **137**, 909; see Haber, *Zeitschrift für physikalische Chemie*, **68**, 752.

² Friedrich A. Weber, "Ueber die Einwirkung von Kohlenoxyd auf Natronlauge" (Doctor-Dissertation), Karlsruhe, 1908. Gorton R. Fonda, "Ueber die Einwirkung von Kohlenoxyd auf Laugen" (Doctor-Dissertation), Karlsruhe, 1910.

³ Unpublished results.

² See Haber and Hodsmann, *Zeitschrift für physikalische Chemie*, **67** (1909), 383.

³ See Haber and Coates, *Zeitschrift für physikalische Chemie*, **69** (1909), 337; Wolokitin, *Zeitschrift für Elektrochemie*, **16**, 814.

property of leguminosae which grow nitrifying bacteria on its root nodules. These natural aids are now insufficient. The yearly deficit in fixed nitrogen is characterized by the fact that the world's demand for fixed nitrogen amounts to three-quarters of a million tons, by far the largest consumer being agriculture. Nowadays, this requirement is supplied mostly from two sources: the main bulk from the Chilian fields in the form of saltpetre and a smaller part from coal in the form of ammonium sulfate. A few years ago anxiety arose whether the Chilian fields would be sufficient to meet the ever-increasing demands for more than a few years to come. To-day we are confident that they will last at least till the middle of our century, even at the present rate of increase of demand. But when we are told that the Chilian factories have replaced their old and primitive methods by new and very efficient ones and at the same time see that the price continues on its upward course, we realize that the richest and most accessible seams have been exhausted. Therefore, the economic future does not look very cheerful, unless a powerful rival steps in.

In regard to the natural store of nitrogen in coal which averages a little over 1 per cent, it is obvious that it is completely lost in burning and only to a small extent, say one-fifth, regained in coking when by-product ovens are used. In Germany these are almost universal. Here in England the older beehive type, which loses the whole nitrogen, has so far not been completely replaced, and in America up till now the by-product ovens are employed only to a small extent. Though the beehive oven will, without doubt, be universally replaced owing to this saving of fixed nitrogen, the increase of the supply of fixed nitrogen that is to be expected from this substitution will meet the increase in demand only for a very short time. These circumstances afford a tremendous stimulus to chemistry in its efforts to fix nitrogen, of which we have a limitless supply in the atmosphere. Elementary nitrogen is everywhere at our disposal. Its separation from oxygen is brought about by various methods which cost only something like $\frac{1}{4}$ cent per lb. Against that, fixed nitrogen in the form of Chile saltpetre or ammonium sulfate from the by-product coke ovens has a value of more than 1.6 cents per lb. This price gives a very high working margin and makes possible and practicable quite a number of chemical fixation processes. Now, this is not the first time chemists have tackled this question. When Solvay's soda process came with its demand for ammonia Ludwig Mond attempted to solve the question. He took the lines suggested by Bunsen and Playfair and followed in the steps of Margueritte and Sourdeval, by heating together coal, nitrogen, and barium carbonate for the production of cyanide which can be decomposed into ammonia. But Mond gave up this process after a detailed study. He returned to the supply of fixed nitrogen in the coal, and increased the yield to 70 per cent by the introduction of what is known now as the Mond gas process. This process is continually spreading, as a market is found for the gas of low calorific value which is the other product of the process. In view of this development we may ask what modern aids allow us to carry through with success the task abandoned by Mond and to find satisfactory methods for the fixation of atmospheric nitrogen on a large scale. The answer is obvious if we consider the various processes which have lately been introduced into the technical world.

PROCESS FOR OXIDATION OF NITROGEN

First of all, we must mention processes which make use of electric energy on a large scale. The first process imitates the example of nature which produces nitrous products in the track of lightning from the nitrogen and oxygen of the air, by producing a high tension arc in a closed vessel through which air is passed. The foundation of this ingenious method has been laid here in England. Cavendish was the first to get nitrous products from air by help of the spark. Sir William Crookes recommended the use of the high tension arc. Lord Rayleigh and later on

McDougall and Howles determined the yield under varying conditions. The technical forms which have risen to importance are connected with the names of Birkeland and Eyde, Pauling, and Schönherr. They have in common the conception that the technical process must be based upon the use of large amounts of air and electric energy in one single arc flame, and that this problem can be successfully solved only if the discharge is spread out. For this enlarging of the arc Pauling uses a stream of air moving at a high velocity which is blown against the point where the arc strikes between narrow electrodes. Birkeland and Eyde gain the same effect by a strong magnetic field. Schönherr ingeniously uses a steady column of discharge of many meters length which is produced and kept steady by an ascending whirlwind of air, which surrounds the arc. Factories have been started at different places, on the largest scale in Norway. They rapidly captured the small market for nitrites, but in the large field of nitrates the production has not come up to expectations. The obstacle that hampers this industry is the fact that the production of fixed nitrogen referred to the kilowatt-hour does not exceed 16 grams, and that this small yield is obtained only in the form of gases containing no more than 2.5 per cent of nitric oxide. These unfavorable results are due to the fact that the thermodynamic equilibrium between N_2 , O_2 and NO has an unfortunate value at all accessible temperatures. The importance of this equilibrium has been pointed out by Muthmann and Hofer, and exact figures for the equilibrium have since been estimated in a very ingenious way by Nernst. The following table gives the percentage amount of nitric oxide which according to him characterizes the equilibrium:

TABLE I—PERCENTAGE OF NO IN EQUILIBRIUM WITH AIR

% NO	° C.
0.1.....	1230
0.5.....	1660
1.0.....	1930
1.5.....	2140
2.0.....	2300
3.0.....	2590
4.0.....	2840
5.0.....	3060

It is obvious that even at the temperature of the arc only a small fraction can combine with the oxygen unless we may surpass the thermodynamic equilibrium by direct transformation of electric energy into chemical energy. Now experiments carried out in my laboratory have proved that to be possible with small arcs,¹ but there is not much hope of doing so under technical conditions. The upshot of this is that this electric fixation of nitrogen grows up only at places where exceedingly cheap power is available. This is not the case in the chief industrial countries. Conditions are more favorable in the case of the process of Frank and Caro. They fix 50 grams of N_2 by use of 1 kilowatt-hour, everything included. The electric power is used in this case for the purpose of making CaC_2 from CaO and coal, the CaC_2 being able, after an initial heating, to form spontaneously the so-called calcium cyanamide. There are 36,000 tons of N_2 fixed yearly by this method. The calcium cyanamide can either be used as a fertilizer, or split up by steam with the production of ammonia.

A similar amount of energy is said to be necessary in the Serpek process, which apparently is not yet commercially working on a large scale. It is based upon the change of aluminium oxide with carbon and nitrogen into aluminium nitride. Electrical energy is here required, as in the processes mentioned before, for the production of the temperature necessary for rapid reaction. Starting from bauxite and treating it according to the well known Bayer process to produce the alumina, the Serpek

¹ See Haber und Koenig, *Zeitschrift für Elektrochemie*, **13** (1907), 725; **14** (1908), 689; **16**, (1910), 789. Holweh und Koenig, *Zeitschrift für Elektrochemie*, **16** (1910), 803.

process may be introduced as the first step with the result that the valuable ammonia is obtained as a by-product.

We see that all these processes owe their success to the use of electric energy. The high tension arc requires an extravagant amount and the two other processes require, though much less, still a considerable amount. On closer inspection we find that this fact is the reflex of the values, which the underlying thermodynamic equilibria possess. In the reaction $N_2 + O_2 = 2NO$, the right side of the equation which contains the desired fixed nitrogen is thermodynamically less favored than in the reactions $Al_2O_3 + 6C + N_2 = 2AlN + 6CO$; and $CaO + 3C = CaC_2 + CO$; $CaC_2 + N_2 = CaCN_2 + C$. But in all three cases the reaction would, in virtue of its thermodynamical properties, never proceed spontaneously at low temperature. High temperature produces the chemical forces required.

In consequence of that, electric energy can be replaced theoretically by other means of obtaining high temperatures. That is the reason why the question of application of flames comes in for the production of nitric oxide from air. But it is clear that the values of the equilibrium between N_2 , O_2 and NO which are so unfavorable even at the temperature of the arc will be a still greater obstacle at the lower temperatures of flames and explosions. The subject has been studied for some time in my laboratory. To give an example we arrived at one molecule of NO with production of 16 molecules of carbonic acid from carbon monoxide. But such results are obtainable only by a large use of the comparatively expensive oxygen to enrich the air and increase the combustion temperature.

Certainly there are enough examples of chemical processes which work successfully on a large scale in spite of the fact that the chemical forces under ordinary conditions are striving to produce the reverse change, from the final products back to the raw materials. The ammonia soda process is an outstanding example. It produces calcium chloride and soda which if simply brought in contact would return to the original form of sodium chloride and calcium carbonate. But in general those reactions are more easily converted into technical processes which are backed by chemical forces tending to change the raw materials into the desired products.

SYNTHESIS OF AMMONIA

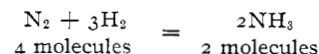
This consideration led our attention some years ago to the reaction of nitrogen and hydrogen to form ammonia. The heat of combination has, according to thermo-chemistry, a positive value, which proves that it is only due to lack of reaction velocity that the gases do not unite at ordinary temperature. It is true that these favorable values of chemical forces become most unfavorable with increasing temperature. It does not need a very high temperature to make the thermodynamical value of the equilibrium a marked hindrance for any appreciable production of ammonia from its elements. Theory teaches us and experiment has proved that the best mixture of N_2 and H_2 for the production of NH_3 has the value of 1 : 3. But with this most favorable mixture the limit of percentage of NH_3 attainable under ordinary pressure is at higher temperatures very small, as will be seen from the first column of this table:

TABLE II—PERCENTAGE AMOUNT OF NH_3 IN THE EQUILIBRIUM OF THE REACTION $N_2 + 3H_2 = 2NH_3$
Temperature ° C.

Pressure in atmospheres	550	650	750	850	950
1	0.0769	0.0321	0.0159	0.0089	0.0055
100	6.70	3.02	1.54	0.874	0.542
200	11.9	5.71	2.99	1.68	1.07

Especially as the temperature approaches the value of 1000° , for which we easily found effective catalysts, the yield is minute. Some hundred degrees below, the much larger though still small amounts given in the table were formerly inaccessible because of the lack of catalysts effective in the neighborhood of 500° .

At first sight one might think that the thermodynamic situation is still worse for the synthesis of ammonia than for the combination of N_2 and O_2 , because the values of the equilibrium content of NH_3 are much smaller than those for the equilibrium content of NO in air given before. But theory shows a way out of this difficulty in the case of ammonia which is not open in the other case. The NO equilibrium is independent of pressure because the number of molecules is the same on both sides of the equation. In the case of ammonia, however, the number of molecules decreases from 4 to 2,



and therefore according to thermodynamics the attainable percentage of NH_3 in equilibrium is proportional to the working pressure over a wide range. Consequently the values of the equilibrium percentage at 100 or 200 atmospheres pressure show a very different aspect, as will be seen from the second and third columns of the table.

It is obvious that technical synthesis is possible if we can succeed in reaching the equilibrium at such pressure and in a short enough time. The current of N_2 and H_2 must circulate in such a way that the ammonia formed by the passage over the catalyst is removed by absorption or cooling before it again passes, mixed with fresh supply of reacting gases. This is the method that was carried through first on a small scale and is now being applied on a large scale. It was necessary to become familiar with the technique of reaction in flowing gases at high pressures. Then catalysts had to be found and studied. The task was somewhat troublesome and I cannot emphasize enough the valuable aid of your countryman Robert Le Rossignol, who was working with me on this question.¹ Earlier experiments had given us the idea that the elements of best catalytic power for producing ammonia from the gases are akin to our first catalysts manganese, iron, chromium and nickel. Thus we tried the metals of the three last groups of the periodic system till we hit upon osmium and uranium. The osmium proved very effective, if used in a very finely divided state, which is easiest obtained by heating osmyl-diamine chloride. The uranium is advantageously used in the form of carbide which in the current of nitrogen and hydrogen changes into nitride which forms a very highly catalytic powder. With these contact substances it was found possible to work in the temperature region of 500° to 600° at high pressures, so that the equilibrium was nearly maintained with a high rate of flow of the gas. The very high pressure limits the space which may be filled with the catalyst, but more than 1 kg. of ammonia is easily produced per hour for each liter of catalyzer space. The reaction itself produces the necessary heat because 13,000 calories are set free in this range of temperature by the formation of 1 gram equivalent of ammonia from the elements. The Badische Anilin and Soda Company have taken over and further developed our results. Starting from the observation that contaminations in certain cases increase the catalytic activity in such heterogeneous reactions, they have been able to raise the activity of poorer catalysts to that of osmium and uranium. The result was obtained only after a careful study of the influence of small impurities, some of which are useful while others, even when present in the smallest traces, act as poisons. They overcame certain difficulties in the construction of high-pressure furnaces which became apparent by prolonged working. They developed the purification methods for the hydrogen which became necessary with the replacement of our electrolytic gas by the impure hydrogen from coal. It seems that the task of managing the process on the largest scale has now been carried through satisfactorily.

Reviewing the whole question of the fixation of nitrogen from an economic standpoint, stress must be laid upon the fact that

¹ See Haber and Le Rossignol, *Zeitschrift für Elektrochemie*, **14**, 181, 513, 688; **19**, 53; *Ber. d. chem. Ges.*, **40**, 2146.

there is no reason why all these processes mentioned should not flourish at the same time. The demand is so large that all the efforts in the different directions will certainly not meet it for some time. Considering the subject from the technical point of view the progress compared with Mond's result is obviously due to the introduction of high temperatures and high pressures: *i. e.*, new physical aids. But looking into the matter from the general standpoint we recognize that the thermodynamic equilibrium questions play the deciding part. Theoretical consideration never replaces experiments, but points out and circumscribes the field in which experiment will probably be fruitful.

There is still a large field to be covered by applied inorganic chemistry, and I trust that the combination of experimental skill in chemical work with physical thinking will lead technical chemists to great results.

CONSERVATION OF NATURAL RESOURCES IN RELATION TO BUSINESS¹

By JOHN J. MILLER
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That the utilization of our natural resources is of vital importance to the people and especially to the chemists of this country no one will question; that the continued prosperity of our chemical industries is dependent upon an early and proper settlement of this problem is admitted by many, but when the method of simultaneously conserving and using our resources without upsetting business is under consideration, agreement upon any proposition seems difficult. The reason for this state of affairs is, we believe, that the logical, scientific or natural plan of conservation and use has not received due attention. As chemists it is our belief that problems of this kind as well as those in natural science are never solved unless the theory of their solution is in harmony with natural law, and, therefore, we propose in this paper to study the subject from that standpoint, first to refer to the law involved and then to build upon it.

In our opinion, the law pertinent to our proposition is: there are naturally two distinct kinds of business, public and private; public business should be owned by the public, whereas private business should be owned by individuals. This is a very simple and almost axiomatic statement and yet it signifies but little unless we explain that by public business is meant enterprises which involve a franchise, a "right of way" or a natural monopoly. All other business is private. Railroads involve rights of way; telephones or telegraphs require franchises; water power control and timber, coal, ore and oil privileges are natural monopolies.

In the conduct of private business let us say as far as this discussion is concerned that competition should reign. It seems natural that this should be so and whatever is natural is best. As against the argument that competition is extremely wasteful, we venture the suggestion that competition has not, in our time, had a fair trial. As we shall show later, much of our industrial wastefulness is due to too much monopoly rather than to a lack of it.

To decide what policy should prevail in the execution of public business (the question in hand) let us proceed negatively, *i. e.*, by casting aside the less desirable propositions.

I. Is private ownership and operation of public business (especially utilization of natural resources) desirable? Experience up to the present time answers emphatically "No." The socialist movement and the existence of the Conservation League are evidences of dissatisfaction with the system now in vogue, which is none other than private ownership and operation. This method means exploitation of the masses by the few and criminal waste of our natural resources.

¹ This article is an application of the fundamental principles set forth by Henry George in his "Progress and Poverty" and "Our Land and Land Policy."

II. The failure of the existing policy relative to public business has led to government control of private ownership and according to Prof. Van Hise, of the University of Wisconsin, this plan (which he broadens by including private coöperation under government control) will eliminate our difficulties [THIS JOURNAL, 5 (1913), 946-7]. To test this proposition let us turn to the work of the Interstate Commerce Commission, which has for some time controlled the railroads and recently the express companies. In some particulars the people have been satisfied, but without fear of being successfully accused of pessimism we will state that there has been considerable trouble. Little differences of opinion as to wages have been amicably settled, but the question of freight rates is becoming serious. Thousands of men were turned out of the railroad repair shops this winter because the roads could not pay dividends and keep up repairs too. Such conditions are intolerable and inexcusable, but we doubt if a rise in freight rates is the remedy. Everyone knows that the railroads are overloaded with watered stock on which dividends are being paid and it would seem only fair that the governing commission should squeeze the water out of such stocks rather than allow repair shops to close and freight rates to rise. This Interstate Commerce Commission has done wonderful work, perhaps all that is possible under the power delegated to it, but in our opinion the dispensation of justice by commissions is bound to be slow, artificial and cumbersome.

Prof. Van Hise's coöperation feature of the "government control plan" has not been published in detail as far as we have been able to learn but his article in THIS JOURNAL, 5, 946-7, indicates that in the case of coal mining and selling he would divide the country into sections and furnish coal for any given section only from the mines in the same district. This would, he says, destroy the wasteful competition in the various sections. With the government controlling coal prices and freight rates, we may fairly conclude that this system will furnish the consumer his coal at moderate cost whereas he is now paying abnormally high prices, but he will have to use the coal from his section whether it is the kind best suited to his needs or not. If he really wants the coal from his section he would be buying it now and there would be no use of imposing the divisions upon the country. If he is not now obtaining the coal produced in his own section it is because it is more economical for him to use another kind and any restrictions of his buying field would involve a greater loss than at present. We venture the idea that the coöperation which travels hand in hand with unfettered competition is the kind to be sought and the type that will exist when privilege in business is destroyed. Coöperation which is not natural is not desirable.

III. Some may conclude at once that public ownership and operation is the best plan, but we beg to dispense with this idea briefly by saying that if there is a better plan of action, government operation should be avoided because of the danger of political control. It has the advantage, however, of being more in accord with natural law than any method yet discussed.

IV. A résumé of the article at this point will show that we would discard (1) private ownership and operation, (2) private ownership under government control and (3) government ownership and operation. One other combination of these two factors remains, namely, government ownership and private operation.

If this can be brought about, we are in exact accord with natural law, to wit: government ownership of all monopolies and private ownership of business where no monopoly is involved. For example, the common ownership of natural resources signifies the impossibility of private monopoly. In mining by private enterprise (and with private tools) of the natural resources (owned by the government) there is no natural monopoly and, therefore, the operating feature may well be