

With proper help and encouragement the American chemist will be able to increase the domestic production of coal tar dyes and to inaugurate the making of intermediates; in the course of time this country may then ultimately look forward to a substantial share of the world's coal-tar dye business.

Hardly any of the valuable or useful intermediates ever were patented. A considerable number of non-German chemists have invented and patented finished dyes made from non-patented intermediates. These inventors had perfect freedom to make the needful intermediates and an *exclusive* right to make, sell and use their new dyes therefrom, yet they bought their intermediates from Germany rather than make them themselves. The patent situation is, therefore, really, that Germany excelled the rest of the world in making patentable combinations from non-patented and non-patentable intermediates and further in making those intermediates in open competition with the rest of the world. So, from one point of view, it appears that the rest of the world, inclusive of the United States, lay back, let the Germans do all the hard work and when the rest of the world finally woke up to the value of what the Germans had accomplished they became very busy making excuses and explaining instead of making a determined, directed, united and effective attempt to recover the ground so lost. That such recovery will require the hardest kind of work on the part of all—users, capitalists, consumers and makers alike—is self-evident and obvious and the question is: Do we want to pay the price? It can be done, if the price be paid.

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GAS MANUFACTURE FROM THE POINT OF VIEW OF PHYSICAL CHEMISTRY¹

By W. F. RITTMAN

In past practice, gas manufacture has been primarily an engineering problem, with the chemist a more or less necessary adjunct for the analysis of coal, coke, oxide, etc. The research chemist, who deals with the processes of manufacture and the phenomena of reactions involved, has been looked upon as a burden unwarranted by returns. In view of the present available raw materials for gas manufacture on the one hand, and the demands of the public on the other, the advisability of continuing the policy of the past becomes a serious question.

There are few industrial operations which, from the standpoint of physical chemistry, are more complex in their nature than the treatment by heat of coal, oil and water in the production of coke, gas, tar, ammonia and cyanogen. In gas manufacture practically all the variables of chemical phenomena are involved. While this fact greatly complicates such industrial problems theoretically and practically, at the same time it greatly enlarges their possibilities; it strongly emphasizes the need of continued scientific research and investigation in connection with them. The heat treatment of coal, oil and water necessitates dealing with the chemical reactions of solids, liquids and gases, and with all the laws, both physical and chemical, which govern these reactions. The finest equipment in the world, designed with utmost mechanical precision, but without regard for the laws which govern the reactions carried out in it, is likely to be less useful than apparatus of the most wretched mechanical construction, but which does consider the chemical changes involved. Obviously, the aim of any industrial operation is perfection, both of process and apparatus.

Problems that are primarily chemical, and which can be attacked most efficiently from a chemical point of view, are common enough in gas manufacture. Who of the gas men present have not, at some time or another, faced the problems resulting from naphthalene, drip oil, fluctuating candle power, deposited carbon, ammonia, sulfur, cyanogen, or any one of a dozen other

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factors? Further, every new development in gas manufacture will create new problems. Every improvement will involve some question or questions peculiar to it. The greater the number of researches, the greater is the progress in a given field, and the greater becomes the number of new problems.

Hitherto, the greatest progress in American gas manufacture has been made along mechanical lines, and, as Americans, we may be proud of this progress. Chemical development, however, has been far behind the mechanical and operative improvements. It may be said that we have been spending too much of our energy investigating the machine rather than what is going on inside of the machine. Were the machine the end product of vital importance, improvements of this character would be unquestionable but the gas factory of the future will earn, or fail to earn, its dividends as it turns out, or fails to turn out, the best relative yields of coke, gas, tar and ammonia. It is true that the machine and the process are vitally related; there may be objections to this point because engineers are constantly working to perfect processes. It seems in gas manufacture, however, that too many of the purely theoretical chemical problems have been left to the mechanical or erecting engineer for solution. A mechanical, electrical or civil engineer, whose primary profession is the building and operation of machines and equipment, whose academic training consisted in the study of chemistry and physics during a part of two years, should not be expected to be as efficient in chemical research as the man who devoted himself exclusively to the study of chemical and physical phenomena; it is the latter, furthermore, whose primary profession to-day is the study of chemical and physical phenomena. To carry out high-grade research and investigation in any line, well-paid specialists must be employed. The able and efficient chemist and chemical engineer can do better things than analyze coal and iron oxide, however efficient he may be at the latter.

The day is past when gas-making is primarily a mechanical operation. Carbureted water gas constitutes approximately two-thirds of the gas made to-day, and it is no longer possible to buy a high-grade paraffin gas oil for 3 cents a gallon. Consequently, the petroleum supply becomes a most vital and important problem to the American gas manufacturer to-day. The importance of the oil problem as related to gas manufacture can be conveyed by the fact that in 1913 Greater New York alone used approximately 3,860,000 barrels of oil in the manufacture of carbureted water gas.¹ During 1913 the same plants used approximately 1,600,000 tons of coal. On the basis of heat units involved, oil has become as important in American gas manufacture as coal. Furthermore, Greater New York constitutes but one center for gas manufacture. I need not elaborate on the importance and seriousness of this oil problem, because you are fully acquainted with it. During the last decade, the increasing price of oil for gas manufacture has created what many gas men regard as a "dangerous" situation; and this is true despite the fact that never before in the history of the United States has so much oil been produced as to-day.

Why is it, then, that gas oil is expensive? Why should hundreds of millions of dollars' worth of oil-carbureting machinery be threatened? What is it that makes the economical use of petroleum one of the chief problems of the gas manufacturer? It is, first, the scientific progress in petroleum refining, and, second, the changing character in composition of the oil from newly discovered fields. Through careful scientific investigation, and through the application of physical-chemical principles, pure and simple, the refiner has perfected processes whereby the oil which you used to buy at 3 cents a gallon is now converted into gasoline and other end products which sell at several times that price. A representative example of this progress can be

¹ *Gas World*, 61 (1914), 76.

had from the testimony of Mr. Frank B. Lewis,¹ Jr., Manager of the Standard Oil Company Refinery at Whiting, Indiana, regarding the Burton process; this was offered at a recent court hearing in Chicago:

"Q. Your Whiting plant is running exclusively on Mid-Continent oil, is it?"

A. Yes, sir.

Q. Now tell us, Mr. Lewis, what percentage of the crude oil is refined into gasoline?

A. With the present method of distillation you can refine it all into gasoline if you wish to.

Q. The entire percentage?

A. You can take it all and convert it all into gasoline, except what coke is left in the still, and a little wax or petroleum tailings.

Q. How long has that method been in use?

A. About one year.

Q. Is that method in use at the Whiting plant to-day?

A. Yes, sir.

Q. To what extent?

A. To convert the fuel oil that we don't have any sale for into lighter product; fuel and gas oil we don't have any sale for and contracts for, into lighter products, making them up into motor fuel, which is practically gasoline."

Furthermore, oil refiners all over the country are working on methods to convert every pound of gas oil into more valuable products. Facing facts, this means that if gas men are to continue the use of petroleum in carbureting water gas, they must resort to one of two alternatives:

1—Greatly increase the yield of gaseous hydrocarbons from a given amount of oil, or

2—Perfect methods of using the millions of barrels of fuel oil which to-day are considered unfit for carbureting water gas.

One often hears the statement that these so-called fuel oils cannot be used in carbureting water gas. What right does any one have to make this statement? Is it the result of scientific study and investigation, or is it the result of experiments carried out under the same old conditions which prevail in the use of Pennsylvania, Ohio or Indiana petroleum?

The purpose in emphasizing the gravity of the petroleum situation in connection with gas manufacture is not to destroy hope nor to disseminate pessimism for the future. On the contrary, I believe that as soon as the gas manufacturer faces facts as they are, and seriously attacks the problem, increased efficiency and economy will result with petroleum still of primary importance as a raw material. Never in the history of the world has so much oil been produced as is being produced to-day. It is estimated that Oklahoma² alone will mine 80,000,000, and California³ will contribute 100,000,000 barrels. Never in the history of the United States has so much oil been in storage as to-day. We are not facing an oil famine. We are facing a famine of knowledge concerning the chemical behavior of inferior petroleum which will facilitate their substitution for higher grade petroleum.

If we accept the statement that the various so-called fuel oils cannot be used to carbure water gas, the necessity for scientific chemical research becomes more acute than ever. It means that carbureted water gas is entering a rapid decline, and is to be replaced by coal gas, by-product coke-oven gas, or some other process gas not developed to-day. The problems involving physical chemistry will not be eliminated. The phenomena of chemical change are involved in any process wherein a solid or liquid is converted into a gas of different constitution.

The machine becomes of vital importance when it favors or hinders optimum conditions for the end products desired. Aside

from operating costs, the relative merits of horizontal *vs.* inclined *vs.* vertical retorts depend entirely upon the influences of the retort's position on physical and chemical changes involved. The relative merits of any mechanical structure used in gas manufacture depend upon its influence on the chemical reactions which produce the ultimate end products. The vertical retort completely filled yields more tar and less gas than the practice of partially filling the vertical retort, simply because the vapors are subjected to different physical conditions which influence the degree of cracking and tend to bring about equilibria concordant therewith. This difference in end products, using the same type of machine, indicates the complexity of the chemical reactions of gas manufacture and the close relations which exist between prevailing conditions and end products obtained. Both coke-oven gas and retort gas are made by the application of heat to coal, yet the two gases vary considerably in their composition. Therefore, should we not look forward to a complete understanding of the composition of the raw materials, coal and petroleum, and the changes and mechanisms of the changes that take place in them under different physical conditions?

When pointing out the seriousness and the dimensions of the gas man's chemical problems, and when referring to the efforts and accomplishments of petroleum refiners, it would be unjust to overlook the excellent research work which has been started within the last three to five years. However, practically all of these investigations deal with coal. They are concerned with determining:

1—The composition of the coal.

2—The initial decomposition products.

3—The final decomposition products under varying temperatures and pressures.

4—The nature of the tars produced under varying temperatures and pressures.

I refer to the valuable work of Parr and Olin,¹ Burgess and Wheeler,² Ame and Pictet,³ Pictet and Bouvier,⁴ Rau and Lambris,⁵ Vignon,⁶ the Bureau of Mines, the United Gas Improvement Company, The Barrett Manufacturing Company, and numerous other investigators.

Much of this work may appear too academic, and questionable from a practical point of view. On the other hand, our industry progresses as the result of just such investigations. Regardless of whether a low-temperature process, for example, is valuable for direct application, the information obtained as to the constitution and chemical behavior of the coal is of utmost importance. The same information with respect to petroleum is equally essential. As a matter of fact, prior to the works above referred to, the extent of change that takes place in the destructive distillation of coal was a question. In other words, do the end products occur in coal as such, or are they formed in the operation? Does benzene occur in coal as benzene, or is it formed in the distillation? To-day these questions appear unnecessary and out of place. We now believe that benzene does not occur perceptibly in the original coal, nor does it occur in appreciable quantities in Eastern gas oils. The fact that it does occur considerably in both water-gas and coal-gas tars of to-day, indicates conclusively that benzene is made in the course of the gas-making process. There has been a transformation, a chemical change. That this change is not a simple one can be observed from the investigations referred to. Further, it is found that when coal is distilled under a vacuum, very little benzene is formed. When the mechanism of benzene formation is fully understood, it will be a relatively simple

¹ Bull., Univ. of Illinois Engr. Expt. Sta., 1912; Compt. rend., 137 (1913), 779.

² Trans. Chem. Soc., 1910, p. 1917; 1911, p. 649; 1914, p. 131.

³ Compt. rend., 157 (1913), 779.

⁴ Jour. f. gasb., 56 (1913), 533, 557, 589.

⁵ Compt. rend., 1912, p. 1514.

¹ The Petroleum Gazette, July, 1914, p. 5.

² Oildom, Aug., 1914.

³ Petroleum Review, 30, 599, 687, 717; 31, 3.

matter to increase or decrease the yield. Benzene is referred to purely as an illustration. The same reasoning applies to all tar, ammonia and cyanogen formation in connection with gas manufacture. If naphthalene is an undesirable product in gas manufacture, its appearance is not conclusive proof that its production cannot be avoided.

The variation in the tar obtained from different processes of coal, oil and coke-oven gases, is entirely due to variations in the prevailing physical conditions. It is a fact that these tars do differ, yet the initial materials used in the process of manufacture may be the same. With the reason for these differences fully understood, the optimum conditions for manufacture of both tar and gas will be understood and better realized. The tars which result from the destructive distillation of coal or oil, under different physical conditions, vary as widely as do the physical conditions under which they are made. In the course of a research carried out by Prof. M. C. Whitaker and the writer,¹ on the destructive distillation of petroleum, it was found that the tar made under greatly diminished pressure was radically different from that obtained by cracking the same oil under atmospheric or increased pressure. The vacuum tar was of much lighter specific gravity; it contained practically no free carbon; no naphthalene or anthracene settled out of the heavier distillates of the tar; the tar combined readily with 1.82 sp. gr. sulfuric acid. Tars resulting from cracking the same oil under increased pressure contained much free carbon; they were of considerably higher specific gravity; naphthalene and anthracene settled out of the distillates; they contained benzene; they would not combine readily with 1.82 sp. gr. sulfuric acid. The gas made under the two conditions was of equally different composition. The vacuum gas was a "dry" gas, in that it contained practically no benzene; on the other hand, it was high in ethylene homologues. The volume of uncombined hydrogen obtained under vacuum conditions was very much less than when the machine was under increased pressure. Further, there was practically no deposit of free carbon when working under a vacuum, whereas when the pressure on the machine was increased to three atmospheres, over fifty per cent, by weight, of the original oil was deposited as carbon.

No.	Reactions	Heats of reaction	Volume changes	Partial pressures	Approximate K_{800}	K_{600}
1.....	$C + 2H_2 = CH_4$	+18900	2 to 1	$K = \frac{CH_4}{(H_2)^2}$	0.077	0.003
2.....	$2C + H_2 = C_2H_2$	-58100	1 to 1	$K = \frac{C_2H_2}{H_2}$	1.1×10^{-13}	5.7×10^{-10}
3.....	$3C_2H_2 = C_6H_6$	+163000	3 to 1	$K = \frac{C_6H_6}{(C_2H_2)^3}$	9×10^{23}	1.2×10^{18}
4.....	$C + H_2O = CO + H_2$	-29300	1 to 2	$K = \frac{CO \times H_2}{H_2O}$	0.2	25
5.....	$CH_4 + H_2O = CO + 3H_2$	-48200	2 to 4	$K = \frac{CO \times (H_2)^3}{CH_4 \times H_2O}$	0.06	3.46
6.....	$CO_2 + C = 2CO$	-39650	1 to 2	$K = \frac{(CO)^2}{CO_2}$	0.1	59

Let us see how far the variables common to any gaseous chemical reactions have been investigated with respect to illuminating and heating gas. They are five in number:

- I—Temperature
- II—Pressure
- III—Concentration (mass action)
- IV—Duration (time)
- V—Contact surface

On the basis of combinations and permutations, it becomes evident that a great variety of manufacturing conditions can be obtained. Opinions naturally differ as to when a field has been properly and sufficiently investigated, and I, therefore, do not pretend to determine what proportion of the work remains to be done. It remains for each individual to form his own opinion. The field of temperature has been widely investigated, but

principally with the machine under atmospheric pressure. Experiment shows that the moment we change the pressure, new results are obtained and a new series of experiments suggested. Certain it is that much remains to be done in the field of concentration, pressure and contact-surface changes. The application of various conditions for different periods of time still offers field for investigation.

I repeat that even if such investigations do not result in radically new processes, they will yield valuable information for a better understanding of, and improvement in, present-day processes. From a practical viewpoint, we may not as yet be able to see the advantages to be gained from the application of such scientific investigations, and, on the contrary, we may see disadvantages. However, this should not prevent our exploring the field. Industrial experience has again and again proven that the theory of to-day is the practice of to-morrow. In the absence of theoretical considerations, applied chemistry to-day would be in the medieval stages. As a typical example, the investigations of Haber¹ concerning the manufacture of ammonia from hydrogen and nitrogen were on a purely theoretical basis. From an initial yield less than 0.25 per cent, the process has been perfected to give a yield of well over 10 per cent of ammonia. From the idea of a man whose principal tools were theoretical chemistry, mathematics and physics, laboratory experiments developed into a process of commercial importance. The same laws maintain in the ammonia production of the gas plant that maintain in Haber's experimental and industrial apparatus.

The combination of nitrogen and carbon in the formation of cyanogen compounds is influenced by varying physical and chemical conditions just as surely as is the production of ammonia, whether from coal distillation or directly from the elements.

The application of physical chemistry, in mathematical terms, to industrial problems furnishes a means for quantitatively expressing yields and reactions taking place. I refer to the equilibrium relationship. Under some conditions it is highly important that the system reach a state of chemical equilibrium; under another condition, it would be fatal for the system to reach such equilibrium. Let us consider a few typical examples:

It becomes evident that for some reactions an elevation in temperature favors the preservation and formation of hydrocarbons, whereas for other reactions the same temperature is destructive. Considering equations 4 and 5, two of the most vital in present carbureted water-gas manufacture, one finds that a temperature of 900° C. is favorable to the CO and H₂ formation of both 4 and 5, but it is unfavorable to the methane preservation of 5. On the other hand, a temperature of 600° C. is unfavorable to the formation and preservation of CO and H₂, but is decidedly more favorable than 900 to the hydrocarbon preservation of 5. At this lower temperature, however, the CO₂ of 6 predominates. From reaction 1 it becomes evident that methane is destroyed by high temperatures.

Numerical equilibrium expressions permit of quantitatively indicating the influence of three of the most important varia-

¹ THIS JOURNAL, 1914, pp. 383, 472.

¹ Z. Elektrochem., 1913, p. 53.

bles of a gaseous reaction, *i. e.*, temperature, pressure and concentration. The value of the equilibrium constant increases or decreases with the temperature. Although pressure and concentration variations do not change the value of the equilibrium constant for a given temperature, the use of such equilibrium enables one to calculate the influence of changes in pressure or concentration for any given temperature. In reactions 1 and 3, referred to above, there is a decrease in the number of volumes due to the reaction; in reactions 4, 5 and 6 there is an increase in the number of volumes due to the reaction; in reaction 2 there is no change in the reacting volumes. According to the principle of Le Chatelier, pressure stimulates those reactions involving contraction, and vacuum stimulates those involving expansion. Pressure and vacuum are without influence on those reactions involving neither contraction nor expansion. For detailed consideration of the application of numerical equilibrium relationships, see articles by Whitaker and Rittman¹ and Rittman.² By a correlation of equilibrium conditions for the various reactions involved in gas manufacture, much help can be had in determining the course of experiments. Unfortunately, equilibrium relationships, as shown, do not indicate the speed of the reaction involved; they indicate the state of affairs after complete reaction has taken place and the system is balanced. Therefore, the information indicated by an equilibrium relationship is not complete in itself. No single reaction can be considered exclusively by itself. All the reactions in a process are vitally inter-related, though any single reaction, or set of reactions, may be extremely important as indicating a tendency.

The shape of the machine cannot change the equilibrium constant for any given reaction. It is easily possible to reach the same equilibrium in entirely different types of machines. The machine is vitally important in so far as its design provides conditions for a favorable or unfavorable equilibrium; or in so far as its design hastens or retards the system in reaching equilibrium. It would be an easy matter to expand indefinitely on the importance and practical application of equilibrium relationships with respect to gas manufacture, but it seems advisable to await further experimental evidence.

In conclusion, I would say that the application of physical chemistry to gas manufacture is stimulating, because gas manufacture is a chemical and chemical-engineering problem. It involves solids, liquids and gases with all the chemical and physical laws governing these three states of matter. The questions of energy and heat transformations determine profit or loss. Nowhere is the question of chemical equilibrium more important. Vapor pressure, surface tension, solubility, dissociation, diffusion, polymerization, catalysis, decomposition, specific heat, latent heats of reaction, speed of reaction constitute fundamentals in physical chemistry, and are all vital to the gas man. The five variables—temperature, pressure, concentration, duration, and contact surface—offer a flexibility which should permit equal flexibility in the character of the end products obtained. Complicated problems become elementary in the light of physical chemistry. The pendulum swings to the extreme where gas manufacture becomes primarily a problem involving theoretical and applied chemistry. Without its application the industry cannot develop. However, in view of the work which has recently been done and which is being done, we can feel that gas manufacture as a chemical problem is gradually coming into its own.

CHEMICAL SECTION OF PETROLEUM DIVISION
BUREAU OF MINES
PITTSBURGH, PA.

¹ THIS JOURNAL, 6 (1914), 383, 472.

² Jour. Soc. Chem. Ind., 1914, p. 626; THIS JOURNAL, 6 (1914), 684; and Metall. Chem. Eng., 1914, p. 475.

THE BROADER APPLICATIONS OF CHEMISTRY BY THE MUNICIPALITY

By HERMANN W. MAHR

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Chemistry has for the last decades been a valuable aid in securing the health and well-being of the dweller in American cities. Its fields of activity have been the inspection of foods, the all-important duty of controlling the quality of the water supply and the disposal of sewage. Beyond this, the science has only in rare instances been called upon for regular aid by the municipality.

In the meantime chemistry has been becoming an important factor in the industrial field. Chemists have improved processes and brought forth new products, many of which are finding wide use in civic housekeeping. The position now occupied by applied chemistry has led the far-seeing to herald the near future as the age of chemistry. With the advance in the industrial field have come additions to the knowledge and improvements in the methods of the science which now enable it to successfully attack special problems confronting our cities.

The chemists at present engaged in the all-important work of aiding in the conserving of the public health are often too well occupied with their duties to give time or attention to the technical problems which arise. Municipal engineers attempt to solve these questions, but are handicapped by a lack of knowledge of industrial chemistry and the ability to think chemically. These conditions give rise to opportunities for the chemist to aid the engineer and become his active co-worker. Members of the profession entering this work must necessarily be well acquainted with the processes of applied chemistry, and the methods of analysis and testing of industrial products, particularly the materials of engineering.

Our federal government has been a pioneer in this respect and its researches have redounded to its material advantage. It now has in its service well informed experts in many branches of industrial chemistry. The results of their investigations have been published and many of them are invaluable to the municipality. The latter should have in its service chemists able to apply the results of these governmental and of other technical investigations to the problems of the city.

A large portion of the expenditure of the municipal corporation is for the purchase of supplies. The value of the chemical laboratory in connection with this work has long been recognized. Some of our railroads were the first organizations to avail themselves of scientific supervision and inspection in this connection. The federal government has followed their lead and carried on the work through the Contracts Laboratory and similar testing stations in the large departments.

The first duty of the chemist concerned with the purchase of supplies is the inspection of materials delivered. Study of the various commodities and the framing of requirements is second only to the work of testing. Many proprietary compounds, of supposedly secret composition, with alleged wonderful properties, are urged on purchasing officials. On being subjected to chemical analysis these materials often prove to be composed of cheap ingredients for which a price greatly in excess of their value is asked.

The fuel bill of the municipality is probably the largest item of its budget for supplies. Competitive bidding, in accordance with well drawn specifications, has been universally adopted among large coal buyers as the best solution of the problem. In spite of its manifest advantages, city officials have hitherto been backward in putting a purchasing method of this nature into operation. The chemist can aid here greatly by studying the composition and heat value of the available coal supplies, drawing up requirements and testing shipments.

His labor in relation to fuel should, however, extend to over-seeing its proper and economical use. The importance of the