INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

EDITORIALS

FIRST STEPS. The Council in its meeting at Kansas City took the first steps in what is unquestionably a very important development within the AMERICAN CHEMICAL SOCIETY. We refer to the adoption of committee reports, one on high school teaching of chemistry, another on accrediting educational institutions offering instruction in chemistry, and the third on enhancing the professional status of the chemist. In reality all these committees are contributing to the improvement of our profession.

In reading the reports which appear in our NEWS EDITION of April 20, some may feel that, after all, very little has thus far been done. It is fortunate if such is the case, for in matters of this importance we must make haste slowly, remembering in our own affairs our preachment to industry—namely, to make errors on a small scale, enabling success to be on a large one. When the Council convenes again in Pittsburgh further reports will undoubtedly show greater progress.

The AMERICAN CHEMICAL SOCIETY is by no means the first important organization to have a real interest in the present educational situation in high and preparatory schools. The report cites a number of others who have studied the problem and reached well-considered conclusions. There has been built up in our generation, with the aid of legislative machinery, a pedagogical trust that until lately has been in a well-nigh impregnable position. Its influence is felt, not alone in this special field in which we are interested, but in many other phases of the profession of teaching. Professors of education have even begun to agree that a student who intends to teach a specialty, say chemistry, should be required to take his advanced degrees, not in the school of science, but in that of education. Some educators hold that, so long as a teacher has a good personality and is skilled in pedagogy, it is quite unnecessary to have any real knowledge of the subject matter. Then, too, the point has been made that a student will learn more from an inspiring teacher who knows method rather than subject than from a poor teacher who may be brilliant in the subject. This point, however, does not need to be argued, for we do not admit such a choice to be necessary. It should be possible to have those who know both method and subject to teach youth, whether their schooling must cease with high schools days or they go on to pursue science as their life work.

The statistics given in the report are enough to cause anyone concerned about the scientist of tomorrow real apprehension. The science of chemistry in this day is one which can scarcely be added for good measure to the duties of one whose primary work is coaching the football team, teaching music, or imitating a "not-otherwise-provided" clause.

But the report must be used as a basis for action and not merely read with approval. As was pointed out in discussion, there are three groups particularly concerned in righting conditions. The first is the state legislatures, with whom doubtless little progress could be made. The second is state departments of education, many of which are keenly alive to shortcomings of the present system. The third is the local board of education which, while it may not subtract from the minimum requirements in its state, may in its own wisdom add to them. There is no necessity for decreasing the pedagogical requirements. We should merely insist upon certain minimum qualifications in chemistry for a teacher who intends to give such instruction. It is difficult to see any justification for the unrestricted certificate now granted by some states.

Let us be sure our teachers first possess adequate knowledge of the subject they intend to teach, and hope there may still be room in their heads for a sufficient number of the latest educational theories.

The next step has to do with accrediting educational institutions offering instruction in chemistry. The committee has begun by recommending changes in By-Law 24, which will give a preference to the graduate of an accredited institution who seeks membership in the AMERICAN CHEMICAL SOCIETY, and then provides for a permanent committee, which is expected to present its first list to the Council in Pittsburgh. No one denies that the preparation of such a list with justice to all concerned is a difficult task. There is certain to be criticism and some feeling of resentment and disappointment. It must be borne in mind, however, that the primary purpose of accrediting schools is to guide those young men and women who wish to become chemists. Whatever disappointment the institution may feel if omitted is as nothing compared with the tragedy too often enacted when, after some years devoted, often at great sacrifice, to gaining an education in a particular school, the student learns with bitterness that he chose the wrong institution. Then, too, the absence of a school from a list need not be permanent. It is one of the best arguments an institutional official could possibly have in going before his board of trustees to secure what may be required in faculty, in laboratory equipment, or in library to make it possible to meet minimum requirements. This committee has a large task before it. It will undoubtedly proceed with caution. It may wish to learn much of the accomplishments of graduates before including some institutions, but in the end it will have accomplished a task which will have an immeasurably beneficial influence upon the trend of chemistry in America.

With these two important subjects receiving the attention they deserve, it is obvious that progress will have been made toward improving the professional status of the chemist. Here, again, the committee begins with specifying those who, for purposes within the AMERICAN CHEMICAL SOCIETY, shall be regarded as chemists. That seems a simple step, but it was one requiring much thought and discussion and forms the basis for the new committee which is to carry this work a step further. Unquestionably some concessions may need to be made, changes of policy undertaken, and points of view altered before the goal which has been set will be achieved. Chemistry *is* a profession and chemists should bear the major share of the burdens in determining who are qualified as professional chemists. Then they must see to it that the public knows of the minimum requirements and is guided accordingly in its professional relationships with the chemist.

All are but first steps. The others will follow, we trust in rapid sequence.

EXPERIENCE FOR SALE. Trouble begins at forty or a little beyond, particularly for men of that age who, for one reason or another, find themselves unemployed. It is relatively easy for men of reputation to change employers at almost any age, but for most this is a real difficulty, particularly in these times when the vogue is for youth. We all appreciate youth with its modern training, its fresh point of view, its ambition, and its energy, and we wish it well, but there is one thing that it cannot possess. That is experience. Employing a man of forty or more years, whose training and record indicate him as capable, affords his employer an advantage somewhat comparable to moving into a new planting a full-grown tree, rather than setting out a sapling. In both cases you are buying time in the only way in which it can be bought.

This analogy can be carried a step further, for we realize that some capable men above the age limit we have given are difficult to transplant. They have developed certain personalities and idiosyncrasies which may make it difficult to fit them into some organizations, but nevertheless after having been through the mill they can help avoid pitfalls, they can make available the negative answers which have been found for many questions, their memories will recall obscure and half-forgotten records and important unpublished information, while a man of the right temperament will provide something of a balance wheel for an otherwise youthful organization. Frequently the older man has become the very specialist the manufacturer seeks to develop.

It is not necessarily true that men of forty who are unemployed are less skilled than their more fortunate colleagues. Many have been simply unfortunate in that their companies liquidated, merged, or became frightened over current social legislation. In some instances it was merely a matter of retrenchment, for a man of forty should receive a better salary, and since in the eyes of the uninformed a chemist is a chemist, why not hire a youthful Ph.D. and save money? It is true that insurance cost and pension matters sometimes bulk large in the picture, but these can be offset by what is gained in the man who has been through the mill.

It all comes down to the policy of many organizations, where a definite and unbending age limit for new employees has been set. It is for the modification of such policies that we plead. By all means employ the young men, but flavor the group with a little of the experience, the wisdom, and the sage advice that can only come from well-spent years.

THE NEGATIVE. We have no statistics to cite, but any large percentage will represent with reasonable accuracy the proportion of papers published in which questions, answered in the positive, are described in detail. But what about the reactions that would not work? What about the questions for which only negative answers have been obtained? Would it not be a service to report these in sufficient detail, either to avoid losses incident to their repetition or to afford sufficient guidance to prevent the same answer being obtained, should another undertake the problem?

We should like to consider for publication some of these questions to which only negative answers have been obtained. They should be stated concisely and with just enough information to guide the reader in future. Have you something to offer that would fit in with such a service to chemistry?

ECONOMIC AND TECHNICAL ASPECTS OF THE RAYON INDUSTRY

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WEAVING was one of the earliest of the crafts practiced by mankind. This art possibly goes back to the time when men were nomads, for we know that flax threads were woven into fabrics during the stone era, eight to ten thousand years ago, when lake dwellings were erected.

Subsequent to the fabrication of linen by the lake dwellers, flax was cultivated in Mesopotamia, Assyria, and Egypt about 5000 to 4000 B. C. It was first used in making lines and nets for fishing and hunting, and also as cords for carrying earthenware vessels. The Egyptians used linen extensively in wrapping embalmed bodies. In Genesis, we read that Pharoah arrayed Joseph "in vestures of fine linen," and in Exodus, that the plague of hail destroyed flax because "the flax was bolled." Among eastern nations the flax fiber was the most important of all vegetable fibers until the close of the eighteenth century when cotton took its place as the supreme vegetable fiber of commerce.

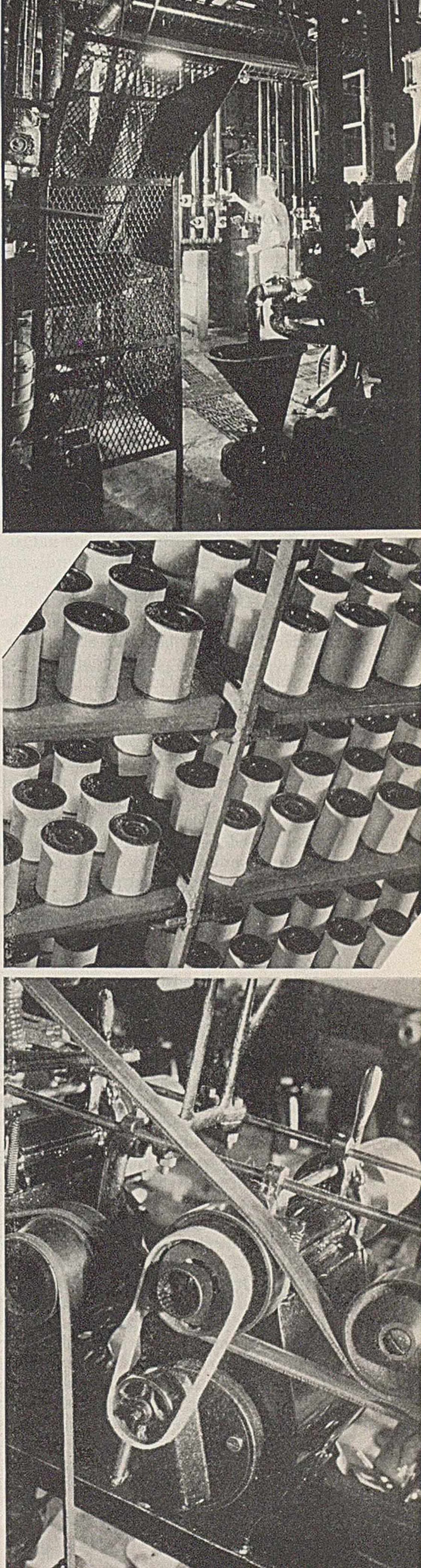
The silk industry originated in China at an unknown date. However, it is known that an Empress of China, about 2600 B. C., encouraged the cultivation of the mulberry tree, the rearing of the worms, and the reeling of the silk.

The history of wool takes us back to the earliest times. Early references to wool and sheep are found in Babylonian records made approximately 4000 B. C., and a certain carving of this era shows figures clad in a ribbed, woolen material. One Babylonian tomb shows a picture of a fulling mill.

The origin of cotton as a textile fiber is probably also prehistoric. The first known account occurs in the Hindu Veda hymn written about 1500 B. C. This hymn mentions cotton in the loom. It is probable that cotton was first employed as a textile in the valley of the Indus.

Early Work on Artificial Fibers

Not until 1664, when a young English physician named Robert Hooke had made for himself a microscope, is there any hint of an artificial textile fiber. Among numerous things which he examined were some samples of



(*Top*) Viscose Mixing and Blending Room
(*Center*) Viscose Yarn on Spools Awaiting Inspection
(*Bottom*) Rear View of Coning Machine

imitation silk. We do not know who made the fabric or its composition, but Hooke's comments constitute at once a report on an imitation of silk which existed at that time and a forecast that a great industry might be based on such a process. Robert Hooke's report has commonly been cited as the oldest written record of a synthetic textile. He suggested the possibility of spinning such a fiber with what we now call a "spinneret," predicted that it could be made superior to silk, and foretold a profitable development. These forecasts have been fairly well realized, although the better part of three centuries was required for their full achievement. Hooke's suggestions were repeatedly offered by others, although it was nearly one hundred years later that Réaumur next made similar suggestions that were a little more to the point.

It would be exceedingly interesting, if time permitted, to trace the work of dozens of scientific experimenters from about 1850 to 1912, during which period artificial silk was brought from the vague and nebulous form of an idea to the stage of small commercial production. We cannot fail, however, to mention the one name which is most commonly associated with the development of the rayon industry—Count Hilaire de Chardonnet. As a student Chardonnet had worked with Pasteur in *l'Ecole Polytechnique*. He knew of Pasteur's work on a silkworm disease which at one time threatened to wipe out the silk industry in France. Chardonnet no doubt considered the possibility of eliminating such hazards by producing artificially a material that would resemble silk and that would replace it in the textile industry. Like many other investigators of contemporary and earlier times, Chardonnet experimented with the sirupy solutions of nitrocellulose, which had been discovered forty years before by Schoenbein. Chardonnet drew heavily on the labors of many other European experimenters, but his chief contribution came from his own patience, persistence, and indefatigable energy. In 1884 he filed with the Academy of Sciences in Paris, a sealed memorandum containing an exact description of his first process for spinning a nitrocellulose solution. Within a year he obtained patents and started at his birthplace in Besançon, northern France, the first factory production of a synthetic textile. Commercially, this venture was a failure, but Besançon is today one of the important European centers for rayon manufacture. Chardonnet died in 1925, having lived to see the industry which he founded produce in one year about 140,000,000 pounds of artificial fiber.

The artificial silk produced by Chardonnet and other contemporary experimenters was neither sufficiently good in quality nor low enough in price to find extensive application in textiles. It happened, however, that the incandescent lamp industry needed cellulose threads from which to produce carbon filaments. This small outlet meant much to the new industry, as the lamp manufacturers did not require filaments of textile grade and they could afford to pay a price in excess of the cost of silk. At the Paris Exposition in 1889 Chardonnet showed lustrous threads made from cellulose nitrate and subsequently denitrated; they were, therefore, not excessively flammable. The principles of the nitrocellulose process, as exemplified by Chardonnet, have continued to the present, although there is now only one factory in the world making this type of yarn (in Hungary). Factories in Belgium, France, and America have closed down, unable to meet the competition of more economical processes.

Chardonnet's exhibit at the Paris Exposition caused a sensation in the world of science and industry, and stimulated interest, not only in the nitrocellulose process but also in other synthetic textile processes.

The flammability of cellulose nitrate and the high price of the severely taxed alcohol-ether mixture used as a solvent were responsible for early efforts to replace the nitrocellulose solution by dissolving cellulose in the cuprammonium solution which Schweitzer had discovered in 1857 and which still bears his name. In 1899 this cuprammonium process was successfully commercialized by Fremery and Urban at Oberbruch, Germany. The stretch-spinning process applied to the cuprammonium yarn was the first to produce artificial filaments finer than those of natural silk. The cuprammonium process is operated in Germany, Italy, Japan, Russia, Great Britain, and the United States, but it has not been able to approach in output the huge quantities made by the viscose and acetate methods.

Viscose and Acetate Rayons

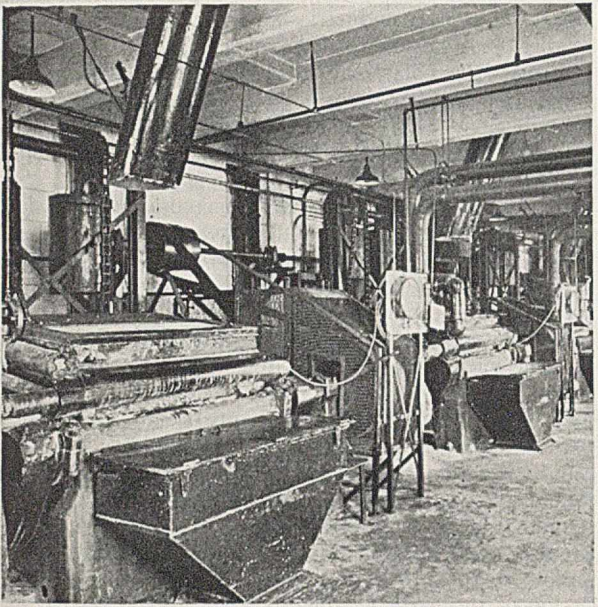
In 1891 the English investigators Cross and Bevan, who contributed so much to the chemical knowledge on which all of the cellulose industries are based, discovered that cellulose which has been treated with caustic soda reacts with carbon disulfide to form a water-soluble alkali salt, sodium cellulose xanthate. Its viscous solution was named "viscose" by the inventors. From this solution, acids and salts precipitate regenerated cellulose, the final composition of viscose yarns. It was not until 1900 that the mechanical developments of the Englishmen, Stearns and Topham, and the accidental discovery of the effect of time on the properties of the viscose solution permitted the rapid development which was soon to enable the viscose process to outstrip its competitors. One hundred and sixty-one viscose rayon factories are now operating in twenty-one countries. The United States alone has twenty such establishments operated by fourteen companies, producing about one-quarter of the world output.

C. F. Cross, one of the inventors of viscose, was the first to patent (in 1894) a process for making synthetic yarn from cellulose acetate. The Americans Mork, Little, and Walker contributed importantly to the early development of the acetate rayon business, and their Lustron Chemical Company of Boston was the first to make the yarn commercially. It remained for the Swiss inventors and promoters, Henri and Camille Dreyfus, to create a large and successful industry with cellulose acetate. Of the twenty-six acetate plants in the world, five are in the United States.

Unique Position of Rayon

It has been shown that early experimentation with artificial textiles was promoted by a desire to make a silk substitute. This was no doubt closely connected with the great prestige held by silk for thousands of years. For many centuries silk was the raiment of royalty and nobility because of its rarity, cost, fineness, and brilliance. Silk symbolized wealth, power. In the early years of commercial production, rayon was prized chiefly because of its superficial resemblance to silk. This no doubt came from the continuity of the filaments and their sheen. As time has passed, the public has recognized the inherent merits of rayon, realizing that it is a distinct and new fiber with its own special characteristics, rather than an imitation of natural silk. For these reasons, in 1924 it was given its own name, "rayon." The field of rayon is not the field of silk or cotton or wool; it has a field of its own. Fabrics can be made from it which cannot be made from other fibers, and its value lies principally in the fact that it is different from all of the natural fibers. This is not alone the claim of rayon manufacturers, but it is the verdict of the world's renowned stylists and fabric houses. The search for artificial silk has brought us to rayon and the original quest is not likely to be renewed.

This is not an unusual sequence in the history of research. Research chemists have frequently taken some natural substance as the goal of their synthesis. Many times they



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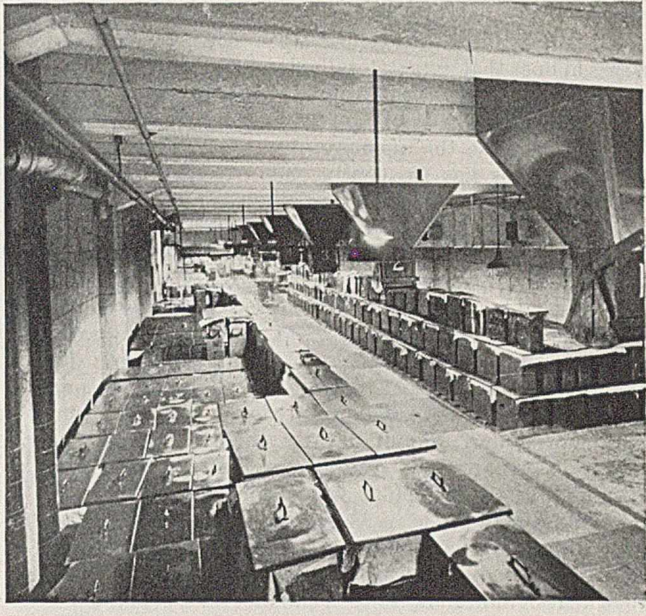

ALKALI CELLULOSE RIPENING

have succeeded in exactly reproducing a natural product. In other cases they have failed in the attempt but have achieved a product surpassing the natural one in many attributes. Research chemists have not duplicated silk—they have given us a unique fiber produced in greater quantity than silk itself, and the first new one in at least four thousand years. Rayon's excellent qualities come not alone from the fact that it is different from all the natural fibers. Because it is chemically produced, control becomes possible. Uniformity is the respect in which rayon excels most. Control can be predicted for any man-made material, given time enough for development. Nature's products, on the contrary, are not only less uniform than man's, but they cannot readily be modified in the making. The silkworm, not being "sales-minded," cannot be persuaded to spin a dull filament. But the luster of rayon is controlled in the manufacturing processes in a range from metallic to chalky. The filaments may be finer than silk or coarser than horsehair, and the predetermined size can be maintained with any reasonable precision. This is a remarkable attainment in view of the fact that in 1 pound of rayon the filament length averages about 1000 miles. These filaments are remarkably alike in dye absorption, cross section, size, and other physical properties.

Steps in Rayon Manufacture

As has been indicated in the brief historical sketch of rayon, cellulose is always the primary raw material. Many chemists believe that it will continue to be the chief basis because of its wide distribution, low cost, and such desirable properties as high molecular weight, chemical stability, and mechanical strength. Many other materials have been tried—for example, the fibroin of waste silk, gelatin, agar-agar, Irish moss, chitin, and others. Casein is even now being advocated in Italy as the source of a yarn intended to be used as a wool substitute. We have all heard of recent developments in the spinning of glass and the weaving of it into fabrics in America.

The essential technical steps in the manufacture of rayon by any one of the four processes are few and simple. First, we must bring cellulose into solution. We may nitrate or acetylate cellulose and then dissolve the ester in organic solvents; we may react it with sodium hydroxide and carbon disulfide to form the xanthate and dissolve in dilute sodium hydroxide; or we may employ Schweitzer's reagent to produce the solution. In each case the objective is the same—namely, to obtain a solution which in the second step may be formed into fine and continuous filaments. The solution obtained is forced through minute apertures in a spinneret; the fine streams of solution emerging are solidified in the third operation to form the filament. With the nitrate and acetate, the solid is obtained by evaporating the volatile solvent; this is called "dry spinning." In the viscose and cuprammonium processes, the spinneret is immersed in a liquid which causes coagulation and regeneration of the cellulose. This method is called "wet spinning." The bundle of continuous filaments from a spinneret is called the "yarn;" it is given a twist to keep the bundle intact.

Nitrocellulose, cuprammonium, and viscose rayons consist of regenerated cellulose. In the acetate process we have cellulose acetate itself as the material constituting the yarn, and this fact readily explains the differences between cellulose acetate and the other types of rayon. The most important of these differences resides in the fact that, whereas the regenerated celluloses all take direct, substantive, or cotton dyes, the acetate is unaffected by them and is dyed only by a special class of colors which were developed for the sole purpose of dyeing acetate yarns. It should not be inferred, however, because nitrocellulose, cuprammonium, and viscose yarns are all regenerated cellulose, that their properties are identical. To the textile man, small differences may become exceedingly important, and these different yarns are clearly recognized as having distinct properties.

The remaining mechanical operations are similar and need not be elaborated. The methods of twisting the filaments together to form the yarn and the packaging in skeins, warps, cones, cops, pirns, and spools, though important as relating to the mechanical quality of the product and the convenience of the millman, need be referred to only as important and necessary adjuncts to the chemical operations of fiber manufacture.

Relation to Other Industries

Man does not live unto himself, and an industry cannot exist without having some effect upon developments and activities in lines that appear totally unrelated. Thus, during the two decades of rapid commercial development of rayon, many problems have had to be solved in order to improve the quality and increase the quantity of output. The solution of these problems has frequently had a bearing on other industries. Let us first consider the cellulose used in making rayon. The wood cellulose originally used in manufacturing viscose rayon was sulfite pulp which had been developed for making bond papers. Ten years ago, a standard pulp for rayon manufacture cost $95.00 per ton and contained about 87 per cent alpha-cellulose. A pulp from the same manufacturer, standard for making rayon, now sells for $70.00 a ton, contains 3 per cent more alpha-cellulose, and the mineral impurities have been reduced to one-quarter their former amount. Simultaneously, the color of the pulp has been greatly improved, and this results directly in whiter yarn. At the same time, pulps approaching cotton linters in alpha-cellulose content have been produced. These statements fail, however, to reflect the most important thing which the pulp companies have accomplished—namely, the improvement in uniformity of their product from bale to bale, lot to lot, and month after month. Precise control is required on all rayon manufacturing processes, and variability of many raw materials had to be overcome before the process could be operated to produce a uniform and high quality of rayon yarn. The pulp companies are to be commended for the vigorous and coöperative way in which they have thus assisted in the development of rayon. The present tendency of the rayon industry towards higher tenacity and finer filament yarns continues to place increasing requirements on the quality of pulp. It is to be expected that the producers of chemical cellulose will be even more strongly pressed in the future for further improvements in the quality of their product.

The improvement of pulp resulting from the demands of the viscose rayon producers has also made it possible for the pulp producers to offer materials for nitration and acetylation. Wood pulp nitrates and acetates are used in the manufacture of a variety of plastics and finishes. Even the paper industry, whose raw material was first used in viscose manufacture, has now employed the new pulps for specialty paper products. They have also partly replaced rags in rag paper and vulcanized fiber for which their purity, uniformity, low cost, and good color are much appreciated. Chemical pulps are also used in filling urea-formaldehyde and phenol-formaldehyde plastics, and in the dialyzers widely used for caustic soda recovery.

All rayon processes have employed purified cotton linters for the cellulosic raw material; some have used it exclusively. Through the installation of their own viscose laboratories, the companies purifying cotton linters have been able to supply a product which gives a better filtering viscose and a whiter finished rayon. Their own experience with the control of the viscosity of viscose solutions made with linters has revealed to them the importance of many factors which had been previously overlooked in linter purification.

It has been shown that the rayon industry was of European origin. The study of cellulose, stimulated by its commercial applications, also has been largely European. Our fundamental concepts of cellulose were laid by Cross, Bevan, Hess, Irvine, Haworth, Denham, Karrer, Staudinger, Heuser, Schwalbe, Meyer, and Mark. But now that America leads the nations of the world in the production of rayon, it, too, is beginning to turn to the exploration of cellulose chemistry. The researches of Hawley, Kraemer, Farr, Sponsler, and Dore are yielding important results. The universities are showing increased interest in the constitution and behavior of cellulose. Certain chemical industries are carrying on fundamental studies in their own laboratories. The Boyce-Thompson Institute, the Forest Products Laboratory, the Paper Institute, and the Textile Foundation have made important contributions. This new American interest in cellulose should lead to a broader knowledge and more applications of cellulose.

Only soap manufacturers consume more sodium hydroxide than the viscose rayon manufacturers. It is estimated that 80,000 tons of sodium hydroxide were required for viscose rayon in 1935. As with pulp, the demand was first toward the elimination of impurities. In the last ten years the quantities of carbonate, sulfate, and chloride have been reduced to about half the former amount, and iron has been brought down to about 8 parts per million. The C. P. grade of reagent sodium hydroxide of ten years ago was probably no better than that produced in huge quantities for industry today. The more recent insistence of rayon manufacturers seems to be in the direction of a constant amount of all impurities rather than further reduction. The price of this high grade of sodium hydroxide has been reduced by at least 40 per cent in the same ten-year period.

One of the early complaints about rayon related to the variable shade produced when the fabric was dyed. At times one might have thought that the fabrics had been produced to display stripes of a different shade. This difficulty not only caused a demand for more uniform yarn, but it also required the dye manufacturers to produce dyes that would minimize the variable dye absorption.

The resistance of cellulose acetate towards the classes of dyes used for dyeing the other natural and synthetic fibers introduced a serious problem. An entirely new class of colors had to be developed for dyeing it, and the whole principle of dyeing had to be altered because, for a long time at least, the most successful acetate dyes were entirely insoluble in water, though soluble in the yarn. This required that the dyes be applied in the form of an extremely fine suspension. Recently, new classes of dyes have been discovered which promise to bridge the solubility-difference between the dye bath and the fiber so that they will be in true solution, yet show good affinity for acetate yarn.

About 40,000,000 pounds of glucose are used annually in the manufacture of viscose rayon. This quantity of glucose is made from about 1,000,000 bushels of corn. The purity of glucose required for the viscose industry is of the same order as that required for the baby food industry. This requirement has actually led one glucose manufacturer into the baby food business.

Machines and Instruments

The fact that the manufacture of synthetic textiles involves a high degree of mechanical precision has been responsible for the development of fine machines and instruments. The electrical spinning motors used for turning the vessels which receive and twist freshly spun viscose rayon are highly developed machines designed to meet the particular requirements of this use. The spinning motors must operate in an atmosphere charged with sulfuric acid mist and hydrogen sulfide gas. They must be operated at 6000 to 10,000 r. p. m., 24 hours a day for long periods of time. About one hundred and twenty-five thousand such motors are in constant use. In addition, there must be about seventy-five thousand other motors of different but very exact specifications.

The spinning pump, which must deliver an exact quantity of the cellulose solution to the spinnerets, is one of the important factors in determining uniformity of filament size. It may be of the multiple-piston or gear type, but in either case the tolerance in dimensions is small. In the gear pump the accuracy is in terms of hundred-thousandths of an inch. The quality of workmanship displayed in the manufacture of these pumps would justify a price of $100.00 each on a small production basis, but with about one-quarter million of such pumps in use, the cost is nearer $10.00.

A constant yarn speed is often essential in winding operations, and, in those cases where a driven bobbin is taking up the yarn, an automatic speed-compensating device has to be employed because of the increasing diameter and peripheral speed. Variable-speed drives of great precision, operated mechanically, electrically, or hydraulically, have been made which show a greater degree of uniformity of speed than most speed-measuring devices.

Improved types of noncorrosive instruments for recording and controlling temperature, humidity, cycles, speeds, and flows have been required. The accuracy, ruggedness, and sensitivity of such devices are now of a high order.

Metallic impurities in rayon may seriously detract from its durability. For this reason the choice of metals for equipment has to be made with a view not so much to long life, as to the danger of contamination of the product by metals. Many of the standards of purity of rayon are in excess of those required for foods, and the problem of finding satisfactory materials has been a serious one. These problems have been solved largely by the metallurgical and mechanical equipment industries. Uniformity of alloys has had to be improved, and new noncorrosive alloys have been developed. Extensive use has been made of hard rubber and phenol-formaldehyde plastics, which have been produced to meet new high standards of strength, precision, and durability.

In the beginning it was necessary that the rayon industry use textile equipment developed for the older fibers. As the quality of the yarn improved and its output increased, it was possible to call for modifications of textile machinery to adapt it better to rayon. As a result of continued contacts with the manufacturers, such textile equipment as twisters, reels, spoolers, creels, warping equipment, slashers, knitting machines, and looms have been more sturdily built, precision of operation has increased, and lubrication systems have been designed to protect the product from contamination. Higher speeds and larger packages have been obtained.

Delustering

We have ordinarily depended upon the oxides and salts of metals for the pigments which are used to produce colors in paints and enamels. It was natural to turn to the known white pigments for a delustering effect when the brilliant luster of rayons was no longer universally desired by fabric designers. The incorporation of titanium oxide, for example, produces various degrees of luster depending upon the amount introduced into the spinning solution; thus we can have any luster from the brilliant, metallic glitter of the old-time rayon to subdued, dull, mat effects similar to cotton and wool; in fact, a chalkiness more pronounced than that seen in any natural fiber has been produced. Inorganic pigments such as titanium oxide are, however, hard, abrasive, and heavy. These objections had to be overcome, and the result was the synthesis of organic materials with pigment qualities. Today we have inert synthetic organic compounds of high refractive index—that is, good covering power—which can be produced in the necessary fine state of division and with a narrower range of particle size than any of those produced from inorganic sources.

The fact that research has enabled man to make a synthetic yarn is not so remarkable if we consider that an ever-increasing group of investigators, for say fifty years, has been engaged in this alluring task. At present, there are literally hundreds of technically trained men striving to improve rayon and to make it adaptable for new applications in textiles. The astonishingly enthusiastic reception by the textile industry does not seem so striking when we realize how starved the

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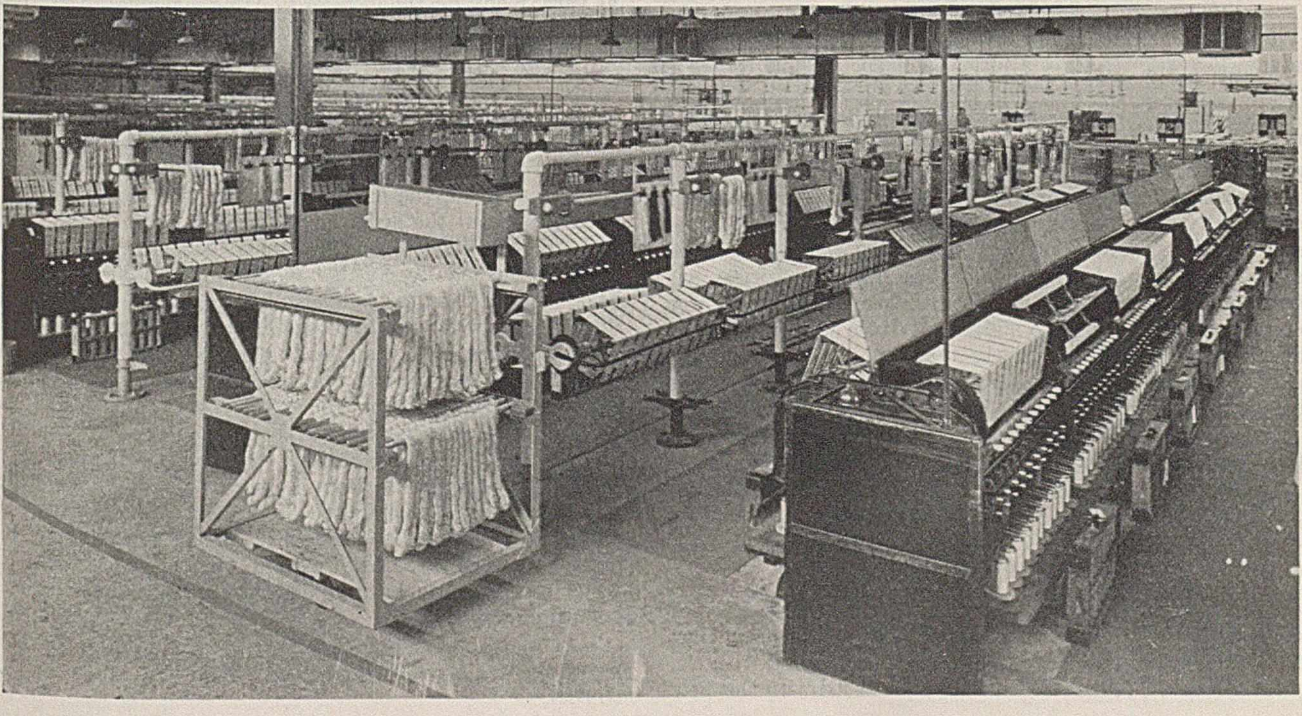

industry has been for ways of producing new and interesting effects. In thousands of years no new basic material was created, and innovations could be made only through new combinations of old fibers, new dyes, and finishes.

Production Figures

In the United States, commercial production of viscose rayon started in 1911, when 360,000 pounds were made. In the next year three times as much was made, and from then on, the United States production grew on the average about 30 per cent a year until 1930. The rate of increase in production was slower during the depression and it required five years for the industry to double its output. Even this is not a bad record for an industry during this most severe depression. One of the junior members of the family, however—the acetate yarn—showed a greater rate of increase. In 1935, 47 per cent more acetate yarn was made than in the previous year, but still nearly 200,000,000 of the 256,000,000 pounds of rayon produced in 1935 were viscose. This involved the making of about 225,000,000 pounds of cellulose xanthate. The author knows of no synthetic organic material produced in larger quantity in America today.

This huge production of rayon furnished employment to about sixty thousand workers. Over $53,000,000 worth of materials were consumed and about $60,000,000 were paid out to employees. In 1935 there were twenty-five plants manufacturing the product, from Massachusetts west to Ohio, and from the Canadian border to Georgia.

World production is approaching the billion-pound mark. In 1929 about 15,000,000 pounds were imported into the United States, but the quantities brought in are now insignificant despite the fact that Japan is pushing the United States for position as the largest producer.

During the first ten years of its domestic manufacture, rayon had a very substantial growth, and by 1921 it had become fully recognized as an important textile fiber. In 1935 the consumption of all textiles was greater than in 1921, but rayon's increase was prodigious. Cotton increased 4 per cent, wool 9 per cent, silk 46 per cent, while rayon increased more than 1000 per cent.

Price Stability

Price has been an important factor in expanding the use of rayon. Rayon is sold in a form which for most purposes is ready to use, while processing costs of the other fibers result in yarn prices that in the case of wool and silk are considerably higher than for rayon, and some cotton yarns are even higher priced than some rayon yarns.

In recent years the prices of all fibers have been greatly affected by disturbed market conditions. The prices of the natural fibers, however, have varied far more than has rayon. Rapid and wide fluctuations in rayon prices are uncommon, and in the last few years these prices have not only been relatively more stable but have worked steadily downward. Speculation in the markets is an insignificant part of the business of a processor of rayon goods, and this has no doubt been one of the factors making for its success.

In the year 1935 United States rayon consumption reached the total of over 250,000,000 pounds. This was four times our consumption of silk, 60 per cent of wool, and about 9 per cent of cotton.

Advantages of Rayon

The low and decreasing cost and the price stability of rayon have contributed to the popularity of the yarn, but these factors have been inconsiderable as compared with the character of the fabrics which can be produced with this new fiber. Rayon resembles silk in that it consists of continuous filaments; it is the only other fiber with the advantage of eliminating long, tedious, and expensive processes involved in producing a yarn from short fibers. The knitting industry was first to adopt rayon in a large way, and its use in knitting has steadily widened. However, while rayon has held its place in the knitting field, 800,000,000 yards of woven fabric were loomed from rayon in 1935, representing 71 per cent of the rayon yarn produced in this country. These woven fabrics varied from sheer cloths made with fine-denier, multifilament yarns to heavy cloths of the wool type. They included delicate transparent velvets and sturdy plushes, light smooth sheers and durable rough crepes, satins with a bright glitter and lusterless "angel-skin" effects. Many fabrics were created with characteristics which could not be achieved by the use of other textile fibers.

But it is not only beauty of appearance and attractiveness of touch and drape that are secured through the use of rayon. This new fiber also contributes to the serviceability of fabrics. For example, it is found satisfactory in such uses as bathing suits and sails for racing boats, where strength and dependability are essential.

It has an important place in the men's wear field. This year many men will wear summer suits made of rayon. Handsome shirtings have been eagerly accepted by the good retail shops because they are cool and pleasant to the touch, and because of the splendid color effects that rayon affords. The diversity of luster, range of filament size, and denier control inherent in rayons have been ingeniously used by fabric designers and stylists to produce the new and interesting textures demanded by exclusive dressmakers of metropolitan centers.

Most of our textiles are made by exceedingly laborious and expensive processes. The operations required to produce yarns from the cocoon of the silkworm, the wool of the sheep, and the seed hair of cotton are tedious and costly operations preliminary to cloth fabrication. Moreover, the idiosyncrasies of individuals of a species, the varying factors of climate and weather, the ravages of disease and insects interfere with the regularity of the fibers. We must take these fibers as we find them; and we do not foresee extensive changes in them through breeding or selection. On the other hand, the continuous, man-made fibers are produced directly as yarn, ready for the loom or knitting machine. The specifications of such fibers can be controlled accurately and over a wide range.

Future of Rayon

These are the facts about textile fiber production today. What of the future? Will fibers be produced embodying the warmth of wool, the elasticity of silk, and the low cost of cotton, without the deficiencies of natural fibers? With the accomplishments of the rayon industry before us, it would take a courageous man to say that these things will never come to pass. We may, on the contrary, look forward to a continued diversification of synthetic textile yarns. Perhaps it is not too much to expect that in the next century the chemical industry will supply raw materials possessing the desirable characteristics of the natural fibers silk, wool, and cotton. We are now too dependent on Nature with its pathetic paucity of offerings and its lax control of products. We may hope for freedom to choose from a large number of synthetic fibers covering a wide range of properties, and with each variety under scientific control. Thus the world may be enriched by low-cost, uniform, and versatile materials from which can be produced more useful, more durable, and more beautiful fabrics.

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CRYSTAL UREA

Industrial Development and Properties

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IN 1812 Davy, studying the action of carbonyl chloride on ammonia (*22*), first synthesized and described but did not recognize urea, "a salt perfectly neutral and dry, but deliquescent by attracting moisture from the air. It is remarkable that on the formation of this ammoniacal salt, gas (phosgene) combines with as much as four times its bulk of ammoniacal gas." The reaction so accurately observed was:

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl$$

Thus it was left for Wöhler (*88*) to announce the synthesis of urea, making memorable the year 1828 and destroying the existing sharp demarcation between organic and inorganic matter. Seventeen years elapsed before the next synthesis of an organic compound—acetic acid by Kolbe. That the Wöhler synthesis could be reversed and urea converted back to ammonium cyanate was not established until 1895 (*79*).

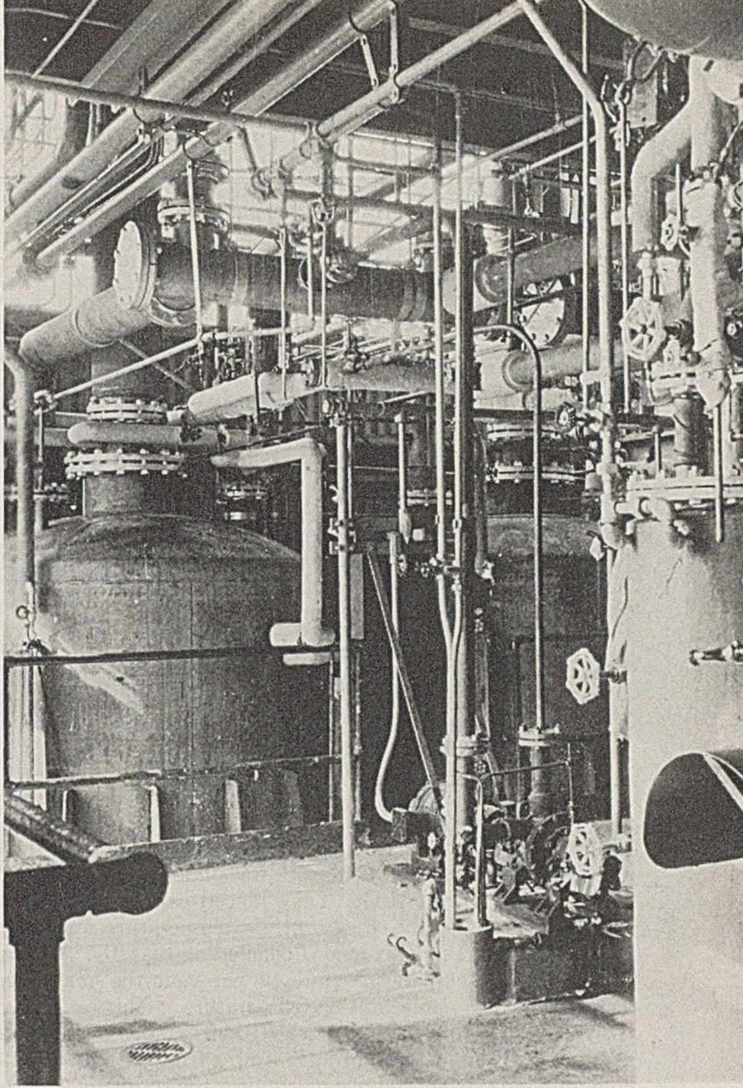
In 1773 Rouelle (*64*) had obtained a "saponaceous extract of urine" by alcoholic extraction of evaporated urine. Twenty-six years later Fourcroy and Vaquelin (*31*) obtained urea in a comparatively pure state from the same source and, recognizing it as a new compound, gave it the name *urée*. Twenty years later Prout (*62*) devised a method for obtaining pure urea from urine and published the first analysis of this compound. In 1829 large quantities of urea were required in the Hospital of St. Antoine in Paris for conducting experiments (which were unsuccessful) on diabetics, and Henry (*38*) developed a method for preparing it in quantity from fresh urine through the use of lead salts for the removal of acids and mucous substances.

Development Process

As mentioned, urea was first synthesized from ammonia and phosgene by Davy in 1812, though Regnault (1838) is usually given credit (*63*) for being the first to prepare urea by this reaction. Well over fifty different methods have since been devised for the synthesis of urea. It is of interest, however, that only two methods have attracted industrial attention, the hydrolysis of cyanamide and the interaction of carbon dioxide and ammonia.

During the World War as an emergency measure, small quantities of urea were manufactured in Canada and by the du Pont Company from calcium cyanamide. A pilot plant for the production of urea by the Lidholm process for the hydrolysis of calcium cyanamide was operated in 1925 at Niagara Falls (*55*).

Until 1935 the world's production of solid synthetic urea was largely controlled by Germany. Early in 1935 the Imperial Chemical Industries, Ltd., Billingham, England, commenced the production of synthetic urea on a relatively small scale. In 1932 E. I. du Pont de Nemours & Company, Inc., developed urea-ammonia liquor, essentially a solution of crude urea in ammonia for use in the ammoniation of superphosphate fertilizer (*13, 60*). This was followed by studies on the high-pressure synthesis of solid urea, and in November, 1935, the first commercial production of synthetic solid urea began in the United States.



ABSORBERS IN CRYSTAL UREA PLANT

All commercial synthetic urea now produced in Germany, England, and the United States is obtained through the reaction of ammonia and carbon dioxide.

In 1868 Basaroff (*2*) first suggested the synthesis of urea from carbon dioxide and ammonia, showing that both ammonium carbamate and carbonate when heated in a sealed glass tube yield urea. Bourgeois (*11*) further studied this reaction to improve the yield but met with little success, obtaining yields from 1.5 to 9.52 per cent urea. He noted the strong corrosive action of the carbon dioxide–ammonia system on iron. In 1882 Mixter (*59*) showed that urea could be formed by passing dry carbon dioxide and ammonia through a heated tube. In 1897 Slosse (*72*) obtained urea by passage of a silent electric discharge through a dry gaseous mixture of one volume of carbon dioxide and two volumes of ammonia. Although the transformation of

TABLE I. PHYSICAL PROPERTIES OF UREA

Mol. weight	60.047
Melting point (decomposes), ° C.	132.7 (*58*)
Melting point at 3000 atm., ° C.	150 (*12*)
Triple point transformation, ° C. at 6535 atm.	102.3 (*12*)
Triple point volume change, kg./cc. (*24*):	
Phase 1 to 2	48.0 (*12*)
Phase 2 to 3	0.6 (*12*)
Sp. gr. at 20°/4° C. (solid)	1.335
Change in sp. gr. per 1° C.	0.000208
Crystalline form	Tetragonal-scalendohedral (*37*)
Crystal constants	Optical sign, positive; axial ratio $A/C = 1:0.833$ (*37*)
Crystal habit	Needles or rhombic prisms
Refractive indices at 20° C.	1.484 and 1.602
Heat of fusion, cal./gram	57.8 (*58*)
Heat of combustion (solid), cal./gram	2,531 (*45*)
Heat of solution in water, cal./gram	−57.8 (*58*)
Heat of solution in methanol, cal./gram	—46.6 (*75*)
Heat of solution in ethanol, cal./gram	−50.2 (*75*)
Free energy of formation at 25° C., cal./mole:	
Solid	−47,120 (*43*)
Aqueous	−48,720 (*43*)
Thermal conductivity of crystals, cal./sec./sq. cm./° C./cm.	0.191
Axial thermal conductivity ($A = B$)	$A/C = 0.79$ (*42*)
Specific heat (20° C.), cal./gram/° C.	0.320 (*41*)
Dissociation constant, 25° C.	1.5×10^{-4} (*80*)
Dielectric constant (22° C.), c. g. s. units at 4×10^8 cycles/sec.	3.5 ± 0.2 (*42A, 74*)

ammonium carbamate to urea had been known for some time, the first markedly successful work was undertaken by Fichter and Becker (*29*) in 1911. They placed carbamate in steel bombs and studied the effects of time, temperature, and packing density on the conversion, concluding that 135° C. was the optimum temperature and 42 per cent the maximum conversion attainable at this temperature. This same year Lewis and Burrows (*50*) published their studies on the free energy of urea and the synthesis of urea from carbon dioxide and ammonia, which tended to confirm the results of Fichter and Becker.

During the war when the problem of nitrogen fixation became acute in France, Matignon and Frejacques (*57*) undertook the study of urea synthesis and showed that, although the temperature exercised no profound influence on the equilibrium, the speed of the conversion is very much affected. The addition of dehydration catalysts accelerated the rate of conversion at the low temperature, but they contributed no appreciable improvement above 150° C.

In 1919 the Fixed Nitrogen Research Laboratory began an investigation of the synthesis of urea from ammonia and carbon dioxide and in 1922 developed a process which was operated on an experimental plant scale (*46*). This consisted of charging briquetted ammonium carbamate into an autoclave maintained at 150° C. and passing the liquid product into a still where the unconverted ammonia and carbon dioxide were recovered and recycled. These studies suggested that higher temperatures would result in higher yields, agreeing with the work of Matignon and Frejacques. Krase and Gaddy further showed that the use of an excess of ammonia over that combined as carbamate materially increased the conversion to urea. Carbon dioxide did not show this effect (*47*). The maximum conversion of ammonium carbamate to urea, which in the absence of excess of ammonia was about 44 per cent, could be increased to 85 per cent by the use of about 300 per cent excess ammonia. The slope of the conversion curve indicated that further excess of ammonia would have little effect on the conversion. The effects of temperature, materials of construction, and a number of other factors were studied by this group (*17, 18, 19, 49*). In 1930 a continuous process for the synthesis of urea from liquid ammonia and carbon dioxide was described. A small unit producing 175 pounds (386 kg.) of urea per day was operated at 35 to 37 per cent conversion at 153° C. (*48*).

While ammonia, carbon dioxide, and water are by themselves practically noncorrosive to steel, when combined they are astonishingly corrosive. Under urea synthesis conditions the mixture will dissolve iron filings rapidly, and ordinary steel plate will dissolve at the rate of about 130 grams per square meter per hour, or more than 10 ounces per square foot per day (*77*). Chrome irons and a number of ordinarily resistant alloys are also rapidly attacked. Lead is attacked at about one-thirteenth the rate of steel.

The primary difference in the manufacture of urea in the United States and in other countries is in the treatment of the unconverted ammonia and carbon dioxide. Both in England and in Germany gypsum conversion plants have been operated in conjunction with the urea synthesis operation. However, in Germany, the present practice is to recycle the unconverted gases at sufficiently high temperature to prevent formation of solid compounds. In this country where there are large amounts of ammonium sulfate available from coke-oven operations, its further production is unattractive. The utilization and handling of the unconverted gases has constituted one of the major problems in the domestic production of urea.

The world's present synthetic urea production capacity is about 190 tons a day. Prior to 1936, with the exception of the small amount produced during the World War, all domestic urea requirements were derived from Germany. There is now sufficient production capacity in the United States

TABLE II. SOLUBILITY OF UREA IN VARIOUS SOLVENTS

Solubility in Water (*44, 61, 70, 81*)

Temp., ° C.	Urea per 100 G. H_2O	Temp., ° C.	Urea per 100 G. H_2O
0	67	70	309
10	84	80	396
20	105	90	508
30	136	100	725
40	163	110	1164
50	205	120	2244
60	246		

Solubility in Methanol (*10, 69, 73, 76*)

	G. Urea per 100 G. Methanol	
Temp., ° C.	Solid phase, $CO(NH_2)_2$	Solid phase, $CO(NH_2)_2 \cdot CH_3OH$
−78	......	0.3
−25	......	2.9
−15	10.9 unstable	3.9
−10	11.6 unstable	4.9
0	14.2 unstable	7.7
+10	17.7 unstable	12.5
15	19.7 unstable	16.4
19	21.4 unstable	20.5
20	22.0 stable	..
30	27.7 stable	..
40	35.3 stable	..
50	46.0 stable	..
60	62.8 stable	..

Solubility in Alcohols (*76*)

	G. Urea per 100 G. Alcohol						
Temp., ° C.	Ethanol (*69*)	*n*-Propanol	Isopropanol	Isobutanol	Isoamyl-alcohol	Capryl alcohol	Allyl alcohol
0	2.6	1.6	..	1.0	..	..	..
10	4.0	2.0	..	1.3	0.7	..	..
20	5.4	2.6	6.2	1.7	1.2	0.6	9.5
30	7.2	3.6	..	2.3	1.6	..	..
40	9.3	4.8	..	3.1	2.1	..	..
50	11.7	6.2	..	3.7	2.7	..	..
60	15.1	7.7	..	4.4	3.4	..	..
70	20.2	9.8	..	5.3	4.1	..	..
80	..	12.3	23	6.3	4.9	..	..
90	..	17.0	..	8.2	5.5	..	..

Solubilities in Other Solvents

Ethyl ether (15–20° C.), g./100 cc.	0.0004 (*35*)
Glycerol (15° C.), g./100 g.	About 50 (*68*)
Pyridine (20–25° C.), g./100 g.	0.96 (*24*)
50% aqueous pyridine (20–25° C.), g./100 g.	21.53 (*68*)
Ethyl acetate (25° C.), g./100 g.	0.080 (*51*)
Ammonia, anhydrous, g./100 g.:	
−26.4° C.	25.1 (*67*)
+23.9° C.	107.6
+50.0° C.	315.2

to satisfy our present and forecastable requirements as well as to allow, for the first time, the exportation of urea.

Physical Properties

Pure urea is a white, odorless, crystalline solid with a cool saline taste resembling sodium nitrate. Urea crystallizes from water in exceedingly long, needle-like crystals without definite terminal faces. However, these are usually well developed when urea is crystallized from alcoholic solution.

The material produced in this country is distinguished from imported urea by difference in crystal habit. It is obtained in compact four-sided rhomblike prisms instead of the usual elongated acicular crystals. The domestic urea is termed "crystal urea." Because of its crystal form, crystal urea is freer-flowing, shows less tendency to mat or cake, and occupies about 25 per cent less space for a given weight—factors of importance in handling, measuring, transporting, and storing.

The essential physical properties of urea are presented in Table I.

Solubility of Urea in Various Solvents

When supersaturated solutions of urea in methanol are rapidly agitated at 0° C., a solid phase, $CO(NH_2)_2 \cdot CH_3OH$, separates. This molecular compound is less soluble in methanol than urea and is stable below +19.25° C., the transition temperature to urea.

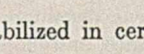
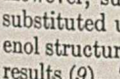
Data on the solubility of urea in various solvents are given in Table II.

Viscosities of Urea-Water Solutions

Chadwell and Asnes (*14*) showed that, although aqueous solutions of urea do not have negative viscosities (relative viscosity less than water), their viscosities are much lower than those of equivalent solutions of ether, ethyl and methyl acetates, and urethane in water. The relative viscosities of urea-water solutions are as follows (densities are in parentheses):

Temp., ° C.	Per Cent by Weight of Urea: 0%	5%	10%	15%
5	1.000 (1.0000)	1.019 (1.0150)	1.046 (1.0296)	1.086 (1.0444)
10	1.000 (0.9997)	1.021 (1.0140)	1.054 (1.0283)	1.094 (1.0428)
15	1.000 (0.9991)	1.030 (1.0132)	1.066 (1.0273)	1.111 (1.0415)
20	1.000 (0.9982)	1.033 (1.0120)	1.071 (1.0257)	1.118 (1.0396)
25	1.000 (0.9971)	1.038 (1.0106)	1.077 (1.0240)	1.126 (1.0376)

Chemical Properties

CONSTITUTION. Urea has long been considered as the diamide of carbonic acid, or carbamide, $NH_2 \cdot CO \cdot NH_2$. Werner has brought together considerable evidence (*86*) to show that this conception does not adequately represent the facts either for the syntheses or for the reactions of urea. He advocates the cyclic formula  $NH{:}C\langle^{NH_3}_{O}$ and visualizes the transient existence of an active tautomeric enol form,  $NH{:}C\langle^{NH_2}_{OH}$, which has been stabilized in certain isoureas. However, substituent groups, such as in the di- and tetra-substituted ureas, are considered to modify the cyclic or the enol structure to such an extent that the carbamide structure results (*9*). The fact that urea acts as a monobasic substance tends to support these views. However, in some reactions, as with aldehydes, malonic acids, and related compounds, it is difficult to justify the cyclic structure. Therefore, while the cyclic or enol structure for urea appears justified, it is probable that under certain conditions and in undergoing some reactions, the carbamide structure prevails.

According to Werner's views, the Wöhler synthesis of urea may be analyzed as follows (*84*):

Dissociation: $NH_4 \cdot OCN \longrightarrow NH_3 + HOCN$ (1)
Rearrangement: $H \cdot O \cdot C{:}N \longrightarrow HN{:}C{:}O$ (2)
Combination: $NH_3 + HN{:}C{:}O \longrightarrow HN{:}C(OH)NH_2$ (3)

Any synthesis of urea is considered to proceed through isocyanic acid, as in No. 3.

HEAT. Dry ammonium cyanate, stable at ordinary temperatures, is rapidly converted to urea at 80° C. Urea heated in a vacuum at 120° to 130° C. sublimes unchanged (*10*). Heated in vacuum at higher temperatures, urea is converted to ammonium cyanate which sublimes (*26*). Heated at ordinary pressures between 130° and 160° C., ammonia is released, ammonium cyanate forms and sublimes, and varying amounts of biuret [or allophanamide, $HN(CONH_2)_2$] remain (*28*, *40*, *83*). Between 160° and 190° C., increasing amounts of biuret as well as cyanuric acid [$C_3N_3(OH)_3$] and ammelide [cyanuromonamide, $NH_2 \cdot C_3N_3(OH)_2$] are formed; above 190° C. the biuret decomposes, yielding cyanuric acid, ammelide, and tricyanourea [$C_3N_3O_3(CONH_2)_3$]. Above 200° C., urea decomposes to ammonia, cyanuric acid, tricyanourea, and ammelide (*36*). Werner suggests that ammelide and tricyanourea are the same. Some confusion still exists (*82*) on the constitution of these complex compounds.

When an aqueous solution of urea is boiled, it is partially converted to ammonium cyanate. The cyanate is then hydrolyzed to ammonium carbonate (*27*, *79*). A urea solution saturated at 73.11° C. showed a loss of urea equivalent to changing the saturation temperature to 69.67° C. by heating at 99° C. for 20 hours (*70*). When heated with water in a sealed tube at 180° C., urea undergoes complete hydrolysis to ammonium carbonate.

ACIDS, BASES, AND SALTS. Urea in cold aqueous solutions is not decomposed by dilute acids or alkalies (*86*). On heating, complete decomposition to ammonia and carbon dioxide is effected. The presence of free ammonia retards the rate of decomposition, and therefore the reaction is more rapid in acid solutions (*25*). The decomposition proceeds through the formation of ammonium cyanate and the hydrolysis of ammonium cyanate to ammonium carbonate. Heating an alcoholic solution of urea with an equivalent amount of alkali at 100° C. results in the formation of the alkali cyanate and ammonia (*25*).

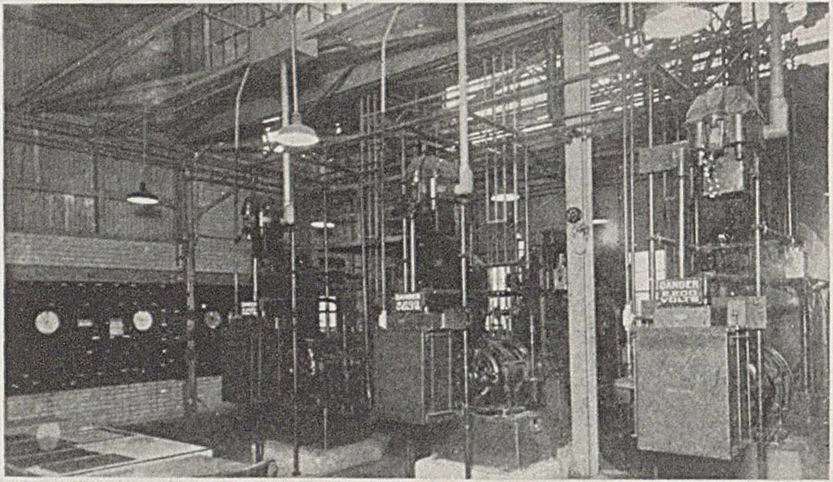
When urea is dissolved in liquid ammonia, it materially increases the electrical conductivity of this solvent and takes on the properties of an acid. In ammonia solutions, it reacts with alkali metals and magnesium with the evolution of hydrogen and with potassium amide to form mono- and dipotassium salts (*8*, *33*, *34*).

Urea forms addition compounds with acids, acting as a monobasic compound. Thus with nitric acid, $CO(NH_2)_2 \cdot HNO_3$ forms; sulfuric acid forms two salts with about the same melting point (70° C.)—namely, $2[CO(NH_2)_2] \cdot H_2SO_4$ and $CO(NH)_2 \cdot H_2SO_4$; oxalic acid also forms two analogous salts (*20*), the monourea oxalate is stable only above 21.22° C.; acetic acid forms large deliquescent crystals, $CO(NH_2)_2 \cdot CH_3COOH \cdot 2H_2O$; only one urea phosphate derivative exists (*56*).

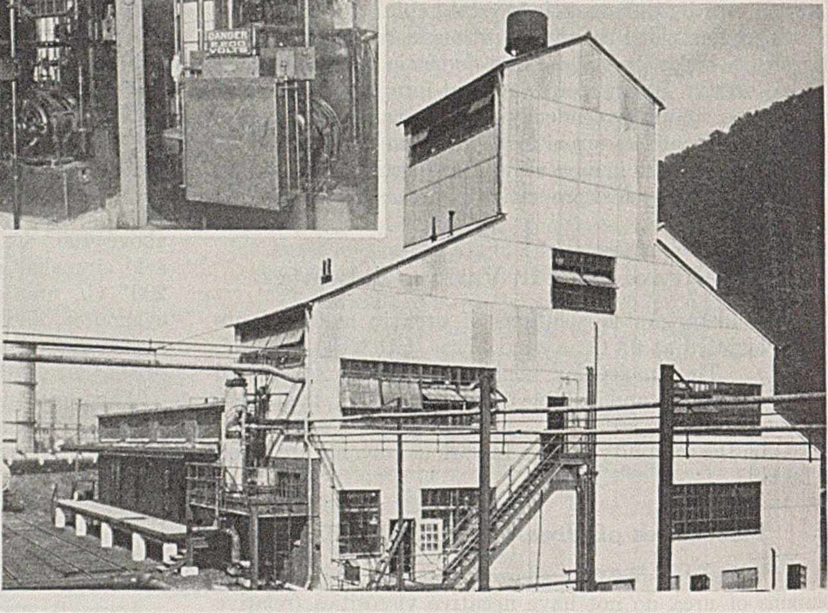
Urea nitrate forms sparingly solute monoclinic crystals, decomposing explosively when heated. Urea nitrate can be detonated and has been considered as a constituent of explosive compositions. Treated with concentrated nitric acid, it decomposes as follows:

$$CO(NH_2)_2 \cdot HNO_3 + HNO_3 \longrightarrow CO_2 + N_2O + NH_4NO_3 + H_2O$$

Concentrated sulfuric acid converts it into nitrourea, $NH_2 \cdot CO \cdot NH \cdot NO_2$, a strong acid.



(*Left*) INTERIOR VIEW OF UREA MELT PLANT



(*Below*) CRYSTAL UREA PLANT OF E. I. DU PONT DE NEMOURS & COMPANY, INC., AT BELLE, W. VA.

Hydrochloric acid apparently forms a mono- and a diurea hydrochloride. Urea hydrochloride heated in an alcoholic solution precipitates ammonium chloride. When heated at 130° C., it gives much better yields of biuret than does urea, since the liberated ammonia reacts with the hydrogen chloride instead of the isocyanic acid (*39*).

Although it is generally assumed that nitrous acid decomposes urea in the same manner that it decomposes all other amides,

$$CO(NH_2)_2 + 2HNO_2 \longrightarrow CO_2 + N_2 + 3H_2O$$

Werner contends that urea and pure nitrous acid do not react except in the presence of a strong acid and that the volume ratio of carbon dioxide to nitrogen (1 to 2) required by the above equation is never obtained. The proportion of carbon dioxide is always much higher and the composition of the gas is affected by the concentration of reactants (*85*). Werner proposed the following mechanism for the reaction in presence of acid:

$$CO(NH_2)_2 + HNO_2 \longrightarrow N_2 + 2H_2O + HNCO$$

The cyanic acid is decomposed in two ways as fast as it is generated, both reactions proceeding simultaneously; the predominance of one over the other is dependent on the conditions:

$$HNCO + H_2O \longrightarrow NH_3 + CO_2$$
$$HNCO + NHO_2 \longrightarrow CO_2 + N_2 + H_2O$$

Urea sulfonic acids, $NH_2{\cdot}CO{\cdot}NH{\cdot}SO_3H$ and $CO(NH{\cdot}SO_3H)_2$ were prepared for the first time in 1931 (*3*).

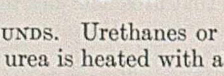
Urea forms crystalline addition compounds with a large number of inorganic and organic compounds. On evaporating a solution containing both urea and sodium chloride, the compound $CO(NH_2)_2{\cdot}NaCl{\cdot}H_2O$ separates in shining prisms (melting range, 60–70° C.). Similar complexes are formed with ammonium chloride and salts of copper, silver, gold, magnesium, zinc, cadmium, aluminum, mercury, lead, and most other metals. Over thirty chromium-urea compounds alone have been described.

Urea also forms metallic salts such as mono- or disodium ureas [$NH_2{\cdot}CO{\cdot}NHNa$ or $CO(NHNa)_2$] obtained by the interaction of urea and alkali or alkali amide in liquid ammonia. Aqueous solutions of urea act on silver oxide to form disilver urea, $CO(NHAg)_2$. A dimercury urea can be similarly prepared (*33*).

Urea forms a crystalline stable compound with hydrogen peroxide, $CO(NH_2)_2{\cdot}H_2O_2$, which decomposes at 85° C. (*4*).

Urea replaces the water of crystallization in many compounds. Gypsum in the presence of an aqueous solution of urea at 30° C. is converted to the complex, $CaSO_4{\cdot}4CO(NH_2)_2$ (*87*); similarly, calcium nitrate forms Calurea, $CaNO_3{\cdot}4CO(NH_2)_2$, a well-known fertilizer material.

OXIDIZING AGENTS. Hypochlorite, hypobromite, or acid permanganate solutions convert urea into carbon dioxide and nitrogen. Neutral or alkaline permanganate solutions do not act on urea. Chlorine acts on fused urea to yield cyanuric acid, ammonium chloride, and nitrogen. Bromine has a similar action (*71*). When chlorine or hypochlorites act on well-cooled or dilute solutions of urea, chloro- and dichlorourea are formed [$NH_2{\cdot}CO{\cdot}NHCl$ and $CO(NHCl)_2$]. These compounds decompose at 71° and 82° C., respectively, when rapidly heated (*7*, *15*, *21*, *54*). Through the chloroureas, hydrazine can be produced in yields up to 60 per cent (*65*). The chloroureas decompose in dilute aqueous solutions to yield chloramines, and bichlorourea on treatment with strong ammonia (*16*, *21*) produces *p*-urazine or diurea,



$$CO\begin{cases}NH{\cdot}NH\\NH{\cdot}NH\end{cases}CO$$

ORGANIC COMPOUNDS. Urethanes or carbamic acid esters are obtained when urea is heated with alcohols:

$$NH_2CONH_2 + ROH \longrightarrow NH_2{\cdot}COOR + NH_3$$

This is a general reaction and can also be applied to dihydric and polyhydric alcohols. However, the yields are relatively low. Evidently alkyl carbonates, $(RO)_2CO_2$, cannot be prepared through the action of 2 moles of alcohol with 1 of urea, the reaction always stopping at the urethane stage.

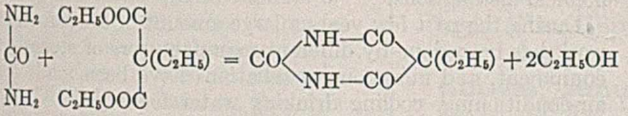
Urea reacts with aldehydes, ketones, acid anhydrides, hydrazines, certain esters, and halogen-substituted compounds. Two reactions, highly important commercially, are the reaction of urea with formaldehyde and with malonic acid derivatives.

Probably the first observation that urea and formaldehyde condense must be credited to Schiff in 1869 (*66*). The commercially important reaction is the formation of the water-soluble crystalline monomethylol and dimethylolurea:

$$NH_2{\cdot}CO{\cdot}NH_2 + CH_2O \longrightarrow NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2OH \text{ (methylolurea)}$$
$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2OH + CH_2O \longrightarrow CO{\cdot}(NH{\cdot}CH_2OH)_2 \text{ (dimethylolurea)}$$

Application of heat or catalyst, or both, to the methylolureas causes further reaction, the methylolurea condensing with itself to form larger and larger molecules; as the reaction continues, the product passes from the true-solution state to the colloidal-solution state and finally to the hard, water-insoluble resin. Further treatment of this resin with heat, such as in the molding operation, forms an insoluble, infusible resin.

Astonishingly large amounts of urea are employed in the manufacture of the malonylureas or barbituric acid derivatives, widely employed soporifics and sedatives. The malonylureas can be obtained through the interaction of urea and substituted malonic acid esters—for example, diethylmalonylurea or diethylbarbituric acid, which as Veronal or Barbital is obtained from diethyl malonic ester and urea:



$$\underset{NH_2}{\overset{NH_2}{CO}} + \underset{C_2H_5OOC}{\overset{C_2H_5OOC}{C}}(C_2H_5) = CO\left\langle\begin{matrix}NH-CO\\NH-CO\end{matrix}\right\rangle C(C_2H_5) + 2C_2H_5OH$$

Urea diethylmalonic ester

Diethylmalonylurea or diethylbarbituric acid (Barbital or Veronal)

Similarly Allonal contains the allyl isopropyl derivative, Luminal and Phenobarbital the ethyl phenyl derivative, Dial the diallyl derivative, etc. Some four hundred barbituric acid derivatives have been described but only about a dozen are in common use.

Analytical Methods

The four principal analytical methods now in use for urea are the Kjeldahl (*52*), urease (*32*), hypobromite (*23*), and xanthhydrol (*30*) methods.

The Kjeldahl method is not specific for urea and is applicable only when no other nitrogenous materials are present. When concentrated sulfuric acid is used for the digestion, the results are somewhat erratic (*78*). It has been noted that the use of dilute sulfuric acid (20 per cent by volume) gives good and consistent results.

The hypobromite method, where the nitrogen evolved is measured, is rapid but not accurate.

In the urease method, urea is hydrolyzed to ammonia and carbon dioxide by the enzyme, urease (obtained from the Jack bean, *Canavalia ensiformis*). This method is specific for urea, but small variations in titration or weighing may cause large percentage errors. For instance, on a 0.1-gram sample, an error of 0.1 cc. of 0.1 *N* acid introduces an error of 0.3 per cent nitrogen.

Urea forms the insoluble dixanthhydrylurea when treated with a methanol solution of xanthhydrol. This may be weighed or dissolved in sulfuric acid and estimated colorimetrically (*5*) or titrated with permanganate (*53*) or dichromate (*1*). The xanthhydrol method is not applicable in the presence of cyanamide, since urea is obtained from cyanamide in the analytical procedure (*32*).

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...VACUUM REFRIGERATION

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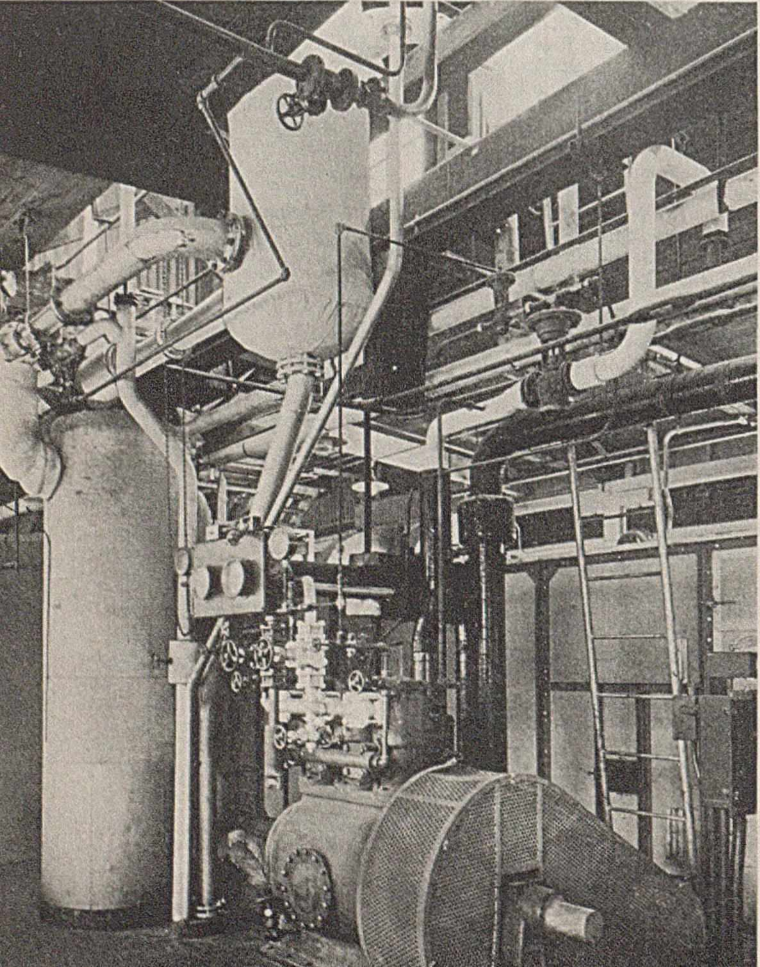
THE chemical engineer and refrigerating engineer have at their disposal a large variety of industrial refrigerants. New ones have frequently been added to the list and some have been quickly and widely adopted with considerable success. Water as a refrigerant is by no means new, but its possibilities were neglected for many years until recent improvements in the steam-jet type of vacuum producer provided economical equipment for applying this method.

Chilling water by partial evaporation at high vacuum has been known for decades. A few isolated cases are recorded where the method was applied in the early part of the century, but the installations proved impractical and were more in the nature of engineering experiments than of practical or economical installations.

Figure 1. Refrigerating Unit of 24 Tons Capacity, with Vertical Vacuum Chamber



During the past few years a large amount of development work has been done by different manufacturers of steam-jet equipment, and numerous installations have been made for air-conditioning, cooling drinking water for large buildings, and cooling a large variety of fluids in chemical process work. A conservative estimate of the total capacity of vacuum refrigerating equipment installed in the past three years is equivalent to 50,000 tons of ice every 24-hour day. The reason for this rather sudden commercial application of an old, well-known principle is interesting. Many of the early attempts to apply this method depended upon reciprocating vacuum pumps to produce the vacuum and draw off the necessary vapor from the high-vacuum evaporating chamber.

The problem can be easily understood by considering a typical case of chilling water required for air-conditioning a medium-size restaurant. Assuming that the required capacity for cooling and dehumidifying the air is 50 tons of refrigeration, a total heat absorption of 600,000 B. t. u. per hour is necessary. Assuming that the required chilled water temperature is 45° F., a vacuum corresponding to an absolute pressure of 0.3 inch of mercury is required. Therefore, sufficient water must be evaporated at 0.3 inch absolute so that the latent heat of evaporation will absorb the 600,000 B. t. u. The latent heat at 0.3 inch is 1066 B. t. u. Dividing 600,000 by 1066 gives 562 pounds per hour of water which must be evaporated. The specific volume of water vapor at 0.3 inch absolute is 2033 cubic feet per pound. The total volume of vapor to be handled, therefore, is 562 × 2033 or 1,142,546 cubic feet per hour (19,042 cubic feet per minute).

Steam-Jet Apparatus

Obviously, then, the vacuum cooling method is not practical with conventional reciprocating vacuum pumps. This type of pump has its advantages for low and moderate vacua, but it is generally agreed that its efficiency falls sharply at high vacuum. A battery of dozens of large-size commercial reciprocating pumps would be required for this duty. On the other hand, the steam-jet type of vacuum producer, operating at high velocity on an entrainment rather than a displacement principle, can handle this capacity in a single medium-size unit which weighs, with its condenser, approximately 3000 pounds.

The reason for the difference is the high velocity of the steam, averaging 4000 feet per second leaving the jets, and the entrainment of the low-density vapor at high velocities as the steam expands. The steam-jet unit also has the advantage of no moving parts.

Figure 1 shows a commercial unit with a capacity of approximately 24 tons of refrigeration. The large vertical vessel at the left is the vacuum evaporating chamber. Suitable internal sprays and baffle equipment are provided in this chamber to give the necessary contact between the water and the vacuum space. The main steam-jet evacuator is bolted onto the connection on top of the vacuum chamber. This unit discharges into a surface or barometric condenser where an intermediate vacuum of approximately 28 inches is maintained. A small two-stage steam-jet evacuator is used to maintain this 28-inch vacuum on the condenser. This comprises the complete equipment with the exception of pump or barometric leg to draw the chilled water from the vacuum chamber.

A brief history is given of the process of chilling liquids by partial evaporation under high vacuum, with reasons for its recent wide commercial application. The steam-jet type of vacuum apparatus for applying the process is described. Curves give actual operating data with figures for steam and water consumption at different chilled water and condenser water temperatures. The discussion includes: vacuum cooling of liquids by direct exposure to vacuum and by an indirect method with a heat-exchanger bundle submerged in chilled water in the vacuum chamber; continuous and batch cooling, with mention of operating economies provided by the latter; and chemical engineering applications, including vacuum crystallization, air-conditioning, chilling mash for distilleries, simultaneous chilling and degasifying of miscellaneous liquids, etc.

The collection of data for different conditions required considerable time and numerous changes in equipment. The steam-jet type of vacuum equipment is highly dependable when operated within reasonable variations of a given set of conditions for which it is designed. However, it is also quite sensitive to appreciable changes in certain operating conditions, such as excessive temperatures of condensing water, low pressure of live steam, etc. The booster steam jet, designed to discharge into a condenser where a vacuum of 28 inches is maintained, will fail when discharging into a condenser where warmer cooling water can produce a maximum vacuum of only 27.5 inches. In order to obtain good efficiency, the internal dimensions of the steam-jet unit have to be extremely accurate and carefully correlated. Therefore, in collecting accurate performance data with different temperatures of cooling water and a constant steam-pressure, it was necessary to change the monel metal steam nozzles frequently and the combining throat into which these nozzles discharge.

An entirely different set of data was obtained by making the main condenser of barometric instead of surface type. In this case the discharge from the steam jet evacuator comes in direct contact with the condenser water and permits a considerably closer terminal difference between the discharge condenser water and the temperature corresponding to the vacuum. This means slightly better efficiency than with a surface condenser where all of the heat must be transferred through tubes, making the terminal difference unavoidably higher. A typical test set-up using a barometric type of condenser is shown in Figure 2. In this case the condenser is operating as a low-head jet condenser since it discharges into a pump instead of into a full-length barometric leg. A low-head jet condenser and a barometric condenser are interchangeable, and their condensing efficiency and performance are equal.

Experimental Data

In collecting experimental data, the vacuum evaporating chamber was tested under its full range of working conditions to be sure that there had been sufficient contact of the water with the vacuum so that the water leaving would be chilled completely to the temperature corresponding to the vacuum. The large steam-jet unit was carefully designed in each case for the exact conditions. The amount of live steam used in the nozzles was calculated from the temperature rise in the condenser water, correcting for the amount of vapor drawn from the vacuum evaporating chamber. The quantity of live steam was checked by calculating the flow from the size of the orifice using standard formulas for this purpose. For each test the design of the steam-jet unit was made according to modern improved practice with efficiency as high as possible.

In testing some of the equipment for maximum vacuum without water in the chilling tank, absolute pressures slightly lower than 1 mm. were obtained. At any absolute pressure less than 3 mm., ice crystals formed in the flow of steam from the jets. The steam supplied to the jets was at a pressure of 100 pounds per square inch gage and a temperature of 338° F., and the steam velocity from the jets was approximately 4000 feet per second. Considering the steam temperature, the exceptionally high velocity, and the fact that the nozzles are only about 4 inches long, the formation of ice crystals seems somewhat anomalous. It is due to the rapid expansion of the steam and the accompanying heat absorption. Some of the steam first condenses into moisture, and, since the absolute pressure is lower than the vapor pressure of ice at 32° F., a part of the moisture reëvaporates, thereby absorbing sufficient heat to produce freezing. Without much extra manipulation a good imitation of a natural snowfall can be produced inside the vacuum vessel.

When operating at vacuum sufficiently high to form ice, the steam consumption of the jets is such that operating costs are usually higher than for mechanical refrigeration, although low-cost steam and relatively cold condenser water in some cases make the steam-jet unit economical and practical even at temperatures a few degrees below freezing. For refrigeration to intermediate temperatures in the neighborhood of 40° F., vacuum refrigeration shows excellent operating economy, as Figure 3 indicates.

Operating data from test units and from commercial installations are given as curves for convenience in Figure 3. They are based on steam at 100 pounds per square inch

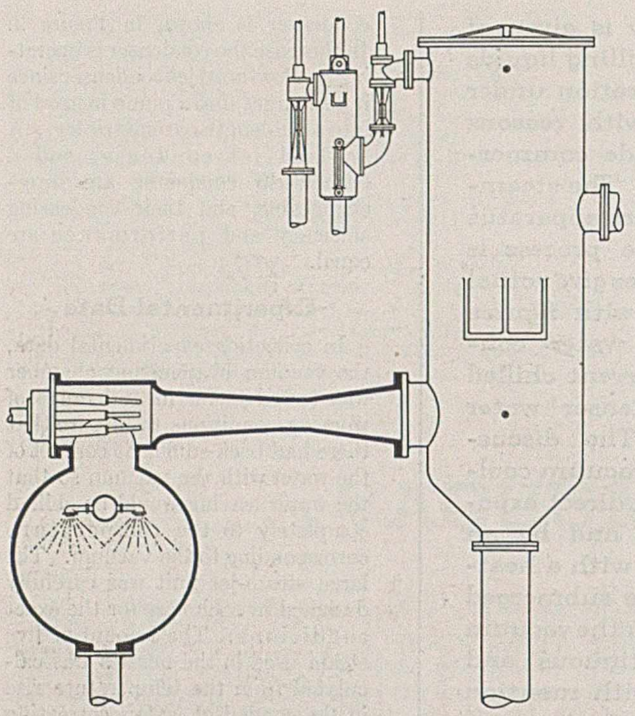


FIGURE 2. TYPICAL ARRANGEMENT OF VACUUM REFRIGERATING EQUIPMENT

pressure and on the use of barometric or low-head jet condensers. Curve *A* gives steam and water consumption figures when chilling water to 40° F. Curves *B*, *C*, and *D* give the same data for chilled water temperatures of 45°, 50°, and 60° F., respectively. The steam consumption figures are expressed in pounds per hour per ton of refrigeration, water consumption figures in gallons per minute per ton of refrigeration. The steam consumption is plotted against the water consumption because one can be compromised against the other. Within certain limits the steam consumption can be reduced by using more water, and vice versa. In using the curves to obtain performance data, it is necessary only to select the proper point somewhere along the curve corresponding to the maximum temperature of the available condenser water. In estimating, the maximum summer temperature of condenser water should always be used; when the weather is mild and the water cooler, its quantity can be reduced.

Many chemical plants have a surplus of exhaust steam at atmospheric pressure or slight positive-pressure, particularly in summer when refrigeration is most necessary. The steam-jet type of cooling equipment has been adapted for using this exhaust steam even though it has no positive pressure above atmospheric. When the proper vacuum is maintained in the main condenser, this atmospheric-pressure steam develops sufficient velocity through the jets to give practical and economical results for many conditions. Of course, steam consumption is greater when using low pressure steam. The quantities required at pressures down to atmospheric were determined but are not available for publication.

Vacuum refrigerating equipment has considerable flexibility. Accurate tests indicate that any unit designed for a definite chilled water temperature can be operated at a variety of different chilled water temperatures at different capacities; for example, a unit designed to produce 100 tons of refrigeration at a chilled water temperature of 50° F. will automatically produce 115 tons of refrigeration at a chilled water temperature of 55° F. If the chilled water temperature is lowered instead of raised, the capacity is also lowered; at a chilled water temperature of 40° F. the capacity drops to 70 tons, and to 55 tons with a chilled water temperature of 35°. Conversely, a unit designed for operation at a relatively low temperature will provide increased heat absorption capacity when operated at slightly higher temperatures.

Batch Cooling

The foregoing operating data apply to cooling by continuous operation. The vacuum process is also adaptable to batch cooling, usually with improvement in operating efficiency. Batch cooling is not practical for air-conditioning or for process work where the temperature range in the chilled water is less than 10° F. However, where the temperature range in the medium to be chilled is more than 10°, batch cooling frequently offers savings, particularly where liquids must be cooled over a range of 100° or more—for example, in the cooling of mash in a whisky distillery. Since the development of vacuum cooling, mash tubs are frequently made to withstand vacuum so that, after the mash has been cooked, it can be quickly cooled in the same vessel by applying the proper vacuum. This is a good illustration of a case where the batch method considerably increases the efficiency. It is necessary to provide some form of agitation for the mash so that, as it is cooled on the surface, it will be thoroughly mixed for homogeneous cooling throughout. The improvement in efficiency in the batch method over the continuous method is obvious when we consider that it permits most of the vapor being removed from the vacuum evaporating chamber at a much lower vacuum than that corresponding to the final chilled temperature. In the case of continuous cooling, it is necessary to maintain maximum vacuum constantly, and all the vapor must be handled at this maximum vacuum. Many data on batch operation of vacuum cooling have been collected, although it is difficult to put them in concentrated

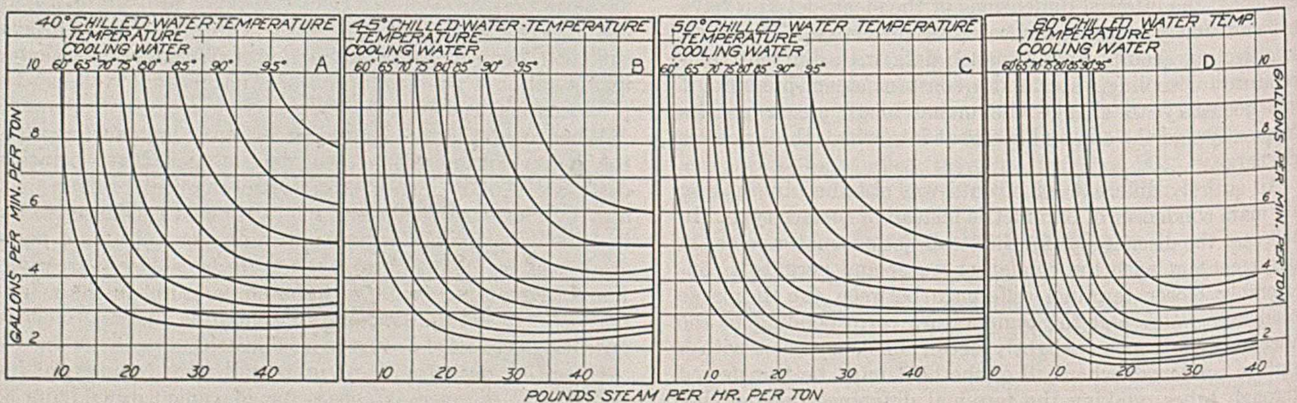


FIGURE 3. OPERATING DATA FROM TEST UNITS AND COMMERCIAL INSTALLATIONS

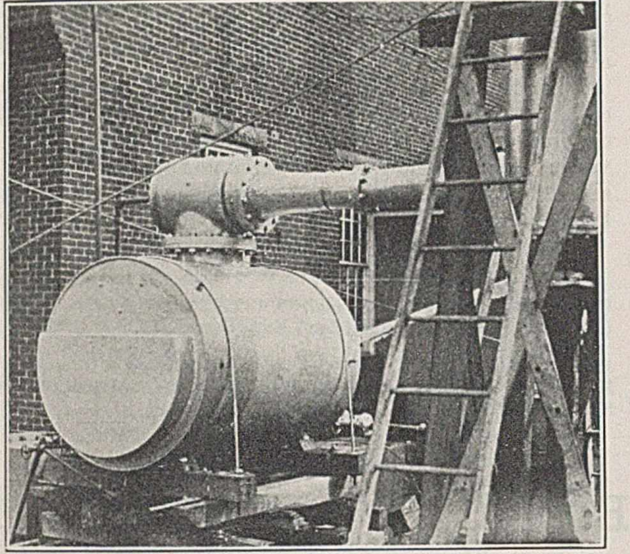
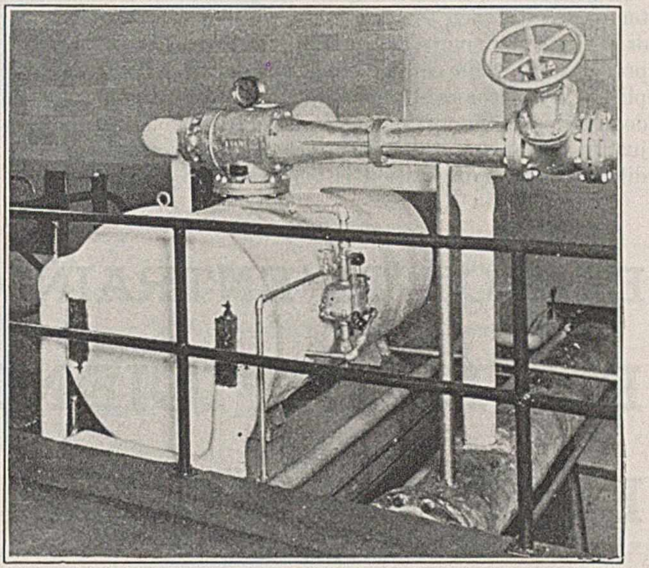


FIGURE 4 (*Left*). EXPERIMENTAL VACUUM REFRIGERATING UNIT WITH SUBMERGED-TUBE INTEGRAL HEAT EXCHANGER

FIGURE 5 (*Below*). VACUUM REFRIGERATING UNIT OF 10 TONS CAPACITY, WITH STEAM-JET EJECTOR



form since conditions of industrial application vary widely. Initial liquor temperatures vary from 220° to 60° F. or even less, and final temperatures down to 15° F. The saving in steam and water consumption on the batch method over the continuous method varies from 50 per cent for large cooling ranges to 10 per cent or less for a cooling range of 10° F.

Indirect Cooling

For fluids which must be cooled without direct contact with vacuum, the vacuum method can still be applied by using any convenient type of heat exchanger. Some of the test results were obtained by submerging a heat-exchanger bundle in the chilled water inside the vacuum evaporating chamber. Figure 4 shows an experimental set-up of this type. This heat exchanger built integral with the vacuum chamber indicated a number of advantages over an external-type heat exchanger in a separate shell: (1) The external heat exchanger requires that water be drawn from the vacuum and pumped through the separate exchanger which involves additional equipment and additional operating cost. (2) The integral heat exchanger has uniform temperature of chilled water and therefore a higher mean temperature difference than in the case of the external heat exchanger where the chilled water is warmed several degrees before it flows back to the vacuum chamber. Some suitable form of agitation in the chilled water may be necessary when using an integral heat exchanger; otherwise, the heat transfer rate would be relatively low. However, in cases where oils or other viscous materials are being handled inside the tubes, the heat transfer rate in the film outside the tubes is not important since there would still be enough thermal circulation to give a better heat transfer rate in the water film outside than there would be in the more viscous film inside with higher velocity.

The integral heat exchanger in the vacuum cooling unit was used on some large commercial work such as chilling lubricating oil in the presence of solvents to remove paraffin and wax. This method was also applied for producing chilled water for industrial process work where it was desirable to maintain the water under its initial pressure without dissipating this pressure in a vacuum chamber.

Applications

Although the largest single application of vacuum cooling is for producing chilled water in air-conditioning, it has also been applied widely to a number of different chemical engineering processes. The most important is doubtless the Swenson process of vacuum crystallization described by Caldwell (*1*). In this case the vacuum serves a double purpose in chilling the mother liquor to temperatures as low as 32° F. and at the same time concentrating it as the chilling progresses, thus increasing the production of crystals. There is further advantage in the fact that the heat is removed from the mother liquor by direct evaporation rather than by being transferred through tubes or metal surfaces, as would be necessary if mechanical refrigeration were used. In the majority of commercial crystallizing operations, the mother liquor is corrosive, which always complicates the heat transfer through metal surfaces. In the vacuum process the crystallizing chamber can be rubber-lined or glass-lined without involving any heat transfer problems, as long as moderate agitation is maintained in the liquor. Most vacuum crystallizing is done on a batch process, although the continuous process is also successful, even though its operating cost is slightly higher in many cases.

Vacuum crystallization is by no means new, although combining it with vacuum refrigeration for subatmospheric temperatures has come only with recent general development in the vacuum refrigerating process. It might also be said that the development of high vacuum crystallizing has in some cases preceded the development of general vacuum refrigeration as the demands of the former process furnished some of the incentive for developing the latter.

The vacuum refrigerating process automatically includes a thorough deaëration or degasification of the liquid being cooled. The drop in temperature of the liquid and the accompanying evaporation of water into large volumes of low-density vapor take out all dissolved gases down to a trace which is usually negligible. This is a decided advantage for many chemical process operations. Dissolved oxygen is frequently the cause of oxidation of chemicals or bacteria growth in miscellaneous liquids. Any possible concentration of dissolved oxygen is entirely removed when a liquid is cooled as much as 10° F. by vacuum evaporation. The same is true of carbon dioxide and many other gases. Some previous data on removal of carbon dioxide by vacuum evaporation at somewhat higher temperatures were published by Jackson and McDermet (*2*).

Preliminary testing on hard water and on carbonated soft water indicates that carbonate removal by vacuum evaporation at low temperatures is practically as efficient as at high temperatures when the evaporation produces a temperature drop of 10° F. or more. There are numerous cases in chemical process work where chilling of various liquids is being accomplished by mechanical refrigeration and where the automatic degasifying action of vacuum refrigeration would more than justify a change to the latter process. There are other conditions where refrigeration is being applied to liquids that must retain certain dissolved gases. In cases of this kind, vacuum cooling can be applied indirectly through tubes or any convenient heat transfer medium.

Preliminary experimental work indicates that vacuum cooling of milk improves its flavor by removing traces of dissolved gases. A pilot plant was installed at Cornell University; experimental work is well under way, and considerable data have been collected. Some of these data will doubtless be published in the near future.

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EFFECT OF ENTRAINMENT ON PLATE EFFICIENCY IN DISTILLATION

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The effect of entrainment in a plate column used for distillation or absorption is to reduce the apparent plate efficiency. This efficiency, E_a, can be calculated by the approximate equation:

$$E_a = \frac{E_v}{1 + \frac{eE_v}{R}}$$

Employing this equation, a relation is developed for the amount of entrainment occurring when the column is operated at the optimum vapor velocity (assuming that the entrainment increases with the fourth power of the velocity): e (at optimum velocity) $= R/3E_v$. Since this value is so high, the importance of large enough down pipes for liquor and of low back pressure through chimneys and caps is emphasized.

THE cost of a plate column for distillation or absorption depends upon both the diameter and height required. The limiting factor in minimizing both of these dimensions by increasing vapor velocity and reducing plate spacing is often the increase of entrainment to a point where the plate efficiency is considerably reduced. To determine the optimum size of column, it is necessary to know both the variation of entrainment with velocity and plate spacing and the effect of a given amount of entrainment on the efficiency. Considerable experimental data have recently been obtained as to the amount of entrainment incurred under various conditions (*1*, *2*, *3*, *5*, *7*). Several theoretical derivations of the effect of entrainment on plate efficiency have been proposed, and the purpose of this study is to carry on these attempts toward a simple relationship which might be generally useful.

Previous Work

The first analysis of the effect of entrainment on plate efficiency was apparently that of Underwood (*8*). He derived Equation 3, expressing the effect of entrainment on the apparent plate efficiency E_a, for the case of total reflux and a dry vapor (Murphree) efficiency, E_v, = 1.0.

Starting from the definition of apparent plate efficiency, E_a,

$$E_a = (Y_n - Y_{n-1})/(y^*_n - Y_{n-1}) \quad (1)$$

where Y_n and Y_{n-1} are apparent values of the composition of vapor leaving the nth and $n-1$th plates, respectively, defined for total reflux, as

$$Y_{n-1} = x_n,\ Y_n = x_{n+1} \quad (2)$$

and where y^*_n is the vapor composition in equilibrium with x_n, and x_n is the composition of liquid leaving the nth plate, Underwood obtained:

$$E_a = 1/(1 + e) \quad (\text{for } E_v = 1,\ L/V = 1) \quad (3)$$

Souders and Brown (*6*) sought an expression for plate efficiency for the general case of any reflux ratio and any vapor efficiency. Their definition of plate efficiency demands a different operating line for each different quantity of entrainment, so that numerical values are not directly comparable with values of plate efficiency based on an operating line determined from a heat balance. That is, Souders and Brown consider the average composition of the dry vapor and entrained liquor entering and leaving a given plate. Defining this quantity as z, the special operating line is defined by the equation,

$$(V + eV)z_n = (L + eV)x_{n+1} + (V - L)x_d \qquad (4)$$

Their definition of plate efficiency, E_S, becomes:

$$E_S = (z_n - z_{n-1})/(y^*_n - z_{n-1}) \qquad (5)$$

Souders and Brown's general equation includes, instead of vapor efficiency, the term $f = y_n/y^*_n$, which is not an explicit function of vapor efficiency but requires also the knowledge of x_n and y_n. These features do not apply to their simplified relation for the case of vapor equilibrium and total reflux, which becomes Equation 3 obtained by Underwood.

Rhodes (*4*) introduced the procedure of applying an efficiency factor to the horizontal step on the distillation diagram to take care of the effect of entrainment. Thus he utilizes a new term E_x, defined as:

$$E_x = \frac{(x_{n+1} - x_n)}{(x'_{n+1} - x_n)} \qquad (6)$$

where x_{n+1} is the actual composition of liquid leaving the $n+1$th plate, and x'_{n+1} is the composition if there were no entrainment. His derivation is developed for the case of equilibrium vapor, although it holds also for the general case. It can be seen by geometry that for the equilibrium case, $E_x = E_a$.

The derivation results in the following equation:

$$E_x = \frac{1}{1 + (e/R)} = \frac{R}{R + e} = \frac{L}{L'} \qquad (7)$$

In case of total reflux and $E_v = 1$ (when $E_a = E_x$), Equation 7 reduces to Equation 3 of Underwood. While this relation is admirable for use in designing a column with set conditions, it requires a complete design to find the effect of a certain amount of entrainment. For general estimating purposes, it would be more desirable to have a simple relation between apparent efficiency and entrainment.

Sherwood and Jenny (*5*) recommend the use of the original material balance equation (Equation 8) in conjunction with the definition of E_v to calculate, successively, vapor and liquid compositions up the column. They also demonstrate a graphical application of these equations on a McCabe and Thiele diagram, which is an alternative to the method of Rhodes. These authors also derived an equation for calculating the amount of color or other nonvolatile impurity in the distillate owing to successive entrainment through the plates.

Apparent Efficiency Related to Liquid Compositions

In case of no entrainment the general material balance relating the amount of low boiler in the vapor leaving the nth plate of a column to that in the liquid reflux entering this plate is customarily written:

$$Vy_n = Lx_{n+1} + (V - L)x_d \qquad (8)$$

In case of entrainment, the vapor stream will carry along eV moles of liquid of composition, x_n, and the reflux will be increased by eV moles. Thus the general material balance considering entrainment is:

$$Vy_n + eVx_n = (L + eV)x_{n+1} + (V - L)x_d \qquad (8a)$$

Dividing through by V and noting that $L/V = R$:

$$y_n + ex_n = (R + e)x_{n+1} + (1 - R)x_d \qquad (8b)$$

This equation can be directly utilized to calculate the composition of liquid leaving the $n+1$th plate from a known value of x_n and a value of y_n calculated using the proper value of dry vapor efficiency. A more convenient procedure is not to determine actual vapor compositions but to consider an apparent efficiency, E_a, to be based upon apparent vapor compositions, Y. Thus,

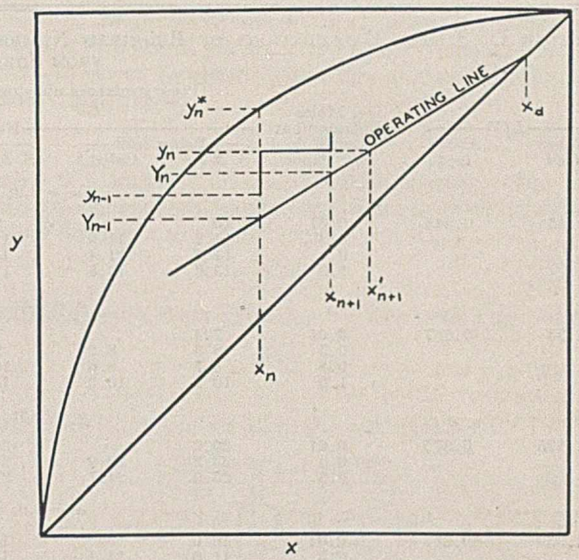

FIGURE 1. COMPARISON OF DESIGN PROCEDURES

BY USE OF E_a:
Given intersection of Y_{n-1} with normal operating line. Vertical step, $Y_n - Y_{n-1}$, is constructed as $E_a \times$ the distance $y^*_n - Y_{n-1}$; Y_n is then extended horizontally to intersect normal operating line.

BY USE OF E_v AND $1/[1+(e/R)]$:
Vertical step $y_n - y_{n-1}$, is constructed as $E_v \times$ the distance, $y^*_n - y_{n-1}$. The horizontal step, $x_{n+1} - x_n$, is made equal to $1/[1+(e/R)] \times$ the distance, $x'_{n+1} - x_n$. This is the method of Rhodes (*4*).

$$VY_n = Lx_{n+1} + (V - L)x_d \qquad (9)$$

and dividing through by V,

$$Y_n = Rx_{n+1} + (1 - R)x_d \qquad (9a)$$

In case of no entrainment, Equation 9 is the usual operating equation with y_n in place of Y_n. As a matter of interest, by comparing Equations 8a and 9, the exact significance of Y is found to be:

$$Y_n = y_n - e(x_{n+1} - x_n) \qquad (10)$$

From Equation 9,

$$E_a = \frac{Y_n - Y_{n-1}}{y^*_n - Y_{n-1}} = \frac{R(x_{n+1} - x_n)}{y^*_n - Rx_n - (1 - R)x_d} \qquad (11)$$

Given the value of E_a, x_{n+1} can be calculated from x_n by use of Equation 11 without needing to calculate the value of vapor composition. Also the values of E_a can be applied directly on a McCabe and Thiele diagram as indicated by Figure 1.

Vapor Efficiency Related to Liquid Compositions

Substituting Equation 8b and an analogous one for y_{n-1} in the definition of dry vapor efficiency, E_v, gives:

$$E_v = \frac{y_n - y_{n-1}}{y^*_n - y_{n-1}} = \frac{R(x_{n+1} - x_n) + e[(x_{n+1} - x_n) - (x_n - x_{n-1})]}{y^*_n - Rx_n - (1 - R)x_d - e(x_n - x_{n-1})} \qquad (12)$$

For the bottom plate, if there is no entrainment from the still, the term $e(x_n - x_{n-1})$ is omitted from Equation 12. For the top plate, if there is no entrainment from it, the term $e(x_{n+1} - x_n)$ is omitted.

TABLE I. SAMPLE CALCULATIONS OF REQUIRED NUMBER OF PLATES WITH VARIOUS AMOUNTS OF ENTRAINMENT (EXPANDED FROM SHERWOOD AND JENNY, *5*)

(Binary mixture obeying Raoult's law: $E_v = 0.5$; $x_f = 0.50$)

L/V		*e*, Moles Entrainment per Mole Dry Vapor	Number of Plates						Ratio Total Plates to Total with No Entrainment	Relative Vapor Velocity, *u*	Relative Column Volume N'/u
Below feed	Above feed		Below feed S. & J.[a]	Below feed Calcd.[b]	Above feed S. & J.[a]	Above feed Calcd.[b]	Total, N' S. & J.[a]	Total, N' Calcd.[b]			
			$\alpha = 3.0$; $x_d = 0.95$; $x_w = 0.05$								
1.45	0.545	0.01	10		9.6		19.6		1.0	1.0	19.6
		0.3	11.2	11.0	12.4	12.1	23.6	23.1	1.2	2.34	10.1
		0.4	11.7	11.4	13.0	13.1	24.7	24.5	1.26	2.51	9.8
		1.0	13.6	13.3	18.4	18.4	32.0	31.7	1.63	3.16	10.1
			$\alpha = 3.0$; $x_d = 0.95$; $x_w = 0.05$								
1.33	0.667	0.01	7.4		7.6		15.0		1.0	1.0	15.0
		0.3	8.3	8.2	9.2	9.3	17.5	17.5	1.17	2.34	7.5
		0.5	8.7	8.8	10.4	10.4	19.1	19.2	1.27	2.66	7.2
		1.0	10.2	10.2	13.4	13.3	23.6	23.5	1.57	3.16	7.5
			$\alpha = 1.5$; $x_d = 0.95$; $x_w = 0.05$								
1.125	0.875	0.01	20.2		20.2		40.4		1.0	1.0	40.4
		0.3	23.2	22.9	24.8	23.7	48.0	46.6	1.19	2.34	20.5
		0.5	25.0	24.7	27.0	26.0	52.0	50.7	1.29	2.66	19.5
			$\alpha = 3.0$; $x_d = 0.98$; $x_w = 0.02$								
1.33	0.667	0.01	10.0		11.0		21.0		1.0	1.0	21.0
		0.3	11.0	11.1	13.0	13.5	24.0	24.6	1.14	2.34	10.2
		1.0	13.5	13.7	19.5	19.3	33.0	33.0	1.57	3.16	10.4
			$\alpha = 3.0$; $x_d = 0.90$; $x_w = 0.10$								
1.33	0.667	0.01	5.1		5.2		10.3		1.0	1.0	10.3
		0.3	5.6	5.65	6.4	6.4	12.0	12.05	1.16	2.34	5.1
		1.0	7.0	7.0	9.1	9.1	16.1	16.1	1.56	3.16	5.1

[a] Calculated in steps by Sherwood and Jenny (*5*) by use of Equation 8.

[b] Calculated by means of Equation 19.

Apparent Efficiency Related to Vapor Efficiency

Substituting for Y_n and Y_{n-1} in Equation 11 their values as given by equations represented by Equation 10 gives:

$$E_a = \frac{y_n - y_{n-1} - e[(x_{n+1} - x_n) - (x_n - x_{n-1})]}{y^*_n - y_{n-1} + e(x_n - x_{n-1})} \tag{13}$$

For purposes of simplification let

$$k = (x_{n+1} - x_n) - (x_n - x_{n-1}) \tag{14}$$

Then Equation 13 becomes:

$$E_a = \frac{y_n - y_{n-1} - ek}{y^*_n - y_{n-1} + e(x_{n+1} - x_n) - ek} \tag{15}$$

From material balance equations for the *n*th and *n*−1th plates, represented by Equation 8b for the *n*th plate, there is obtained:

$$x_{n+1} - x_n = \frac{y_n - y_{n-1}}{R} - \frac{ek}{R} \tag{16}$$

Substituting this value of $x_{n+1} - x_n$ in Equation 15 gives:

$$E_a = \frac{y_n - y_{n-1} - ek}{y^*_n - y_{n-1} + \frac{e(y_n - y_{n-1})}{R} - \frac{e^2k}{R} - ek} \tag{17}$$

Dividing numerator and denominator by $y^*_n - y_{n-1}$:

$$E_a = \frac{\frac{y_n - y_{n-1}}{y^*_n - y_{n-1}} - \frac{ek}{y^*_n - y_{n-1}}}{1 + \frac{e(y_n - y_{n-1})}{R(y^*_n - y_{n-1})} - \frac{ek(e + R)}{R(y^*_n - y_{n-1})}} \tag{17a}$$

Substituting E_v for $(y_n - y_{n-1})/(y^*_n - y_{n-1})$:

$$E_a = \frac{E_v - \frac{ek}{y^*_n - y_{n-1}}}{1 + \frac{eE_v}{R} - \frac{ek(e + R)}{R(y^*_n - y_{n-1})}} \tag{18}$$

The term *k* represents the difference in successive *x* increments and will be very small unless the slopes of the operating and equilibrium curves are widely different. It is further observed that the term involving *k* in the numerator will affect the value of E_a in the opposite direction from that in the denominator, so that the effect of dropping them both will be a minimum change in the value of the fraction.

Hence for all but extreme precision, Equation 18 simplifies to:

$$E_a = \frac{E_v}{1 + \frac{eE_v}{R}} \tag{19}$$

For $E_v = 1$, this simplifies to the ratio obtained by Rhodes, and for $E_v = 1$, $R = 1$, it becomes Equation 3 of Underwood. Equation 19 shows, as brought out by Souders and Brown (*6*), that the higher the reflux ratio, the more entrainment can be tolerated.

An example has been solved to find the exact difference in values of E_a as calculated by the exact and approximate equations, for conditions where the equilibrium and operating lines are not parallel. The conditions chosen are: total reflux ($R = 1$) in which case the slope of the operating line is unity, and a straight line for the equilibrium curve with a slope of 2. Thus the angle between the two lines is 18.5°; $E_v = 0.75$; $e = 0.5$. At a value of $x_n = 0.3$, ek is found from a McCabe and Thiele diagram to be 0.026 and $y^*_n - y_{n-1}$ to be 0.25. Then by Equation 18, $E_a = 0.53$ and by Equation 19, $E_a = 0.545$. The error in using the approximate equation is thus only 3 per cent, which is well within the usual uncertainty in values of E_v and e.

A set of curves is given by Figure 2 to represent Equation 19, and the slopes of the curves indicate that the proportionate effect of entrainment is greater the higher the dry vapor efficiency.

While E_a should properly be applied in each vertical step, the approximate procedure of stepping off the required number of perfect plates and dividing that number by E_a might have occasion to be used. To show that in many cases this procedure is reasonably accurate, additional columns have been added to the table of Sherwood and Jenny (*5*) (Table I), in which the number of plates with entrainment is computed from the number with negligible (1 per cent) entrainment by multiplying by the ratio, E_v/E_a, as obtained from Equation 19.

Consideration of Average Liquid Composition

Equation 19, as well as the equations of Underwood and of Rhodes, is based on the assumption that the entrained liquid carried onto a plate is of the same composition as the liquid leaving the plate from which it is entrained. There are two ways in which conditions do not fulfill this assumption, but they fortunately tend to counterbalance: (1) The composition of liquid on any plate is greater in low-boiling content than the exit composition, so that the liquid carried upward is richer than the exit liquid. (2) As the entrained drops are carried upward, transfer between vapor and the liquid drops presumably continues, thereby reducing the low-boiler content of the drops. The exact evaluation of these two effects cannot be readily made, although it is apparent that they tend to counterbalance each other; for the present, therefore, there is justification for accepting the above assumption at least as a first approximation.

Economic Velocity

Although the vapor velocity in a plate column is usually maintained below the point where appreciable entrainment occurs because of the danger of loading caused by surges in the boil-up, it is of general interest to calculate how high it is economical to raise the vapor velocity. That is, at what point does the cost of increased number of plates (required because of lowered efficiency) counterbalance the saving in column cross-sectional area?

For a given plate spacing, experimental entrainment data can be approximately correlated according to the equation:

$$e = au^n \qquad (20)$$

where a and n are constants for any given column over the considered range of velocities. The cost, C, of the column is assumed to be proportional to the cross-sectional area, A, and to the number of plates; the number of plates is equal to the number of theoretical plates, N, divided by the plate efficiency, E_a. Thus,

$$C = bAN/E_a \qquad (21)$$

where b is a constant for a given plate spacing. Now the cross-sectional area can be expressed in terms of the quantity of vapor flowing in unit time:

$$A = V/u \qquad (22)$$

Substituting for u from Equation 20, and letting $m = 1/n$:

$$A = \frac{Va^m}{e^m} \qquad (23)$$

Substituting for A and for E_a in the cost equation:

$$C = \left[\frac{bNVa^m}{e^m}\right]\left[\frac{1 + eE_v/R}{E_v}\right] \qquad (24)$$

or

$$C = bNVa^m\left[\frac{1}{E_v\, e^m} + \frac{e^{1-m}}{R}\right] \qquad (25)$$

The rate of change of cost with entrainment is then found,

$$\frac{dC}{de} = bNVa^m\left[-\frac{m}{E_v e^{1+m}} + \frac{1-m}{Re^m}\right] \qquad (26)$$

For the minimum cost, $dC/de = 0$, and

$$-\frac{m}{E_v\, e^{1+m}} + \frac{1-m}{Re^m} = 0 \qquad (27)$$

Solving for the value of e which corresponds to the minimum cost and replacing $1/n$ for m:

$$e_{\text{opt.}} = R/(n-1)E_v \qquad (28)$$

In some cases the exponent n has been found to be 4. For these cases Equation 28 becomes:

$$e_{\text{opt.}} = R/3E_v \qquad (29)$$

A small error may be made in the value assumed for n without affecting appreciably the final value of $e_{\text{opt.}}$.

Thus it is economic to design a column to operate at such high velocities that even considerable entrainment occurs. For example, for a reflux ratio $R = 0.8$, $n = 4$, and $E_v = 0.8$, the optimum velocity is that causing an entrainment of 0.33 mole of liquid per mole of vapor. Down pipes may not be large enough to take care of the additional liquid, and the column may load. Because of the rapid rate of increase of entrainment with vapor velocity, it is not advisable to operate too near the loading point, and hence it is believed advisable to design for velocities somewhat less than the optimum from the standpoint of plate efficiency. The main interest in Equation 29 is therefore the variables involved rather than the numerical values.

A practical conclusion which may be drawn is that, when it is desired to push a column to its highest capacity, it will probably be found that the limiting factor is not an excessive falling-off in efficiency of separation, but loading. This may be caused either by the inability of the down pipes to take care of the high liquid load augmented by entrainment or by an excessive pressure drop due to friction in the slots of the bubbler caps over and above the liquid head in the down pipes. For this reason it is recommended that whenever possible the down pipes and bubbler caps be designed for an excess load so that columns may be pushed to a maximum in case of necessity.

Based on the assumptions that the entrainment is proportional to the fourth power of the linear vapor velocity and that the cost of the column is proportional to the number of plates and to the cross-sectional area of the column, the rela-

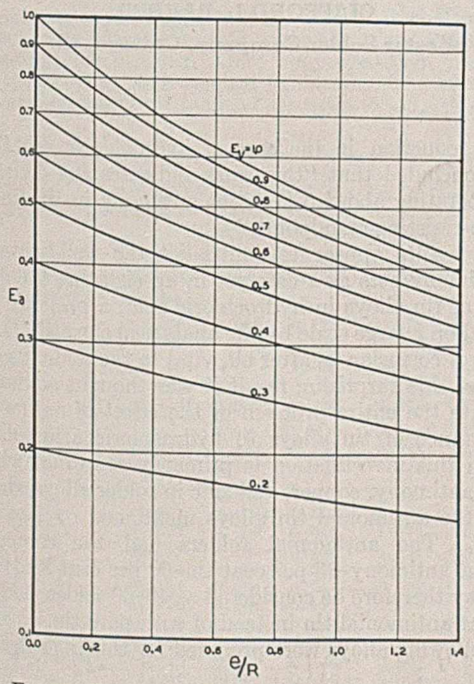

Figure 2. Relation of Apparent Plate Efficiency, E_a, to Dry Vapor Efficiency, E_v, Moles Entrainment per Mole Dry Vapor, e, and the Reflux Ratio, $R = L/V$, by Equation 18

tive column volumes were calculated for the conditions in the cases calculated by Sherwood and Jenny. The results are given in Table I. They show that, while the number of plates necessary for a given separation increases as the increase in entrainment cuts down the efficiency, the increased vapor velocity tends to cut down the column volume by decreasing the cross-sectional area. The relative column volume, N'/u, therefore passes through a minimum which is shown in Table I to correspond approximately to an entrainment of 0.4 mole of liquid per mole vapor, as predicted by Equation 29.

Acknowledgment

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Nomenclature

R = L/V = reflux ratio
V = moles of dry vapor per hour
L = moles of reflux (exclusive of entrainment) per hour
L' = total liquid overflow (including entrainment) per hour
e = moles of entrained liquid per mole of dry vapor
C = cost of column
N = no. of theoretical plates
N' = no. of actual plates
A = cross-sectional area
x_n = mole fraction of low boiler in liquid leaving nth plate
x_d = mole fraction of low boiler in product
x_f = mole fraction of low boiler in feed
y_n = mole fraction of low boiler in dry vapor leaving nth plate
y^*_n = mole fraction of low boiler in dry vapor in equilibrium with x_n
Y_n = apparent composition of vapor when entrainment occurs, as defined by Equation 9 or 10
z_n = av. mole fraction of low boiler in vapor and entrained liquid leaving nth plate
E_a = apparent plate efficiency, defined by Equation 11
E_v = dry vapor (or Murphree) efficiency, defined by Equation 12
E_s = entrainment efficiency applied to liquid concentration steps, defined by Equation 6
E_S = special efficiency used by Souders and Brown, defined by Equation 5
x'_n = apparent value of x_n, defined by Equation 6
u = vapor velocity, moles per unit time and unit cross-sectional area
α = relative volatility, $= y^*(1 - x)/(1 - y^*)x$

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Effect of Impurities on Corrosion Resistance of—

SOLDER

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THE effect of impurities on solder has long been the subject of controversy. Unfortunately, nearly all the practical questions dealing with solder appear to remain indefinitely suspended in a realm of speculation, fancy, or superstition, and only rarely do they ever descend to that plane of realism where they are finally stripped of their veil of secrecy and examined in the cold light of experimental measurement. A notable example is the effect of certain impurities, particularly antimony, on the corrosion resistance of solder—an example illustrating the prevailing tendency for much popular discussion but little experimentation.

The question of the effect of antimony on the corrosion of tin and its alloys was, however, investigated by Hoar (*2*), who compared the corrosion resistance of rolled pure tin with that of 5 per cent antimonial tin partly immersed in 0.1 *M* hydrochloric and citric acids and certain tap waters. Hoar observed that "the addition of 5 per cent antimony to tin is usually beneficial from the point of view of resistance to corrosion by the liquids used" and that "there is a slight reduction in the attack by citric acid in the presence of air and a marked reduction in the case of hydrochloric acid." He finally concluded that "this work indicates the desirability of incorporating about 5 per cent antimony in tin from the corrosion-resisting standpoint."

These results appear to contradict the well-known fact that antimony acts as a catalyst in accelerating the decomposition of tin alloys in hydrochloric acid, a principle which is utilized on a large scale by the analytical chemist (*1*). The question of corrosion is, after all, vital to the solder user, and in view of this surprising result it was thought advisable to investigate the entire problem of the effect of antimony on the resistance of tin alloys to hydrochloric acid solutions. Although this investigation is primarily concerned with the effect of antimony, copper, and zinc in solder alloys, the pure tin and the antimonial tin alloys mentioned by Hoar were included. The antimonial solders had the composition 2 per cent antimony–38 per cent tin–60 per cent lead; these alloys may therefore be considered as 40–60 solder made with 5 per cent antimonial tin instead of with pure tin.

The following alloys were prepared for this investigation:

1. These samples were poured bars machined down in a lathe to a perfect cylinder:

Pure tin	100% Sn
Antimonial tin	5% Sb–95% Sn

In one set of samples the cylinder was 81 mm. long and 10.1 mm. in diameter and had a surface of about 2800 sq. mm.; in another set the dimensions were 85 × 13.7 mm. and the total surface was about 4000 sq. mm.

2. These alloys were poured bars machined down in a lathe to a cylinder 65 mm. long, 12.7 mm. thick, and 2900 sq. mm. in total surface:

Tin-lead alloys	40% Sn-60% Pb
Antimony-tin-lead alloys	2% Sb-38% Sn-60% Pb
Copper-tin-lead alloys	0.5% Cu-39.5% Sn-60% Pb
Zinc-tin-lead alloys	0.5% Zn-39.5% Sn-60% Pb

3. These alloys were rectangular extruded bars, 8.7 mm. square, 118 mm. long, and 4200 sq. mm. in total surface:

Tin-lead alloys	40% Sn-60% Pb
Antimony-tin-lead alloys	2% Sb-38% Sn-60% Pb

This list includes an assortment of extruded and poured bars; these are the forms in which solder is actually made. (The rolled alloys mentioned by Hoar are not produced commercially to any extent.) Since it is obvious that the weight loss of a sample is a function of the surface exposed, it was necessary to machine down the irregular poured bars to a definite geometric form in order to measure their surfaces.

"Chempur" tin of 99.99 per cent purity (containing about 0.003 per cent antimony) and electrolytic lead of 99.99 per cent purity were used throughout all tests.

Continuous Immersion Test

The first test was to compare the solution rate of antimonial solder with that of nonantimonial solder continuously immersed in various concentrations of hydrochloric acid, and also to compare the solution rate of pure tin with that of antimonial tin in 0.1 *M* hydrochloric acid.

First, seven samples of 40-60 extruded bars were stamped with the odd numbers 1, 3, 5, 7, 9, 11, and 13; at the same time seven samples of the 2-38-60 bars were stamped with the even numbers 2, 4, 6, 8, 10, 12, and 14. There were therefore seven pairs of samples, each pair consisting of one antimonial and one nonantimonial solder. An eighth pair was added by selecting cylinders of pure and of antimonial tin; these were stamped 17 and 18, respectively (Table I). In all tests, pairs were made up from samples of the same size.

All samples were polished a little with steel wool, washed in soap and water followed by cold water alone, and finally washed repeatedly in hot distilled water; they were then dried with a cloth, cooled in air, and weighed (Table I). The samples were then placed separately, in inclined positions, in tall, 1-liter bottles. Seven concentrations of hydrochloric acid were then prepared ranging from 36 to 0.36 per cent (0.1 *M*); these were added to the bottles in such manner that both samples comprising any one pair were exposed to acid of the same strength, but so that each individual pair was exposed to acid of different strength, each sample being immersed in about 1 liter of liquid. [An exception is that 0.36 per cent (0.1 *M*) hydrochloric acid was used for the high-tin pair and also for one of the solder pairs.] The bottles were then covered with a watch glass and allowed to stand at room temperature. After the acid had reacted for a desired period on any pair, the acid was discarded, the samples were removed, washed well in hot water, dried, cooled, and weighed as before, and the weight loss was noted. The samples were then replaced in the bottles and fresh acid was added as before. The results are summarized in Table I.

TABLE I. RELATIVE SOLUTION RATES OF PURE AND IMPURE SOLDERS IN HYDROCHLORIC ACID SOLUTIONS (CONTINUOUS IMMERSION)

Sample[a]	HCl Reagent Per cent	Original Weight Grams	Loss, Grams 1 hr.	2 hr.	3 hr.	4 hr.	5 hr.	Difference Per cent
1(P)	36	82.818	0.068	0.178	0.337	0.516	0.830	
2(I)		80.529	1.266	6.136	11.746	16.344	21.596	2500
			4 hr.	22 hr.	40 hr.	45 hr.	60 hr.	
3(P)	24	83.697	0.037	0.091	0.160	0.219	0.314	
4(I)		81.414	0.059	0.325	4.266	12.444	23.721	7500
			4 days	7 days	9 days	12 days	18 days	
5(P)	18	82.774	0.118	0.167	0.241	0.313	0.441	
6(I)		80.538	0.150	0.278	0.618	1.745	18.318	4000
			1 wk.	4 wk.	8 wk.	20 wk.	26 wk.	
7(P)	9	82.593	0.104	0.510	1.395	5.993	7.733	
8(I)		81.027	0.099	0.544	1.433	6.317	12.707	64
9(P)	4	82.378	0.100	0.454	1.221	5.119	6.658	
10(I)		80.771	0.101	0.494	1.367	5.330	7.701	16
11(P)	1	83.102	0.084	0.341	0.894	....	....	
12(I)		81.090	0.084	0.411	1.058	....	....	18
13(P)	0.36	82.672	0.072	0.226	0.551	1.460	....	
14(I)		80.705	0.070	0.240	0.558	1.452	....	None
17(P)	0.36	75.142	0.062	0.149	0.302	0.910	....	
18(I)		74.944	0.062	0.150	0.303	0.911	....	None

[a] Samples 1 to 14, rectangular extruded bars, 8.7 × 8.7 × 118 mm.; odd numbers, 40-60 (Sn-Pb); even numbers, 2-38-60 (Sb-Sn-Pb). Samples 17 and 18, machined cylindrical poured bars 10.1 × 81 mm.; 17, pure tin; 18, 95-5 (Sn-Sb). P = pure; I = impure.

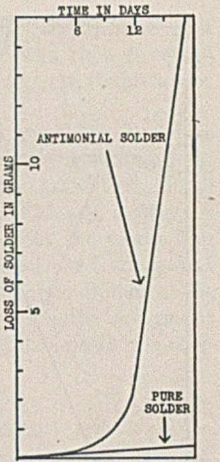


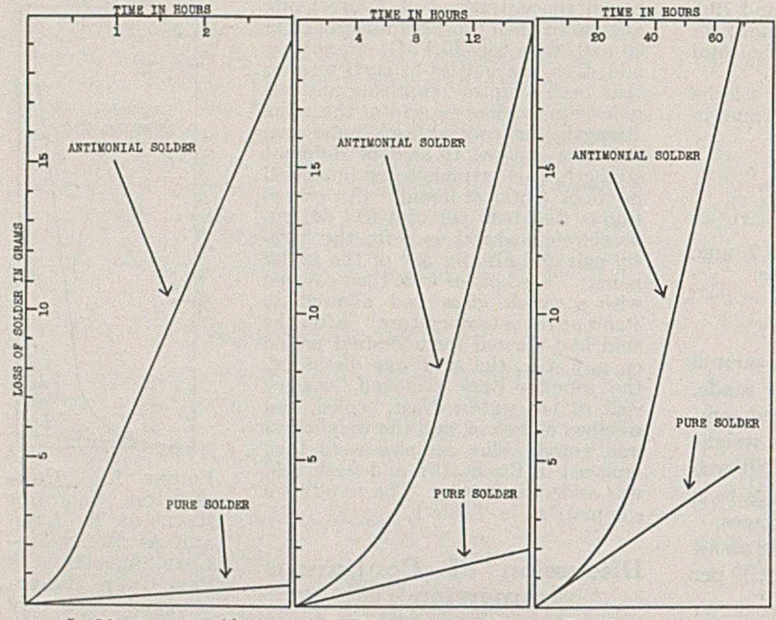
FIGURE 1. COMPARATIVE SOLUTION RATES OF TIN-LEAD AND ANTIMONY-TIN-LEAD SOLDERS IN 18 PER CENT HYDROCHLORIC ACID BY CONTINUOUS IMMERSION

Discussion of Continuous Immersion Test

In this continuous immersion test the antimonial solder dissolves 16 to 7500 per cent faster than the nonantimonial in solutions where the hydrochloric acid content is 1 per cent or greater. The general shape of a typical decomposition curve is particularly significant (Figure 1). For the first 9 days the extreme difference in solution rates is about 250 per cent. During the next 9 days, however, something seems to "break," and during this period the difference jumps from 250 to 4000 per cent. Attention may also be called to the behavior of the samples in 9 per cent acid. At the end of a week the antimonial solder has lost less than the straight 40-60, but by the end of 26 weeks, it has lost 64 per cent more. These significant facts perhaps account for much of the disagreement and discrepancies among various workers. Probably certain investigators have been led to false conclusions because they did not carry their tests over a sufficiently long period.

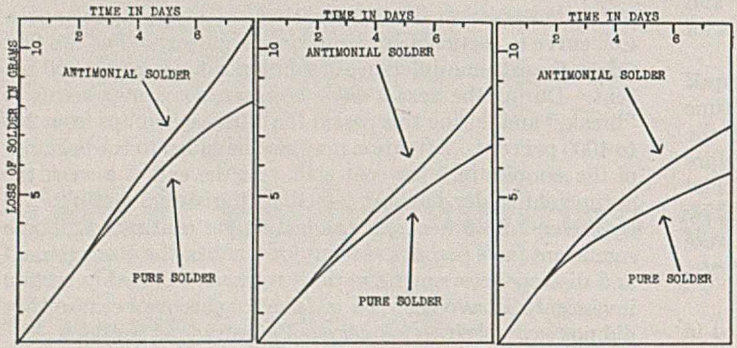
Although a completely satisfactory explanation of the phenomenon is not available at present, it appears most plausible that there was originally a film of oxide on the surface of the solder and that the corroding agent broke through this protective film relatively slowly. Although all samples were polished just prior to weighing and immersion, there is a possibility that the process of polishing only "flowed" oxide-trapped metal over the surface of the sample. This would cause all samples to show similar behavior during the first period of immersion. There is also a possibility that some investigators compared freshly manufactured samples with older ones covered with heavier oxide films, and that they did not take into account the greater resistance to corrosion which the older sample would naturally offer. Throughout the investigation, all samples comprising any one pair were produced at the same time and under the same conditions.

Turning now to the case of the weaker solutions (0.36 per cent), there is no appreciable difference in the solution rates of the antimonial and the nonantimonial metals. In order to understand this, it will be necessary to consider for a moment the mechanism of the reaction between hydrochloric acid and an antimonial metal. The acid first exerts a slight solvent



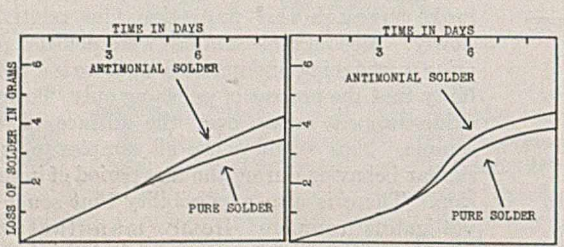
In 36 per cent acid In 24 per cent acid In 18 per cent acid

FIGURE 2. COMPARATIVE SOLUTION RATES OF TIN-LEAD AND ANTIMONY-TIN-LEAD SOLDERS IN HYDROCHLORIC ACID BY INTERMITTENT IMMERSION



In 9 per cent acid In 4 per cent acid In 1 per cent acid

FIGURE 3. COMPARATIVE SOLUTION RATES OF TIN-LEAD AND ANTIMONY-TIN-LEAD SOLDERS IN HYDROCHLORIC ACID BY INTERMITTENT IMMERSION



In 0.36 per cent (0.1 *M*) hydrochloric acid In 0.1 *M* citric acid

FIGURE 4. COMPARATIVE SOLUTION RATES OF TIN-LEAD AND ANTIMONY-TIN-LEAD SOLDERS IN HYDROCHLORIC ACID BY INTERMITTENT IMMERSION

action on the tin or lead, leaving untouched the black flakes of precipitated antimony which are insoluble in pure hydrochloric acid. Actually the acid contains small amounts of dissolved oxygen which cause some of the antimony to go into solution, thus forming a catalyst which actively accelerates further solvent action. In case the acid is very weak, the solution action is very feeble and the flakes of metallic antimony are only precipitated on the surface of the metal, requiring more oxygen for their solution than would be the case in a stronger acid. Gradually the surface of the metal becomes covered with a protective coating of metallic antimony which is insoluble in hydrochloric acid. As long as the sample is immersed in the liquid or otherwise kept away from air or as long as the protective film is not broken or ruptured, the solution action may be no greater than that of pure solder.

Intermittent Immersion Test

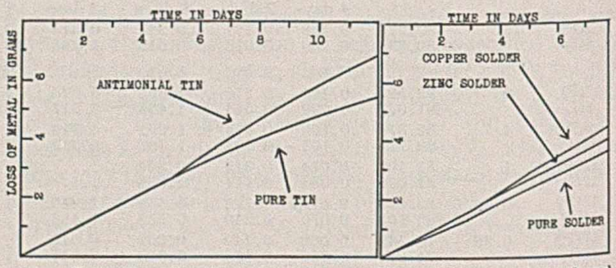
Of course, such an ideal condition is seldom realized in commercial practice, and actual solder is continually exposed to air. Actual conditions would be more closely approximated if the sample were exposed simultaneously to the action of acid and air or if it were exposed intermittently to these two agents.

An apparatus was therefore built which would continually lower and raise a sample into a liquid and out of it, thus subjecting the sample to alternate immersion and emersion. The apparatus consisted essentially of a multiple rocker arm arrangement operated by an electric motor. From the end of each rocker arm was suspended a small steel ring mounted in a bearing. In order to attach the metal sample to the rocker arm a strand of wire of the same composition as the sample was inserted through a hole drilled in the end of the sample and then to the steel ring at the end of the rocker arm. As the latter moved up and down, the sample traveled in and out of the liquid, and any friction, due to the fact that the rocker arm described a small arc, was absorbed in the bearing. The sample therefore always hung vertically, and there was no wear on it due to friction. The speed of travel was such that a sample underwent one complete immersion every 10 seconds.

The experimental procedure used to illustrate comparative solution rates of antimonial and nonantimonial metals intermittently immersed in the corroding liquid differed essentially from the previous test only in this method and manner of immersion. Larger bottles, however, were used and samples were immersed in 2 liters of liquid instead of 1. Samples 1 to 16 involved eight pairs of antimonial and nonantimonial solders, and samples 17 and 18 a pair consisting of tin and antimonial tin. Samples 19, 20, and 21 involved the tin-lead, copper-tin-lead, and zinc-tin-lead alloys previously described (Table II). The corroding agent used was hydrochloric acid in all cases except that of samples 15 and 16, where 0.1 *M* citric acid was used.

Discussion of Intermittent Immersion Test

The results of the intermittent immersion test are summarized in Table II. The antimonial solders dissolve from 21 to 2370 per cent faster under these conditions than pure solder, and the antimonial tin dissolves 24 per cent faster



Pure tin and antimonial tin Tin-lead, copper-tin-lead, and zinc-tin-lead solders

FIGURE 5. COMPARATIVE SOLUTION RATES IN 0.36 PER CENT (0.1 *M*) HYDROCHLORIC ACID BY INTERMITTENT IMMERSION

Table II. Relative Solution Rates of Pure and Impure Solders in Hydrochloric Acid Solutions (Intermittent Immersion)

Sample[a]	HCl Reagent	Original Weight	Loss, Grams						Difference
			0.5 hr.	1 hr.	1.5 hr.	2 hr.	2.5 hr.	3 hr.	
	Per cent	*Grams*							*Per cent*
1(P)	36	81.976	0.126	0.240	0.380	0.485	0.615	0.773	
2(I)		79.594	1.902	5.124	8.669	11.621	14.680	19.106	2370
			2 hr.	4 hr.	6 hr.	12 hr.	16 hr.		
3(P)	24	82.217	0.233	0.455	0.687	1.436	1.918	....	
4(I)		79.803	0.518	1.225	2.185	10.798	19.602	....	922
			10 hr.	20 hr.	30 hr.	40 hr.	50 hr.	70 hr.	
5(P)	18	82.552	0.950	1.598	2.115	2.771	3.422	4.796	
6(I)		79.422	0.915	1.713	3.443	7.006	10.022	20.493	327
			2 days	3 days	4 days	5 days	6 days	8 days	
7(P)	9	80.591	2.590	3.838	4.873	5.982	6.796	8.071	
8(I)		79.614	2.496	4.017	5.264	6.658	7.617	10.573	31
9(P)	4	80.755	2.357	3.148	4.053	4.854	5.406	6.648	
10(I)		79.411	2.341	3.427	4.384	5.462	6.250	8.584	29
11(P)	1	82.071	2.545	...	...	4.158	....	5.802	
12(I)		79.437	2.785	...	...	5.301	....	7.386	27
			4 days	6 days	9 days				
13(P)	0.36	74.132	1.818	2.772	3.420	....	....	....	
14(I)		73.725	1.690	3.360	4.144	....	....	....	21
15(P)	[b]	74.205	1.366	3.082	3.938	....	....	....	
16(I)	[b]	74.402	1.312	3.457	4.392	....	....	....	12
			2 days	5 days	8 days	10 days	12 days		
17(P)	0.36	89.372	1.127	2.517	3.930	4.722	5.436	....	
18(I)		90.517	1.065	2.691	4.393	5.681	6.749	....	24
			3 days	5 days	8 days				
19(I)	0.36	76.807	1.565	2.834	4.293	....	....	....	22
20(P)		72.714	1.396	2.310	3.540	....	....	....	..
21(I)		73.431	1.568	2.613	3.917	....	....	....	11

[a] Samples 1 to 12, rectangular extruded bars, 8.7 × 8.7 × 118 mm.; odd numbers, 40–60 (Sn-Pb); even numbers, 2–38–60 (Sb-Sn-Pb). Samples 13 to 16, machined cylindrical poured bars, 12.7 × 65 mm.; odd numbers, 40–60 (Sn-Pb); even numbers, 2–38–60 (Sb-Sn-Pb). Samples 17 and 18, machined cylindrical poured bars, 13.7 × 85 mm.; 17, pure Sn; 18, 95–5 (Sn-Sb). Samples 19 to 21, machined cylindrical poured bars, 12.7 × 65 mm.; 19, 0.5–39.5–60 (Cu-Sn-Pb); 20, 40–60 (Sn-Pb); 21, 0.5–39.5–60 (Zn-Sn-Pb). P = pure; I = impure.

[b] 0.10 *M* citric acid.

than the pure tin. In 0.1 *M* citric acid the antimonial solder dissolves about 12 per cent faster than does pure solder. Copper and zinc also cause solder to dissolve 22 and 11 per cent faster, respectively, under these conditions.

The decomposition graphs (Figures 2 to 5) show the typical differences in corrosion rates for total given periods of immersion. It is significant that the tendency, already noted, for antimonial solder to manifest a sharp break in its decomposition rate appears in all cases from the strongest to the weakest acids. Expressed in terms of the decomposition rate of pure solder, the impure alloys appear to pass through two stages—first, a period in which their corrosion rate is comparable to that of the pure metal or even slightly less, and then a period in which it is vastly greater. It is particularly significant from a practical point of view that the pure and the antimonial solder may, under certain conditions, exhibit apparently identical behavior for weeks or even months, but that eventually the latter alloy reaches a stage where the decomposition rate changes very sharply.

It should again be emphasized that perhaps neither the continuous immersion nor the intermittent immersion test exactly duplicates the actual conditions encountered in practice. It is the purpose of any accelerated test to show a trend or indicate a probability, and it is contended that the intermittent immersion test just described is so designed as to include in a specific way those factors which are generally operative in causing corrosion in practice.

Short Partial-Immersion Test

A short partial-immersion test was conducted, employing essentially the technic of Hoar. Machined cylinders of pure and of 5 per cent antimonial tin 81 mm. long and 10.1 mm. in diameter were placed in inclined positions in separate 250-cc. beakers; 0.1 *M* hydrochloric acid was then added to each beaker so that each sample was about half immersed. A 2-liter beaker was then inverted over each smaller one; these were removed for a few minutes once a day.

At the end of 6 days the pure tin had lost about 60 mg. in weight, and the antimonial tin 55. The pure tin was evenly etched while the attack on the antimonial metal was spotty or highly localized, indicating that the oxide film on the latter metal was penetrated somewhat more slowly but that once through this film, the attack was rapid. These results are about what would be anticipated on the basis of previous tests.

Conclusions

1. Antimony decreases the resistance of solder to the action of hydrochloric acid and air from 20 to several thousand per cent, depending on the strength of the acid, the time of exposure, access to air, and possibly other factors.

2. The mathematical value of these corrosion differences may be varied widely by an arbitrary selection of conditions.

3. In very weak hydrochloric acid and under certain ideal or carefully controlled conditions, antimonial solders may acquire a protective film of metallic antimony over the surface of the metal which retards further action to the point where the corrosion rate is about comparable with that of pure solder.

4. Antimony decreases the corrosion resistance of solder to 0.1 *M* citric acid and air.

5. The addition of 5 per cent antimony to tin makes it much less resistant to 0.1 *M* hydrochloric acid and air.

6. Under no condition was antimony found to increase resistance to corrosion.

7. Copper and zinc decrease the resistance of solder to the corrosive attack of 0.1 *M* hydrochloric acid under ordinary conditions.

8. This work indicates that antimony, copper, and zinc should be excluded from tin alloys from the corrosion-resistance standpoint.

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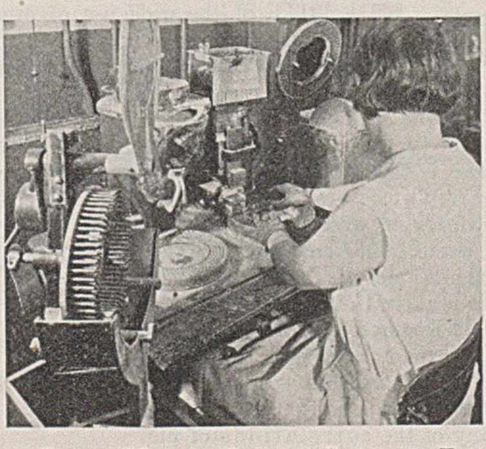
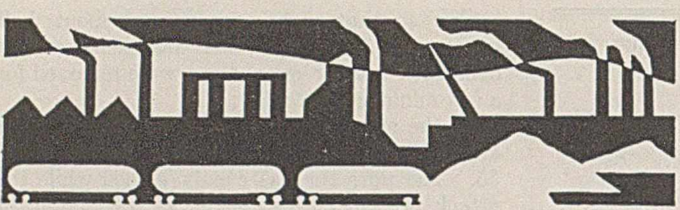


Capsule Filling Machine Showing Filling of Extralin in Liver Department, Eli Lilly and Company



SYMPOSIUM
on
HEAT
TRANSMISSION

Held under the auspices of the
Division of Industrial and Engineering Chemistry
of the American Chemical Society at Yale University,
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HEAT-TRANSFER COEFFICIENTS IN VERTICAL-TUBE FORCED-CIRCULATION EVAPORATORS

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IN SPITE of the wide use of evaporators and the large number of tests that have been run on commercial evaporating equipment, no satisfactory general equation has been proposed for predicting the coefficients of heat transfer in any particular type. One type of evaporator in common use in the chemical industries is the vertical-tube forced-circulation evaporator. Badger (*1*, *3*) measured, in a semi-commercial forced-circulation evaporator, over-all coefficients for the evaporation of sulfite waste liquor and caustic soda solutions. Additional experiments (results not published) were made at the University of Michigan Chemical Engineering Laboratory and also by the manufacturers of such equipment. No general correlation of these data has previously been reported nor have any of the correlations of film coefficients of heat transfer been usefully applied to this problem.

As a result of the work reported in this paper, the over-all coefficients of heat transfer for the work of Logan, Fragen, and Badger (*8*) on the evaporation of sucrose solutions were correlated within ±10 per cent by the use of a comparatively simple equation involving only the velocity of the liquid entering the heating tubes, the viscosity of the liquid being evaporated, and the over-all temperature drop from the condensing steam to the liquid. The viscosity and temperature drop were based on a temperature of the liquid corresponding to the boiling point of the solution at the pressure existing in the vapor space of the evaporator (apparent boiling point corrected for boiling point elevation). It was necessary to use this apparent temperature because the liquid is heated as it passes through the tubes, and its average true temperature cannot be predicted by any known methods. The apparent boiling point is readily obtained, and data for making the correction for boiling point elevation are usually available.

The same equation was applied to data reported by Badger (*2*, *3*) for the evaporation of sulfite waste liquors and impure sugar solutions. The experimental data for these tests were within ±15 per cent of the values predicted by the equation. The apparatus used in these tests contained tubes of nearly the same dimensions as in the work of Logan, Fragen, and Badger.

Over-all coefficients of heat transfer for the evaporation of distilled water were measured by Kleckner and Badger (*7*) in a vertical-tube forced-circulation evaporator containing tubes of the same length as, but of different diameter from, those in the evaporator used by the authors. Other coefficients were measured by Hebbard and Badger (*5*) in an apparatus of the same type but containing one tube of a greater length than the tubes in the authors' apparatus. A revised equation was derived that included the effects of tube length and diameter. This revised equation is presented with some hesitation and should be more rigidly established by further experimentation. However, the size of the tubes used by the authors is that generally used in commercial evaporators.

A detailed description of the apparatus and procedure was previously reported by Logan, Fragen, and Badger (*8*). Only a brief description will be given:

> The apparatus used was a Swenson semi-commercial forced-circulation

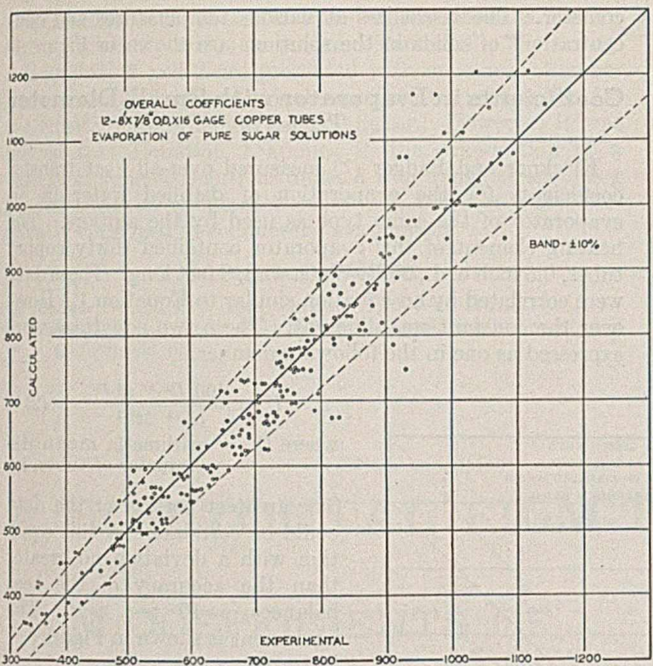

FIGURE 1

evaporator having twelve copper tubes (8 feet long) in the heating element. Eleven of these tubes were $^7/_8$ inch o.d., 16 B.W.G. (Birmingham wire gage) wall, and one tube was 1 inch o.d. and had an 11 B.W.G. wall. Solution was pumped through the tubes and steam was condensed on the outside of the tubes.

In the experimental procedure, the principal operating variables and the ranges covered were: concentration of sucrose in solution, 22 to 65 per cent; apparent boiling point of the solution, 160° to 210° F.; velocity of the liquid entering the tubes, 7 to 17 feet per second; apparent over-all temperature drop, 9° to 65° F. The system of changing these variables was such that in any one set of experiments three of the variables were held constant while the fourth was varied over the entire range.

The heat input was measured by determining the volume of the condensed steam. Heat balances checking within 10 per cent were obtained by using steam that was slightly superheated and by adequately insulating the outside of the steam chest from its surroundings. Hence, the heat lost by the condensing steam was a true measure of the heat transferred through the walls of the tubes. Steam and liquid temperatures were obtained by pressure measurements and were checked by the use of thermocouples. Concentrations of the solution were determined by taking the gravities of the samples at frequent intervals. The viscosities of the solutions, taken from the data reported in the International Critical Tables (*6*) by the Bureau of Standards (*4*), were fitted into an equation which was used to interpolate and extrapolate the reported data.

A large number of over-all heat transfer coefficients in forced-circulation evaporators were correlated by the equation:

$$U = \frac{435u^{0.45}}{\mu^{0.25}\ \Delta t^{0.1}}$$

Several hundred determinations on distilled water, sucrose solutions, molasses, and sulfite liquor were correlated by this equation. Terms for tube length and tube diameter were also included but are based on too few determinations to have much weight.

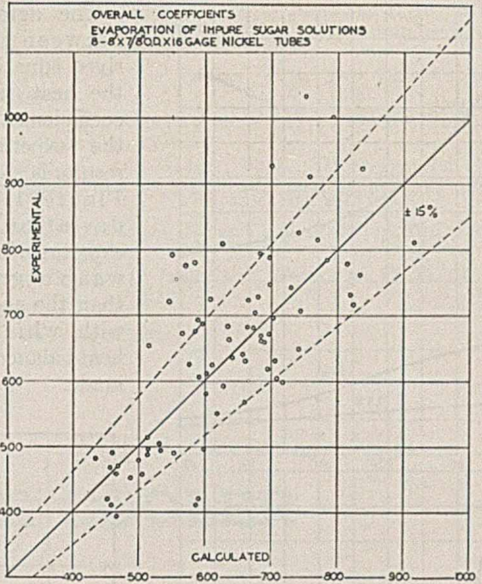

FIGURE 2

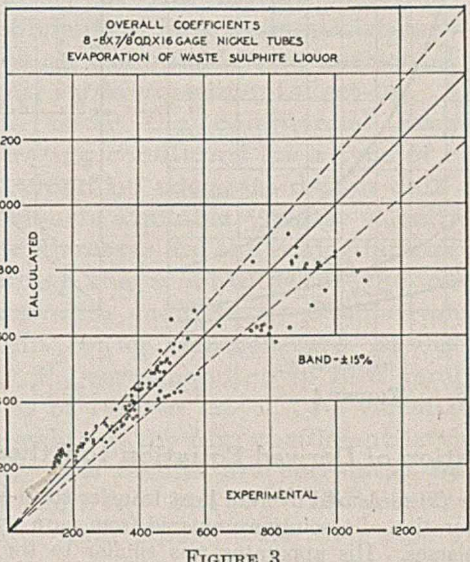

FIGURE 3

Derived Equation

The empirical equation derived may be expressed as:

$$U = \frac{435u^{0.45}}{\mu^{0.25}\Delta t^{0.1}} \qquad (1)$$

where U = over-all coefficient of heat transfer based on arithmetic mean area of heating surface, B.t.u./sq. ft./hr./° F.

u = linear velocity of liquid at tube entrance, ft./sec.

μ = viscosity of solution being evaporated, lb./hr./ft. = (2.42) (centipoises)

Δt = over-all apparent temperature drop corrected for boiling point elevation—i. e., difference between temperature of saturated steam and temperature of liquid boiling at pressure existing in vapor space of evaporator

The experimental range was:

U = 302 to 1143
u = 7.1 to 17.0
μ = 1.05 to 20.6
Δt = 8.9 to 64.8

The agreement between the derived equation for the heat transfer coefficients and the experimental results is shown in Figure 1. The deviation of the experimental data was no greater than the accuracy with which the heat balances were made.

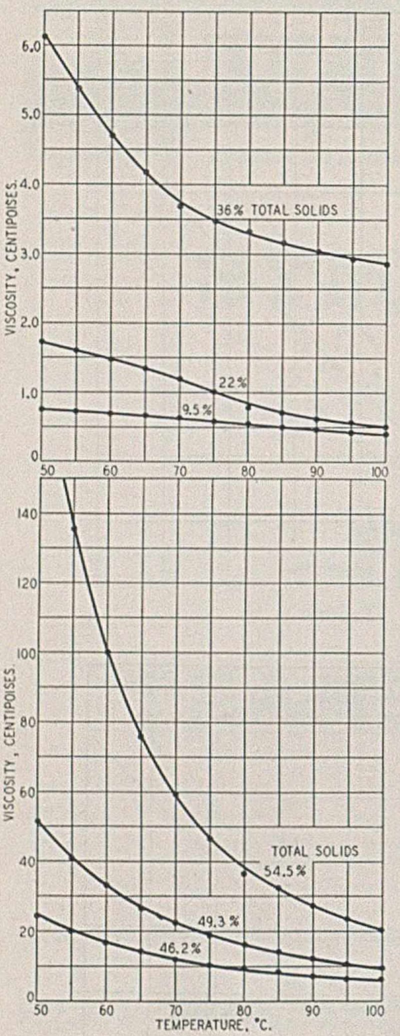

Figure 4

Application of Derived Equation to Other Data

Badger (*2*) measured over-all heat transfer coefficients for the evaporation of a solution prepared from pure sugar and cane molasses. His apparatus was similar to the experimental evaporator used by the authors but contained eight nickel tubes, $^7/_8$ inch o. d., 16 B. W. G. wall, and 8 feet long. The derived equation was applied to those data, and the resulting agreement was within ±15 per cent. This agreement is shown in Figure 2. The range of the variables was:

$$U = 400 \text{ to } 1000$$
$$u = 7.6 \text{ to } 14.1$$
$$\mu = 2.0 \text{ to } 21.6$$
$$\Delta t = 11.3 \text{ to } 50.9$$

Badger (*1*) also measured over-all heat transfer coefficients in this same apparatus for the evaporation of neutralized, sulfite waste liquors. The derived equation also applied to these data with a fair degree of accuracy. The agreement is shown in Figure 3. The range of the variables was:

$$U = 200 \text{ to } 900$$
$$u = 2.7 \text{ to } 11.1$$
$$\mu = 1.2 \text{ to } 242$$
$$\Delta t = 19.6 \text{ to } 53.3$$

The data of Moore (*9*) was used to determine the boiling point of the sulfite solutions, and the viscosities were determined experimentally by the use of a MacMichael viscometer. The viscosities at various temperatures and concentrations of solids in the solutions are shown in Figure 4.

Coefficients in Evaporator with Small-Diameter Tubes

Kleckner and Badger (*7*) measured over-all heat transfer coefficients for the evaporation of distilled water in an evaporator of the same type as used by the authors. The heating element of this evaporator contained thirty copper tubes, 0.5 inch o. d., 20 B. W. G. wall, 8 feet long. These data were correlated by an equation similar to Equation 1. However the constant was different. These two equations were expressed as one in the following manner:

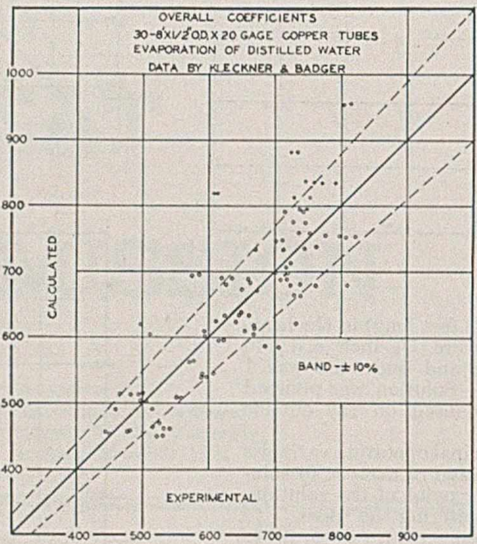

Figure 5

$$U = \frac{490\, D^{0.57}\, u^{0.45}}{\mu^{0.25}\, \Delta t^{0.1}} \qquad (2)$$

where D = arithmetic mean diameter of tubes, in.

The greatest portion of the data could be correlated by this equation with a deviation no greater than the accuracy of the heat balances, ±10 per cent. The agreement is shown in Figure 5.

Coefficients in Evaporator with Longer Tube

Hebbard and Badger (*5*) measured over-all heat transfer coefficients for the evaporation of distilled water in a single-tube, forced-circulation evaporator containing one copper tube, 1 inch o. d., 11 B. W. G. wall, and 12 feet long. These data were successfully correlated by an equation similar to Equation 2, except for the exponent of velocity:

$$U = \frac{490\, D^{0.57}\, u^{3.6/L}}{\mu^{0.25}\, \Delta t^{0.1}} \qquad (3)$$

where L = tube length, ft.

The agreement of this set of data and Equation 3 is shown in Figure 6. Equation 3 will successfully correlate all of the

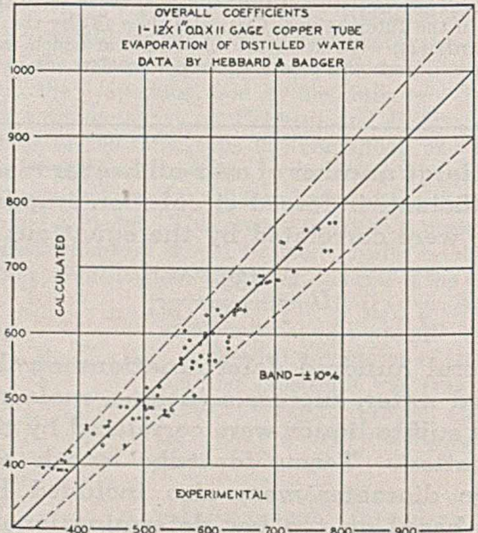

Figure 6

experimental data obtained from the evaporators having heating tubes of various lengths and diameters.

Equations 2 and 3 are presented with some hesitation because of the lack of additional experimental verification for the effects of tube length and diameter. However, it was proved that Equation 1 applies to the evaporation of a variety of aqueous solutions under a wide range of operating conditions in an evaporator containing tubes of a size frequently employed in commercial evaporators.

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A HORIZONTAL FILM-TYPE COOLER

FILM COEFFICIENTS OF HEAT TRANSMISSIONS

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Fundamental data were determined in a study of the factors affecting film coefficients of heat transmission for water films on the outside of a horizontal pipe cooler in an experimental set-up. These data cover the commercial range of operating conditions for a type of cooler on which no adequate design data were previously available. Water velocity and pipe diameter are the major factors controlling the magnitude of the outside water film coefficient. Over a range in cooling-water temperature of 52° to 177° F., corresponding to film temperatures of 146° to 196° F., no variation in the value of the film coefficient is apparent. The results are correlated by the equation, $h_0 = 24.4\ (C^{0.39}/D^{0.61})$, for 2-inch and 4-inch pipe. One-inch pipe yields values of the coefficient which are 80 per cent of those calculated by the equation.

FILM-TYPE heat exchangers offer certain advantages for heating and cooling liquids and for the condensation of vapors on account of the high coefficients of heat transmission which they afford. In this type of apparatus the tubes may be arranged vertically with the liquid passing down through the inside of the tubes, or they may be arranged horizontally in banks with the liquid flowing over the outside of the tubes and falling from one tube to the next below it. This latter arrangement is common in the so-called trombone cooler in use by the heavy chemical, coke, brewing, dairy, petroleum-refining, and refrigeration industries. It has the distinct advantage of lower cost due to the use of only one set of tubes without the necessity of surrounding tubes or shell to confine the liquid. It may be constructed to fit any desired floor arrangement and is readily accessible for cleaning, alteration, or replacement of tubes. When used as a cooler, the water requirements of such an exchanger are extremely low.

That the importance of the horizontal film type of liquid heat exchanger has not been generally appreciated is evident from the dearth of design data covering its operation, particularly as regards the outside film coefficient. The uncertainty in the value of this coefficient is further accentuated in many cases by the presence of scale and dirt. Hence little attention has been paid to the inside film coefficient, which frequently is the major resistance to heat flow and is readily calculable. As a result, many of the present installations operate inefficiently.

Van der Ploeg (*6*), working on a trombone cooler composed of twenty-four tubes of a flattened, irregular cross section, determined outside film coefficients for the top sixteen tubes by measuring outside wall temperatures. He obtained values of the water film coefficients from 470 to 695 B. t. u. per hour per square foot per ° F. for water velocities of 1000 to 2100 pounds per hour per foot and cooling water temperatures of 50° to 104° F. He gives an empirical equation for calculating water film coefficients, which recalculated to English units becomes:

$$h_0 = 53.4\ \frac{C^{0.27}}{L^{0.05}}\ (1 + 0.0099t)$$

Davis (*2*) worked with small single wires, electrically heated, which he moved through water and several hydrocarbons at various velocities. His results were expressed by McAdams (*4*) as follows:

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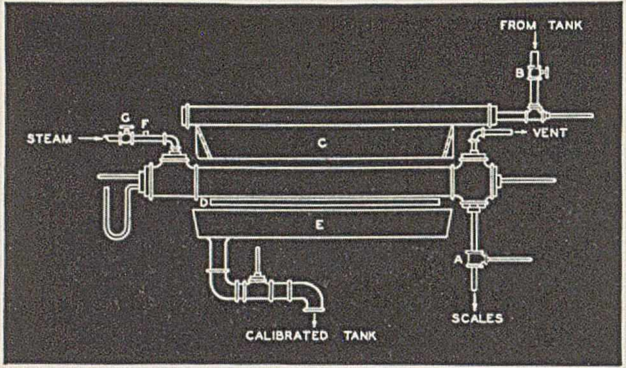

FIGURE 1. ARRANGEMENT OF TUBE AND CONNECTIONS

$$\frac{\frac{h_0 D}{k}}{\left(\frac{c_p \mu}{k}\right)^{0.3}} = 0.86 \left(\frac{D V \rho}{\mu}\right)^{0.43}$$

The only other available data even remotely connected to this problem are those of Bays and Blendemran (*1*) who studied the heat transmission coefficients for a falling liquid film inside a vertical tube. Their results are correlated by the dimensionless equation:

$$h_0 \left(\frac{C^2}{k^3 \rho^2 g}\right)^{0.33} = 0.0025 \left(\frac{c_p \mu}{k}\right)^{0.70} \left(\frac{4C}{\mu}\right)^{1.05}$$

The application of any of these equations to the design of trombone coolers is unproductive, unless the specific design of the apparatus being constructed is similar to that for which the equations were obtained. The general design of coolers of this type requires a knowledge of the fundamental factors affecting the liquid film coefficient.

From the above equations and a critical analysis of the problem, it is apparent that liquid velocity, tube diameter, and the properties of the liquid outside the tube are the important variables. Water was selected as the cooling medium in this study because of its general use and ready availability. Variation in the properties of the liquid was therefore limited to that possible because of change in water temperature. The variables studied were therefore water rate, tube diameter, and water temperature.

The apparatus was designed by Kepner and Lewis (*3*) to give a direct determination of the water film coefficient. Steam at atmospheric pressure passed through a horizontal copper tube, over the outside of which the cooling water flowed. The quantity of steam condensed in the tube, the quantity of cooling water, and its inlet and outlet temperatures were measured. The average surface temperature of the tube was determined by means of thermocouples set in the tube wall, the tube itself serving as one element of the couples. In this way a direct determination of the water film coefficient became possible, and any need for exact knowledge of the steam film coefficient was eliminated.

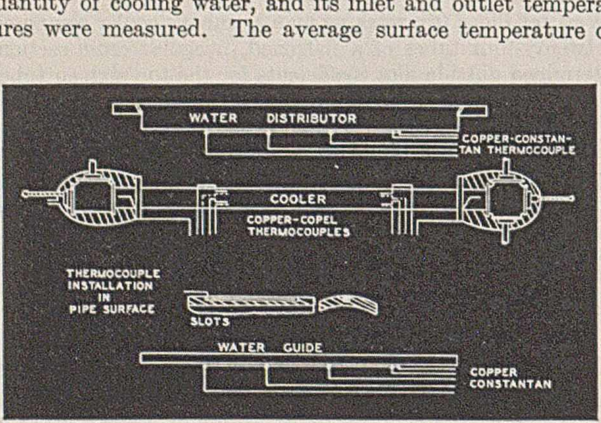

FIGURE 2. ARRANGEMENT OF THERMOCOUPLES

Copper was chosen for the tube material since it is not subject to oxidation and scale formation. It also forms, in conjunction with copel wire, a sensitive thermocouple over the range of temperatures measured.

Apparatus

The actual arrangement of the tube and its connections is shown in Figure 1:

One-inch, two-inch, and four-inch copper tubes were used, each 4 feet long. In each case a length of 3.39 feet was exposed to the cooling water. The ends of the tube were carefully lagged with magnesia, and access of cooling water to them was prevented by stuffing boxes. The tubes were slightly tilted so that the condensate would drain toward the outlet.

Dry steam, supplied at 30 pounds per square inch gage pressure, was reduced through a throttling valve to atmospheric pressure before entering the tube. The condensate drained through a trap, *A*, and sight glass, whence it passed to a galvanized-iron can (partially filled with cold water to prevent evaporation losses) placed upon a scale. The weight of condensate was therefore obtained directly. Uncondensed steam escaped through a vent at the end of the tube to eliminate air binding.

Cooling water was supplied from a city water line, to which was connected a steam line for heating the water. From a tank of constant level head, the water passed through a valve, *B*, to a standard 2-inch pipe, directly above and parallel to the cooler tube. The top of this pipe was drilled with $^1/_{16}$-inch holes, causing the water to flow out and around the pipe before it reached the wooden distributor board, *C*, thus insuring an even flow of water over the whole tube. The water leaving the tube was directed by a collection board, *D*, into a sloping galvanized steel trough, *E*, whence it flowed to one of two duplicate 54-gallon calibrated steel drums. Since for runs with high cooling-water temperatures the steam line connected to the water supply was insufficient to heat the water to the temperature desired, a small rotary pump was installed to recirculate hot water, which had passed over the apparatus, back to the constant-head tank.

Inlet and outlet temperatures of cooling water and steam were measured with thermometers at appropriate points as indicated in Figure 1. Cooling-water temperatures were also measured by means of copper-constantan thermocouples arranged on the distribution and collection boards as shown in Figure 2. Tube surface temperatures were measured by embedding eight No. 22 copel wires in shallow grooves ($^1/_{16} \times {}^1/_{16} \times 1^1/_2$ inches) cut in the tube parallel to the tube length at points on the circumference 45° from the vertical diameter (Figure 2). The wires were placed in two groups of four at points one foot on each side of the mid-section of the tube. In some of the early work the wires were placed on the vertical and horizontal diameters. Copper wires soldered to each end of the tube, which formed the second element of the thermocouple, together with the copel wires, led through a mercury cold-junction bottle to a set of knife switches.

Procedure

All the thermocouples used were calibrated by immersion in a water bath over a series of known temperatures, and calibration curves were prepared. The thermometers were also checked at the boiling point of water; the maximum error of any thermometer was 1° F.

The cooling-water collection drums were calibrated by pouring in weighed amounts of water at known temperature and recording the height of water on the measuring stick. The condensate scales were checked against known weights and found to be accurate.

About one hour before commencing a series of runs the cooling water was turned on in order to obtain thorough soaking of the apparatus and a complete water film over the tube. At the same time a few drops of benzyl mercaptan were inserted through opening *F* (Figure 1) into the steam line. This procedure insured dropwise condensation of the steam throughout the investigation (*8*).

In the first and third series of runs, in which the effect of water velocity and pipe diameter were investigated by Parker (*5*) and Reid (*7*), the temperature of the cooling water was kept approximately constant and its rate adjusted by means of valve *B* (Figure 1). In the second series of runs, in which the effect of cooling-water temperature was investigated by Reid (7), the water valve was sealed, giving an approximately constant water rate, and the temperature was varied by means of the steam line up to inlet water temperatures of 120° F. Above this temperature, however, it was necessary to operate the pump to recirculate the cooling water. In all experiments care was taken that there was an overflow of water from the constant-level tank.

After the cooling-water rate and temperature were adjusted, steam valve *G* was regulated so that a small excess of steam escaped continuously from the vent.

When conditions became steady, as indicated by thermometer and thermocouple readings, a run was started. Thermometer and thermocouple readings were taken at the beginning, middle, and end of each run, which covered periods of 10 to 20 minutes, depending upon the time necessary to fill the calibrated tank with cooling water.

At high cooling-water temperatures there was considerable difference in the readings of the inlet and outlet cooling-water thermometers and the corresponding thermocouples, owing to evaporation as the water flowed over the boards. The thermocouple readings were therefore adopted in all calculations.

Calculation of the Water Film Coefficient

Water film coefficients were calculated by means of the equation:

$$Q/\theta = h_0 A \, \Delta t$$

The total heat transferred during the run was given by the product of the weight of the condensate and its enthalpy change. The latter was obtained from steam tables, since the condensate and entrance steam temperatures were known. The change in heat content of the water (measuring the water temperature either by thermometer or thermocouple), was always less than the total heat transferred, owing to evaporation of some of the cooling water. The arithmetic mean of the tube surface temperatures, indicated by the thermocouples, was assumed to be the average surface temperature of the tube. The average cooling-water temperature was estimated as the arithmetic mean of the inlet and outlet water temperature. The temperature drop through the water film was therefore taken to be the difference between these two quantities. Since the surface area of each of the tubes was known, the water film coefficient, h_0, was calculated.

The precision of the rate of heat flow, as determined by the various measurements involved was better than 2 per cent, the radiation and convection being found to be negligible. Inlet-water temperatures varied over a range of less than 3° F. during a run, and the thermocouple measurements of the temperatures of the water and tube were accurate within 2° F. The precision of the temperature difference, calculated from these measurements, was about 5 per cent. Consequently, the precision of the heat transmission coefficient was certainly better than 6 per cent.

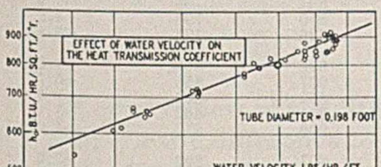

Figure 3

Discussion of Results

The effect of water velocity on the outside film coefficient for a 2-inch tube is shown in Table I and Figure 3. The temperature of inlet cooling water was maintained within 3° of 56° F. during the series of runs. The coefficient increased with the 0.39 power of water velocity, expressed as pounds of water per hour per foot length of tube. The range of water velocities used covered the desired spread in operating conditions; lower velocities showed incomplete

Table I. Effect of Water Velocity on Outside Film Coefficient of Heat Transmission for 2-Inch Tube[a]

Run No.	Water Velocity *Lb./hr./ft.*	h_0 Obsvd.	h_0 Calcd.	Deviation[b] %
1	252	546	564	3.3
2	298	606	604	−0.3
3	309	619	616	−0.5
4	325	660	623	−5.6
5	326	666	625	−6.1
6	342	643	636	−1.1
7	344	657	643	−2.1
8	345	659	643	−2.4
9	350	651	643	−1.2
10	419	717	682	−4.9
11	426	723	695	−3.9
12	427	717	695	−3.1
13	428	704	695	−1.3
14	429	712	695	−2.4
15	519	763	755	−1.0
16	519	769	755	−1.8
17	540	806	760	−5.7
18	551	791	774	−2.1
19	553	790	774	−2.0
20	580	821	787	−4.1
21	598	802	794	−1.0
22	598	802	794	−1.0
23	616	817	807	−1.2
24	648	846	820	−3.1
25	667	844	826	−2.1
26	669	819	826	0.9
27	669	875	826	−5.6
28	670	830	833	0.4
29	699	843	846	0.4
30	701	830	846	1.9
31	710	880	846	−3.9
32	725	906	853	−5.8
33	730	841	859	2.1
34	733	846	865	2.2
35	739	896	865	−3.5
36	745	914	865	−5.4
37	750	907	865	−4.6
38	752	856	865	1.1
39	756	883	865	−2.0
40	757	893	865	−3.1
41	759	891	872	−2.1
42	760	868	872	0.5
43	760	885	872	−1.5
44	760	895	872	−2.6
45	760	900	872	−3.1
46	761	891	872	−2.1
			Average	2.6

[a] Outside diameter of tube = 0.198 foot.

[b] Per cent deviation = $\left(\frac{h_0 \text{ calcd.} - h_0 \text{ obsvd.}}{h_0 \text{ obsvd.}}\right) \times 100.$

Table II. Effect of Water Temperature on Outside Film Coefficient of Heat Transmission for a 2-Inch Tube[a]

	Temperature						
Run No.	Inlet water ° *F.*	Water film ° *F.*	h_0 Obsvd.	Water Velocity *Lb./hr./ft.*	h_0 Cor.	h_0 Calcd.	Deviation[b] %
47	52	146	685	405	630	683	−0.3
48	52	147	637	352	612	650	2.0
49	53	149	603	329	597	630	4.5
50	53	151	543	344	527	637	17.3
51	61	151	595	348	577	643	8.1
52	62	150	540	342	529	637	18.0
53	76	157	627	349	608	643	2.6
54	76	161	576	324	576	630	9.4
55	77	158	627	349	608	643	2.6
56	90	164	626	328	620	630	0.6
57	92	163	588	320	588	623	6.0
58	92	164	640	329	633	630	−1.6
59	95	167	591	336	579	637	7.8
60	99	169	609	321	609	624	2.5
61	101	169	580	290	604	597	2.9
62	101	171	545	290	567	597	9.5
63	101	171	616	310	622	617	0.2
64	110	174	595	277	630	591	−0.7
65	115	177	543	281	570	591	8.8
66	119	178	553	275	586	584	5.6
67	122	178	579	318	579	623	7.6
68	148	188	548	291	570	597	8.9
69	151	189	543	305	554	610	12.3
70	159	190	577	306	589	610	5.7
71	171	196	508	327	503	630	24.0
72	172	195	513	303	524	610	18.9
73	177	196	590	321	590	624	5.8
Average			584	320	584		7.0
Average deviation, %			5.7	6.7	4.6		

[a] Outside diameter of tube = 0.198 foot.

[b] Per cent deviation = $\left(\frac{h_0 \text{ calcd.} - h_0 \text{ obsvd.}}{h_0 \text{ obsvd.}}\right) \times 100.$

wetting of the surface, and higher velocities caused excessive splashing.

The effect of inlet-water temperature between 52° and 177° F. on the coefficient was determined on the same tube at an average water velocity of 320 pounds per hour per foot. The results are reported in Table II. Since film temperatures determine the properties of the film and therefore might be expected to influence the heat transmission coefficient, they are tabulated in column 3. The coefficients show an average deviation from their mean of 5.7 per cent, and no trend with temperature.

In column 6 the coefficients are corrected to a constant water velocity of 320 pounds per hour per foot, using the relation derived from Figure 3 that $h_0 = f(C)^{0.39}$. This calculation gives the same average coefficient of 584 but reduces the average deviation to 4.6 per cent, and still no trend with temperature is apparent. This observation justifies the conclusion that in the range investigated—that is, with film temperatures of 146°–196°F.—the coefficient is independent of film temperature.

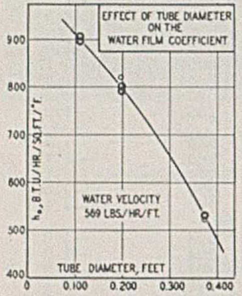

Figure 4

The effect of tube diameter on the coefficient is shown in Figure 4 for an average water velocity of 569 pounds per hour per foot. The coefficient increases rapidly as the tube diameter is decreased, but the increase for the one-inch tube is less than might be expected. This behavior is probably due to the fact that the water is used less effectively on the smaller size.

The application of van der Ploeg's equation to these data shows its limitations. For example, with a constant water rate and tube diameter, his equation requires the coefficient to increase by 80 per cent with a temperature increase from 52° to 177° F.; the corrected coefficients reported in Table II, column 6, show a decrease in this range of 4 per cent which is within the precision of these data. Furthermore, the effect of water rate on the coefficient determined by van der Ploeg is much less than that found in the present investigation.

Reid (*7*) proposes to correlate these data with a dimensionless equation of the Nusselt type:

$$\frac{h_0 D}{k} = K\left(\frac{DC}{2x\mu}\right)^m \left(\frac{c_p \mu}{k}\right)^n$$

It is evident that this equation is similar in form to those of Davis and of Bays and Blenderman already cited.

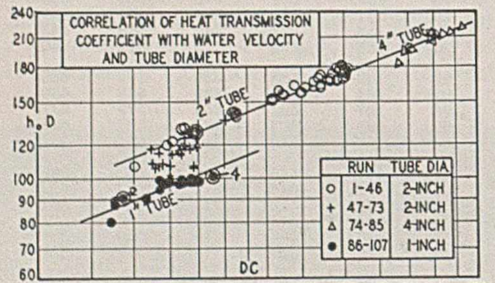

Figure 5

Since it has been shown that the film coefficient is independent of film temperature in the range studied, and if we assume constant thickness of water film, this equation may be simplified to give:

$$h_0 D = K'(DC)^m$$

In Figure 5 the results of all the runs are presented, plotting h_0D vs. DC on a logarithmic scale. Runs 1 to 46 on a 2-inch tube fall on the same straight line as runs 74 to 85 on a 4-inch tube. Runs 47 to 73 at various temperatures are clustered near one end of this line and slightly below it. Runs 86 to 107 on a 1-inch tube are well represented by a straight line parallel to the first line but somewhat below it. From this plot the equation for the larger sizes becomes:

$$h_0 = 24.4\,\frac{C^{0.39}}{D^{0.61}}$$

For the 1-inch tube, values 80 per cent of this obtain, or

$$h_0 = 19.5\,\frac{C^{0.39}}{D^{0.61}}$$

Using these two equations, film coefficients of heat transmission were calculated for comparison with the observed values. The calculated values for varying water velocity on a 2-inch tube (Table I) check the observed with an average deviation of 2.6 per cent. The values observed for varying water temperatures on a 2-inch tube (Table II) average 7.0 per cent below those calculated from the equation. This effect may be explained by differences in cleanliness of the tube, thermocouple location, water distribution, or amount of steam vented although these differences between runs were so small that they were probably not due to any one alone, but rather to a combination of them. The calculated values for the 4-inch and 1-inch tubes (Table III) average within 1.7 and 2.4 per cent, respectively, of the observed.

TABLE III. EFFECT OF WATER VELOCITY ON OUTSIDE FILM COEFFICIENT OF HEAT TRANSMISSION

Run No.	Water Velocity *Lb./hr./ft.*	h_0 Obsvd.	h_0 Calcd.	Deviation[a] %
	4-In. Tube (Outside Diam., 0.375 Ft.)			
74	534	486	515	6.0
75	548	524	520	−0.8
76	558	531	524	−1.3
77	565	529	524	−0.9
78	628	565	546	−3.4
79	628	550	546	−0.7
80	629	564	546	−3.2
81	634	552	550	−0.4
82	648	565	555	−1.8
83	673	570	564	−1.1
84	696	577	573	−0.7
85	749	587	586	−0.2
			Average	1.7
	1-In. Tube (Outside Diam., 0.110 Ft.)			
86	404	732	780	6.6
87	410	815	788	−3.3
88	413	803	788	−1.9
89	425	830	795	−4.2
90	429	826	795	−3.8
91	484	825	840	1.8
92	520	907	855	−5.7
93	523	858	862	0.5
94	526	890	862	−3.1
95	546	906	870	−4.0
96	573	897	892	−0.6
97	580	898	900	0.2
98	586	907	900	−0.8
99	591	902	900	−0.2
100	613	901	915	1.6
101	620	915	922	0.8
102	624	906	922	1.8
103	639	904	930	2.9
104	680	928	952	2.6
105	680	929	952	2.5
106	680	930	952	2.4
107	687	930	952	2.4
			Average	2.4

[a] Per cent deviation $= \left(\frac{h_0 \text{ calcd.} - h_0 \text{ obsvd.}}{h_0 \text{ obsvd.}}\right) \times 100.$

It is therefore evident that these equations apply satisfactorily in the range investigated to the film coefficient of heat transmission on the outside of a film-type horizontal pipe cooler of circular cross section. The equations, in conjunction with existing equations for calculating coefficients of heat transmission inside pipes, will permit the design of coolers of this type. Due allowance must be made for the thermal resistance of the tube and possible scale formation.

Nomenclature

A = area, sq. ft.
C = rate of flow of cooling liquid, lb./hr./ft.
c_p = sp. heat of liquid in film, B. t. u./lb./° F.
D = outside diam. of tube, ft.
g = gravitational constant
h_0 = film coefficient of heat transmission, B. t. u./hr./sq. ft./° F.
K, K' = constants
k = thermal conductivity of liquid in film, B. t. u./hr./sq. ft./° F./ft.
L = length of travel of liquid over wetted surface, ft.
m, n = exponents
Q = total heat transferred, B. t. u.
t = cooling liquid temp., ° F.
Δt = temp. drop through liquid film, ° F.
V = velocity, ft./hr.
x = thickness of water film, ft.
μ = viscosity of liquid in film, lb./hr./ft.
ρ = density of liquid in film, lb./cu. ft.
θ = time, hr.

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MEAN TEMPERATURE DIFFERENCE CORRECTION IN MULTIPASS EXCHANGERS

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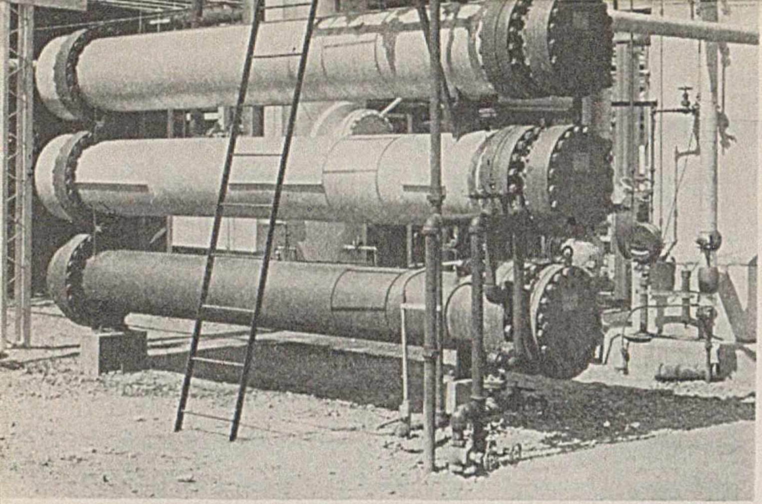
A brief review of the literature on mean temperature difference to date is included with a comparison of the results obtained by the different methods for several special cases. The formulas given by Underwood for single-pass shell with multipass tubes are repeated. There are no data in the literature covering shells with more than two passes. The writer derives an equation for extending the results given by Nagle to exchangers with any number of shell passes. A table gives solutions of this equation for two-, three-, four-, and six-pass shells. The data for three-, four-, and six-pass shells are also given in the form of curves.

THE use of the so-called logarithmic mean temperature difference in the design of heat transfer equipment has been accepted for some time. Its validity, based on the assumption of constant heat transfer rate and constant specific heat, can easily be demonstrated for the case of countercurrent or parallel flow. Unfortunately, the designer is usually limited for mechanical reasons to what might be called "mixed flow"—that is, two or more tube passes for each shell pass. It is obvious that in such an exchanger the true mean temperature difference is somewhat lower than if counterflow were used but higher than for parallel flow. It is only within the last five years or so that a mathematical solution for this type of *MTD* has been developed. Prior to that time, while the designer was well aware that the logarithmic *MTD* based on counterflow was too high, there was no standard way of correcting it, and he usually called that value the "mean difference" and penalized his heat rates to compensate for it. Frequently the average of the counter- and parallel flow *MTD*'s was used. Where there is any temperature crossing, this value is obviously too low, but where the temperatures do not approach too closely, the agreement with sounder methods is surprisingly good. Another method was to consider the tube-side fluid as being at a constant temperature midway between the inlet and outlet temperature and to take the logarithmic mean of the difference between this value and the shell-side temperatures. In the light of more recent knowledge the results of this method were fairly good but ran a little high.

In 1931, Davis (*1*) published curves of factors by which the logarithmic *MTD* was multiplied to give the true mean. No description of the method was given. In 1932 Nagle (*2*) published a mathematical analysis of the problem. The final equation of his solution is solved by a graphical integration based on a trial-and-error solution of a semi-final equation. Complete data are given for single- and two-pass shells with multipass tubes, the correction factor being expressed as a function of temperature ratios. Solutions were made for one-two, one-four, and one-six exchangers. The results were quite close to one another, and the author concluded that for practical purposes the same correction factor could be used for all cases.

SOON after the publication of Nagle's paper, Underwood (*4*) succeeded in differentiating the equations involved and thus eliminated the necessity for a trial-and-error and graphical solution. The equation he derived for the mean temperature of a single-pass shell with two-tube passes is:



TWO GASOLINE-TO-GASOLINE HEAT EXCHANGERS WITH TWO SHELL PASSES, EACH IN SERIES, FOLLOWED BY A GASOLINE-TO-WATER COOLER

$$\frac{\sqrt{(T_1 - T_2)^2 + (t_2 - t_1)^2}}{\theta m} = \ln \frac{T_1 + T_2 - t_1 - t_2 + \sqrt{(T_1 - T_2)^2 + (t_2 - t_1)^2}}{T_1 + T_2 - t_1 - t_2 - \sqrt{(T_1 - T_2)^2 + (t_2 - t_1)^2}} \quad (1)$$

The equation for the correction factor is:

$$F = \frac{\eta \ln \frac{\theta_1}{\theta_2}}{\ln \left[\frac{\theta_1(\eta + 1) - \theta_2(\eta - 1)}{\theta_2(\eta + 1) - \theta_1(\eta - 1)}\right]} \quad (2)$$

$$\text{where } \eta = \frac{\sqrt{1 + \left(\frac{t_2 - t_1}{T_1 - T_2}\right)^2}}{1 - \frac{t_2 - t_1}{T_1 - T_2}}$$

$$\theta_1 = T_1 - t_2;\ \theta_2 = T_2 - t_1$$

In those cases where the tube temperatures are higher than the shell temperatures, these equations involve the logarithm of a negative number. Experience indicates that in such a case the correct answer is obtained by assuming that the temperatures are interchanged.

The results are naturally a little more accurate than those of the original paper, but the disagreement between the two sets of results is not more than about 3 per cent. Considering the accuracy of the other calculations involved in heat exchanger design and the fact that the correction factor curves are quite steep when plotted against the temperature ratio, the results of the two papers can be considered essentially equal. Underwood presents a solution for a single-pass shell and four-pass tubes as well as one for the two-pass tubes. The equation for a single-pass shell with four tube passes is:

$$\frac{\mu(T_1 - T_2)}{2\theta m} \coth \left\{\frac{\mu(T_1 - T_2)}{2\theta m}\right\} + \frac{t_2 - t_1}{4\theta m} \tanh \left\{\frac{t_2 - t_1}{4\theta m}\right\} = \frac{T_1 + T_2 - t_1 - t_2}{2\theta m} \quad (3)$$

$$\text{where } \mu = \sqrt{1 + \frac{(t_2 - t_1)^2}{4(T_1 - T_2)^2}}$$

This equation requires a trial-and-error solution. An approximate solution is also included, but it gives results which agree with those of Equation 3 less closely than do those of Equation 1. While the results of Equations 1 and 3 are not identical, the additional accuracy gained from using a separate equation or set of curves for each number of tube passes does not seem to justify the complication of design procedure.

The problem of cross flow is studied by Smith (*3*) in an analysis of several types of cross flow, classified according to whether the fluid is completely mixed or unmixed as it flows through the exchanger. The results obtained are useful for finned-tube air coolers, etc., where a relatively large volume of one of the fluids is handled. The case of completely mixed flow on both sides is also of interest in shell and tube application. This corresponds to the flow which exists in an exchanger with one shell pass and an infinite number of tube passes. The fluid in the shell must be considered to be thoroughly mixed by "cross" or "disk and doughnut," baffles as was done in the derivation of the equations for two and four passes.

4 IN ORDER to show the relative results obtained by the various methods, several examples were worked out for single-pass shells. The temperatures for the various examples are:

	θm	Ratio
(1) $T_1 = 300°$, $T_2 = 200°$, $t_1 = 100°$, $t_2 = 200°$ C.:		
Countercurrent flow	100	1
One-two pass exchanger (Nagle)	80	0.80
One-two pass exchanger (Underwood)	80.4	0.804
One-four pass exchanger (Underwood)	79.8	0.798
One-∞ pass exchanger (Smith)	79	0.79
(2) $T_1 = 290$, $T_2 = 190$, $t_1 = 100$, $t_2 = 200$:		
Countercurrent flow	90	1
One-two pass exchanger (Nagle)	66.1	0.735
One-two pass exchanger (Underwood)	66.7	0.741
One-four pass exchanger (Underwood)	66	0.734
One-∞ pass exchanger (Smith)	65	0.722
(3) $T_1 = 300$, $T_2 = 200$, $t_1 = 150$, $t_2 = 200$:		
Countercurrent flow	72.5	1
One-two pass exchanger (Nagle)	59.1	0.815
One-two pass exchanger (Underwood)	60.1	0.829
One-four pass exchanger (Underwood)	59.6	0.821
One-∞ pass exchanger (Smith)	58.5	0.807
(4) $T_1 = 290$, $T_2 = 190$, $t_1 = 150$, $t_2 = 200$:		
Countercurrent flow	61.6	1
One-two pass exchanger (Nagle)	43.1	0.70
One-two pass exchanger (Underwood)	43.15	0.701
One-four pass exchanger (Underwood)	42.3	0.688
One-∞ pass exchanger (Smith)	42.0	0.683

These four examples show good agreement among the four systems, and apparently the choice of the one to use depends on its ease of application.

11 EVIDENTLY there are many instances in which it will be desirable to work to such close temperatures that a single-pass multipass exchanger will fail to work. In such cases the obvious solution is to use two passes on the shell side since this more nearly approaches true counterflow. Nagle and Underwood have presented solutions for this case, and their results show a considerable gain over a single-pass shell. In analyzing the problem they have assumed that the heat transfer through the longitudinal baffle can be neglected and also (tacitly) that the baffle is tight against leakage. Let us consider the probable validity of these assumptions.

The three principal methods of designing exchangers with two shell passes are:

(1) The use of two separate and complete sections connected in series.

(2) The use of an integral longitudinal baffle and splitting the floating head into two parts to permit the removal of the tube bundle.

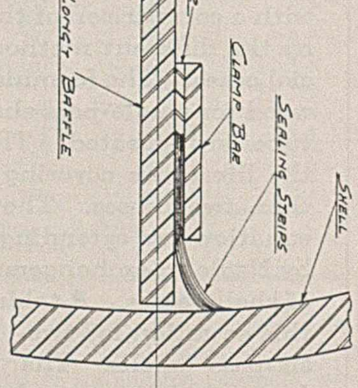


FIGURE 1. DIAGRAM OF SEAL FOR LONGITUDINAL BAFFLE

(3) Making the longitudinal baffle a part of the tube bundle structure so that bundle and baffle will come out of the shell as a unit.

The first method is, as a rule, the most expensive, but all danger of leakage of heat or fluid between passes is eliminated. The second method eliminates any fluid leakage, but there can be heat transfer through the baffle. The amount of this transfer depends on the proportions of the unit—i. e., the area of the baffle compared to the tube area and the temperature difference across the baffle. Ordinarily the assumption of no heat transfer seems justifiable. The second type of unit is more expensive than the third because there are two floating heads which also means additional center bolts with, consequently, a larger shell diameter. In the third type of unit, since the longitudinal baffle is not permanently joined to the shell, there may be some fluid leakage as well as a small amount of heat leakage. The amount of this fluid leakage can be kept to a very small value by the use of a reliable method of sealing between the baffle and the shell. One such method is shown in Figure 1. The effect of this small deviation of conditions in an actual exchanger from those assumed in the derivation of the *MTD* correction is probably quite small when the correction factor is near unity. As the correction factor becomes smaller, the error, no doubt, becomes larger. Referring to the curves presented by Nagle (*2*, Figure 5), we should expect the bottoms of the curves to move slightly to the left if it were possible to evaluate the effect of leakage. Consequently, it seems that the theoretical results should not be trusted too explicitly in the region where the curves mentioned are quite steep.

APPLICATIONS frequently arise where it is desirable to bring the temperatures so close together that even a two-pass exchanger is inoperative. In such cases, as many additional shell passes must be added as are necessary to make the unit operative. Where removable tube bundles with split rings are desired, it is not feasible to put more than two passes in one shell because of the difficulty of sealing the longitudinal baffle inside the shell cover or bonnet. Consequently the usual method of obtaining more shell passes is the use of several single- or two-pass exchangers in series. Where nonremovable tube bundles are used, the limitation of the number of passes is only that of manufacturing feasibility.

Unfortunately, the previous investigators did not consider more than two passes and, consequently, the designer finds some difficulty in determining the number of passes he must use to have an efficient unit. The writer has developed a method for extending the data for a single-pass exchanger to an exchanger of any number of passes. The work of Nagle was chosen as a basis for this extension since the correction factors were worked out for a large number of cases, and the system of presenting the data lends itself to the type of calculations used in making the extension. It is pointed out by Nagle that the correction factors for the individual passes of a two-pass shell are the same and are, of course, equal to the over-all correction factor. It was observed that this same fact holds true for any number of passes as long as the surfaces in the various passes are equal. Making use of this fact in the following equation, we can solve for the temperature ratios which correspond to a given correction factor for any number of passes:

$$\frac{Q_0}{Q_i} = \frac{A_0U_0MTD_0F_0}{A_1U_1MTD_1F_1} = Y \qquad (4)$$

From observation $F_0 = F_1$; by assumption $U_0 = U_1$.

$$N = \frac{A_0}{A_1}$$

$$Y = N\frac{MTD_0}{MTD_1} \qquad (5)$$

$$MTD_0 = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln\dfrac{T_1 - t_2}{T_2 - t_1}}$$

$$MTD_1 = \frac{(T_1 - t_2) - (T_a - t_a)}{\ln\dfrac{T_1 - t_2}{T_a - t_a}}$$

$$T_1 - t_2 = (T_1 - t_a) - (t_2 - t_a) = (X_1 - 1)(t_2 - t_a)$$

$$T_a - t_a = (X_1 - R)(t_2 - t_a)$$

$$T_2 - t_1 = [Y(1 - R) + (X_1 - 1)](t_2 - t_a)$$

Substituting in Equation 5, we obtain:

$$Y = NY\frac{\ln\dfrac{X_1 - 1}{X_1 - R}}{\ln\dfrac{X_1 - 1}{Y(1 - R) + (X_1 - 1)}}$$

$$Y = \left[\left(\frac{X_1 - R}{X_1 - 1}\right)^N - 1\right]\left(\frac{X_1 - 1}{1 - R}\right) \qquad (6)$$

By definition:

$$X_0 = \frac{T_1 - t_1}{t_2 - t_1} = \frac{T_1 + Y(t_2 - t_a) - t_2}{t_2 + Y(t_2 - t_a) - t_2}$$

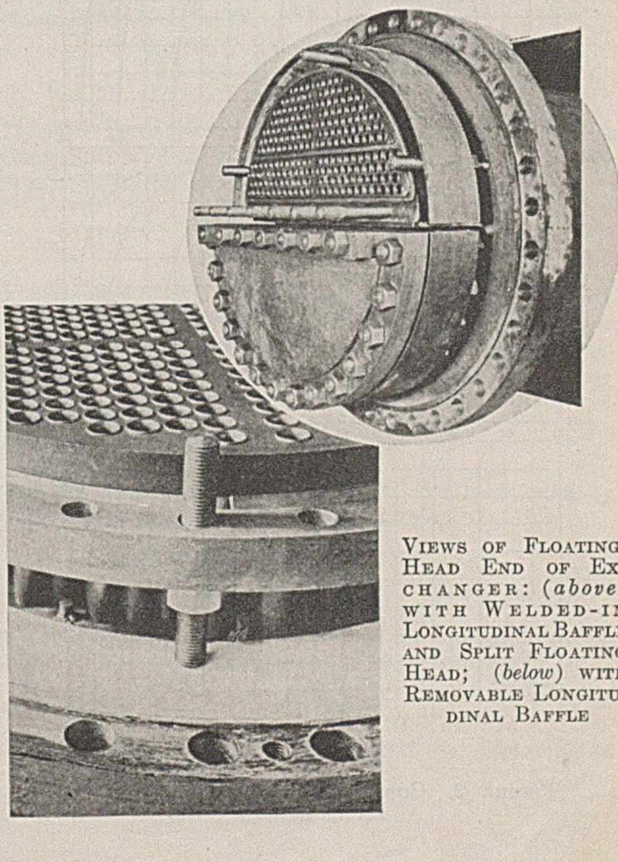
$$X_0 = \frac{Y + X_1 - 1}{Y} \qquad (7)$$

Substituting Equation 6 in 7 we obtain:

$$X_0 = \frac{R - \left(\dfrac{X_1 - R}{X_1 - 1}\right)^N}{1 - \left(\dfrac{X_1 - R}{X_1 - 1}\right)^N} \qquad (8)$$

Thus we obtain an equation which gives X_0 in terms of X_1, R, and N. For a given correction factor we can determine X_1 from the table given by Nagle, and by substitution in Equation 8 we find what X_0 would be for the same correction factor in an exchanger with any number of shell passes.

When $R = 1$, Equation 8 becomes indeterminate. Where R is unity, it is evident that the *MTD* is the same for all



VIEWS OF FLOATING-HEAD END OF EXCHANGER: (*above*) WITH WELDED-IN LONGITUDINAL BAFFLE AND SPLIT FLOATING HEAD; (*below*) WITH REMOVABLE LONGITUDINAL BAFFLE passes—in other words, $Y = N$. Substituting for Y in Equation 7, we obtain,

$$X_0 = \frac{N + X_1 - 1}{N} \qquad (9)$$

which holds true only when R is equal to unity. Solving Equations 8 and 9 for X_1, we obtain the data for Table I.

An analysis was also made based on the last shell pass. While the resulting equation was of slightly different form, the results were identical with those given in Table I.

THE data given in Table I for three-, four-, and six-pass exchangers are plotted in Figure 2. The curves break sharply and come down in a line that is nearly vertical. This tendency becomes more pronounced with an increasing number of passes. With three or more shell passes it almost seems possible to say that the exchanger works either with a fairly good factor or not at all. Also, it can be said that the curves serve more to determine the number of passes necessary than to correct the MTD for a given number of passes.

In the solution of the MTD correction problem, it was assumed that the heat transfer rate and the specific heats of the fluid are the same throughout the exchanger. As a rule, neither of these assumptions is strictly true, but they are the same as those made in the development of the formula for logarithmic MTD and are approximately true as long as there is no change of state.

As pointed out already, this solution applies only when the shell passes are of equal surface; otherwise the correction factor for the different passes would be different. In most cases, where the passes are of unequal surface, a trial-and-error solution must be used to determine the temperature between passes. Each pass can then be figured separately.

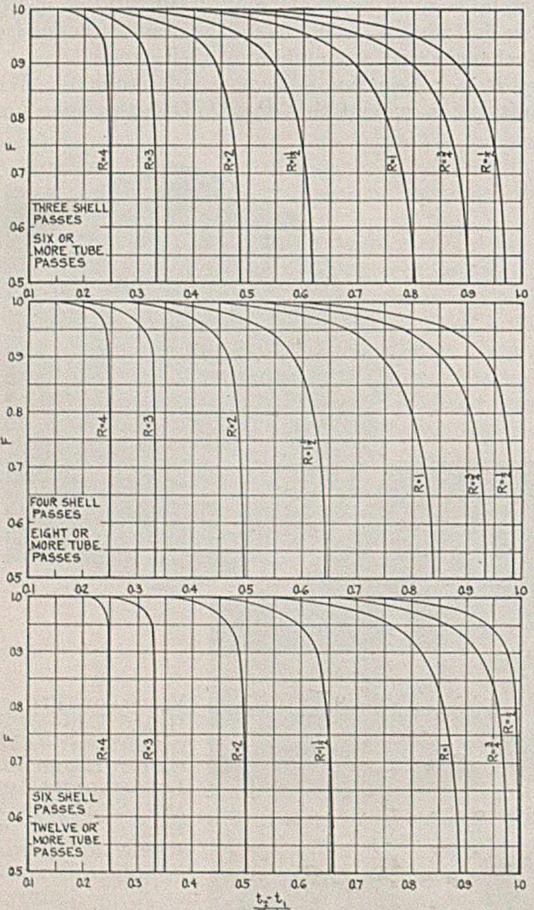


FIGURE 2. CORRECTION FACTOR FOR HEAT EXCHANGERS

TABLE I. DATA FROM SOLUTION OF EQUATIONS 8 AND 9

		$\frac{t_2 - t_1}{T_1 - t_1}$				
R	F	$N = 1$[a]	$N = 2$	$N = 3$	$N = 4$	$N = 6$
4	0.975	0.125	0.183	0.213	0.229	0.2434
	0.950	0.155	0.213	0.232	0.242	0.2484
	0.90	0.181	0.228	0.243	0.247	0.2497
	0.80	0.203	0.239	0.247	0.2494	0.2499
	0.50	0.217	0.245	0.2491	0.2498	....
	0	0.2192	0.245	0.2495	0.2499	....
3	0.975	0.146	0.221	0.263	0.289	0.315
	0.95	0.185	0.260	0.295	0.313	0.327
	0.90	0.224	0.291	0.3162	0.326	0.3314
	0.80	0.257	0.312	0.327	0.331	0.3331
	0.50	0.276	0.321	0.330	0.3326	0.3332
	0	0.2793	0.322	0.331	0.3327	0.3333
2	0.0975	0.182	0.282	0.344	0.388	0.437
	0.95	0.234	0.341	0.398	0.434	0.470
	0.90	0.288	0.392	0.440	0.466	0.489
	0.80	0.336	0.431	0.468	0.485	0.496
	0.50	0.376	0.457	0.484	0.4936	0.4990
	0	0.382	0.460	0.486	0.4945	0.4992
1.5	0.975	0.227	0.356	0.429	0.485	0.551
	0.95	0.285	0.42	0.493	0.541	0.596
	0.90	0.348	0.481	0.547	0.587	0.628
	0.80	0.407	0.532	0.589	0.619	0.648
	0.50	0.458	0.571	0.617	0.640	0.658
	0	0.465	0.577	0.621	0.642	0.659
	0.975	0.275	0.432	0.533	0.603	0.696
	0.95	0.350	0.519	0.617	0.682	0.764
	0.90	0.428	0.599	0.692	0.749	0.818
	0.80	0.501	0.669	0.751	0.802	0.859
	0.50	0.575	0.73	0.803	0.844	0.890
	0	0.5858	0.739	0.809	0.85	0.894
0.75	0.975	0.328	0.569	0.623	0.701	0.799
	0.95	0.411	0.603	0.713	0.783	0.866
	0.90	0.504	0.696	0.795	0.855	0.920
	0.80	0.592	0.774	0.860	0.907	0.960
	0.50	0.659	0.827	0.900	0.939	0.975
	0	0.6667	0.889	0.905	0.942	0.976
0.5	0.975	0.379	0.585	0.710	0.792	0.888
	0.95	0.475	0.688	0.804	0.872	0.943
	0.90	0.576	0.784	0.882	0.933	0.977
	0.80	0.672	0.861	0.936	0.969	0.993
	0.50	0.754	0.916	0.968	0.988	0.9981
	0	0.764	0.921	0.971	0.989	0.9984

[a] From Nagle.

Acknowledgment

The writer wishes to express his gratitude to W. M. Nagle for the helpful suggestions on the preparation of this paper.

Nomenclature

A_0 = area of entire exchanger
A_1 = area of first shell pass
F_0 = MTD correction, entire exchanger
F_1 = MTD correction, first shell pass
MTD_0 = mean temp. difference for entire exchanger
MTD_1 = mean temp. difference for first pass
N = number of shell passes
Q_0 = heat transferred by entire exchanger
Q_1 = heat transferred by first shell pass
$R = \frac{T_1 - T_2}{t_2 - t_1}$
T_1 = inlet temp., shell side
T_2 = outlet temp., shell side
T_a = temp. between first and second passes, shell side
t_1 = inlet temp., tube side
t_2 = outlet temp., tube side
t_a = temp. between first and second shell passes, tube side
U_0 = heat transfer rate of entire exchanger
U_1 = heat transfer rate of first shell pass
$X_0 = \frac{T_1 - t_1}{t_2 - t_1}; \quad X_1 = \frac{T_1 - t_a}{t_2 - t_a}$
$Y = \frac{Q_0}{Q_1} = \frac{T_1 - T_2}{T_1 - T_a} = \frac{t_2 - t_1}{t_2 - t_a}$
θm = true mean temp. difference

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HEATING AND COOLING RECTANGULAR AND CYLINDRICAL SOLIDS

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This paper deals with the estimation of surface and central temperatures as functions of time in cases of heating or cooling solids of various shapes by convection. A pair of Schack-type charts is presented for the infinite cylinder, and Schack's charts are reproduced for the infinite slab. It is shown how the charts can be used singly or in pairs to estimate the surface and central temperatures of finite shapes such as rectangular bars, brick shapes (rectangular parallelepipeds), short cylinders, etc., when these shapes are exposed to convective heating or cooling. Mathematical proofs of these new methods are presented. The same methods can be applied to the Gurney-Lurie charts which have been reproduced in several reference works.

THE purpose of this paper is to review the published work on the solution of problems involving heat transfer by convection to and from solid slabs and cylinders, and to extend the utility of the methods which have been developed to other rectangular and cylindrical shapes.

In 1923 Gurney and Lurie (*3*) presented a set of charts for the slab, infinite cylinder, sphere, and semi-infinite solid. By the use of the appropriate chart, it is possible to predict the temperature at any time and at any location within the solid, given the constant temperature of the fluid medium to or from which heat is being transferred by convection, the initial uniform temperature of the solid, the surface coefficient of heat transmission (film coefficient), and the density, specific heat, thermal conductivity, and significant dimension of the solid. The Gurney-Lurie charts have been widely accepted by American authors of reference books (*4*, *5*, *9*, *12*).

In 1930 Schack (*10*) published a chart based upon the same theory as used by Gurney and Lurie. Instead of attempting to present on a single chart the information necessary to determine the temperature and any location in the solid, Schack used one chart for the surface of the solid and another for the center. Other Schack charts could be plotted for intermediate locations within the solid, but in most practical cases the temperature history at the surface and at the center is all that is needed. The Schack charts for the slab have also been published in reference works (*1*, *11*) and are reproduced here as Figures 1 and 2.

Gurney and Lurie did not publish the mathematical equations underlying their charts, but they were derived independently by the writer in connection with the analogous case of liquid water transfer in the drying of porous solids (*6*) and checked with the equations published by Gröber and Erk (*2*). In order to show how the use of the charts may be extended, it is necessary to present a brief mathematical analysis. The following nomenclature is a modification of that used by McAdams (*5A*):

Nomenclature

t = temp., varying with time and location in solid
t_0 = initial uniform temp. of solid
t_s = constant temp. of surroundings (fluid medium)
x, y, z, r = distance from center of solid in x, y, z, or r direction
θ = time
k = thermal conductivity
C = specific heat
ρ = density
$\alpha = k/C\rho$ = thermal diffusivity
h = surface or film coefficient of heat transmission
R = radius of cylinder
a, b, c = half-thickness of rectangular solid in x, y, and z directions, respectively
m_a, m_b, m_c, m_R = respectively, k/ha, k/hb, k/hc, k/hR, dimensionless ratios
Nu_a, Nu_b, Nu_c, Nu_R = modified Nusselt No. = $1/m_a$, $1/m_b$, etc.
X_a, X_b, X_c, X_R = $\alpha\theta/a^2$, $\alpha\theta/b^2$, etc.

Rectangular Shapes

The general partial differential equation for heat flow in rectangular coördinates is:

$$\frac{\delta t}{\delta \theta} = \alpha \left(\frac{\delta^2 t}{\delta x^2} + \frac{\delta^2 t}{\delta y^2} + \frac{\delta^2 t}{\delta z^2} \right) \tag{1}$$

If heat is permitted to flow only in the x direction, there is no temperature gradient in the y or z directions, and the equation reduces to that of the slab:

$$\frac{\delta t}{\delta \theta} = \alpha \left(\frac{\delta^2 t}{\delta x^2} \right)$$

For a slab of thickness $2a$, the central plane being at $x = 0$, the case of heating or cooling by convection at the surfaces $x = \mp a$ is represented by the above partial differential equation and by the following conditions:

$$\pm k \frac{\delta t}{\delta x} = h(t_s - t) \text{ at } x = \mp a \tag{2}$$

Each side of this equation represents the heat quantity passing across unit surface area in unit time.

$$k \frac{\delta t}{\delta x} = 0 \text{ at } x = 0 \tag{3}$$

representing the condition where there is no heat flow across the central plane of the slab on account of symmetry.

$$t = t_0 \text{ when } \theta = 0 \tag{4}$$

indicating uniformity of temperature at the beginning of heating or cooling.

$$t = t_s \text{ when } \theta = \infty \tag{5}$$

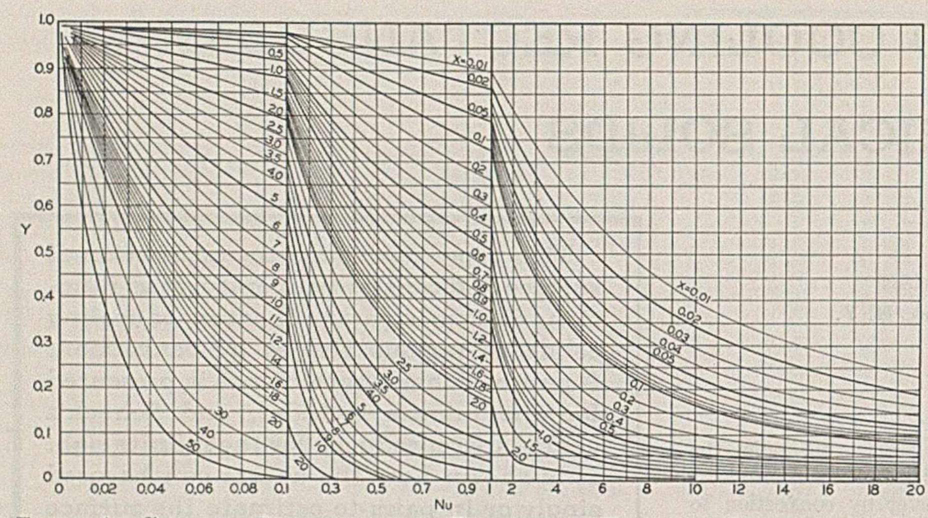

FIGURE 1. CHART FOR DETERMINING THE TEMPERATURE HISTORY OF POINTS ON THE SURFACES OF RECTANGULAR SHAPES

indicating that eventually the whole slab will be heated or cooled to the temperature of the surroundings.

An equation, in dimensionless form, satisfying the differential equation and the other imposed conditions is

$$\frac{t_s - t}{t_s - t_0} = 2\sum_{n=1}^{\infty} A_n e^{-\beta_n^2 X_a} \cos\left(\beta_n \frac{x}{a}\right) = Y_x$$

where

$$A_n = \frac{m_a}{(1 + \beta_n^2 m_a^2 + m_a)\cos\beta_n}$$

and β_n is defined by $\cot\beta = m_a\beta$, and values β_1, β_2, etc., being the first, second, etc., roots of this equation. Tabulated values of β were published by Newman and Green (8). Y_x is set up as a convenient symbol for later use. Figure 1 gives Y_x plotted as ordinate against $Nu_x = 1/m_x$ as abscissa for the case of $x = \mp a$, and each curve represents a fixed value of $X_a = \alpha\theta/a^2$. Figure 2 gives corresponding values for the case of $x = 0$.

If it were desired to set up the condition that heat was to flow only in the y direction then the partial differential equation would be

$$\frac{\delta t}{\delta\theta} = \alpha\left(\frac{\delta^2 t}{\delta y^2}\right)$$

and the solution, complying with the same type of boundary conditions, would be

$$\frac{t^s - t}{t_s - t_0} = 2\sum_{n=1}^{\infty} A_n e^{-\beta_n^2 X_b} \cos\left(\beta_n \frac{y}{b}\right) = Y_y$$

It is obvious that Figures 1 and 2 would apply equally well to this case.

If heat were permitted to flow in the x and y directions, but not in the z direction, the differential equation would be:

$$\frac{\delta t}{\delta\theta} = \alpha\left(\frac{\delta^2 t}{\delta x^2} + \frac{\delta^2 t}{\delta y^2}\right)$$

This is the case of a rectangular bar of which the length is very great as compared with the dimensions of a cross section. The thickness of the bar in the x direction is $2a$ and in the y direction $2b$. It can be proved that an equation satisfying the conditions for this case is:

$$\frac{t_s - t}{t_s - t_0} = Y_x Y_y$$

The proof is carried out by evaluating the partial derivatives:

$$-\frac{\delta t}{\delta\theta} = Y_x\frac{\delta Y_y}{\delta\theta} + Y_y\frac{\delta Y_x}{\delta\theta}$$

$$-\frac{\delta^2 t}{\delta x^2} = Y_y\frac{\delta^2 Y_x}{\delta x^2} \text{ and}$$

$$-\frac{\delta^2 t}{\delta y^2} = Y_x\frac{\delta^2 Y_y}{\delta y^2}$$

Substituting these values in the partial differential equation for the bar gives:

$$Y_x\frac{\delta Y_y}{\delta\theta} + Y_y\frac{\delta Y_x}{\delta\theta} = \alpha\left(Y_y\frac{\delta^2 Y_x}{\delta x^2} + Y_x\frac{\delta^2 Y_y}{\delta y^2}\right)$$

From the definitions of Y_x and Y_y in the cases of unidirectional heat flow,

$$\frac{\delta Y_x}{\delta\theta} = \alpha\left(\frac{\delta^2 Y_x}{\delta x^2}\right) \text{ and } \frac{\delta Y_y}{\delta\theta} = \alpha\left(\frac{\delta^2 Y_y}{\delta y^2}\right)$$

Substituting these values in the equation immediately preceding, both sides become identical. By similar methods, all of the other conditions can be shown to be satisfied and the equation proved valid.

For the rectangular parallelepiped (brick shape), the solution is

$$\frac{t_s - t}{t_s - t_0} = Y_x Y_y Y_z$$

and the general form of differential Equation 1 is satisfied. Thus the single pair of charts for the case of a slab (Figures 1 and 2) can be used for rectangular bars heated or cooled on four sides and brick shapes on six sides. The procedure is

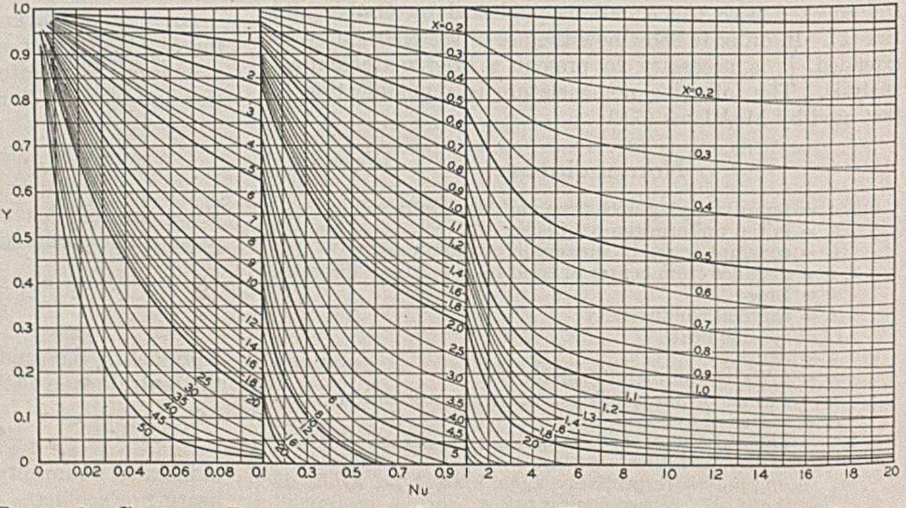

FIGURE 2. CHART FOR DETERMINING THE TEMPERATURE HISTORY OF POINTS AT THE CENTERS OF RECTANGULAR SHAPES

simply the multiplication of the numerical values of the proper ordinates read from the charts.

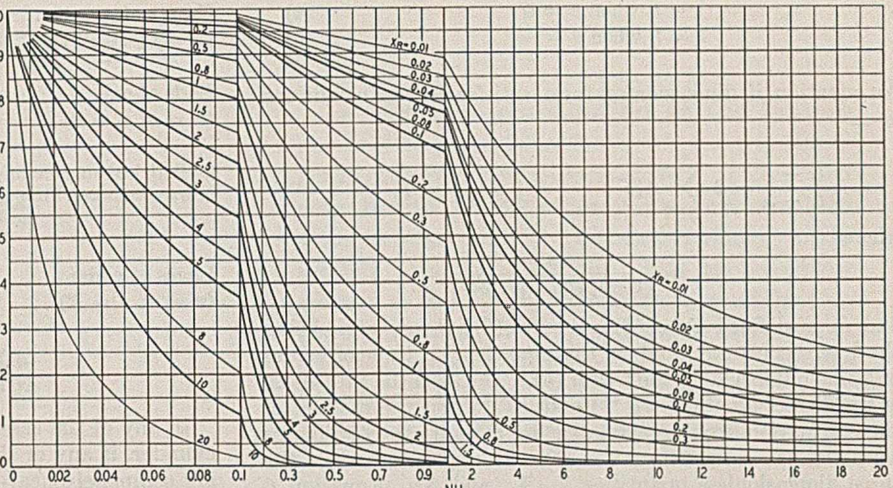

Figure 3. Chart for Determining the Temperature History of Points on Cylindrical Surfaces

Numerical Example for Heating Rectangular Shapes

A fire brick of dimensions 9 × 4.5 × 2.5 inches, initially at 70° F., is suspended in a flue through which furnace gases at 300° F. are traveling at a rate which produces a surface coefficient of h = 4.1 B. t. u. per square foot per hour per ° F. Estimate the temperatures at the following points at the end of one hour: the center of the brick, any corner of the brick, the center of the 9 × 4.5 inch faces, the centers of the 9 × 2.5 inch faces, the centers of the 4.5 × 2.5 inch faces, the middle of the long edges. The data are as follows:

k = 0.3 B. t. u. ft./sq. ft. hr. ° F.
ρ = 103 lb./cu. ft.
C = 0.25 B. t. u./lb. ° F.
$\alpha = k/C\rho$ = 0.01164 sq. ft./hr.
$t_s = 300$; $t_0 = 70$; $\theta = 1$
a = 0.375 ft.; b = 0.1875 ft.; c = 0.104 ft.

From the above:

$X_a = 0.0828$; $X_b = 0.3313$; $X_c = 1.073$
$Nu_a = 5.125$; $Nu_b = 2.562$; $Nu_c = 1.425$

From the charts:

	For $x, y, z = 0$	For $x, y, z = a, b, c$
Y_x	0.98	0.325
Y_y	0.75	0.29
Y_z	0.43	0.245

For all cases:

$$\frac{t_s - t}{t_s - t_0} = \frac{300 - t}{300 - 70} = \frac{300 - t}{230}$$

Center of brick: ($x = 0$; $y = 0$; $z = 0$) $\frac{300 - t}{230} = (0.98)(0.75)(0.43) = 0.316$
$t = 300 - 72.6 = 227.4$° F.

Corner of brick: ($x = a$; $y = b$; $z = c$) $\frac{300 - t}{230} = (0.325)(0.29)(0.245) = 0.023$
$t = 300 - 5.3 = 294.7$° F.

Center of 9 × 4.5 face: ($x = 0$; $y = 0$; $z = c$) $\frac{300 - t}{230} = (0.98)(0.75)(0.245) = 0.18$
$t = 300 - 41.5 = 258.5$° F.

Center of 9 × 2.5 face: ($x = 0$; $y = b$; $z = 0$) $\frac{300 - t}{230} = (0.98)(0.29)(0.43) = 0.122$
$t = 300 - 28 = 278$° F.

Center of 4.5 × 2.5 face: ($x = a$; $y = 0$; $z = 0$) $\frac{300 - t}{230} = (0.325)(0.75)(0.43) = 0.105$
$t = 300 - 24.2 = 275.8$° F.

Middle of long edge: ($x = 0$; $y = b$; $z = c$) $\frac{300 - t}{230} = (0.98)(0.29)(0.245) = 0.0695$
$t = 300 - 16 = 284$° F.

As would be expected, the temperatures are in the following order, from lowest to highest: center of brick, center of 9 × 4.5 face, center of 9 × 2.5 face, center of 4.5 × 2.5 face, middle of longest edge, corner.

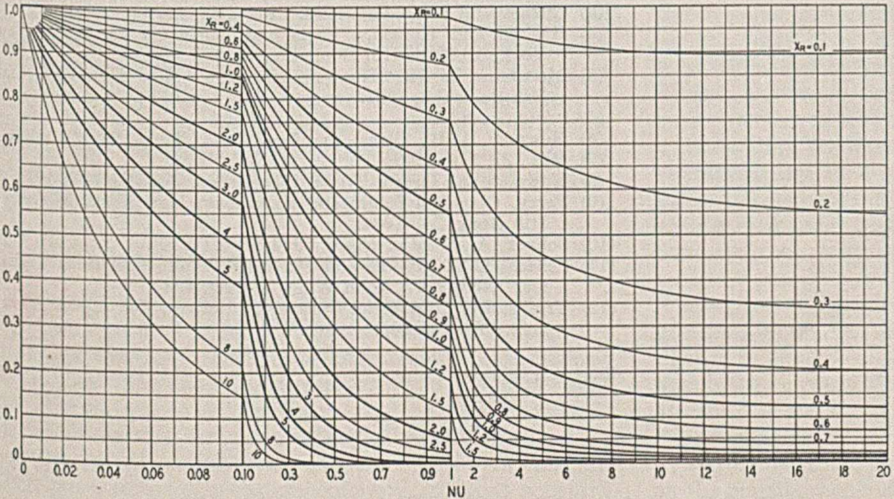

Figure 4. Chart for Determining the Temperature History at the Axes of Cylindrical Shapes

Cylindrical Shapes

The simplest case is a circular solid cylinder of infinite length or its equivalent (short cylinder with insulated ends). For this case, the partial differential equation in cylindrical coördinates is:

$$\frac{\delta t}{\delta \theta} = \alpha \left(\frac{\delta^2 t}{\delta r^2} + \frac{1}{r} \frac{\delta t}{\delta r} \right)$$

For cylinder of radius $r = R$, the axis being at $r = 0$, the case of heating or cooling by convection is represented by the differential equation and by

$$k \frac{\delta t}{\delta r} = h(t_s - t) \text{ at } r = R \quad \text{(2A)}$$

$$k \frac{\delta t}{\delta r} = 0 \text{ at } r = 0 \quad \text{(3A)}$$

$$t = t_0 \text{ when } \theta = 0 \tag{4}$$
$$t = t_s \text{ when } \theta = \infty \tag{5}$$

An equation, in dimensionless form, satisfying these conditions is

$$\frac{t_s - t}{t_s - t_0} = 2\sum_{n=1}^{\infty} A_n e^{-\beta_n^2 X_r} J_0\left(\beta_n \frac{r}{a}\right) = Y_r \tag{6}$$

where

$$A_n = \frac{m_r}{(1 + \beta_n^2 m_r^2)[J_0(\beta_n)]}$$

and β_n is defined by $J_0(\beta) = m_r \beta J_1(\beta)$; β_1, β_2, etc., being the first, second, etc., roots of this equation. A table of values of β was published by the writer (*6*). The essential properties of the Bessel functions $J_0(\ )$ and $J_1(\ )$ and the method of transformation from rectangular to cylindrical coördinates were also given by the writer (*7*). Taking as variables the three dimensionless quantities Y_r, X_r, and Nu_r, Equation 6 was reduced to a set of tables which were used to plot the curves of Figures 3 and 4, analogous to Figures 1 and 2.

The case of the right circular solid cylinder with convection at the cylindrical surface and the plane ends is represented by

$$\frac{\delta t}{\delta \theta} = \alpha\left(\frac{\delta^2 t}{\delta r^2} + \frac{1}{r}\frac{\delta t}{\delta r} + \frac{\delta^2 t}{\delta x^2}\right)$$

where x is the distance along the axis, and the point $x = 0$, $r = 0$ is the center of gravity. If the length is $2a$ and the diameter $2R$, the solution for this case is

$$\frac{t_s - t}{t_s - t_0} = Y_r Y_x$$

and solutions of numerical problems may be effected by the use of Figures 1 to 4.

Numerical Example for Cooling a Cylindrical Shape

A circular fire-clay cylinder 4.5 inches in diameter and 5 inches long, initially at a uniform temperature of 300° F., is suspended in a cooling duct through which air at 70° F. is passing at a rate which produces a surface coefficient of h = 4.1 B.t.u. per square foot per hour per ° F. Estimate the temperatures at the following locations at the end of one hour: the center of gravity, the ends of the axis, the cylindrical surface midway between the ends, the edges at the ends.

The data are the same as were given for the previous example except:

$t_s = 70$; $t_0 = 300$
$a = 0.208$ ft.; $R = 0.1875$ ft.

From the above:

$X_a = 0.2682$; $X_r = 0.3313$
$Nu_a = 2.85$; $Nu_r = 2.562$

From the charts:

	For $x, r = 0$	For $x, r = a, R$
Y_x	0.83	0.36
Y_r	0.525	0.215

For all cases:

$$\frac{t_s - t}{t_s - t_0} = \frac{70 - t}{70 - 300} = \frac{t - 70}{230}$$

Center of gravity: ($x = 0$; $r = 0$)

$$\frac{t - 70}{230} = (0.83)(0.525)$$
$$t = 70 + 100 = 170° \text{ F.}$$

Ends of axis: ($x = a$; $r = 0$)

$$\frac{t - 70}{230} = (0.36)(0.525)$$
$$t = 70 + 43.5 = 113.5° \text{ F.}$$

Cylindrical surface midway between ends:

$$\frac{t - 70}{230} = (0.83)(0.215)$$
$$t = 70 + 41 = 111° \text{ F.}$$

Edges at ends: ($x = a$; $r = R$)

$$\frac{t - 70}{230} = (0.36)(0.215)$$
$$t = 70 + 17.8 = 77.8° \text{ F.}$$

Miscellaneous Notes

In any of the cases given in this paper, except the infinite cylinder, if any of the plane faces not parallel to each other are completely heat-insulated, it is necessary only to double the dimension perpendicular to each insulated face and then to carry out the calculations in the usual way. If a pair of parallel faces is insulated, the corresponding dimension is eliminated.

In the case of a laminated solid, in which the thermal conductivity may be different along the various axes, the value of thermal diffusivity may be correspondingly adjusted for the different directions, and the calculation carried out as usual.

If the surface coefficient, h, is different at the various faces, these different values of h may be used, the only limitation being that of maintaining symmetry; the value of h must be the same for any pair of parallel faces.

The data for the solution of problems may be taken from the Gurney-Lurie plots; the Schack-type plots are preferred by the writer merely on account of easier reading and interpolation.

Acknowledgment

The writer wishes to acknowledge the assistance rendered by Boris Gouguell, who computed the tables underlying Figures 3 and 4 and checked the derivations and calculations given in this paper.

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Permeability of Paint Films to Moisture

Effect of Humidity, Temperature, and Aging

In further investigation of the factors controlling penetration of paint films by moisture, the permeability of the film was found to be closely proportional to the water vapor concentration only within certain limits. The absorption of water by the paint film parallels the permeability. The temperature coefficient is small and shows a slight decrease in permeability with rise in temperature. Upon aging or exposure to weather, the permeability of a paint film follows a typical course which includes, first, a decrease, followed later by a substantial increase in permeability, which eventually reaches a very low value at failure of the paint film.

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THIS paper continues the report on the investigations of permeability of paint films being carried out at this laboratory. The first paper in the series, by Wray and Van Vorst (*7*), described the experimental methods employed, and established among other things, the following fundamental relations:

1. The moisture impedance (or resistance) of a paint or varnish film is proportional to the thickness (within working limits).
2. In aluminum paints the moisture impedance increases regularly with increase in the aluminum powder concentration.
3. In aluminum paints of the same pigment concentration, the moisture impedance increases as the mesh size of the powder decreases or the covering area (*1*) increases.
4. The superior effect of aluminum bronze powder in increasing the moisture impedance of a vehicle appears to be related to the structure presented by overlapping flakes, which gives a greatly increased diffusion path.

In the title to this paper, the term "permeability" is employed because it has been commonly used and its significance is readily apparent. The permeability of a coating is expressed as the milligrams of moisture diffusing through one square centimeter of film per hour. In comparing data, however, it is frequently more convenient to employ the reciprocal of permeability, which has been termed the "moisture impedance" of the film. As previously stated, the moisture impedance is proportional to the thickness of the film. For example, the moisture impedance of a film is doubled by doubling the thickness.

Effect of Water Vapor Concentration

In the first report (*7*) the moisture impedances of the coatings were measured under a single condition of temperature and vapor pressure. Most of the measurements were made at 80° F. (26.7° C.) and with atmospheres of 0 and 95 per cent humidity on the two sides of the coating. It is important to know how the moisture permeability changes with change in the water vapor concentration on the moist side of the film. Therefore a series of measurements was made at constant temperature (80° F.) with dry air, 0 humidity, on one side of the paint film, and with atmospheres of different humidities on the other side of the paint film. In successive tests, the relative humidity was varied from about 10 to 100 per cent.

In making these tests, aluminum paint films applied on amalgamated tin plate and later stripped, were sealed to the opening of flat crystallizing dishes containing a drying agent, activated alumina. The moisture penetrating the paint film and absorbed by the activated alumina in any given period was determined by weighing the dish with the attached paint film. One series of measurements was made by placing the dishes in desiccators containing sulfuric acid, adjusted in concentration to give the desired water vapor concentration in the atmosphere in the desiccator. Under these conditions, reliance must be placed on diffusion processes to maintain the atmosphere at the surface of the paint film at the required water vapor concentration. Accordingly, check tests were made by placing the dishes with the attached paint films in a large cabinet with circulating air where, by suitable regulating devices, an atmosphere of constant temperature and constant moisture content was maintained.

These data are shown in Table I and Figure 1. With air containing less than about 20 grams of moisture per cubic meter (80 per cent humidity at 80° F.), the moisture permeability of the film is closely proportional to the water vapor concentration at the moist face. Above this concentration, moisture penetration of the film increases at a more rapid rate. The form of the graph suggested that the amount of moisture absorbed by the film itself might show a similar variation with change in humidity. A series of tests was therefore made in which the moisture absorption of the paint film itself was determined at 80° F. and in atmospheres of different water vapor concentrations. These data were also plotted on Figure 1, and the resulting curve shows a decided point of inflection in the neighborhood of 80 per cent humidity, just as did the curves showing the relationship between permeability and moisture content.

TABLE I. MOISTURE PENETRATION AND IMPEDANCE OF ALUMINUM PAINT[a] IN AIR OF DIFFERENT MOISTURE CONTENTS

		Total Weight of Moisture Penetration		Moisture Impedance[b]			
				Observed		Interpolated[c]	
Relative Humidity of Air	Moisture Content of Air	In desiccator over sulfuric acid	In cabinet with circulating air	In desiccator over sulfuric acid	In cabinet with circulating air	In desiccator over sulfuric acid	In cabinet with circulating air
Per cent	*G./cu. m.*	*Gram*	*Gram*				
10	2.50	0.013	...	122	..	203	..
20	5.02	0.027	...	59	..	98	..
25	6.12	0.039	0.044	41	36	68	60
37	9.27	0.063	0.071	25	22	42	37
51	12.76	0.096	0.113	16	14	28	23
72	18.01	0.152	0.167	10	9.5	17	16
80	20.02	0.187	...	8.5	..	14	..
90	22.50	...	0.236	...	6.7	...	11
100	25.00	0.314	...	5.0	..	8.3	..

[a] Made with 2 pounds of aluminum paste per gallon of long-oil varnish (240 grams per liter).

[b] Moisture impedance = $\frac{\text{area of film in sq. cm.} \times \text{hours}}{\text{mg. of moisture penetration}}$.

[c] Based on a film thickness of 0.025 mm.

A similar relationship between moisture absorption and humidity was observed for other organic materials such as wood, cellulose, etc. Seborg and Stamm (*4*), Sheppard and Newsome (*5*), and Stamm and Loughborough (*6*), for example, have published graphs showing the moisture content–humidity relations for wood and wood pulp; these graphs are similar in shape to those of Figure 1. They show a more rapid absorption of water (departure from linear relationship) as the humidity rises above 80 per cent at 25° C. Similar results have been obtained by Pidgeon and Maass (*3*) for wood and cellulose.

One explanation offered in the case of cellulose, wood pulp, etc., is that up to about 80 per cent humidity at 25° C. the moisture is adsorbed on the intermicellar surfaces. Above that point the moisture concentration becomes so high that, in effect, moisture condenses in the intermicellar spaces and swelling takes place. Whether or not that is the explanation, the phenomenon is qualitatively the same in the paint films examined as in the case of cellulose. Most observations recorded in the literature, as well as those of the writers, have for convenience been made with air at about 95 per cent humidity, or even with saturated air, on one side of the film and with dry air on the other. Some authors have calculated the permeability or diffusivity constants for paint films from experiments made with moisture-saturated atmospheres. These constants, however, do not apply, even with the usual partial pressure corrections, to paint films under the commonest conditions of service—namely, below about 80 per cent humidity at summer temperatures.

The permeability of a paint film in contact with liquid water was found to be lower than in an atmosphere of 100 per cent humidity. For example, a film with a moisture impedance of 13 at 100 per cent humidity and 80° F. (26.7° C.) showed a moisture impedance of 18 in contact with liquid water at the same temperature. It seems probable that the water does not wet the paint film well and that surface tension reduces the effective concentration of water vapor at the interface between water and paint film.

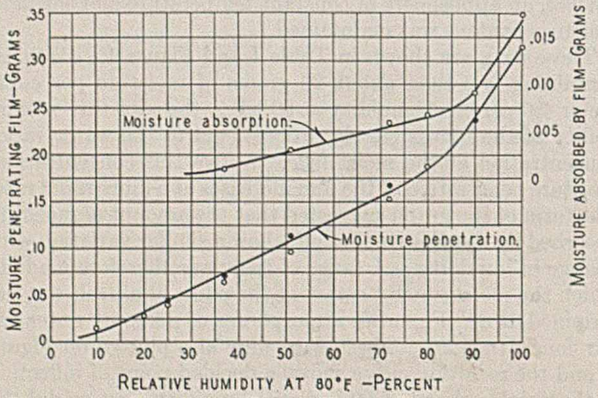

FIGURE 1. EFFECT OF WATER VAPOR CONCENTRATION ON MOISTURE PENETRATION AND MOISTURE ABSORPTION BY ALUMINUM PAINT FILM

Effect of Temperature

A few experiments were made to determine the temperature coefficient of moisture impedance. In these tests, the moisture impedances of two paint films were determined at four temperatures from 60° to 90° F. (15.6° to 32.2° C.); the moisture content of the air was maintained at 12.8 grams per cubic meter in each test, so that the observed differences in permeability might be ascribed entirely to the effect of temperature:

		Moisture Impedance[b] at Relative Humidity of:			
Al Paint[a]	Obsvd. Film Thickness	100% at 60° F. (15.6° C.)	72% at 70° F. (21.1° C.)	51% at 80° F. (26.7° C.)	37% at 90° F. (32.2° C.)
	Mm.				
Varnish A	0.015	19	22	22	22
Varnish B	0.016	47	62	73	71

[a] Made with 2 pounds aluminum paste per gallon (240 grams per liter).

[b] Based on film thickness of 0.025 mm. per coat.

The differences observed were relatively small and indicated that the moisture impedance increased slightly with rise in temperature. The data secured were quite insufficient, however, to establish the temperature coefficient with any degree of precision, and the observations should be considered only qualitative in nature. In this connection another analogy

TABLE II. COMPOSITION OF PAINTS

Paint Coating	Wet Basis		Dry Basis
	% by weight	*% by vol.*	*% by vol.*[a]
Aluminum paint:			
Standard Varnish powder	22	9	16
Varnish A[b]	78	91	84
Standard Lining powder	22	9	16
Varnish A	78	91	84
Extra Fine Lining powder	22	9	16
Varnish A	78	91	84
Standard Paste pigment	13	4.9	11.3
Varnish A	87	95.1	88.7
Standard Varnish powder	22	9	18
Varnish B[c]	78	91	82
Standard Varnish powder	22	9	15
Varnish C[d]	78	91	85
White lead–zinc oxide (varnish):			
White lead (in oil)	37 (dry)	18	26
Zinc oxide (in oil)	24 (dry)		
Linseed oil (from pastes)	10	82	74
Varnish A	29		
White lead–zinc oxide (oil):			
White lead	36	24	26
Zinc oxide	23		
Inert material	7		
Linseed oil and thinner	34	76	74
Lithopone in varnish:			
High-strength lithopone	58	22	37
Varnish A	42	78	63
Lithopone in oil:			
High-strength lithopone	67	30	30
Linseed oil and drier	33	70	70

[a] Determined by calculation using values for density given by Gardner and Levy.

[b] Varnish A: 80-gallon ester gum varnish; 50 per cent nonvolatile content.

[c] Varnish B: glycerol phthalate varnish; 46 per cent nonvolatile content.

[d] Varnish C: 50-gallon Bakelite resin varnish; 58 per cent nonvolatile content.

may be noted between the behavior of the paint films and cellulose or wood. According to Stamm and Loughborough (*6*), for example, the so-called fiber saturation point (equilibrium moisture content) of wood decreases with increase in temperature. This decrease is about 0.1 per cent for each rise in temperature of 1° C. Similarly, it is probable that the paint films absorb less moisture at the higher temperatures and hence show a lower permeability. The temperature-permeability effect, however, is apparently small and, under most conditions, negligible.

Effect of Aging

The data so far given in this paper, as well as in the previous paper (*7*), are for what might be called the "initial" moisture impedance of the paint film. The paint films are in a state of change from the moment they are applied. The greatest change takes place when the wet and mobile paint film dries to a relatively solid and nontacky coating. Change does not stop here, however, for the dry paint film undergoes a process of aging which may be rapid if exposed to the weather or similar deteriorating agencies. During this aging process, the paint film usually becomes harder and less distensible and eventually reaches a brittle stage where its effective properties are seriously impaired. In the early stages of drying, chemical changes such as the absorption of oxygen may be an important factor. Later on, however, the hardening of the paint film may be the result of a change of liquid phase to solid (*2*).

During this aging process, the moisture impedance of a paint film follows a typical cycle. There is an initial period during which the moisture impedance shows little change or else a gradual increase. In nearly every case, however, the moisture impedance eventually shows a sharp increase. This increase appears to be associated with a marked hardening of the paint film, and soon thereafter the paint film begins to show a decrease in moisture impedance. This decrease may be very rapid, typical of the less durable paints, or it may be gradual and the moisture impedance may still remain at a substantial figure over an extended period. Paint films which take only a short initial period to rise to a maximum moisture impedance, generally show a sharp and rapid decline in moisture impedance. Aluminum paints, and especially those made with synthetic resin vehicles of good quality, require an extended period before the peak of moisture impedance is reached; thereafter the decline is much slower. This behavior gives the paint a long period throughout which it shows adequate moisture-proofing power. Table II gives the composition of the various paints tested.

Table III gives the moisture impedance of various paint films as applied and after weather exposure. These films were applied to metal panels by spinning and were exposed on the roof of the laboratory, at a 45° angle facing south, for various periods; the longest period reported here was 36 months. Some of these tests are being continued. The panels were removed from the test rack at intervals of 6 months; circular disks of paint film were then cut and stripped from the panels for moisture impedance tests. The bare spot on the panel was then recoated with aluminum paint and the panel returned to the roof for further exposure.

The first four aluminum paints given in Table III show the behavior on exposure of aluminum paint films made with aluminum powders of varying degrees of fineness and with aluminum paste. These films show that the finer powders have a greater effect in increasing the moisture impedance of the paint film. The finer mesh powders also give a paint film which maintains its moisture impedance for a longer period. Although the three paints (Table III) made with dry powder contained 2 pounds of powder per gallon of vehicle (240 grams per liter), the one made with aluminum paste pigment contained 2 pounds of paste with a metal content of 60 per cent. These latter paint films, therefore, carried only a little more than half as much metal powder as the paint made with Standard Varnish powder, for example, but showed

Table III. Moisture Impedance of Paint Films after Weather Exposure

Paint Coating[a]	No. of Coats	Film Thickness *Mm.*	Moisture Impedance[b] after: Initial	6 mo.	12 mo.	18 mo.	24 mo.	36 mo.
Al paint in varnish A, Standard Varnish powder	1	0.028	7.0	9.4	4.2	1.3	0.2	[c]
	2	0.049	17	16	25	22	18	14
	3	0.073	27	23	27	33	28	24
Al paint in varnish A, Standard Lining powder	1	0.021	12	18	37	6.9	3.6	[d]
	2	0.038	25	28	42	26	66	..
	3	0.054	36	38	44	35	79	..
Al paint in varnish A, Extra Fine Lining powder	1	0.019	13	19	36	13	12	[d]
	2	0.035	27	28	32	28	120	..
	3	0.054	36	35	35	34	56	..
Al paint in varnish A, Al paste pigment (Standard grade)	1	0.016	7.8	13	0.3	0.2	[c]	..
	2	0.028	17	20	28	14	11	[d]
	3	0.042	24	29	31	28	72	..
Al paint in varnish B	1	0.035	7.1	14	16	18	10	4.3
	2	0.056	16	21	38	44	39	30
	3	0.085	33	29	33	48	48	37
Al paint in varnish C	1	0.040	11	16	14	10	1.9	0.3
	2	0.075	24	22	21	24	25	27
	3	0.120	36	30	35	43	39	38
White lead–ZnO in varnish A	1	0.038	2.7	[c]	..	..	..	..
	2	0.082	6.4	[c]	..	..	..	..
	3	0.181	8.6	12	[c]	..	..	..
White lead–ZnO in linseed oil	1	0.055	1.2	1.6	[c]	..	..	..
	2	0.110	2.2	3.0	[c]	..	..	..
	3	0.165	3.8	4.8	0.5	[c]	..	..
High-strength lithopone in varnish A	1	0.020	6.6	[c]	..	..	..	..
	2	0.048	12	[c]	..	..	..	..
	3	0.092	18	3.1	[c]	..	..	..
High-strength lithopone in linseed oil	1	0.021	2.4	[c]	..	..	..	..
	2	0.052	3.7	[c]	..	..	..	..
	3	0.093	5.2	3.6	[c]	..	..	..
Gray glycerol phthalate enamel	1	0.021	3.1	4.5	[c]	..	..	..
	2	0.039	7.9	9.5	21	12	2.0	[c]
	3	0.076	11	13	41	18	15	12
Gray Bakelite enamel	1	0.018	7.2	[c]	..	..	..	..
	2	0.049	11	12	[c]	..	..	..
	3	0.098	13	14	[c]	..	..	..
Clear varnish B	1	0.018	4.2	15	1.9	0.6	[c]	..
	2	0.035	6.0	18	25	5.0	[c]	..
	3	0.060	7.9	24	34	19	22	[c]
Clear varnish C	1	0.025	4.7	10	0.6	[c]	..	..
	2	0.055	7.9	20	17	10	5.5	3.2
	3	0.075	9.4	26	23	14	16	9.8
Al primer (varnish A) + 2 coats white lead–ZnO paint	3	0.114	9.7	5.3	[c]	..	..	..
Al primer (varnish B) + 2 coats white lead–ZnO paint	3	0.160	11	14	20	1.8	0.1	[c]

[a] Where not otherwise stated, the Standard Varnish grade of aluminum powder was used in the aluminum paint.
[b] Based on film thickness of 0.025 mm. per coat.
[c] Film was too brittle to remove intact for measurement.
[d] Tests not yet complete.

about as good retention of moisture-proofing power. The difference in behavior may be ascribed generally to the much finer mesh size of the powder in the paste, and hence to the great number of flakes in unit weight.

The high-strength lithopone in varnish A showed almost as good value as the Standard Varnish powder in reinforcing the moisture impedance of the vehicle. Upon exposure, however, a different performance is apparent. The film made with the high-strength lithopone, even in three coats, was too brittle for removal and testing after 12-month exposure, whereas all the aluminum paints in two and three coats, and even some in one coat, could be removed and measured after 36-month exposure. Qualitatively the high-strength lithopone showed a similar behavior in linseed oil. A similar effect of pigment may be noted by comparing the aluminum paint in Bakelite varnish C and the gray Bakelite enamel. The aluminum paint in one, two, or three coats is still in fair condition after 36-month exposure, whereas the Bakelite enamel with gray pigment could not be removed for measurement after 12-month exposure.

The fact that a paint film was too brittle for removal and measurement does not necessarily prove that its protective value was at an end. It does, however, indicate the approach of a period when it may check, crack, or otherwise increase markedly in moisture permeability. A comparison along these lines may be obtained by a study of Table IV in connection with Table III. Table IV gives the moisture impedance of various paints on 0.25-inch (0.635-cm.) wood panels initially and after weather exposure for various periods. In these tests, of course, the paint films were not removed from the wood for measurement, but the moisture resistance of the paint and wood was determined in combination. Here again the moisture impedance of the painted wood eventually reaches a maximum and thereafter declines. The high-strength lithopone in varnish A which, as a separate film, was too brittle for handling at 12 months, also was failing on wood after 18-month exposure. The relative order of failure of these paints on wood followed that of the same paint films on metal. Unfortunately, part of the tests shown in Table IV had to be discontinued after 18 months since no more test pieces were available.

As a class, the synthetic resin vehicles have high moisture impedance; some are quite superior in this respect. Table V shows the moisture impedance of a group of aluminum paints made with fourteen different varnish vehicles. The typical rise in moisture impedance with aging of the paint film was also observed here. The changes in the mechanical properties of some of the paint films of Table V are shown in Table VI; the data show the tensile strength and elongation before and after exposure to the weather for different periods. The tensile strength rises to a maximum and thereafter declines. The elongation decreases from the start, the rate of change gradually slowing up as the aging of the film progresses.

TABLE IV. MOISTURE IMPEDANCE OF PAINTS ON 0.635-CM. PINE PANELS AFTER WEATHER EXPOSURE

Paint Coating	No. of Coats	Moisture Impedance[a] after: Initial	6 mo.	12 mo.	18 mo.	24 mo.	36 mo.
Al paint in varnish A	1	9.0	10	9.3	15[b]	...	...
	2	47	71	89	82[b]	...	...
	3	63	100	95	96[b]	...	...
Al paint in varnish B	1	20	14	15	17	7.6	...
	2	77	52	66	57	74	26
	3	112	108	111	153	243	123
Al paint in varnish C	1	32	22	22	19	10	...
	2	61	59	72	64	79	57
	3	117	111	103	127	233	160
White lead–ZnO in varnish A	1	8.0	5.1	4.1	...	...	...
	2	16	16	11	11[b]	...	...
	3	34	35	12	7[b]	...	...
White lead–ZnO in linseed oil	1	4.9	2.6	2.0	...	...	...
	2	16	15	18	13	7.8	...
	3	23	21	26	27	28	6.1
High-strength lithopone in varnish A	1	12	4.2	3.7	...	...	...
	2	22	11	4.0	...	...	...
	3	31	18	14	11[b]	...	...
High-strength lithopone in linseed oil	1	10	4.5	4.1	...	...	...
	2	16	13	7.7	8[b]	...	...
	3	20	26	19	13[b]	...	...
Gray glycerol phthalate enamel	1	6.1	8.2	6.0	10[b]	...	...
	2	15	24	22	34[b]	...	...
	3	27	36	40	48[b]	...	...
Gray Bakelite enamel	1	10	6.5	5.9	8[b]	...	...
	2	22	28	20	25[b]	...	...
	3	29	39	31	36[b]	...	...
Clear varnish B	1	8.2	6.2	5.4	3.7	...	...
	2	17	15	16	19	20	8.4
	3	18	16	16	18	21	12
Clear varnish C	1	14	11	9.6	11	6.5	...
	2	24	18	18	22	22	11
	3	36	27	26	35	36	21
Al primer (varnish A′)[c] + 2 coats white lead–ZnO paint	3	35	33	38	40	29	5.3
Al primer (varnish B) + 2 coats white lead–ZnO paint	3	48	53	52	63	104	22
Bare wood panel[d]	0	3.3	2.8	3.4	4.5	4.8	3.2

[a] Each impedance is the average of tests on duplicate specimens.
[b] Test discontinued after 18 months.
[c] Varnish A′ is a modification of varnish A with less China wood oil.
[d] Not exposed but run as a blank at each period.

TABLE V. MOISTURE IMPEDANCE OF ALUMINUM PAINT FILMS

Paint Coating[a]	No. of Coats	Film Thickness *Mm.*	Moisture Impedance[b] after: Initial	3 mo.	6 mo.	12 mo.	18 mo.
Al paint–glycerol phthalate varnish No. 1	1	0.035	16	20	25	62	46
	2	0.056	30	35	41	52	224
Al paint–glycerol phthalate varnish No. 1[c]	1	0.020	11	19	134	171	45
Al paint–glycerol phthalate varnish No. 2	1	0.035	17	34	46	13	1.1
Al paint–glycerol phthalate varnish No. 3	1	0.033	6.8	9.2	10	17	9.6
Al paint–glycerol phthalate varnish No. 4	1	0.033	4.9	7.0	10	20	20
Al paint–phenolic resin varnish No. 1	1	0.026	22	62	95	47	1.2
	2	0.047	44	29	31	23	44
Al paint–phenolic resin varnish No. 2	1	0.029	9.3	20	23	1.8	d
	2	0.054	23	31	36	23	155
Al paint–phenolic resin varnish No. 3	1	0.030	15	15	38	45	33
Al paint–phenolic resin varnish No. 4	1	0.035	13	25	41	55	0.7
Al paint–phenolic resin varnish No. 5	1	0.032	16	16	34	30	30
Al paint–modified phenolic resin varnish	1	0.029	16	18	58	39	3.6
	2	0.053	31	29	54	56	43
Al paint–coumaron resin varnish	1	0.030	9.3	15	19	2.6	d
	2	0.050	27	24	28	24	35
Al paint–chlorinated diphenyl resin varnish	1	0.030	14	12	12	15	5.9
Al paint–petroleum resin varnish	1	0.037	13	12	38	33	19
Al paint–ester gum varnish	1	0.024	4.7	7.1	7.7	0.3	d
	2	0.044	19	18	19	28	32
White lead–ZnO paint (oil base)	1	0.098	1.4	2.6	d	...	...
	2	0.174	2.8	4.6	0.3	d	...
White lead paint (oil base)	1	0.054	1.3	0.1	d	...	...
	2	0.098	2.5	4.0	d	...	...

[a] Aluminum paint made with 2 pounds of Standard Varnish powder per gallon of vehicle (240 grams per liter) except where paste is noted.
[b] Based on film thickness of 0.025 mm. per coat.
[c] Aluminum paint made with 2 pounds of aluminum paste per gallon of vehicle.
[d] Film was too brittle to remove intact for measurement.

Table VI. Mechanical Properties of Aluminum Paint Films

Paint Coating[a]	No. of Coats	Initial	2 weeks in lab.	1 mo. in lab.	3 mo. on roof	6 mo. on roof	12 mo. on roof	18 mo. on roof
		Tensile Strength in Lb. per Sq. In.[b] after:						
Aluminum paint–glycerol phthalate varnish No. 1	1	200	303	385	1034	1750	2635	1815
	2	344	...	...	809	1222	2105	2220
Al paint–glycerol phthalate varnish No. 1[e]	1	369	...	...	1400	2830	2680	2985
Al paint–phenolic resin varnish No. 1	1	1079	...	...	2010	1760	2790	480
	2	1084	...	...	1872	2883	3055	3425
Al paint–phenolic resin varnish No. 2	1	455	620	750	1470	1283	280	[c]
	2	798	...	...	1228	1673	1610	1735
Al paint–modified phenolic resin varnish	1	556	...	...	1134	1734	1535	785
	2	584	...	...	1000	1209	1428	1765
Al paint–coumaron resin varnish	1	423	...	...	960	613	700	[c]
	2	652	...	...	700	850	1010	1335
Al paint–ester gum varnish	1	63	86	100	375	392	[c]	..
	2	189	...	...	570	648	859	915
White lead–ZnO paint (oil base)	1	252	...	...	623	[c]	..	..
	2	384	...	...	628	[c]	..	..
White lead paint (oil base)	1	55	28	78	[c]	..	..	..
	2	72	...	...	350	[c]	..	..
Clear glycerol phthalate varnish No. 1	1	60[d]	...	...	..	..	..	..
		Per Cent Elongation						
Al paint–glycerol phthalate varnish No. 1	1	19.88	15.54	15.11	2.42	0.86	0.45	0.40
	2	36.07	...	...	5.78	2.60	1.27	1.33
Al paint–glycerol phthalate varnish No. 1[e]	1	50.92	...	...	8.70	1.58	1.88	0.98
Al paint–phenolic resin varnish No. 1	1	7.32	...	...	1.66	0.74	0.45	0.04
	2	12.96	...	...	5.27	1.40	1.85	1.29
Al paint–phenolic resin varnish No. 2	1	11.94	10.60	7.66	1.97	0.76	0.00	[c]
	2	12.26	...	...	5.84	2.10	1.18	1.25
Al paint–modified phenolic resin varnish	1	12.58	...	...	4.06	0.96	0.99	0.23
	2	21.89	...	...	7.75	4.64	2.51	1.48
Al paint–coumaron resin varnish	1	15.50	...	...	0.96	0.53	0.00	[c]
	2	24.64	...	...	7.30	3.12	2.04	1.14
Al paint–ester gum varnish	1	27.18	26.48	30.16	3.36	0.41	[c]	..
	2	31.46	...	...	9.02	2.22	1.40	1.06
White lead–ZnO paint (oil base)	1	17.06	...	...	0.54	[c]	..	..
	2	24.89	...	...	1.72	[c]	..	..
White lead paint (oil base)	1	12.23	12.58	17.91	[c]	..	..	..
	2	14.56	...	...	0.68	[c]	..	..
Clear glycerol phthalate varnish No. 1	1	31.56[d]	...	...	..	..	..	..

[a] Aluminum paint made with 2 pounds of Standard Varnish powder per gallon of vehicle (240 grams per liter), except where paste is noted.

[b] 1000 lb. per sq. in. = 70.3 kg. per sq. cm.

[c] Film was too brittle to remove intact for measurement.

[d] Not exposed.

[e] Aluminum paint made with 2 pounds of aluminum paste per gallon of vehicle.

Table VII. Moisture Impedance of Aluminum Paint Films Air-Dried and Baked One Hour at Different Temperatures

Aluminum Paint[a] Coating	Coats	Moisture Impedance[b] Air-dried	Moisture Impedance[b] Baked	Baking Temp. ° F. (° C.)
With Varnish A	1	7.8	18	250 (121.1)
	2		33	250 (121.1)
With Varnish B	1	10.5	28	250 (121.1)
	2		84	250 (121.1)
With Varnish C	1	40	57	250 (121.1)
	2		73	250 (121.1)
	1		60	150 (65.6)
	1		28	200 (93.3)
	1		70	300 (148.9)
	1		113	350 (176.7)

[a] Made with 2 pounds of Standard aluminum paste per gallon of vehicle (240 grams per liter).

[b] Based on film thickness of 0.025 mm. per coat.

Effect of Drying Temperature

Since harder films are obtained by baking or drying at elevated temperatures, it would be expected that the moisture impedance of a paint film would be increased by baking. This is in fact the case, and Table VII gives figures on the moisture impedance of aluminum paints made with three different varnishes in the air-dried condition and baked one hour at different temperatures. Roughly speaking, the moisture impedance is about doubled by the baking treatment. Increasing the temperature of baking generally increases the moisture impedance although there would be a practical limit to such a relationship. The films baked for one hour at 300° and 350° F. (about 150° and 175° C.) are probably "overbaked" as far as durability is concerned. In Table VII one coat of aluminum paint made with varnish C, baked for one hour at 200° F. (93.3° C.), is substantially lower than a similar paint film baked for one hour at 150° or 250° F. (65.6° or 121.1° C.). For no apparent reason the value appears to be out of line, particularly since a check test gave a value for the moisture impedance of 45 instead of 28. It may be well to point out that small differences in the weights of moisture penetrating a paint film represent a larger percentage when the total amount of penetration is small—that is, when the moisture impedance is large. The same degree of concordance cannot be expected, therefore, nor is it observed with films of high moisture impedance. The general trend of results is, however, clearly indicated by the data.

The moisture resistance of a paint film is now generally recognized as an important fundamental property. In paints on wood it controls the interchange of moisture between wood and atmosphere. On metal it is the controlling factor in keeping from the metal, moisture without which the metal will not corrode. With the fundamental data now available, paint manufacturers and paint users should have a much better understanding of the subject.

Acknowledgment

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PROPYLENE POLYMERIZATION

ZINC CHLORIDE AS CATALYST

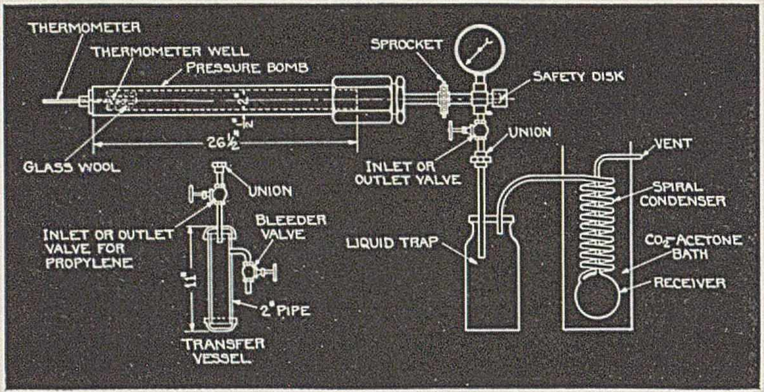

Figure 1. Pressure Bomb and Recovery System

In the present investigation a study was made of the polymerization of propylene, using anhydrous zinc chloride as catalyst. Experiments were conducted in a closed-pressure apparatus, and various conditions of temperature, pressure, and time of contact were employed with the object of determining which set of conditions produced a maximum yield of liquid product of gasoline type. For each set of experimental conditions investigated a quantity of liquid product sufficient to enable close fractionation was prepared. Examination of the resultant fractions gave information concerning the nature of their constitutents.

THE recent activity in the field of polymerization of gaseous olefins is readily understood when we consider that there is available per year approximately 300 billion cubic feet of olefin-containing gas from the petroleum cracking industry. Thus, for 1930 Dunstan, Hague, and Wheeler (*2*) estimated the volume of such gas produced as 275 billion cubic feet, from which the quantities of gaseous olefins obtainable, expressed in million of cubic feet, were about as follows: ethylene, 16,500; propylene, 22,000; butylenes, 11,000. A recent publication by Ipatieff and Egloff (*9*) describes the polymerization of such material to yield a highly antiknock gasoline.

In 1933 Gayer (*7*) reported results on the polymerization of propylene at atmospheric pressure and temperatures of 340° to 350° C. Activated Floridin, synthetic aluminum silicate, and alumina-on-silica were found to be active catalysts; the last mentioned was most effective. The portion of the polymeric product boiling up to 150° C. consisted of a series of homologous olefins from C_5 to C_9, inclusive (the C_6 fraction was the largest), and a small proportion of paraffin hydrocarbons. A comprehensive review of the decomposition and polymerization of the olefinic hydrocarbons, including propylene, by thermal, chemical, electrical, and alpha-particle action was given by Egloff, Schaad, and Lowry (*4*).

Materials

The propylene used in this experimental work was obtained from the Carbide and Carbon Chemicals Corporation. The gas analyzed 97 per cent propylene, the remainder being chiefly propane. Finely ground Baker's anhydrous c. p. zinc chloride was employed as catalyst for the experiments at 290° to 310° C.; for the experiments at 200° to 210° C. and at 150° to 160° C. the zinc chloride catalyst was distributed on the surface of pea-size pumice by heating these substances together, atmospheric moisture being excluded, until incipient fusion of the salt caused its adherence to the pumice surface.

Apparatus and Experimental Procedure

The apparatus used in the polymerization experiments is shown in Figure 1:

> The steel pressure bomb, of approximately 1400 cc. capacity, was mounted in a horizontal, electrically heated furnace, and could be rotated at approximately 25 r. p. m. In each experiment the catalyst was distributed along the length of the pressure bomb to secure better contact of catalyst and reactant. The weight of propylene used was found from the difference in weight of the transfer vessel when filled with liquid propylene from the supply cylinder and its weight after transfer of the propylene to the pressure bomb. After introduction of the catalyst and the propylene, the pressure bomb was heated to and maintained at

Table I. Results of Typical Polymerization Experiments

Expt. No.	Weight of $ZnCl_2$	Molar Ratio, $ZnCl_2$/C_3H_6	Temp.	Time at Working Temp.	Pressure Drop		Max. Pressure		Yield of Liquid Product	Sp. Gr. $\left(\frac{15}{15}\right)$ of Liquid Product
	Grams		° *C.*	*Min.*	*Lb./sq. in. gage*	*Kg./sq. cm.*	*Lb./sq. in. gage*	*Kg./sq. cm.*	*Weight %*	
1	74.3	0.12	290–300	90	750	52.7	1500	105.4	61.4	0.7547
2	[a]	0.10	290–300	90	1040	73.1	1775	124.8	62.0	0.7543
3	[a]	0.10	290–310	90	980	68.9	1600	112.5	74.2	0.7571
4	0.0 (control)	..	290–308	92	275	19.3	2475	174.1	4.3	0.7665$\left(\frac{20°}{4}\right)$
5	74.3	0.11	200–209	60	400	28.1	1700	119.5	31.6	0.7535
6	75.0	0.11	200–210	60	600	42.2	2100	147.6	34.1	0.7527
7	75[b]	0.11	200–208	60	750	52.7	2050	144.1	43.5	0.7491
8[c]	0.0 (control)	..	200–215	60	100	7.03	2150	151.1	0.3	....
9	150[b]	0.11	150–160	360	2800	196.8	3400	239.0	64.4	0.7441$\left(\frac{20°}{4}\right)$
10[c]	0.0 (control)	..	150–160	360	500	35.1	3350	235.5	0.2	....

[a] The same sample of catalyst was used in experiments 1, 2, and 3.

[b] Distributed on 72 grams of pumice.

[c] In these control experiments 72 grams of pumice were placed in the pressure bomb to correspond to the pumice carrier used in the experiments made under corresponding conditions.

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the desired temperature for a given time. Regular and frequent observations of time, temperature, and pressure were made. At the conclusion of each experiment the pressure bomb was removed from the furnace and cooled to room temperature in a current of air. Liquid product was then collected in the liquid trap of the recovery system, any unreacted propylene being slowly vented through the spiral condenser and receiver cooled to −35° to −40° C. At this temperature any highly volatile product that might otherwise have escaped from the liquid trap during release of the unreacted propylene was recovered and added to the main body of product collected in the liquid trap. The latter was then allowed to stand for 8 to 10 hours at room temperature while connected to a condenser and receiver at 0° to −10° C. in order to permit evolution of dissolved gases without loss of volatile product. After weighing, the liquid product was stored in a dark, cold room until the time of examination.

Examination of Liquid Products

The combined liquid products collected for each set of experimental conditions investigated were carefully distilled through a fractionating column designed after that described by Guthrie and Higgins (*8*), and equipped with a Kester and Andrews' type of still head (*14*). Characteristics of the column were as follows: length, 3 feet (91.4 cm.); internal diameter, 0.75 inches (1.9 cm.); packing, approximately 0.5-inch (1.27-cm.) lengths of 4-mm. bore glass tubing. Adiabatic control was effected by means of a dead air space and electrically heated jacket encircling the column. A reflux ratio of approximately 20 to 1 was maintained, and the distillation rate was such as to give 1 cc. of distillate per minute. At the time the distillations were made, the barometric pressure was 744 (±2) mm. Except where otherwise noted, fractions were collected for each 10° F. (5.6° C.) rise in temperature, as read from an A. S. T. M. thermometer. During collection of the lower boiling fractions, suitable precautions were taken to guard against loss through volatilization. Each fraction was stored in the dark under an atmosphere of carbon dioxide until ready for use. As an additional precaution the lower boiling fractions were kept in a refrigerator at 40° F. (4.4° C.). The results of the distillations are expressed graphically by plotting the volume (in cc.) of distillate per given fraction *vs.* the average boiling temperature of the fraction.

Specific gravities ($\frac{20}{4}$), refractive indices (n_D^{20}), and iodine numbers were determined for the various fractions. The iodine numbers were found by the Johansen method (*13*), in which a correction for iodine substitution is applied. Molecular weights were estimated by the method of Francis (*5*). From the molecular weights and iodine-addition values the percentage unsaturation of the fractions was calculated.

Results of Polymerization

The findings of typical polymerization experiments are given in Table I. The liquid products possessed the following characteristics: light straw color, slight fluorescence, neutral reaction to litmus, negative Beilstein halogen test response, and sweet pleasant odor characteristic of lower members of the olefin series. In a separate experiment (not shown in Table I) a maximum yield of 81.5 per cent by weight of liquid product was obtained at 260° to 270° C., 3225 pounds per square inch pressure (226.7 kg. per sq. cm.), and a time period of 75 minutes. In the 150–160° C. experiments it was necessary, because of the slow reaction rate, to employ a higher pressure and a longer time period to secure satisfactory yields of liquid products.

The sample of catalyst described for experiment 7, Table I, was used for a series of eight experiments under conditions closely approximating those for experiment 7. An average yield of 35.6 per cent by weight of liquid product was obtained. At the end of the series the catalyst had produced an amount of liquid product equal to 7.7 times its own weight, and still retained 87 per cent of its initial activity. Similarly, the sample of catalyst described in experiment 9 was employed in a series of five experiments under conditions corresponding to those for experiment 9. At the end of this series a weight of liquid product equal to 6.5 times that of the catalyst was obtained, while the activity of the latter had dropped to 50 per cent of its initial value.

Tables II to V record the data secured by fractionating and examining the fractions from the combined liquid products of the 290–310° C., 200–210° C., and the 150–160° C. experiments. The corresponding distillation curves are shown in Figures 2, 3, and 4. Table V shows that the C_6 and C_9 fractions from the original fractionation of the 150–160° C. product were refractionated into closer boiling fractions. These latter were then examined.

While the composition of the gaseous hydrocarbons accompanying the liquid polymers was not determined, it is of interest that liquefied samples of the gases from the 150–160° C. and the 200–210° C. experiments distilled off at a temperature corresponding to that for liquid propylene (−47° C.). This would tend to indicate that in these cases the gaseous products consisted essentially of unreacted propylene.

The control experiments, in which no zinc chloride catalyst was present, showed practically no conversion of propylene to liquid products, particularly at 200° to 210° C. and at 150° to 160° C. The 4.3 per cent by weight conversion in the control experiment at 290° to 310° C. (experiment 4, Table I) may have resulted from the mild catalytic action of the steel walls of the pressure apparatus, since Dunstan, Hague, and Wheeler (*3*) obtained an 80 per cent by weight conversion of propylene into liquid products by using a mild steel autoclave, a temperature of 400° to 404° C., a pressure of 71 kg. per sq. cm., and a time period of 2.5 hours.

Further, the data in Tables II to IV and the distillation curves shown in Figures 2 to 4, inclusive, demonstrate that as the experimental temperature was lowered (from 290–310° C. to 200–210° C., and then to 150–160° C.), a larger percentage by volume of the product distilled in the gasoline range (to 200° C.); likewise, a larger percentage by volume of the product corresponded to the tripolymer of propylene.

This paper presents the results obtained in a study of the polymerization of propylene at elevated temperatures and pressures in the presence of zinc chloride as catalyst. Experiments were conducted in a closed pressure apparatus under three different conditions of temperature, pressure, and time. Liquid polymer yields as high as 74.2, 43.5, and 64.4 per cent by weight were obtained under the three respective conditions. A total of 74.5 per cent by volume of the 290–310° C. product, 85.9 per cent of the 200–210° C. product, and 92 per cent of the 150–160° C. product distilled in the motor gasoline range (to 200° C.). The data obtained on fractionation of the polymeric products and examination of the resultant fractions are given, together with a discussion of their probable chemical composition.

Table II. Fractionation and Examination of Liquid Product from 290–310° C. Experiments

(Volume fractionated = 520 cc.; specific gravity $(^{20}_{4})$ = 0.7557)

Group	B. P. of Fraction ° C.	Average B. P. ° C.	Volume Cc.	Per Cent by Vol. Distd.	Sp. Gr. $(^{20}_{4})$	Re-fractive Index (n^{20}_{D})	Iodine Addition Value, N	Iodine Substitution Value	Mol. Wt., M	Per Cent Unsatn.
C_5	30.5–40.5	35.5	19		0.6431	1.3765	145	0.0	72	41
	40.5–50.0	45.2	11		0.6360	1.3721	132	0.0	77	40
			30	5.8						
C_6	50– 60	55	13.8		0.6531	1.3752	128	0.0	82	41
	60– 70	65	20.4		0.6570	1.3865	141	0.0	87	48
	70– 80	75	18.4		0.6706	1.3938	161	0.25	92	58
			52.6	10.1						
C_7	80– 90	85	11.0		0.6826	1.3980	123	1.2	96	47
	90–100	95	19.5		0.6845	1.4060	125	5.1	101	50
			30.5	5.9						
C_8	100–110	105	20.5		0.7012	1.4061	122	8.1	107	51
	110–120	115	15.2		0.7075	1.4120	134	7.8	112	59
	120–128	124	31.5		0.7192	1.4162	115	11.4	116	52
			67.2	12.9						
C_9	128–130	129	8.0		0.7235	1.4190	111	12.2	118	52
	130–139	134.5	50.1		0.7281	1.4218	131	18.5	121	62
	139–140	139.5	6.0		0.7311	1.4240	132	13.0	124	64
	140–148	144.0	29.0		0.7367	1.4252	115	10.3	126	57
	148–150	149.0	4.2		0.7410	1.4290	124	10.3	128	62
			97.3	18.7						
C_{10} to C_{12}, inclusive	150–160	155	15.8		0.7476	1.4311	112	13.0	132	58
	160–170	165	22.0		0.7601	1.4370	90	33.8	136	48
	170–180	175	20.2		0.7665	1.4404	86	34.6	141	48
	180–190	185	23.0		0.7714	1.4440	85	34.4	146	49
	190–200	195	29.0		0.7780	1.4481	70	41.4	151	41
	200–210	205	16.0		0.7923	1.4550	39	40.0	156	24
	210–220	215	16.0		0.8052	1.4613	38	37.0	162	24
			142.0	27.3						
C_{13}	220–230	225	13.0		0.8109	1.4653	30	44.0	167	20
	230–234	232	11.5		0.8190	1.4681	19	51.0	170	13
			24.5	4.7						

Residue = 61 cc. = 11.7 per cent; per cent by volume distilling to 200° C. = 74.5.

represented by the C_9 compounds. Moreover, at 290° to 310° C. the liquid product contained an appreciable amount of C_5, C_7, and C_8 hydrocarbons, as compared to the relatively small amounts of these compounds in the liquid products from the lower temperature experiments. Gayer (*7*) referred to the presence of these nonmultiple polymers in the liquid product resulting from the polymerization of propylene. It is probable that, by lowering the experimental temperature still more (below 150° C.), the polymerization reaction could be further controlled so as to yield a still higher percentage of the lower polymers, such as the dimer and trimer compounds; but slower reaction rates at lower temperatures might prove objectionable.

With reference to polymerization by means of chemical reagents, such as zinc chloride and anhydrous ferric and aluminum chlorides, Brooks (*1*) says that all such cases probably involve addition of the reagent to the double bond, followed by dissociation or decomposition of the addition product to give hydrocarbon residues having at the moment bivalent or trivalent carbon atoms. Combination of these residues results in polymer formation.

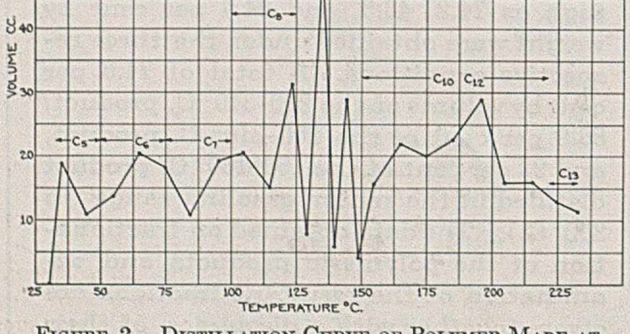

Figure 2. Distillation Curve of Polymer Made at 290–310° C.

Probable Composition of Main Fractions of Liquid Products

The fractions of the liquid products of most interest were naturally those present in largest amounts; these fractions comprised the main peaks of the distillation curves shown in Figures 2, 3, and 4. By comparison of the properties of these fractions with those for known hydrocarbons[1] of similar boiling points, the following conclusions as to the approximate composition of the polymer fractions were drawn:

Product at 290° to 310° C. The data for the C_5–C_9, inclusive, fractions of this product (Table II) indicated them to consist predominantly of olefinic and paraffinic hydrocarbons. The high specific gravities and refractive indices of the naphthenic, cycloölefinic, and aromatic hydrocarbons eliminate the possibility of their presence in the fractions, except in very small amounts. Moreover, treatment of the C_9 fraction of 134.5° C. average boiling point with fuming nitric acid, as in the Garner method (*6*), and consequent renitration of the fuming nitric extract, failed to yield any crystalline nitroaromatic derivatives of the xylenes (meta and para), which

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[1] A long list of hydrocarbons with their boiling points, specific gravities, refractive indices, and literature references is contained in the thesis of O. L. Brandes from which this paper is taken.

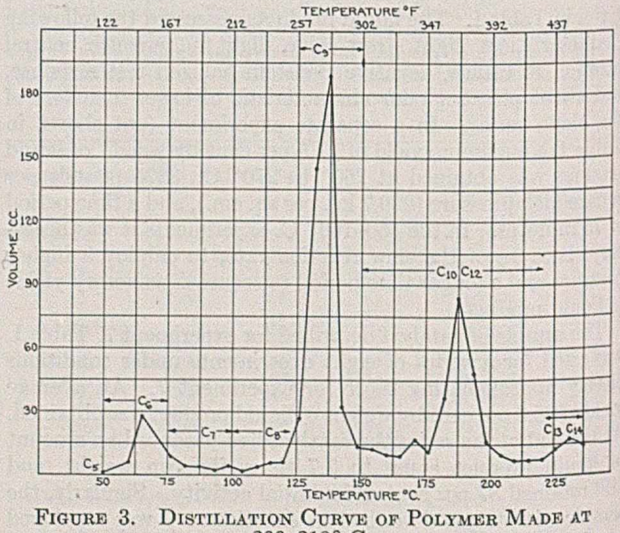

Figure 3. Distillation Curve of Polymer Made at 200–210° C.

have boiling points within the range of this fraction. The specific gravity of known olefins and paraffins and the relatively high iodine substitution values of the C_9 fractions indicate that an appreciable content of branched-chain hydrocarbons, such as the methyl octanes, methyl octenes, and the dimethyl heptanes, was present.

TABLE III. FRACTIONATION AND EXAMINATION OF THE LIQUID PRODUCT FROM 200–210° C. EXPERIMENTS

(Volume fractionated = 860 cc.; specific gravity ($^{20}_{4}$) = 0.7523)

Group	B. P. of Fraction ° F.	B. P. of Fraction ° C.	Average B. P. ° C.	Volume Cc.	Per Cent by Vol. Distilled	Sp. Gr. ($^{20}_{4}$)	Refractive Index (n^{20}_{D})	Iodine Addition Value, *N*	Iodine Substitution Value	Mol. Wt., *M*	Per Cent Unsatn.
C_5, C_6	100–134	44.4–56.7	50.5	0.6	0.07						
C_6	134–144	56.7–62.2	59.4	5.0		0.6868	1.3930	214.5	0.0	84	71
	144–154	62.2–67.8	65.0	28.1		0.6846	1.3948	221.0	0.0	86	75
	154–164	67.8–73.3	70.5	18.5		0.7036	1.4009	213.0	0.0	89	75
	164–174	73.3–78.9	76.1	8.2		0.7045	1.4030	209.0	0.0	92	76
				59.8	7.0						
C_7	174–184	78.9–84.4	81.6	4.0							
	184–194	84.4–90.0	87.2	4.0							
	194–204	90.0–95.6	92.8	2.0							
	204–214	95.6–101.1	98.3	4.0							
				14.0	1.6						
C_8	214–224	101.1–106.7	103.9	2.0							
	224–234	106.7–112.2	109.4	3.6							
	234–244	112.2–117.8	115.0	6.0							
	244–254	117.8–123.3	120.5	6.0							
				17.6	2.0						
C_9	254–264	123.3–128.9	126.1	26.1		0.7383	1.4209	141.0	8.9	117	65
	264–274	128.9–134.4	131.6	144.0		0.7418	1.4235	136.0	5.2	120	64
	274–284	134.4–140.0	137.2	188.0		0.7436	1.4258	139.0	3.5	123	67
	284–294	140.0–145.6	142.8	31.6		0.7514	1.4280	138.0	3.8	125	68
	294–304	145.6–151.1	148.3	14.0							
				403.7	47.0						
C_{10} to C_{12}, inclusive	304–314	151.1–156.7	153.9	12.0							
	314–324	156.7–162.2	159.4	10.0							
	324–334	162.2–167.8	165.0	9.0							
	334–344	167.8–173.3	170.5	17.0							
	344–354	173.3–178.9	176.1	11.0							
	354–364	178.9–184.4	181.6	36.0		0.7696	1.4370	87.0	24.0	145	50
	364–374	184.4–190.0	187.2	84.0		0.7766	1.4392	84.6	24.5	148	49
	374–384	190.0–195.5	192.7	48.0		0.7764	1.4405	85.5	25.0	150	50
	384–394	195.5–201.1	198.3	16.0							
	394–404	201.1–206.6	203.8	10.0							
	404–414	206.6–212.2	209.4	7.0							
	414–424	212.2–217.8	215.0	7.5							
	424–434	217.8–223.3	220.5	8.2							
				275.7	32.0						
C_{13}, C_{14}	434–444	223.3–228.9	226.1	13.0							
	444–454	228.9–234.4	231.6	17.0							
	454–464	234.4–240.0	237.2	14.6							
				44.6	5.2						

Residue = 40 cc. = 4.6 per cent; per cent by volume distilling to 200° C. = 85.9.

In the case of the C_{10-12} fractions from each of the liquid products (Tables II, III, and V), the percentage unsaturation is observed to be lower than that of the lighter fractions, particularly in the 200–210° C. and the 150–160° C. products, while the iodine substitution values are correspondingly higher. These facts would indicate that larger amounts of compounds, such as branched-chain olefins and paraffins, which contain secondary and tertiary hydrogen atoms capable of substitution by iodine, were present in the heavier fractions. Here also the high specific gravities and refractive indices of the aromatic hydrocarbons boiling in this range led to the belief that they were not present in significant amounts. Support for the presence of naphthenic hydrocarbons was found, however, from the fact that the observed specific gravities of the fractions were higher than could be explained on the basis of known olefins and paraffins present to the extent indicated by the degree of unsaturation. Thus, if we select the fraction of 180–190° C., boiling point from the 290–310° C. product (Table II), and choose from the literature representative hydrocarbons of similar boiling point, the calculated specific gravity of the fraction becomes:

1. Assuming only olefins and paraffins were present,
   0.49 (% unsatn.) × 0.7630 (1-undecene) = 0.3739
   0.51 × 0.7655 (2,6-dimethyl-3-isopropylheptane) = 0.3904
   0.7643
   Observd. sp. gr. = 0.7714
2. Assuming olefins, paraffins, and naphthenes were present
   0.49 × 0.7630 (1-undecene) = 0.3739
   0.30 × 0.7655 (2,6-dimethyl-3-isopropylheptane) = 0.2296
   0.21 × 0.801 (pentamethylcyclohexane) = 0.1682
   0.7717

Here the assumption of 21 per cent of a naphthene in the saturated portion of the fraction gives a calculated specific gravity close to that observed.

PRODUCTS AT 200–210° C. AND 150–160° C. The unsaturation of the C_6 fractions from these products was from 19 to 36 per cent higher than for the corresponding fractions from the 290–310° C. product. Also, in the case of the 150–160° C. product, the specific gravity passes through a minimum in going from 134° to 146° F. (56.7° to 63.3° C.). The same behavior is noted for the 200–210° C. product in going from 134° to 154° F. (56.7° to 67.8° C.). This minimum was not observed in the C_6 fractions from the 290–310° C. product. As the specific gravities of the 56.7–62.2° C. fraction from the 200–210° C. product, and the 56.7–59.4° C. and 59.4–62.2° C. fractions from the 150–160° C. product were higher than could be explained on the basis of known olefins of similar boiling point, the presence of cyclic hydrocarbons in the saturated portion of these fractions was inferred. For purposes of illustration, let it be assumed that the saturated portion of the 59.4–62.2° C. fraction from the 150–160° C. product (Table V) was composed entirely of naphthene hydrocarbons. The calculated gravity of this fraction would then be:

0.71 (% unsatn.) × 0.6817 (2-methyl-1-pentene) = 0.4840
0.29 × 0.6946 (1,2,3-trimethylcyclopropane) = 0.2014
0.6854
Obsvd. sp. gr. = 0.6867

Probably, then, the saturated portion of the fractions just cited contained appreciable amounts of naphthenes. The other C_6 fractions had properties indicating a high content of olefinic and paraffinic hydrocarbons. An explanation for the absence of naphthenic hydrocarbons in the corresponding C_6 fractions of the 290–310° C. product is suggested by the research of Ipatieff and Rutala (*11*) and of Ipatieff and Huhn (*10*). In the polymerization of ethylene by zinc chloride the

TABLE IV. FRACTIONATION OF LIQUID PRODUCT FROM 150–160° C. EXPERIMENTS

(Volume fractionated = 1240 cc.; specific gravity $(\frac{20}{4})$ = 0.7400)

Group	B. P. of Fraction ° F.	B. P. of Fraction ° C.	Average B. P. ° C.	Volume Cc.	Per cent by Vol. Distd.
C_5, C_6	110–134	44.4–56.7	50.5	3.5	0.3
C_6	134–144	56.7–62.2	59.4	24.0	
	144–154	62.2–67.8	65.0	92.0	
	154–164	67.8–73.3	70.5	13.0	
	164–174	73.3–78.9	76.1	3.0	
				132.0	10.6
C_7	174–184	78.9–84.4	81.6	5.0	
	184–194	84.4–90.0	87.2	3.0	
	194–204	90.0–95.6	92.8	5.0	
	204–214	95.6–101.1	98.3	2.0	
				15.0	1.2
C_8	214–224	101.1–106.7	103.9	4.0	
	224–234	106.7–112.2	109.4	4.0	
	234–244	112.2–117.8	115.0	6.0	
	244–254	117.8–123.3	120.5	7.0	
				21.0	1.7
C_9	254–264	123.3–128.9	126.1	28.0	
	264–274	128.9–134.4	131.6	378.0	
	274–284	134.4–140.0	137.2	240.0	
	284–294	140.0–145.6	142.8	31.0	
	294–304	145.6–151.1	148.3	16.0	
				693.0	55.9
C_{10} to C_{12}, inclusive	304–314	151.1–156.7	153.9	10.0	
	314–324	156.7–162.2	159.4	8.0	
	324–334	162.2–167.8	165.0	6.0	
	334–344	167.8–173.3	170.5	10.0	
	344–354	173.3–178.9	176.1	17.0	
	354–364	178.9–184.4	181.6	56.0	
	364–374	184.4–190.0	187.2	116.0	
	374–384	190.0–195.5	192.7	40.0	
	384–394	195.5–201.1	198.3	13.0	
	394–404	201.1–206.6	203.8	5.0	
	404–414	206.6–212.2	209.4	5.0	
	414–424	212.2–217.8	215.0	6.0	
	424–434	217.8–223.3	220.5	7.0	
				299.0	24.1
C_{13}, C_{14}	434–444	223.3–228.9	226.1	11.0	
	444–454	228.9–234.4	231.6	12.3	
	454–464	234.4–240.0	237.2	10.0	
	464–474	240.0–245.5	242.7	15.0	
				48.3	3.9

(Residue = 28 cc. = 2.3 per cent; per cent by volume distilling to 200° C. = 92.0)

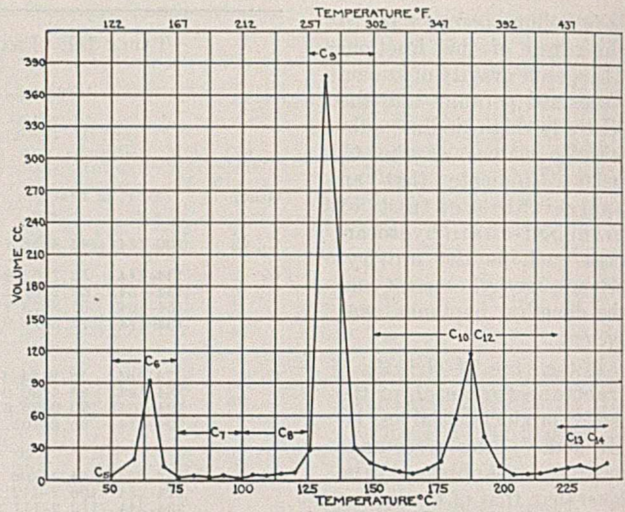

FIGURE 4. DISTILLATION CURVE OF POLYMER MADE AT 150–160° C.

former authors observed that polymerization began at 275° C. and that no lower naphthenes were formed. They concluded that at this temperature the zinc chloride probably produced an isomerization of lower naphthenes to olefins.

The distillation curves of the liquid products under consideration (Figures 3 and 4) reveal very pronounced peaks corresponding to C_9 compounds and representing the trimer stage of polymerization. Similarly, Tables III and IV show that, for the 200–210° C. and the 150–160° C. products, the percentages by volume distilling in the C_9 range were 47 and 55.9, respectively. A comparison of the properties of the C_9 fractions of these products with those of known hydrocarbons of similar boiling point indicated that the fractions contained, in addition to olefinic and paraffinic hydrocarbons, approximately 15 per cent of naphthenes. It was concluded that aromatics were not present, except possibly in very small amounts: (1) because of their very high specific gravities and refractive indices, as compared to the corresponding values for the fractions; and (2) because of the low experimental temperature. Cycloölefins may have been present in small amounts (probably not exceeding 5 per cent).

Similar considerations for the C_{10-12} fractions that were examined (Tables III and V) led to the logical assumption of the presence of 30 to 45 per cent of naphthenes, in addition to olefins and paraffins, taking into account the observed specific gravities of the fractions, their percentage unsaturation, and the properties of known hydrocarbons of similar boiling point. The presence of more than small amounts of aromatic hydrocarbons was unlikely, for reasons previously indicated.

TABLE V. PROPERTIES OF FRACTIONS FROM LIQUID PRODUCT OBTAINED IN 150–160° C. EXPERIMENTS

Group	B. P. of Fraction ° F.	B. P. of Fraction ° C.	Average B. P. ° C.	Volume Cc.	Sp. Gr. $(\frac{20}{4})$	Refractive Index (n^{20}_{D})	Iodine Addition Value, N	Iodine Substitution Value	Mol. Weight, M	Per Cent Unsatn.
C_5, C_6	110–134	44.4– 56.7	50.5	5.0	0.6950	1.3860	198	0.0	79	62
C_6	134–139	56.7– 59.4	58.0	4.6	0.6915	1.3879	205	0.0	83	67
	139–144	59.4– 62.2	60.8	4.4	0.6867	1.3891	214	0.0	84	71
	144–146	62.2– 63.5	62.7	17.4	0.6838	1.3921	222	0.0	85	74
	146–148	63.3– 64.4	63.8	31.0	0.6870	1.3940	223	0.0	86	75
	148–150	64.4– 65.6	65.0	26.0	0.6883	1.3956	222	0.0	86	76
	150–152	65.6– 66.7	66.1	13.0	0.6912	1.3972	221	0.0	87	76
	152–154	66.7– 67.8	67.2	6.2	0.6946	1.3985	220	0.0	88	76
	154–164	67.8– 73.3	70.5	9.0	0.6942	1.3984	219	0.0	89	77
	156–164	68.9– 73.3	71.1	12.0	0.6944	1.3995	212	0.0	89	74
	164–176	73.3– 80.0	76.6	9.2	0.7003	1.4012	205	0.0	92	74
				132.8						
C_9	254–259	123.3–126.1	124.7	4.2	0.7347	1.4209	138	0.0	116	63
	259–264	126.1–128.9	127.5	6.4	0.7372	1.4230	134	1.0	118	62
	264–266	128.9–130.0	129.4	32.0	0.7384	1.4224	138	4.7	119	65
	266–268	130.0–131.1	130.5	22.0	0.7398	1.4235	139	3.4	119	65
	268–270	131.1–132.2	131.6	45.0	0.7416	1.4239	137	5.0	120	65
	270–272	132.2–133.3	132.7	143.8	0.7428	1.4250	139	3.0	120	66
	272–274	133.3–134.4	133.8	146.6	0.7441	1.4252	141	2.2	121	67
	274–276	134.4–135.6	134.9	123.0	0.7455	1.4268	142	1.1	121	67
	276–278	135.6–136.7	136.1	53.0	0.7466	1.4274	140	2.7	122	67
	278–280	136.7–137.8	137.2	15.0	0.7488	1.4280	137	3.5	123	66
	280–284	137.8–140.0	138.9	10.0	0.7492	1.4289	136	3.3	123	66
	284–294	140.0–145.6	142.8	5.5	0.7527	1.4298	130	0.5	125	64
	294–304	145.6–151.1	148.3	2.0	0.7564	1.4310	128	0.5	128	65
				608.5						
C_{10} to C_{12}, inclusive	354–364	178.9–184.4	181.6	56	0.7731	1.4388	80	27.2	145	46
	364–374	184.4–190.0	187.2	116	0.7763	1.4402	74	27.1	148	43
	374–384	190.0–195.5	192.7	40	0.7811	1.4420	80	26.0	150	47
				212						

It is interesting to recall at this point that Ivanov (*12*) reported in 1933 that the condensate obtained by the polymerization of so-called ethylene concentrate in the presence of zinc chloride at 320–360° C. and superatmospheric pressure was made up of a mixture of paraffin, aromatic, naphthene, and olefin hydrocarbons. The amount of the olefins present was stated not to exceed 30 per cent.

Conclusions

The following data were obtained from the fractionation of the liquid products under the various conditions shown in Table I:

Exptl. Temp. ° *C.*	Chief Constituents Present in Liquid Product C_5	C_6	C_7	C_8	C_9	C_{10-12}	Product Distilling in the Motor Gasoline Range (to 200° C.)
	Per cent by volume						
290-310	5.8	10.1	5.9	12.9	18.7	27.3	74.5
200–210	0.07	7.0	1.6	2.0	47.0	32.0	85.9
150–160	0.3	10.6	1.2	1.7	55.9	24.1	92.0

As the experimental temperature was lowered, a successively higher percentage of the liquid product corresponded to the tripolymer of propylene, represented by the C_9 compounds.

Corresponding to the above data, the distillation curve of the 290–310° C. product showed prominent peaks pointing to C_8, C_9, and C_{10-12} compounds, with somewhat lower peaks for the C_5, C_6, and C_7 compounds. The distillation curves of the 200–210° C. and 150–160° C. products had very pronounced peaks corresponding to C_9 compounds, and somewhat lower peaks for C_{10-12} compounds. The C_5, C_7, and C_8 compounds were present only in small amounts.

From a comparison of the properties of the fractions comprising the peaks of the distillation curves with those of known hydrocarbons of similar boiling point, conclusions were drawn regarding the probable composition of the fractions. No evidence was found of the presence of aromatic hydrocarbons. The data indicated the presence of appreciable amounts of naphthenic hydrocarbons in certain of the fractions, in addition to olefins and paraffins.

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4-CHLOROACETOPHENONE

Catalytic Oxidation in the Liquid Phase

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The oxidation of 4-chloroacetophenone in the liquid phase, using manganese dioxide as a catalyst and air as the oxidizing agent, is studied. An apparatus is described, and optimum conditions of temperature and time for the production of 4-chlorobenzoic acid are determined. Yields of the acid in excess of 90 per cent are obtained.

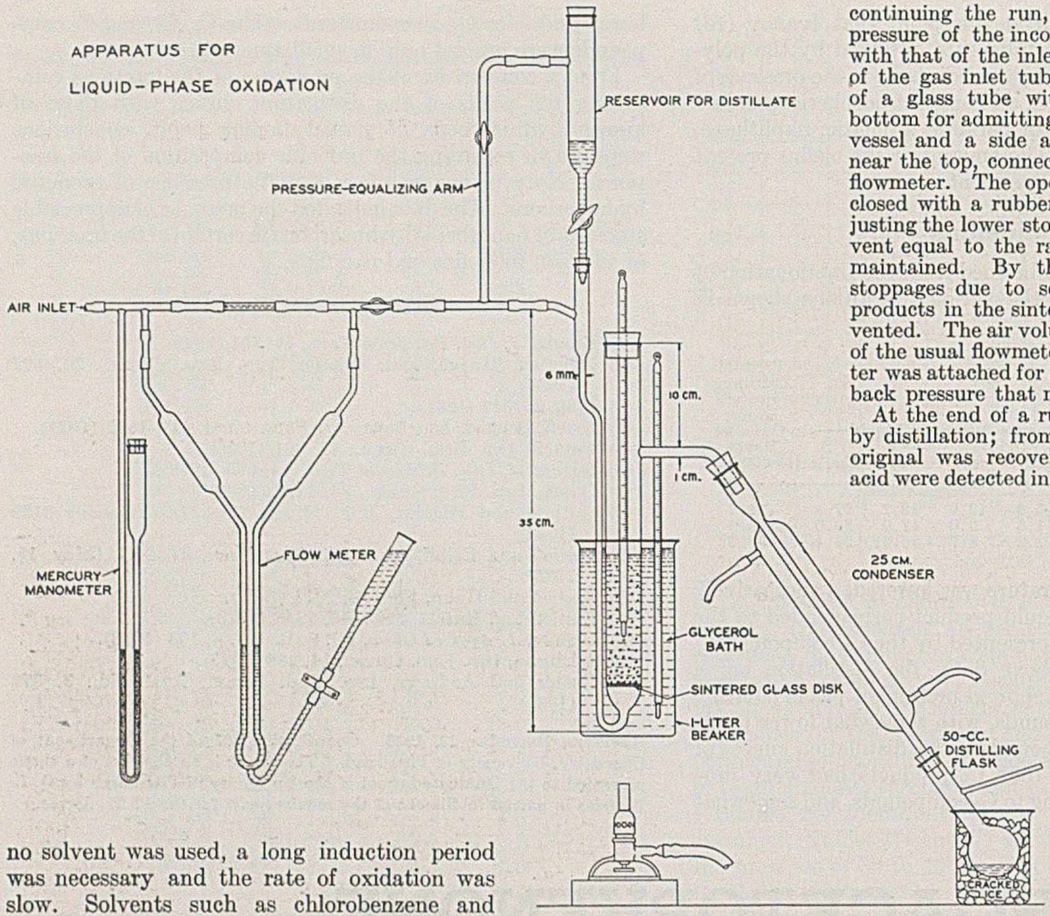
ACETOPHENONE and its derivatives are easily oxidized by the usual oxidizing agents to the corresponding benzoic acids. Recently VanArendonk and Cupery (*6*) showed that 4-chloroacetophenone and other derivatives can be oxidized in good yields with sodium hypochlorite. The writers (*5*) found that, although under carefully controlled conditions good yields of acetophenone could be obtained by the catalytic oxidation of ethylbenzene in the liquid phase, there was a tendency toward further oxidation of the ketone to benzoic acid; this behavior was especially evident at slightly elevated temperatures. Flemming and Speer (*1*) recently extended the scope of their patented process for the liquid-phase oxidation of aliphatic ketones to include the oxidation of acetophenone. A yield of 25 grams of benzoic acid and 7 grams of formic acid is claimed when 50 grams of acetophenone in acetic acid is oxidized for 12 hours at 105° C. in the presence of a small quantity of manganese acetate by means of air bubbled through a filter plate at the rate of 5 liters per hour.

The recent work of Groggins and Nagel (*2*) showing that both acyl groups of acid anhydrides can be made to react with aromatic compounds in the Friedel and Crafts condensation by using increased proportions of aluminum chloride indicates that acetophenones might well be used as a starting material for the production of certain substituted benzoic acids. Thus, Newton and Groggins (*3*) described the preparation of 4-chlorobenzoic acid by the oxidation of 4-chloroacetophenone with chromic anhydride, 95 per cent yields being obtained.

The purpose of the present investigation was to determine the optimum conditions of temperature and of time for the production of 4-chlorobenzoic acid by the liquid-phase catalytic oxidation of 4-chloroacetophenone, using atmospheric oxygen as the oxidizing agent.

Oxidation Experiments

The experiments in general consisted of passing air, dispersed by a sintered glass disk, through a solution of 10 grams of 4-chloroacetophenone in 100 ml. of glacial acetic acid in the presence of 0.5 gram of specially prepared manganese dioxide (*4*). Preliminary experiments had shown that, when



no solvent was used, a long induction period was necessary and the rate of oxidation was slow. Solvents such as chlorobenzene and xylene were found unsatisfactory.

Almost immediately after an experiment was started, the color of the reaction mixture changed from brown to dark cherry red. When this color was maintained, the oxidation appeared most vigorous, as evidenced by the evolution of carbon dioxide. At times, especially at the beginning of an experiment when a large excess of ketone was present, there was a tendency for the manganese dioxide to dissolve in the acetic acid, forming a colorless solution. When entirely dissolved, the catalyst showed no activity whatever. The reduction of the catalyst to this inactive state could be prevented by increasing the flow of air, by lowering the temperature, or by adding the ketone in small increments during the reaction. The rate of flow of air was maintained at 250 ml. per minute, since that was the approximate capacity of the apparatus.

Run No.	Temp.	Catalyst	Time	4-Chlorobenzoic Acid	
	° C.		*Hours*	*Grams*	%
1	110–112	None	3	0	0
2	100	Prepared MnO_2[a]	3	8.34	82.3
3	110–112	Same	2	8.10	80.0
4	110–112	Same	2.5	8.80	86.9
5	110–112	Same	3	9.29	91.7
6	110–112	Same	3	9.20	90.8
7	125[b]	Same	3	9.20	90.8
8	110–112	Same	5	9.00	88.8
9	110–112	Manganese acetate	3	8.84	87.2
10	110–112	Commercial MnO_2[c]	3	4.40	43.4

[a] The preparation of this catalyst was described in a former paper (*4*).
[b] Propionic acid used as solvent.
[c] Pulverized 85 per cent MnO_2.

The figure shows diagrammatically the apparatus used in the experiments:

The reaction vessel consisted of a Pyrex glass cylinder, with a diameter of 31 mm. and a capacity of 175 ml.; a sintered glass disk was fused in near the bottom, and a small-bore glass inlet tube was sealed on below for admitting air. In order to return any solvent which distilled over during the reaction without discontinuing the run, a reservoir in which the pressure of the incoming air could be equalized with that of the inlet tube was placed at the top of the gas inlet tube. This reservoir consisted of a glass tube with a glass stopcock at the bottom for admitting the solvent to the reaction vessel and a side arm with a glass stopcock, near the top, connected to the air line from the flowmeter. The opening of the reservoir was closed with a rubber stopper. By properly adjusting the lower stopcock, a steady flow of solvent equal to the rate of evaporation could be maintained. By thus returning the solvent, stoppages due to separation of solid reaction products in the sintered glass disk could be prevented. The air volume was measured by means of the usual flowmeter, and a mercury manometer was attached for the purpose of detecting any back pressure that might develop in the system.

At the end of a run the solvent was removed by distillation; from 80 to 90 per cent of the original was recovered. Only traces of formic acid were detected in the distillate. The 4-chlorobenzoic acid was then dissolved in 10 per cent sodium hydroxide solution, filtered to remove manganese hydroxide, and subsequently extracted with ether to remove any unreacted ketone. The aromatic acid was then precipitated with dilute hydrochloric acid, filtered, washed with water, and dried in the oven. In the experiments in which maximum yields were obtained, the aromatic acid was recovered by distilling off the solvent, during which process the manganese dioxide was converted to manganous acetate. The residue was washed with approximately 600 ml. of water, filtered, and dried. This treatment gave a product with a neutralization equivalent of 156 and a melting point of 238° to 240° C.; the melting point of 4-chlorobenzoic acid is 242.5° to 243.4° C. When this product was dissolved in sodium hydroxide, filtered, extracted with ether, and precipitated with hydrochloric acid as in the first method, the melting point was 240° to 242° C.; the neutralization equivalent remained the same.

The table includes data on temperature and time variations with a specially prepared manganese dioxide catalyst (*4*). The highest yields were obtained at 110° to 112° C. during 3 hours. Since this temperature was the maximum that could be obtained when acetic acid was used as a solvent, a run was made with propionic acid at 125° C., and approximately the same yield was obtained. The yield of acid was not raised by increasing the duration of the run from 3 to 5 hours.

A comparison of the catalytic efficiency of manganese acetate and of commercial precipitated manganese dioxide (85 per cent) with the specially prepared manganese dioxide indicates that the latter is a superior catalyst.

Acknowledgment

The writers are indebted to H. P. Newton of this division for suggesting the possibility of preparing 4-chlorobenzoic acid from 4-chloroacetophenone by this method of oxidation.

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NICOTINE PEAT

A New Insoluble Nicotine Insecticide

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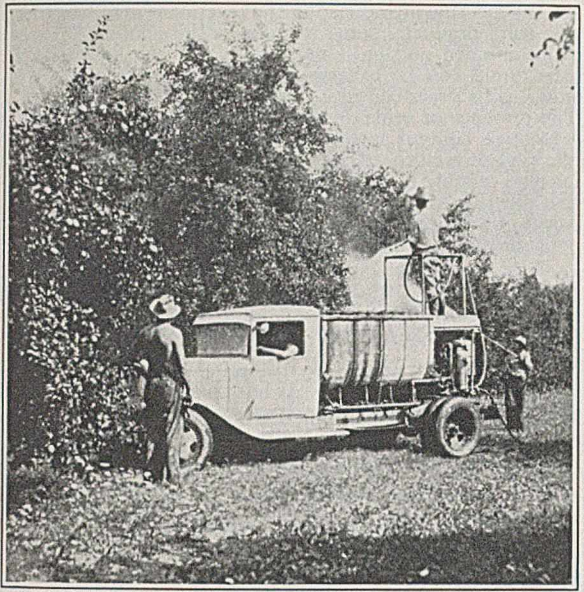
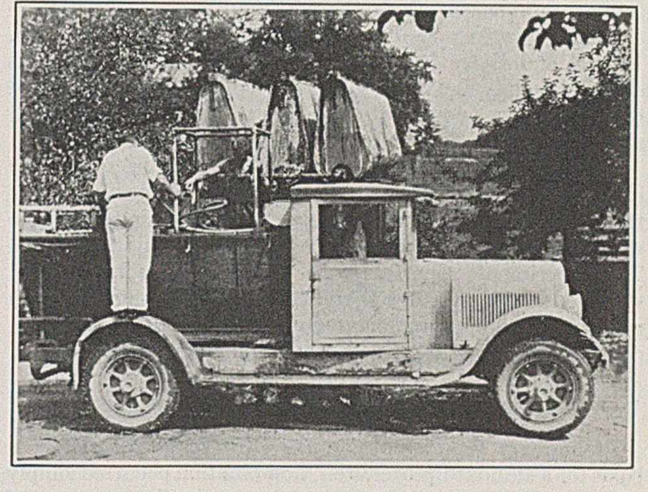


(*Above*) Experimental Spraying of Apple Trees at Kearneysville, W. Va.



(*Right*) Filling the Spray Tank from Water Tanks in the Rear, for Experimental Spraying at Kearneysville, W. Va.

The desirability of having available water-insoluble nicotine products for insect control has recently been recognized and has stimulated research in that direction. For many years nicotine has been used as an insecticide in the free state or combined with sulfuric acid, but these materials are water-soluble and are used principally against the sucking insects. If it becomes possible to develop a water-insoluble nicotine preparation of satisfactory toxicity, such a product will be adaptable for the control of certain chewing insects. It might also displace the hazardous inorganic insecticides such as those containing lead, arsenic, and fluorine.

Recently two such nicotine insecticides were developed and subjected to entomological tests, chiefly against the codling moth, for which the standard control material is lead arsenate. These products are nicotine tannate (*3*) and nicotine bentonite (*5*).

A third insoluble nicotine preparation is here presented for the first time. This is the reaction product of nicotine and peat, for which the designation "nicotine peat" is proposed. Peat is an organic type of soil which is widely distributed. Its chemistry is imperfectly understood even after many years of investigation. An important ingredient is a group of acidic substances known collectively as "humic acid," the constitution of which has not been established. This humic acid is combined more or less, according to environmental conditions, with basic elements, chiefly calcium, magnesium, iron, and aluminum, thus giving peats of acidity ranging from a pH of less than 4 to a pH of 7 or more.

A water-insoluble insecticide can be formed by the reaction of nicotine and peat in aqueous solution. A study of the factors involved showed that the nicotine content of the product is not greatly affected by the concentration of nicotine, the degree of dilution, or the ratio of peat to nicotine. The coarser particles of peat are combined with more nicotine than the finer ones. The presence of acid in the reaction reduces the nicotine content of the product.

Peats vary in their capacity for holding nicotine. The highly acid peats combine with a greater amount of nicotine than the less acid or neutral peats. When peat is first treated with acids to remove inorganic basic constituents (calcium, magnesium, iron, aluminum, etc.) the nicotine content is increased, and the proportion of soluble nicotine is reduced. The peats that are benefited most by the acid treatment are those of least natural acidity.

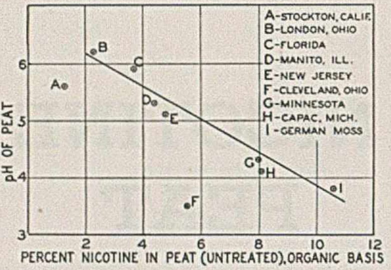


FIGURE 1. RELATION BETWEEN THE ACIDITY OF A PEAT AND THE NICOTINE CONTENT (ORGANIC BASIS) OF NICOTINE PEAT MADE FROM IT

It is due to the presence of free acid that peat is able to combine with nicotine, a fairly strong organic base.

Scholl and Davis (*4*) showed that peat combines with liquid (anhydrous) ammonia at high temperatures and pressures to form a product in which the added nitrogen is largely insoluble in water and is no longer in the ammoniacal form. Feustel and Byers (*2*), who worked with peat and aqueous ammonia solutions at 150° C. under slight pressure, also found that there was combination between the two, the added nitrogen being chiefly nonammoniacal but soluble.

The chemical natures of ammonia and nicotine are similar in that both are weak nitrogenous bases. It was therefore thought possible that nicotine might also be made to combine with peat, and the data here presented show this to be true. The experiments reported, with the single exception noted, were conducted at atmospheric pressure. In contrast to the results reported for ammoniated peat, the added nitrogen was completely recoverable as nicotine on distillation with alkali.

Experiments with Florida Sedge Peat

Preliminary experiments on a Florida sedge peat laid the basis for a standard procedure. Combination occurred simply by bringing together nicotine and peat in the presence of water. The concentration of nicotine, or of peat, and the volume of water may be varied over a considerable range. In practice it is desirable to work with a moderate excess of peat in order to utilize fully the more expensive nicotine. A peat-nicotine ratio of 20 to 3 was selected as standard:

Twenty grams of peat (air-dried) and 3 grams of nicotine are brought together in the presence of 100 cc. of water. The reaction is conducted at steam-bath temperature (about 100° C.) which results in higher nicotine yields than can be obtained at lower temperatures. At 200° C., under pressure, the nicotine content falls off appreciably. No experiments were made at intermediate temperatures, but there is probably no advantage in going above open-steam-bath temperature. A uniform time of 2 hours is generally allowed for each experiment, although the same results can be achieved in 15 minutes.

The air-dried peat is first ground to about 60 mesh. An interesting but not well-understood factor is the size of particle as affecting the nicotine content of the product. Coarse particles (coarser than 40 mesh) seem to produce higher nicotine products than do finer particles (80 mesh or above). This behavior may be due to varying segregation of active and inert matter, or to greater removal of nicotine from the finer particles by the wash water, or to still other causes. Since this experiment was performed on only one sample of peat, it should not be concluded that the behavior is typical of all peats.

After the reaction, the solid matter is separated by filtration, centrifuging, or settling, and is ultimately washed until the wash water shows only a negligible amount of nicotine (opalescence with silicotungstic acid). The product is then air-dried and ground to 200 mesh, in which condition it is suitable either for dry-dusting or for use in a spray mixture.

All the nicotine introduced in the reaction cannot be recovered in the solid product; some remains in the solution. However, the uncombined portion is not wasted but can be regenerated, or the liquid can be otherwise processed for its nicotine in a manner to be described in a future publication.

The presence of acids during the reaction is to be avoided, as the nicotine content is thereby lowered. An experiment with acetic acid showed that the percentage of nicotine in the product is lowered roughly in proportion to the amount of acid present. When nicotine and acid are present in equivalent amounts (as in a salt of nicotine) there is still combination but less than when there is no acid at all.

Preliminary Treatment of Peat with Acid

The nicotine content of a nicotine peat can be markedly raised by treating the peat with an acid before submitting it to the nicotine reaction. As has been stated, the acid constituents of peat are combined wholly or in part with bases, such as the alkaline earths, iron, and aluminum, and, to a smaller degree, the alkali metals. With the removal of these bases by an acid, and the consequent liberation of the free peat acids, the nicotine-combining power is increased, especially in the case of the slightly acid, neutral, and alkaline peats which are rich in basic elements. Hydrochloric, nitric, and sulfuric acids are about equally effective in this regard, while acetic acid is somewhat less so.

Nicotine-Combining Power of Various Peats

Table I summarizes the results of tests on nine samples of peat. The standard procedure mentioned previously was followed throughout:

A mixture of 3 grams of nicotine, 20 grams of peat, and 100 cc. of water was allowed to react on the steam bath for 2 hours. The solid matter was separated by centrifuging, washed on a Büchner funnel, air-dried, ground to 200 mesh, and then analyzed. Where preliminary acid treatment was given, the same quantity of peat was immersed overnight in 3 per cent hydrochloric acid, washed free of excess acid and dissolved salts, and used further without drying in the nicotine reaction.

The values for total and for water-soluble nicotine were obtained by the silicotungstate method. The determination of water-soluble nicotine is important, since it affords an index of the water-resisting properties of the product. This value should be kept as low as possible in order that the maximum amount of nicotine shall be retained under wet conditions on the surface to be protected. Water-soluble nicotine is determined at an arbitrary dosage of 5 pounds of nicotine peat to 100 gallons of water, which on a laboratory scale becomes 1 gram to 166 cc. The mixture is held at room temperature (25° C.) over a 24-hour period

TABLE I. ANALYSES OF NICOTINE PEATS FROM DIFFERENT PEAT SAMPLES

						Nicotine			
						Air-Dry Basis			
Peat	Degree of Decomposition[a]	Acidity of Peat	Moisture	Ash	Organic Matter	Total	Water-sol.	Insol.	Organic Basis, Total
		pH	%	%	%	%	%	*% of total*	%
				Untreated					
Florida sedge	C	5.9	8.05	5.52	86.43	3.17	0.81	74	3.67
Capac, Mich., sedge	B	4.1	6.53	4.84	88.63	7.21	0.95	87	8.13
New Jersey reed	D	5.1	8.44	9.24	82.32	4.76	1.12	76	5.78
Minnesota reed	B	4.3	7.50	10.14	82.36	6.56	0.98	85	7.97
German moss	A	3.8	6.72	1.63	91.65	9.71	1.19	88	10.59
Manito, Ill., reed	E	5.3	8.42	19.52	72.06	3.16	0.65	79	4.39
Cleveland, Ohio, reed	D	3.5	7.85	14.68	77.47	4.30	1.00	77	5.55
London, Ohio, reed	E	6.2	7.87	30.99	61.14	1.43	0.60	58	2.34
Stockton, Calif., tule	B	5.6	6.50	40.95	52.55	0.67	0.17	75	1.28
				Treated with Hydrochloric Acid					
Florida sedge			7.03	1.56	91.41	8.78	1.01	89	9.61
Capac, Mich., sedge			6.06	3.35	90.59	9.00	0.88	90	9.93
New Jersey reed			6.82	3.55	89.63	12.25	1.03	92	13.67
Minnesota reed			6.13	7.63	86.24	10.23	0.99	90	11.86
German moss			7.09	0.80	92.11	9.99	0.86	91	10.85
Manito, Ill., reed			5.48	14.91	79.61	9.37	0.89	91	11.77
Cleveland, Ohio, reed			5.65	10.30	84.05	8.41	0.90	89	10.01
London, Ohio, reed			4.52	26.27	69.21	9.11	1.05	88	13.16
Stockton, Calif., tule			3.60	39.25	57.15	6.36	0.92	86	11.11

[a] A, poorly decomposed (closest to living plant); B, slightly decomposed; C, partly decomposed; D, largely decomposed; E, well decomposed. Classification according to Dachnowski-Stokes (*1*).

and is shaken vigorously at hourly intervals during the working day. The amount of nicotine dissolved is determined as usual in an aliquot of the clear filtrate. Repeated aqueous extraction of the product continues to dissolve out nicotine, but very slowly. At present it is believed that the rate of dissolution is slow enough to afford an adequate period of protection, but this point awaits settlement by special investigation.

In addition to total and water-soluble nicotine, analyses were made for moisture and ash, which permit the conversion of total nicotine to a basis of 100 per cent organic matter. Moisture is the loss on drying at 80° C. for 24 hours; ash is the residue after ignition at low red heat. From a practical standpoint the air-dry basis is the important one, but it is informative also to compute values to the organic basis, since this permits us to compare the active matter in the various peats.

Determinations of pH were made with the hydrogen electrode on a suspension of peat in water at a ratio of 1 to 5.

Conclusions

Several conclusions can be drawn from the foregoing data. In the first place, the highly acid peats, such as German moss, the Capac, Michigan, and Minnesota peats, are distinctly superior to the less acid types, exemplified by the peats from London, Ohio, and Stockton, Calif. Figure 1 shows graphically the relation between pH and nicotine content on the organic basis. If the Stockton, Calif., and Cleveland, Ohio, peats are disregarded, the various points fall close to the straight line shown. Too much importance should not be attached to this apparent correlation between pH and nicotine content, since acidity in some cases may be due partly to inorganic constituents and hence is not a measure of active organic matter upon which the reaction depends.

Secondly, acid treatment in every case raises the nicotine content, and the increase is least for those peats that are naturally very acid and greatest for the more neutral types. The explanation is that, as the basic elements are removed, the acids in the peat are correspondingly freed to combine with nicotine, a process equivalent to base replacement. In this way a peat—New Jersey reed, for example—which in its natural state possesses a low combining power, can be converted to one ranking among the highest. Of the untreated peats, German moss shows the highest combining power, and acid treatment improves it so little as to make it inferior to other acid-treated peats. Probably also the nature of the peat acids is an important factor. Peat acids of the black, well-decomposed peats (mucks) in general have greater combining power than those of the lighter, less decomposed peats.

Thirdly, the nicotine contained in nicotine peat is largely insoluble in water. In the case of untreated peats the insoluble nicotine reaches a value of 88 per cent of the total amount of nicotine present. The nicotine in the acid peats (German moss, the Capac, Michigan, and Minnesota peats) is less soluble than that in the more neutral peats (such as the London, Ohio, and Florida peats). Preliminary acid treatment increases the proportion of insoluble nicotine to over 90 per cent for the better products. This improvement is least for the acid peats, which show a high percentage even in the untreated state, and marked for the more neutral types.

The question of how the nicotine is held in nicotine peat can only be speculated upon at this time. Clearly it is not a case of free nicotine being adsorbed on the peat, because the product gives a definitely acid reaction which is inconsistent with the presence of a free, strong base. Since nicotine is basic and peat acidic, it is reasonable to infer that a typical acid-base reaction occurs, producing a nicotine salt that is substantially insoluble in water. The practical aim—having the nicotine insoluble—is achieved, irrespective of the explanation.

From the commercial standpoint, nicotine peat is a practical product. Peat itself is available in large quantities at a low price (a few dollars per ton), and the process of manufacture is simple.

Nicotine peat, like all nicotine salts, is incompatible with alkaline fungicides. If water-insoluble nicotine insecticides are to be applied with fungicides, the latter should be of a neutral type.

Letters patent covering this product and the process of making it have been applied for under the Act of March 3, 1883, as amended.

Acknowledgment

Acknowledgment for making the pH determinations with the hydrogen electrode is kindly made to E. H. Bailey, of the Bureau of Chemistry and Soils. M. S. Anderson, of the same bureau, checked the value for the Cleveland, Ohio, peat with the glass electrode.

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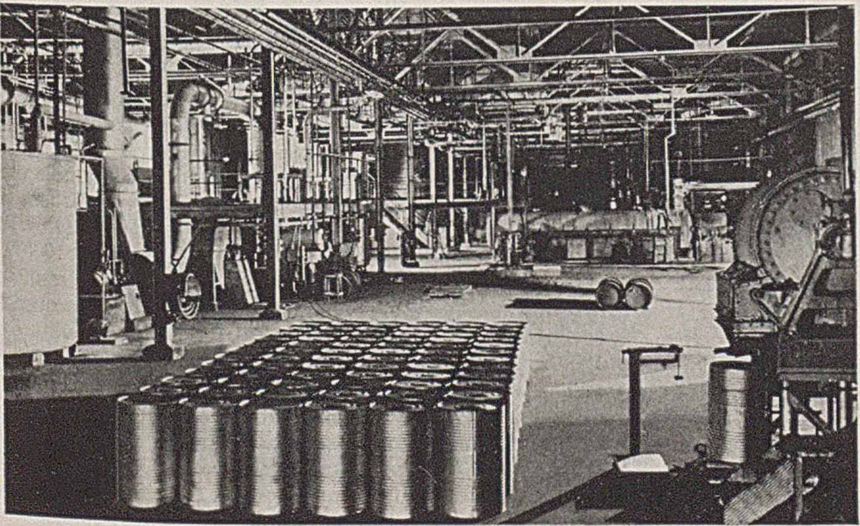

Plant for Manufacturing Improved Flake Form of Sodium Acetate

Courtesy, Dow Chemical Company

Catalytic Oxidation of Carbon

JESSE E. DAY AND
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Columbus, Ohio

The rate of oxidation of "amorphous" carbon by air over the temperature range 200° to 450° C. is greatly increased by the presence of admixed copper or zinc chromite. The quantitative increase in oxidation speed due to the presence of the chromite is shown to be a function of the rate of activated adsorption of oxygen by the chromite used.

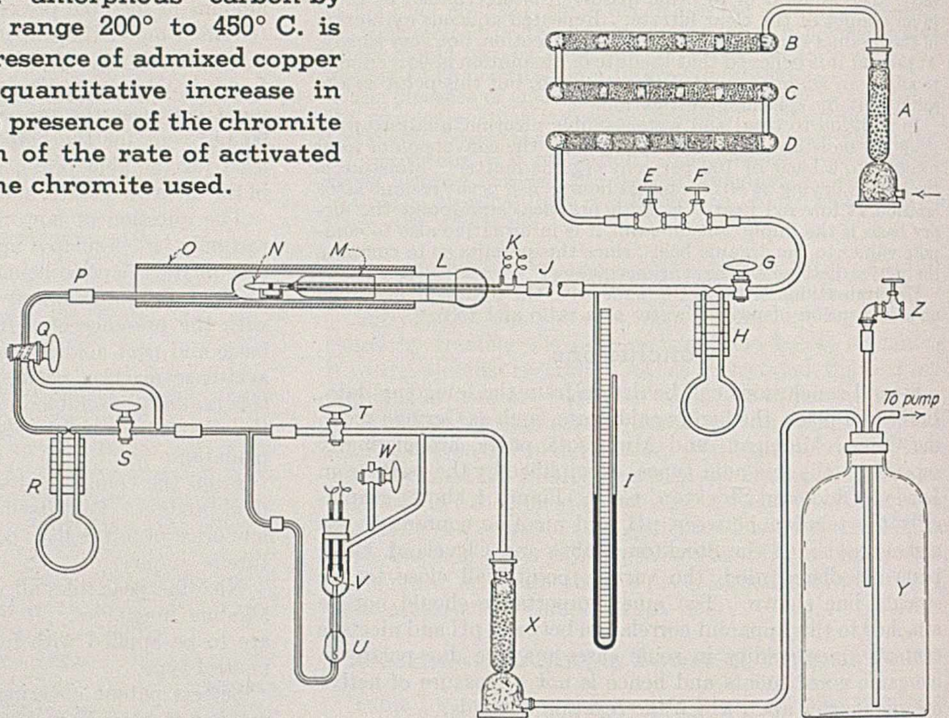

FIGURE 1. DIAGRAM OF APPARATUS

IN A PREVIOUS paper Day and others (*3*) reported a method of preparation of a pure form of "amorphous" carbon and presented the results of a study in which the carbon was admixed with certain inorganic oxides and burned in a stream of oxygen gas. The effects of the various substances on the rate of oxidation were compared with the rate of oxidation of the pure carbon samples as a standard.

Two of the various oxides used were especially effective in increasing the rate of oxidation of carbon at 300° C.—namely, the double chromium oxides of copper and zinc, or chromites.

The present paper offers the results of a continued and more detailed study of the rates of oxidation of pure carbon and of carbon-chromite mixtures by air over the temperature range 200° to 450° C.

Materials and Experimental Method

Acetylene-black carbon (designated "acetylene A" carbon in the previous paper) was prepared by the method developed by Day and co-workers (*3*). The method was based on the incomplete combustion of purified acetylene gas in purified air. The carbon was dried for several hours at 110° C. and sieved through a Tyler 325-mesh screen. The ash residue after burning consisted of about 0.05 per cent of the original carbon (including volatile matter). Samples of the carbon were prepared for reaction by compressing 0.150 gram, together with 0.05 gram of the chromite (if added), in a tablet press of 0.8-cm. bore under a pressure of 458 kg. per sq. cm. The acetylene carbon samples were thus obtained in the form of small right cylinders with a smooth lateral surface that was oxidized while supported in a streamline holder similar to, but smaller than, the one used by Mayers (*7*). The apparent density of compressed acetylene carbon is 0.8. The iodine retentivity of this carbon was determined by shaking 0.200-gram samples in 20 cc. of 0.05 *N* iodine in benzene for 22 hours. The residual iodide was titrated after removal of the carbon, the carbon retaining 7 mg. of iodine per gram.

A "conditioned" carbon was kindly furnished by K. D. Detling of this laboratory and was the identical sample used by him in a study of the adsorption of oxygen on carbon. It was prepared from the acetylene black just described by the steam-air method of activation in a muffle furnace at 1000° C. and was allowed to cool in air. Two grams of the resulting product were placed in a silica bulb which was subsequently evacuated to a pressure of 0.1 to 0.01μ at a temperature of 1000°, after which it was allowed to cool to room temperature and oxygen gas was admitted to it. This procedure was carried out with the 2-gram sample innumerable times in the course of the adsorption study. Before it was used in this investigation, the sample was degassed at 1000° C. and allowed to cool to room temperature *in vacuo*. Its iodine retentivity measured 39 mg. per gram, and its ash content 0.3 per cent.

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[1] Because of the sudden death of Dr. Day on April 19, 1935, the junior author was deprived of the benefits of his final criticism and kind advice in the preparation of this paper.

This carbon could not be molded by pressure in a press because no binding seemed to occur. Consequently a glass boat was constructed of such a design as to hold 30 mg. of the carbon in loose form, plus 10 mg. of chromite, when added, and to offer a known gross oxidizable surface. In the loose condition the apparent density of the carbon is 0.1.

A "degassed" carbon was prepared by simple degasification (oxygen flushing steps omitted) of the activated acetylene black at 1000° C. and cooling *in vacuo.*

The cupric and zinc chromites were also those used by Detling in an adsorption study. Both had been passed through a 325-mesh screen and, after the completion of the adsorption studies, were degassed at 450° C. and allowed to cool *in vacuo.* The desired weights of these chromites were thoroughly mixed with the carbon samples by shaking them together for a half-hour to an hour in a glass vial. In the compressed condition copper and zinc chromites have apparent densities of 1.3 and 1.4, respectively; in the loose condition both apparent densities are 0.6. The cupric chromite was prepared by a method essentially that of Adkins and Connor (*1*), while that of zinc was prepared as described by Taylor and Kistiakowsky (*8*). The formula of the zinc compound is approximately $2ZnO \cdot Cr_2O_3$.

The apparatus train used for the determination of the rate of oxidation of the samples is shown diagrammatically in Figure 1:

The air used in the oxidation was purified by passage through packings of soda lime and anhydrous calcium chloride, ascarite, anhydrous calcium chloride, and phosphorus pentoxide in *A*, *B*, *C*, and *D*, respectively. The air flow velocity over the sample, as measured by calibrated flowmeters *H* and *R*, was controlled by valves *E*, *F*, and *G* and was maintained constant throughout the investigation at the value 0.03 cm. per second. The pressure in the reaction tube was measured by manometer *I* and maintained at 700 mm. by the controlled leakage of air through valve *Z* into buffer bottle *Y*. The gas entered the Pyrex glass reaction tube, *L*, by way of the center tube, *J*, sealed in a ground-glass joint. The gas was caused to flow around the baffle at *M* and over the sample in a Pyrex glass streamline holder at *N*. The temperature at this point was determined by use of a platinum and platinum-rhodium wire (0.025 cm. diameter) junction. The reaction tube surrounded by an iron core, *O*, was heated over the temperature range at a rate of 4° C. per minute. Capillary tubing was used for the gas exit, *P*, to reduce the time of flow to the absorption tube, *U*, to less than one minute. Stopcocks *Q*, *S*, and *T* provided gas by-passes.

The effluent gas bubbled through 17 cc. of barium hydroxide solution in the Pyrex glass cell, *U*, contained in a thermostat at 25.2° C. with a variance of ±0.01°. The cell was so constructed that the flow of gas through it caused a circulation of the electrolyte over the protected platinized conductivity electrodes, *V*. The concentration of the solution (about 0.1 *N*) was that prescribed as the optimum for the absorption-resistance method of continuously analyzing for carbon dioxide by Cain and Maxwell (*2*). The surface tension of the barium hydroxide solution was depressed to facilitate bubble formation by the addition of *n*-butyl alcohol to the extent of 0.5 per cent. The rate of evolution of carbon dioxide was determined by the rate of change of the resistance of the solution, using a Leeds and Northrup Kohlrausch slide-wire in a Wheatstone bridge circuit with tuned earphones and referring to the more recent data of Leopold and Luck (*6*). The hydroxide solution, however, did not absorb all the carbon dioxide which flowed into the cell; nevertheless, it was shown that the rate of absorption of carbon dioxide at a constant-area gas-liquid interface is a first-order process (*5*) dependent upon the partial pressure of the gas at the interface and also upon the hydroxide-ion concentration. Thus the efficiency of the absorption should remain constant over a wide range of carbon dioxide partial pressures for a given gas flow rate with uniform bubble formation. The efficiency of the absorption was found by comparing the loss in sample weight with the total amount of carbon dioxide absorbed as indicated by the total resistance change. Within the limits of the weighing error, this factor remained constant for the gas flow rate (15 cc. per minute) used throughout this investigation. The correction factor involved by the concentration change of the hydroxide solution during the course of a run was so small as to be negligible.

Stopcock *W* aided in cleaning and refilling the absorption cell. Tower *X*, packed with soda lime, prevented back-flow of carbon dioxide.

Experimental Data

The resulting data are given in Table I. The rate of evolution of carbon dioxide was determined for each of the various types of samples in ambient nitrogen as well as in air. The rates are expressed in hundredths of micromoles of carbon dioxide evolved per square centimeter of gross carbon surface per second. Complete data on the conditioned carbon were not obtained because of the limited amount of the sample.

The various types of carbon are arranged in the order of the ease of oxidation by air. As might be expected, the nonactivated carbon is the most easily oxidized. This may be attributed, at least in part, to the oxidation of volatile tarry hydrocarbon matter associated with this type of carbon, since appreciable quantities of it were found in the exit tube (*P*, Figure 1) at the ends of the runs with this type of carbon.

The results indicate that all of the various types of pure carbon samples evolve carbon dioxide when heated in pure nitrogen gas. This phenomenon is undoubtedly due to the desorption of previously adsorbed oxygen or carbon dioxide from the carbon. The rate of desorption is highly reproducible and may be given the symbol Δ.

In air, the rate of evolution of carbon dioxide from the nonactivated acetylene carbon is increased, as would be expected with the introduction of the process of oxidation of the exposed carbon surface by the oxygen of the air. It is reasonable to suppose that the rate of desorption of carbon dioxide from the interior of the sample would proceed undisturbed by a process of oxidation taking place only on the surface. It thus becomes apparent that the rate of evolution of carbon dioxide from pure carbon samples in air is in

Table I. Rates of Evolution of Carbon Dioxide (in Moles per Sq. Cm. of Gross Surface per Second × 10^8) from Various Types of Carbon

		Observed						Calculated				
		In nitrogen			In air							
Type of Carbon	Temp. ° *C.*	C alone Δ	Cupric chromite mixed with C Δ'_{Cu}	Zinc chromite mixed with C Δ'_{Zn}	C alone $\Omega+\Delta$	Cupric chromite mixed with C $\Omega'_{Cu}+\Delta'_{Cu}$	Zinc chromite mixed with C $\Omega'_{Zn}+\Delta'_{Zn}$	Ω	Ω'_{Cu}	Ω'_{Zn}	$\Omega'_{Cu}-\Omega$	$\Omega'_{Zn}-\Omega$
Acetylene black	225	0.9	1.1	0.9	2.1	4.1	2.7	1.2	3.0	1.8	1.8	0.6
	250	1.3	1.7	1.5	2.7	5.9	3.6	1.4	4.2	2.1	2.8	0.7
	275	2.3	3.1	2.6	5.2	9.4	6.6	2.9	6.3	4.0	3.4	1.1
	300	3.3	4.5	3.7	7.8	12.9	9.7	4.5	8.4	6.0	3.9	1.5
Conditioned carbon	350	..	..	..	0.9	2.0	1.7	..	..	..	1.1	0.8
	375	..	..	..	1.2	2.9	2.4	..	..	..	1.7	1.2
	400	..	..	..	1.5	4.6	3.6	..	..	..	3.1	2.1
Degassed carbon	350	0.19	0.19	0.19	0.19	0.44	0.36	0.0	0.25	0.17	0.25	0.17
	375	0.26	0.24	0.24	0.24	0.54	0.44	0.0	0.30	0.20	0.30	0.20
	400	0.30	0.29	0.29	0.28	0.68	0.58	0.0	0.39	0.29	0.39	0.29
	425	0.35	0.33	0.33	0.31	0.80	0.69	0.0	0.47	0.36	0.47	0.36
	450	0.39	0.36	0.36	0.33	0.93	0.82	0.0	0.57	0.46	0.57	0.46
Activated carbon	300	0.12	0.10	0.11	0.14	0.15	0.15	0.02	0.05	0.04	0.03	0.02
	325	0.15	0.14	0.15	0.16	0.24	0.20	0.01	0.10	0.05	0.09	0.04
	350	0.19	0.19	0.19	0.18	0.33	0.25	0.0	0.14	0.06	0.14	0.06
	375	0.28	0.28	0.24	0.25	0.44	0.34	0.0	0.16	0.10	0.16	0.10
	400	0.38	0.38	0.29	0.37	0.56	0.43	0.0	0.18	0.14	0.18	0.14
	425	0.50	0.45	0.42	0.49	0.63	0.57	0.0	0.18	0.15	0.18	0.15
	450	0.63	0.51	0.55	0.62	0.69	0.72	0.0	0.18	0.17	0.18	0.17

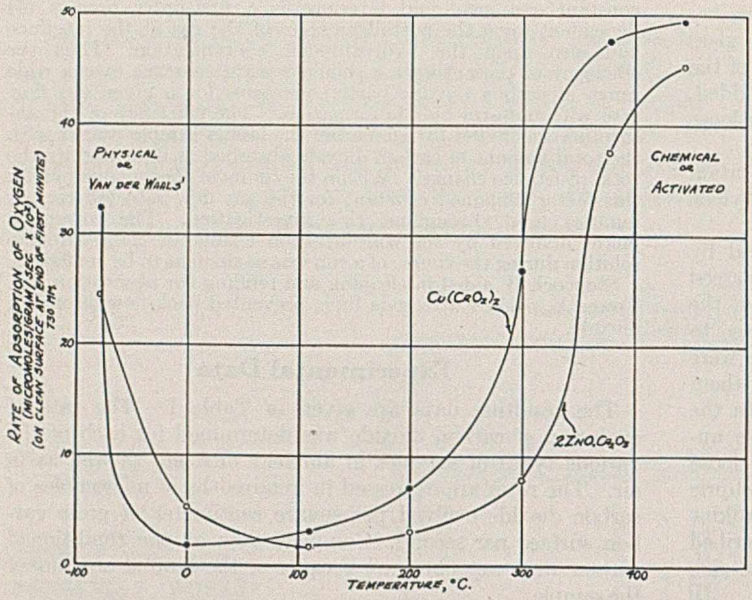

Figure 2. Adsorption of Oxygen on Cupric and Zinc Chromites

reality the sum of two rates—that of desorption from the interior, Δ, and that of surface oxidation, symbolized Ω.

On the other hand, Table I shows that the activated black and the other carbons prepared from it, evolve carbon dioxide at practically the same rate in air as in nitrogen. The conclusion is that the carbon dioxide evolution from these samples in air is derived entirely from the desorption process and not at all from oxidation.

When a mixture of carbon and chromite is heated in nitrogen, the resultant evolution of carbon dioxide may also be attributed largely to desorption, but in this case the rate of desorption may be influenced by the presence of the added chromite. The chromite might also be reduced. In any case, let the symbol Δ′ represent the rate of evolution of carbon dioxide from the carbon-chromite samples in nitrogen. The data show little, if any, difference between Δ and Δ′ in the case of the activated carbons, but considerable difference may be noted in the case of the nonactivated acetylene black, thus again demonstrating the great resistivity of the activated carbons to oxidation.

The large increase in the rate of oxidation of all the carbons by air when chromite is present is remarkable. The measured rate in this case is composed of the rate of desorption and reduction, Δ′, and the rate of oxidation of the carbon surface by air as influenced by the presence of the catalyst. The latter rate is given the symbol Ω′.

The increase in the rate of surface oxidation due to presence of the chromite is equal to Ω′ − Ω.

Theory of Catalysis

In an endeavor to find an explanation for the peculiar oxidation catalytic effects, Detling and Day (*4*) completed a study of the rate and degree of adsorption of oxygen gas on the two chromites over a considerable temperature range. A portion of their results is given in Figure 2. The data obviously represent the sum of two different, but simultaneously occurring, processes of adsorption—namely, physical or van der Waals' adsorption, and chemical or activated adsorption. Physical adsorption possesses a negative temperature coefficient and comes to equilibrium rapidly; chemical adsorption has a well-defined positive temperature coefficient and approaches equilibrium relatively slowly and evidently possesses an energy of activation—hence the name "activated adsorption." The temperature range of Detling and Day's study was limited in the upper region by a peculiar depressing effect, presumably a sintering of the adsorbent surfaces. The obvious differences between the adsorption curves of the two chromites suggests that activated adsorption might be the means whereby the differences in the effects of the presence of each of these adsorbents in a carbon surface undergoing oxidation could be explained.

The values corresponding to the rates of activated adsorption of oxygen gas by the added chromite over the temperature range of the present study are given under A in Table II in hundredths of micromoles of oxygen per gram of chromite per second.

The rate of activated adsorption of oxygen by the chromites is a function of the Maxwellian probability of the impinging oxygen molecules having the necessary energy of activation to adsorb. Detling and Day (*4*) and others showed that this energy value varies with the amount of the gas adsorbed.

Table II. Rate of Adsorption of Oxygen by Chromites in Moles per Gram per Second × 10⁸

Temp., ° C.	Cupric Chromite	Zinc Chromite	Temp., ° C.	Cupric Chromite	Zinc Chromite
225	A = 8	A = 4	350	A = 43	A = 31
250	12	5	375	47	35
275	17	6	400	48	41
300	26.8	7.8	425	49	44
325	37	20	450	49	46

The heterogeneous reaction between the carbon surface and the oxygen actively adsorbed on the chromite surface might be responsible for the peculiar anomalous increase in the rate of oxidation of carbon surfaces in air in the presence of the chromites. It is probable that, if this is the case, the chromite surface is not in equilibrium with the atmospheric oxygen because of the peculiar slowness with which activated

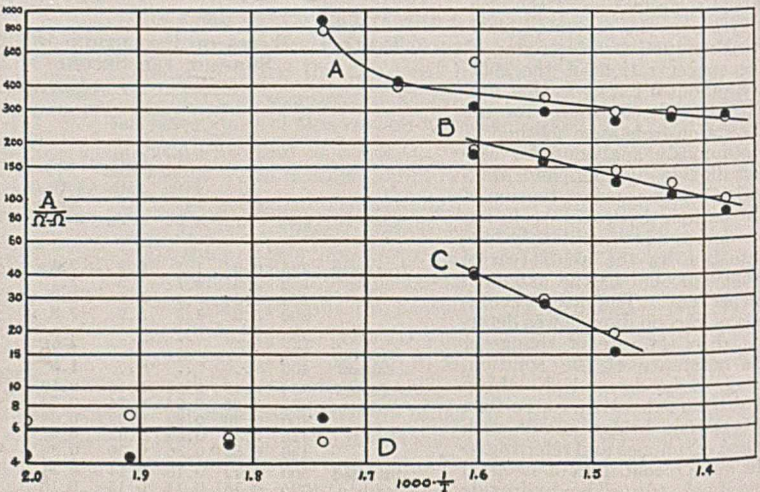

Figure 3. Logarithm of Ratio of Rate of Oxygen Adsorption by Catalyst to Increase in Oxidation Rate as a Function of Temperature

A. Activated carbon	*C.* Conditioned carbon
B. Degassed carbon	*D.* Acetylene black
● Cupric chromite	○ Zinc chromite

adsorption approaches this state. Assuming a Maxwellian distribution of energy among the adsorbed molecules of oxygen, then only those molecules possessing the necessary energy of activation, E, will react with the carbon surface; thus,

$$\mathrm{A}e^{-E/RT} = K\,(\Omega' - \Omega)$$

$$\text{and } \log \frac{\mathrm{A}}{\Omega' - \Omega} = \frac{E}{R}\left(\frac{1}{T}\right) + \log K$$

Since the energy of activation, E, of the reaction is probably constant after the induction period during which the active points on the surface are destroyed, then $\log \mathrm{A}/(\Omega' - \Omega)$ should be practically a linear function of $1/T$. The values of $\mathrm{A}/(\Omega' - \Omega)$ are plotted semi-logarithmically against the reciprocal temperature in Figure 3 for various types of carbon.

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PRODUCTION OF KOJIC ACID FROM XYLOSE BY ASPERGILLUS FLAVUS

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A NUMBER of investigators (*4, 7, 9, 10, 13, 14, 22, 23, 26, 28–31*) have shown that kojic acid, 2-hydroxymethyl-5-hydroxy-γ-pyrone, is produced during the growth of different species of *Aspergilli* upon solutions of a variety of organic substances. Of the carbon sources tested, xylose was used with varying success as to the yields obtained (*1, 2, 3, 5, 8, 11, 27*).

The purpose of this investigation was to determine the effects of environmental changes upon the quantity of kojic acid produced by a strain of *Aspergillus flavus* growing upon xylose solutions and to learn if any change occurs in the stability of that strain of *A. flavus* over a period of 4 years with regard to kojic acid production. One series of experiments was carried out in 1931, a second in 1935.

The mold employed was probably introduced into the laboratory on pods of *Gymnocladus sp.* and was identified as an *A. flavus* by Charles Thom of the Bureau of Chemistry, United States Department of Agriculture.

The experimental results of a study of the effects of environmental changes upon the ability of a strain of Aspergillus flavus to produce kojic acid from xylose are presented. Yields corresponding to over 20 per cent weight per weight conversion of xylose were obtained consistently. The fermentation process is similar to that in which citric acid is made commercially and, likewise, could probably be adapted to the production of kojic acid in commercial quantities.

The structure of kojic acid is such that it lends itself to the preparation of numerous derivatives; probably this acid will prove a useful substance either through its known derivatives or those to be prepared in the future.

Xylose, procured from the Swann Corporation, Birmingham, Ala., was a technical product containing a slight acid residue and a small quantity of a second impurity which reduced Fehling solution and was optically active. Quantities obtained at different times varied to some extent as to the quantity of acid required to bring fermentation media to a given initial pH.

Methods

Stock cultures were maintained continuously on a dextrose–corn meal agar medium of the following composition in grams per liter: ammonium nitrate, 1.0; potassium dihydrogen phosphate, 0.6248; $MgSO_4 \cdot 7H_2O$, 0.5; dextrose, 200; gelatin powder, 10; and Bacto corn meal agar, 19. Transfers were made at regular intervals. Previous to the fermentation experiments, the stock mold was transferred to and grown for several generations upon a xylose–corn meal agar medium, the composition of which was the same as that just given, except that the dextrose was replaced by 150 grams of xylose per liter. Spores developed on this medium were used to inoculate the xylose solutions to be fermented.

Fifty cubic centimeters of prepared xylose solutions were fermented in 125-cc. Erlenmeyer flasks in which the ratio of area to volume was approximately 0.6, and the flasks and contents were autoclaved for 15 minutes at 15 pounds per square inch (1.05 kg. per sq. cm.) pressure before inoculation. All fermentations were run in duplicate and all runs were repeated.

Evaporation and absorption by the mycelial mats somewhat reduced the volume of the solutions from the original 50 cc. When fermentation was complete, the mats were removed and washed with water sufficient to restore the original volume. Two separate 5-cc. aliquots were taken from the fermented liquor of each flask, and each one was diluted with water to 50 cc. The kojic acid in one aliquot was measured by titrating with 0.1 N sodium hydroxide, using phenolphthalein as an indicator, and titrating to full red color over a source of diffused light. In the second aliquot the kojic acid was neutralized with 0.1 N sodium hydroxide and precipitated with 0.1 N copper acetate; the precipitate was dried at 100° C. and weighed as its copper salt, $Cu(C_6H_5O_4)_2 \cdot 1/2\ H_2O$ (*13*). With solutions of carefully purified kojic acid, these methods checked well with each other and with

TABLE I. EFFECT OF PHOSPHATE VARIATION (1931)

(Composition of media, grams per liter: xylose, 150; NH_4NO_3, 2.25; $MgSO_4 \cdot 7H_2O$, 0.5)

Time, Days	KH_2PO_4, Grams per Liter: 0.469	0.625	0.781	0.937	1.093	1.250	1.406	1.562
	Kojic Acid, Grams per Culture							
6	0.19	0.47	0.62	0.61	0.62	0.67	0.47	0.50
7	0.46	0.69	0.71	0.75	0.82	0.89	0.69	0.74
9	0.79	0.97	0.99	0.98	0.98	1.09	1.04	0.93
11	1.01	1.11	1.12	1.07	1.11	1.10	1.05	0.99
12	1.19	1.30	1.26	1.10	1.14	1.14	1.05	1.02
13	1.41	1.44	1.29	1.13	1.06	1.09	1.11	1.04
14	1.37	1.31	1.23	1.10	1.04	0.94	1.08	..

TABLE II. EFFECT OF PHOSPHATE VARIATION (1935)

(Composition of media, grams per liter: initial pH extremes, 3.5 to 3.7; xylose, 150; NH_4NO_3, 1.0; $MgSO_4 \cdot 7H_2O$, 0.5)

Time, Days	KH_2PO_4, Grams per Liter: 0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
	Kojic Acid, Grams per Culture									
4	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
6	[a]	0.24	0.55	0.55	0.43	0.43	0.30	0.42	0.38	0.31
8	[a]	0.60	0.95	1.05	0.89	0.80	1.12	0.89	1.21	0.80
10	[a]	1.17	1.37	1.33	1.31	1.20	1.21	1.48	1.06	1.09
13	[a]	1.48	1.27	1.31	1.26	1.26	1.30	1.38	1.27	1.32
16	[a]	1.04	0.72	0.82	0.75	0.73	1.09	0.80	0.83	0.82

[a] No more than traces of kojic acid.

TABLE III. EFFECT OF AMMONIUM NITRATE VARIATION (1931)

(Composition of media, grams per liter: xylose, 150; KH_2PO_4, 0.625 and 1.250; $MgSO_4 \cdot 7H_2O$, 0.5)

Time, Days	NH_4NO_3, Grams per Liter: 0.50	1.00	1.50	1.75	2.25	2.75	3.25	3.75
	Kojic Acid, Grams per Culture							
	0.625 Gram KH_2PO_4 per Liter							
7	..	..	..	..	0.21	0.07	0.04	
9	..	..	..	..	0.60	0.64	0.56	
10	0.12	1.70	0.98	1.31	..	..	..	
11	..	..	..	..	1.29	0.99	0.85	
13	0.23	2.07	1.65	1.66	1.45	1.02	0.67	
16	..	..	..	..	1.31	0.77	0.43	
17	0.29	1.93	1.41	1.17	..	..	..	
	1.250 Grams KH_2PO_4 per Liter							
7	..	..	..	..	0.67	0.73	0.57	0.33
8	..	..	..	..	0.83	0.79	0.58	0.28
10	0.09	1.45	1.54	1.46	..	..	..	..
11	..	..	..	..	1.01	0.68	0.34	0.04
13	0.12	1.88	1.37	1.22	..	..	..	..
17	0.20	1.60	0.82	0.74	..	..	..	..

TABLE IV. EFFECT OF AMMONIUM NITRATE VARIATION (1935)

(Composition of media, grams per liter: initial pH extremes, 3.45 to 3.50; xylose, 150; KH_2PO_4, 0.625; $MgSO_4 \cdot 7H_2O$, 0.5)

Time, Days	NH_4NO_3, Grams per Liter: 0.00	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25
	Kojic Acid, Grams per Culture									
4	..	..	..	..	..	..	..	..	..	..
6	..	..	..	0.24	0.85	0.80	0.55	0.40	0.50	0.43
8	..	..	..	0.38	1.35	1.11	1.11	1.04	0.71	0.40
10	..	..	..	0.84	1.49	1.29	0.92	0.92	0.84	0.86
13	..	..	..	1.25	1.24	0.87	0.43	..	..	..
16	..	..	0.46	1.27	0.82	0.40	..	..	..	..

TABLE V. EFFECT OF pH VARIATION (1935)

(Composition of media, grams per liter: xylose, 150; NH_4NO_3, 1.0; KH_2PO_4, 0.625; $MgSO_4 \cdot 7H_2O$, 0.5)

Time, Days	Initial pH: 2.25	2.50	2.75	3.20	3.45	4.60	5.10	5.40	5.75	5.90
	Kojic Acid, Grams per Culture									
4	..	..	..	..	..	..	..	..	..	..
6	0.81	0.57	0.52	0.42	0.37	0.28	..	..	..	..
10	1.59	1.76	1.01	1.41	1.57	1.30	1.45	1.16	1.02	0.77
13	1.82	1.79	1.11	1.14	1.50	1.64	1.65	1.70	1.66	1.42

calculated values. With experimental solutions, however, the titration method gave results which were high approximately to the extent of the buffer effect, which varied with the conditions of the experiment from 0.4 to 1.5 cc. After the sixth day of fermentation the difference between analyses of a sample by the two methods was no greater on the average than 0.7 cc. The kojic acid analytical data listed in the tables were obtained by the copper precipitation method and represent averages.

Residual xylose, when measured, was determined by means of the polariscope. The pH adjustments of solutions to be fermented were made by additions of 0.1 *N* sulfuric acid or 0.1 *N* potassium hydroxide. The pH measurements of fermented solutions were made with the quinhydrone electrode. The temperature of fermentation was 35° C.

The following factors affecting mold growth were varied individually: potassium dihydrogen phosphate, ammonium nitrate, pH, xylose, $MgSO_4 \cdot 7H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$, and time of fermentation. The results obtained in 1931 and 1935 are presented. Because of the necessity of checking back on the variables in the earlier part of the work, the 1931 results cannot always be compared with each other or with those of 1935. The 1935 results are comparable.

Influence of Phosphate Concentration

The ammonium nitrate concentration used in the 1931 phosphate experiments was chosen because it had been found to give the best kojic acid yield over an arbitrarily chosen 10-day period. In subsequent experiments of the same year, the smaller concentration (1.0 gram per liter) was found to be optimal and was used, therefore, in the 1935 experiments.

The general effect of phosphate increase from a certain minimum was to increase the rate of fermentation and to decrease the yield. However, within the range of phosphate concentrations used, there developed consistently in the 1931 experiments (Table I) two concentrations favorable to kojic acid formation at roughly 0.6 and 1.2 grams potassium dihydrogen phosphate per liter. It was thought desirable to use both of these concentrations as a basis for the variation of the other constituents even though there was considerable difference between the kojic acid yields corresponding to the two apparent maxima. A repetition of the phosphate experiments in 1935 (Table II) showed a widening of the interval between the maxima.

Influence of Ammonium Nitrate Concentration

In preliminary experiments, different inorganic salts containing the ammonium and nitrate radicals were tested for their suitability in this fermentation. Salts containing the ammonium group were found to be much the better (*6*), and ammonium nitrate seemed to be particularly well adapted (*3*, *13*, *26*).

The data given in Tables III and IV afford a good comparison between the 1931 and 1935 fermentations. The most favorable ammonium nitrate concentration was 1.0 gram per liter, above which the yield gradually decreased. This behavior held for both low and high phosphate concentrations, although the low phosphate gave a slightly higher maximum yield. Increased kojic acid production resulting from the use of lower concentrations of available nitrogen than are usually employed in culture media appears to bear out the observations of Kinoshita (*10*), Kluyver (*11*), and Currie (*6*).

Influence of pH Variation

Results of the 1931 experiments led to the conclusion that the optimum pH for kojic acid production was the lowest that the strain of mold would tolerate. In almost all trials the most favorable initial pH was approximately 3.5; however, in a few isolated cases yields were obtained as high as that corresponding to 36 per cent weight per weight conversion of xylose in solutions where the initial pH was well down toward 2.0. Tamiya (*26*) concluded 5.5 to be the optimum pH.

The 1935 data (Table V) confirm this conclusion generally but give the additional information that good yields resulted not only at the initial pH 3.5 but also consistently within the lower 2.0 to 3.0 pH range (*8*, *9*, *11*).

Influence of Xylose Concentration

In the conversion of xylose into kojic acid, there was little difference between the 150 and 200 grams per liter xylose concentrations on the low phosphate concentration (Tables VI and VII); however, on the high phosphate concentration the 200-gram concentration was the more efficient (Table VI). Where only 50 grams of xylose per liter were used, all of the sugar was utilized by the organism for vegetative growth and as a source of energy. Xylose disappeared entirely from those solutions containing 150 grams or less per liter when fermentation was allowed to proceed 22 days.

Influence of Magnesium Concentration

After a minimum concentration of $MgSO_4 \cdot 7H_2O$ (0.1 gram per liter) was reached, further increase had relatively little effect although a continuous increase or decrease in yield did not follow a continuous increase of $MgSO_4 \cdot 7H_2O$ (Table VIII).

The fermentation of xylose solutions with this strain of *A. flavus* was almost always accompanied by the formation of a small quantity of a yellow compound with indicator properties. The quantity of this substance was appreciably increased in those solutions, the $MgSO_4 \cdot 7H_2O$ concentration of which ranged between 0.00 and 0.05 gram per liter.

Influence of Iron and Calcium Concentrations

Additions of iron as $Fe(NO_3)_3 \cdot 9H_2O$ and calcium as $Ca(NO_3)_2 \cdot 4H_2O$ were inhibitory in an irregular manner except at one calcium and two iron concentrations where there were no appreciable effects. This behavior does not eliminate possible stimulating influences of traces of iron and calcium which might have been present in the materials of which the solutions were made.

These results are in harmony with Currie's conclusion (*6*) regarding the influence of iron in citric acid production but not with that of Di Capua (*7*) regarding the influence of iron in kojic acid production.

The data in Table IX show also that continuous increases in the concentrations of iron and calcium did not occasion a continuous increase or decrease in yields.

Influence of Zinc Concentration

An accumulation of experimental evidence indicates that a small concentration of zinc stimulates the growth of *A. niger* (*12, 16, 18, 20*) and *A. flavus* (*15*), and is even required for normal growth and development (*19, 25*). Porges (*17*) showed that zinc favors acid production by *A. niger* although Currie (*6*) had concluded earlier that zinc is unnecessary for that purpose.

Because of the seeming importance of zinc in mold metabolism, comparative experiments were carried out to find what influence zinc might have upon kojic acid production from xylose by *A. flavus*. For this purpose a concentration of 2 to 3 parts per million of zinc ion furnished by $ZnSO_4 \cdot 7H_2O$ was chosen. Previously this concentration of zinc with the same strain of *A. flavus* had markedly increased kojic acid yields with another carbon source (*24*).

The results of the experiments with xylose media containing zinc were identical with those without zinc, showing that zinc at this concentration range has no effect upon the production of kojic acid from xylose. Spore formation was retarded to some extent; the mats were somewhat thinner and possessed a whitish appearance, especially in the earlier stages of fermentation.

Table VI. Effect of Xylose Variation (1931)

(Composition of media, grams per liter: NH_4NO_3, 2.25; KH_2PO_4, 0.625 and 1.250)

Time, Days	Xylose, Grams per Liter:							
	150	200	250	300	150	200	250	300
	Kojic Acid, Grams per Culture				Per Cent Yield Kojic Acid, Weight per Weight			
	0.625 Gram KH_2PO_4 per Liter							
6	0.29	0.14	0.03	..	3.90	1.40	0.25	...
8	0.63	0.56	0.33	0.21	8.40	5.60	2.60	1.40
10	1.13	1.16	0.96	0.87	15.10	11.60	7.70	5.80
12	1.42	1.60	1.79	1.27	18.90	16.00	14.30	8.50
16	1.63	2.17	2.54	2.50	21.70	21.70	20.30	16.70
18	1.34	2.05	2.39	2.54	17.90	20.50	19.10	16.90
	1.250 Grams KH_2PO_4 per Liter							
6	0.31	0.20	0.22	..	4.10	2.00	1.75	...
8	0.92	0.69	0.84	0.62	12.30	6.90	6.70	4.10
10	0.95	1.03	1.41	1.17	12.70	10.30	11.30	7.80
12	1.04	1.68	2.11	1.99	13.90	16.80	16.90	13.30
16	0.93	1.85	2.29	2.71	12.40	18.50	18.30	18.10
18	0.91	1.65	1.74	2.45	12.10	16.50	13.90	16.30

Table VII. Effect of Xylose Variation (1935)

(Composition of media, grams per liter: initial pH extremes, 3.5 to 3.9; NH_4NO_3, 1.0; KH_2PO_4, 0.625; $MgSO_4 \cdot 7H_2O$, 0.5)

Time, Days	Xylose, Grams per Liter:									
	50	100	150	200	250	50	100	150	200	250
	Kojic Acid, Grams per Culture					Per Cent Yield Kojic Acid, Weight per Weight				
4	..	..	..	..	..	..	...	...	...	...
6	..	0.70	0.85	0.67	..	..	14.00	11.30	6.70	...
10	..	0.62	1.56	1.80	1.52	..	12.40	20.80	18.00	12.20
13	..	..	1.31	1.93	2.19	..	...	17.40	19.30	17.50

Table VIII. Effect of $MgSO_4 \cdot 7H_2O$ Variation (1935)

(Composition of media, grams per liter: initial pH, 3.55; xylose, 150; NH_4NO_3, 1.0; KH_2PO_4, 0.625)

Time, Days	$MgSO_4 \cdot 7H_2O$, Grams per Liter:									
	0.00	0.005	0.01	0.05	0.10	0.30	0.50	0.70	0.90	1.10
	Kojic Acid, Grams per Culture									
4	..	..	..	..	..	..	..	..	..	..
6	..	..	..	0.47	0.60	0.54	0.60	0.63	0.64	0.65
10	..	..	0.80	1.26	1.58	1.51	1.65	1.53	1.65	1.60
13	..	..	1.66	1.14	1.36	1.36	1.56	1.65	1.55	1.56

Table IX. Effect of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ Variation (1935)

(Composition of media, grams per liter: xylose, 150; NH_4NO_3, 1.0; $MgSO_4 \cdot 7H_2O$, 0.5; KH_2PO_4, 0.625; pH extremes, 2.05 to 3.60 when iron was varied, 3.50 to 3.55 when calcium was varied)

Metal	Time, Days	$Fe(NO_3)_3 \cdot 9H_2O$ or $Ca(NO_3)_2 \cdot 4H_2O$, Grams per Liter:								
		0.005	0.01	0.05	0.25	0.50	1.00	1.50	2.00	2.50
		Kojic Acid, Grams per Culture								
Fe	6	0.43	0.57	0.41	0.21	0.26	0.65	..	..	..
	13	1.41	1.24	1.26	1.07	0.94	1.32	1.47	1.36	..
Ca	6	0.57	0.60	0.37	..	0.35	0.18	..	..	..
	13	1.36	1.43	1.20	0.40	1.14	0.92	0.80	0.72	0.58

Table X. Effect of Time Variation (1931)

(Composition of media, grams per liter: initial pH, 3.4; xylose, 150; NH_4NO_3, 2.25; KH_2PO_4, 0.625; $MgSO_4 \cdot 7H_2O$, 0.5)

Time	Kojic Acid per Culture	Xylose Consumed	Weights of Mats	pH
Days	*Grams*	*Per cent*	*Gram*	
3	..	10.7	0.0896	3.06
4	..	21.2	0.2960	2.11
5	0.14	32.0	0.3840	2.13
6	0.48	43.8	0.3845	2.29
7	0.56	48.3	0.3820	2.50
8	0.93	68.0	0.4600	3.60
10	1.43	92.3	0.6679	4.17
11	1.54	93.1	0.7902	4.19
12	1.63	93.4	0.7973	4.29
13	1.58	94.5	0.8365	4.04
14	1.44	94.5	0.8787	4.04
15	1.33	96.1	0.8401	3.90
16	1.32	97.5	0.8451	3.85

Table XI. Effect of Time Variation (1935)

(Composition of media in grams per liter: initial pH, 3.5; xylose, 150; NH_4NO_3, 1.0; KH_2PO_4, 0.625; $MgSO_4 \cdot 7H_2O$, 0.5)

Time	Kojic Acid per Culture	pH	Time	Kojic Acid per Culture	pH
Days	*Grams*		*Days*	*Grams*	
4	..	2.45	10	1.65	4.00
6	0.60	3.50	13	1.36	4.10
8	1.15	3.90	16	0.77	4.25

Influence of Time Variation

The rate of kojic acid production was not constant during the progress of fermentation. In 1931 experiments (Table X) an initial 5-7 day unproductive period was usually found. This period was accompanied by a slow rate of sugar consumption and a slow rate of increase in mycelial weight. During this period there was considerable pH adjustment. In the 1935 experiments (Table XI) the lag was formed somewhat earlier. There was also a marked drop in pH consistently from the original over the first 3 or 4 days, and, until there had been a certain amount of pH recovery, fermentation proceeded slowly.

In 1931, maximum yields were obtained on the twelfth or thirteenth day; in 1935 they were obtained on about the tenth day. The fact that the 1931 and 1935 maximum yields are approximately equal is not interpreted as indicating that the concentrations of 1.00 and 2.25 grams of ammonium nitrate per liter are equally favorable, since these and other data (Tables III and IV) appear to show that 4 years of culturing decreased moderately the maximum yield and increased the rate of fermentation.

Discussion of Results

The fermented solutions were analyzed for kojic acid by two different methods—titrating with standard alkali and weighing as the copper salt. The fact that the analytical data for individual samples checked within the limits of the buffer effect leads us to the conclusion that acidic organic compounds other than kojic acid, if present, were in negligible quantities.

Examination of the 1931 and 1935 results shows that 4 years of culturing modified moderately the strain of *A. flavus* in its ability to convert xylose into kojic acid. The interval between the phosphate maxima increased from about 0.6–1.2 in 1931 to 0.2–1.4 in 1935, the organism became tolerant to a greater hydrogen-ion concentration, and the maximum yield was lowered appreciably.

In a number of instances during the course of these experiments, a continuous increase or decrease in yield of kojic acid did not accompany a continuous increase of one of the variants. This behavior was particularly apparent in the variation of the initial pH, iron, calcium, and, to some extent, phosphate and magnesium. It may be objected that in some cases the differences noted are too small to be significant. But in view of the consistency with which repeated experiments indicated this behavior, such variations in yields can scarcely be fortuitous although they may be relatively unimportant numerically. Similar observations were made by Lohmann (*12*) who found optimum zinc concentrations for *A. niger* at 0.8 and at 132 mg. per hundred, and by Rossi and Scandellari (*21*) who found that continuously increasing ammonium nitrate and potassium dihydrogen phosphate concentrations gave first an increase, then a decrease, and finally an increase of invertase production by *A. niger*. A possible explanation may be suggested for this behavior. It is recognized that the availability of phosphate to plant life in general is dependent upon the form in which the phosphate exists which, in turn, is partially dependent upon the heavy metal and hydrogen-ion concentrations. It is conceivable that the combined effects of the heavy metals and hydrogen ion may modify the availability or utilization of phosphate in fermentation processes which may govern the production of invertase or other necessary enzymes, as suggested by the work of Rossi and Scandellari (*20*, *21*).

Summary

1. The fermentation of xylose solutions with a strain of *A. flavus* was carried out over a period of 4 years. The acidic organic product was almost exclusively kojic acid. The medium most favorable to kojic acid production at 35° C. had the following composition in grams per liter: xylose, 150; ammonium nitrate, 1.0; potassium dihydrogen phosphate, 0.625; and $MgSO_4 \cdot 7H_2O$, 0.5.

2. There were two optimal pH values, approximately 2.5 and 3.5.

3. Maximum yields were obtained over intervals of 13 (1931) and 10 (1935) days.

4. A minimum of 150 grams of xylose per liter was required for good kojic acid yields. When fermented for 22 days, the sugar disappeared entirely.

5. The ammonium radical was much better than the nitrate radical in furnishing nitrogen. Ammonium nitrate served excellently for this purpose.

6. Iron and calcium were inhibitory except at one calcium and two iron concentrations where there was no appreciable effect. Zinc exerted no influence.

7. In the phosphate, iron, calcium, magnesium, and pH experiments the continuous increase of a variant was not followed by a continuous increase or decrease in yield of kojic acid, possibly because of variations in the availability of the phosphate.

8. Low magnesium concentrations favor the formation of a yellow compound with indicator properties.

9. Over a period of 4 years there was a moderate change in the stability of the mold with respect to kojic acid production. The interval between phosphate maxima widened, the tolerance of the mold to acid increased, and the maximum yield decreased.

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Ammoniation of SULFITE WASTE LIQUOR

When sulfite waste liquor is made alkaline with lime to a pH of 9.6, the free sulfur dioxide and part of the combined sulfur dioxide are precipitated as calcium sulfite. The resulting liquor can be directly ammoniated to give a solid and liquid portion, both of which contain combined nitrogen. The solid material is physically suitable for fertilizer.

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SHORTLY after the announcement by Davis and Scholl (*2*) of the ammoniation of peat and its possible usefulness as a fertilizer, work was started on the ammoniation of sulfite waste liquor (S. W. L.). Their complete paper (6) mentioned the ammoniation of dried S. W. L. residue. Phillips, Goss, Brown, and Reid (*5*) studied the ammoniation of dried S. W. L. residue by heating it with concentrated ammonium hydroxide at 200° and 220° C. for 4 to 20 hours, finding from 7.30 to 10.55 per cent total nitrogen. They also found the ammoniated solid a beneficial fertilizer on a test millet crop. A German patent (*3*) claims the treatment of S. W. L. with ammonia and heating under pressure to 200° C. Peat or sawdust may be added to the S. W. L.

This investigation had a different aspect from that of the other workers who had used a dried S. W. L. residue. The well-known difficulty of evaporating and drying S. W. L. makes this product difficult to obtain and greatly decreases the technical value of the previously described ammoniation processes. This work was started from the viewpoint of ammoniation of the concentrated S. W. L. obtained from the digesters. This liquor can be obtained with 10 to 12 per cent solids. The direct ammoniation of this material avoids evaporation, and therefore the continued study of this particular method was considered worth while.

Lime End Point

First, it was observed that the addition of ammonium hydroxide to the concentrated S. W. L. gave only a minute amount of precipitate even when a great excess of ammonium hydroxide was used. It was concluded that the ammonium sulfite formed from the free sulfur dioxide must prevent precipitation, so lime was added to the liquor to precipitate the free sulfur dioxide as calcium sulfite. The neutralized liquor gave considerable precipitate with ammonium hydroxide. The amount of precipitate varied with the amount of lime used, the optimum being the point where the lime just begins to precipitate organic matter from the liquor. This lime end point was later studied in detail by Leitz, Sivertz, and Kobe (*4*) who employed the glass electrode for pH determinations. In this work the Wulff indicator strip method was used. It was found that the maximum precipitate with ammonium hydroxide was obtained when the liquor had a pH of 9.6. The relationships between pH and the weight of precipitate obtained with lime, and with ammonium hydroxide when the liquor is first brought to the indicated pH with lime, are shown in the figure. The percentage ash in the lime precipitate indicates the amount of organic matter in the precipitate.

After determining the lime end point, all S. W. L. used was made alkaline to this point with lime, and the precipitated calcium sulfite was separated from the liquor.

Ammoniation

Six liters of the alkaline S. W. L. were placed in an autoclave (*1*), and ammonia gas was passed in until the liquor was satu-

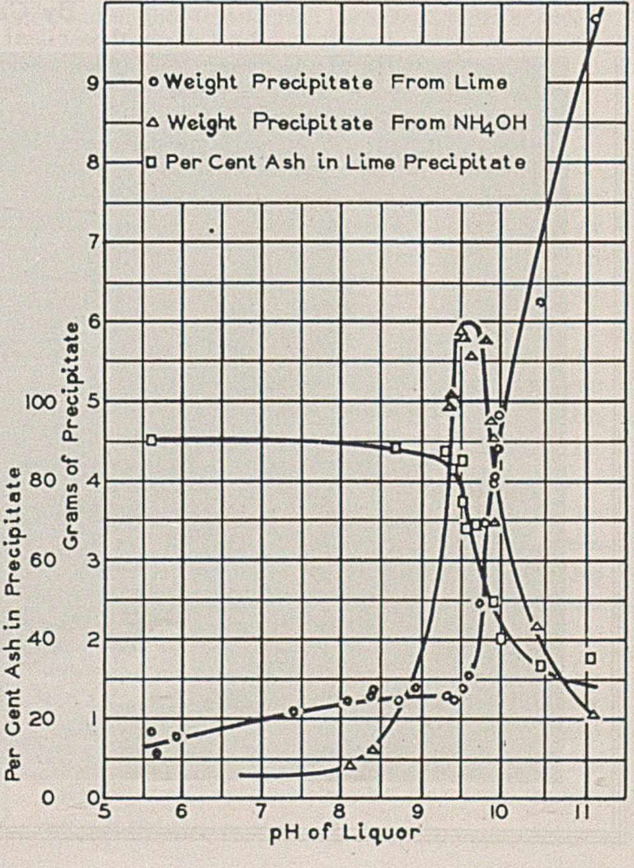

TABLE I. RESULTS OF AMMONIATION

Run No.	Time	Initial NH₃ Gage Pressure		Temp.	Gage Pressure		Per Cent N_2 in: Precipitate	Per Cent N_2 in: Residue from filtrates
	Hr.	*Kg./ sq. cm.*	*(Lb./ sq. in.)*	*° C.*	*Kg./ sq. cm.*	*(Lb./ sq. in.)*		
1	1	0.35	(5)	20	0.35	(5)	0.43	..
2	2	..	..	20	8.8	(125)	0.54	..
3	2	..	..	150	15.5	(220)	2.67	..
4	40	..	..	175	21.1	(300)	4.55	..
5	10	1.41	(20)	103	21.1	(300)	3.50	6.20
6	10	2.81	(40)	82–105[a]	35.1	(500)	3.10	5.66
7	10	1.05	(15)	166	70.3	(1000)	5.61	9.63
8	10	0.35	(5)	149	35.1	(500)	4.02	8.02
9	10	0.00	(0)	184	21.1	(300)	4.01	..

[a] Leak developed; temperature was increased from 82° to 105° C. to maintain constant pressure.

rated. The autoclave was connected directly to an ammonia tank so that the ammonia pressure in the liquid could be regulated up to the vapor pressure of liquid ammonia. The autoclave was rotated and the charge heated for a definite time, the pressure was released, the autoclave contents were removed, and the solids were separated. The filtrate was evaporated to dryness for a number of the runs. Nitrogen was determined in the precipitated solid and in the residue from the evaporated filtrate. The data are given in Table I.

A material balance was made in run 8, all weights being calculated to a nitrogen-free basis. The initial lime treatment to the lime end point removed 4 per cent of the solids, and the ammoniation removed 69 per cent, leaving 27 per cent of the solids in the liquor. The precipitated solids analyzed 4.02 per cent nitrogen, and the soluble material 8.02 per cent. Apparently the soluble carbohydrate material in the liquor ammoniated to a greater extent than the lignin, and remained in solution. Part of the material still in solution was precipitated by the addition of lime, so that a further recovery could be effected. However, the high nitrogen content of these dissolved solids required that all of this soluble material be recovered.

The dried precipitated material is a very fine, dark brown powder which dusts easily. Although the nitrogen content of this material is not as high as that obtained from the evaporated S. W. L. (*5*), the use of higher temperatures and pressures may give equal values. However, the use of a precipitation method rather than an evaporation method to give a fertilizer material appears to be a great technical advantage.

Pot fertilizer tests are being carried out by the Soils Section, Department of Agronomy, Washington State College.

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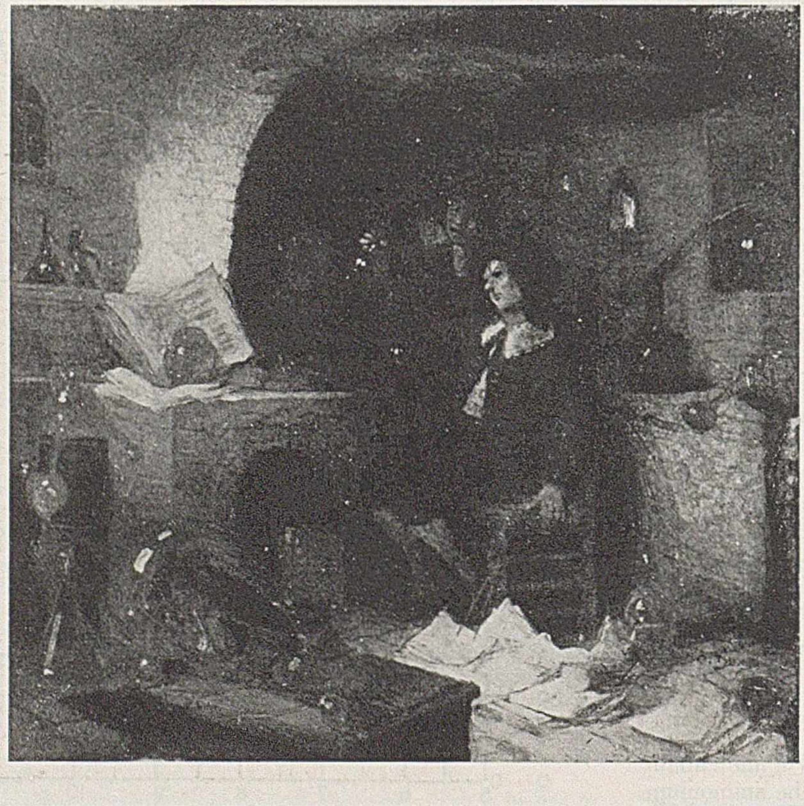
By Carl Duxa



◉ In presenting No. 65 in the Berolzheimer Series of Alchemical and Historical Reproductions we express our appreciation to Mr. Benno Lowy, a member of the American Chemical Society in San Francisco, who kindly made arrangements for the photographing of the original painting which he purchased in Vienna a few years ago, and who gave Mr. Berolzheimer permission to publish this reproduction.

Carl Duxa, the painter, was born in Vienna in 1871 and studied at the Vienna Academy under Trenkwald from 1888 to 1895. In 1912 he was awarded the Dumba Prize of the Vienna Artists' Association.

The original painting is 14 by 15 inches, and in its style and coloring resembles the work of Thomas Wijck, although some of the glass apparatus shown appears quite modern.

◉

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Commercially Important Systems of Organic Solvents . .

Vapor-Liquid Equilibrium Data for the Ternary System *n*-Butanol–*n*-Butyl Acetate–Water

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IN A PREVIOUS article of this series (*1*) data were presented for the vapor-liquid equilibrium relations of the system *n*-butanol–*n*-butyl acetate. In the present paper the equilibrium relations are given for the ternary system including water as the third component. Rosanoff, Schulze, and Dunphy (*9*) studied ternary systems and presented their results by plotting the two binaries and several ternary mixtures for each different boiling point on isosceles right-angle triangles, giving the compositions of the liquid and the vapor in equilibrium with it. In this paper an attempt is made to correlate the data obtained in a new and different way in the hope that it may be useful in designing fractionating equipment.

Determination of Water-Saturation Curve at 20° C.

The introduction of water as third component to the system *n*-butanol–*n*-butyl acetate–water produces a heterogeneous system over a considerable range; hence it was necessary to study the solubility relations of the system before distillation data could be interpreted. The butyl acetate is practically insoluble in the water, and likewise the water is nearly insoluble in the acetate. For the alcohol-water pair, Hill and Malisoff (*5*) determined the mutual solubilities of water and alcohol by volumetric measurements at 25° C. and found that the water layer contained 7.37 per cent alcohol by weight, and the alcohol layer contained 20.27 per cent water by weight.

Stockhardt and Hull (*10*) determined the solubility of water in the alcohol layer at 25° C. by gravimetric methods and found it to be 20.5 per cent water and 79.5 per cent alcohol.

In the present investigation it was necessary to know the water saturation values not only for pure butanol and butyl acetate, but for mixtures of all portions of these two components. The saturation line or boundary between the homogeneous and the heterogeneous phases was determined by two different methods:

METHOD 1. A series of known mixtures of butanol and butyl acetate was made up in weighed, glass-stoppered, Erlenmeyer flasks. A small buret provided with a stopper fitting snugly into the necks of these flasks was filled with distilled water and connected to one of them. The water was slowly added dropwise at a temperature slightly below 25° C. until cloudiness first appeared. While the water was being added, the flasks were shaken vigorously. When the cloudiness appeared, one more drop of water was added, and the flasks were immersed in the thermostat and allowed to come to temperature. The mixtures were thus just saturated at 25° C. The criterion for saturation was a small drop of water in excess. Mixtures which had an excess of more than the small drop were discarded. The flasks were weighed again; the increase in weight was the water picked up by the mixtures.

METHOD 2. An apparatus was developed which proved quite satisfactory and more rapid than shaking flasks by hand (Figure 1). It consisted of a small Pyrex glass bulb 2 inches (5 cm.) in diameter provided with a small stopcock at the bottom and two necks at the top. One neck had a ground joint to fit a small buret; the other somewhat larger neck was provided with a mercury seal and a glass stirrer. The stirrer was run by a small variable-speed motor. The apparatus containing a weighed mixture of alcohol and acetate was placed in the thermostat, the buret attached, and the stirrer started. Water was added dropwise until the cloudiness just appeared. The speed of the stirrer was increased for several minutes to break up the cloudiness. The stirrer and buret were then removed and the opening in the necks closed with glass stoppers provided for the purpose. The apparatus was removed from the thermostat, dried, and weighed to determine the amount of water added. A small loop blown in the top of the bulb served to suspend the

The specific gravities and compositions for all possible mixtures of *n*-butanol–*n*-butyl acetate–water were determined at 25/25° C., and plotted on rectangular and triangular coördinates. The method of Stockhardt and Hull was used to determine vapor-liquid equilibrium curves for saturated and unsaturated mixtures of *n*-butanol–*n*-butyl acetate–water. The results were correlated by two new methods. Data for the composition of saturated mixtures of *n*-butanol–*n*-butyl acetate with water at the boiling point were also determined and presented, and the composition of the heterogeneous azeotrope of *n*-butyl acetate and water was established. This mixture boils at 90.5° C. (760 mm. pressure), and has a composition of 29.44 mole per cent acetate and 70.56 mole per cent water. The ternary system possesses no true azeotropic mixture.

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[1] Present address, The Lummus Company, New York.

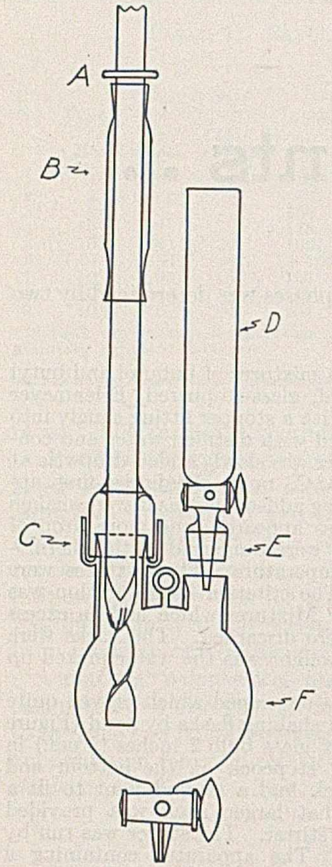

FIGURE 1. APPARATUS FOR DETERMINING AMOUNT OF WATER REQUIRED TO SATURATE MIXTURES OF BUTANOL AND BUTYL ACETATE

A. Bearing surface
B. Glass bearing
C. Mercury seal
D. Detachable buret
E. Standard tapers to fit ground stoppers
F. Diameter, 5 cm.

apparatus by a fine platinum wire from the balance arm during weighing. A similar bulb containing shot was used as a counterpoise.

In a similar manner pure distilled water was saturated with butanol and then with butyl acetate. The solubility was so small in both cases that it was deemed unnecessary to determine more than the two points to fix the position of the upper limits of the heterogeneous phase.

The specific gravity of each of the saturated mixtures was determined immediately after the weight of the added water had been found. The results of these determinations are presented in Table I, on both the weight per cent and the mole per cent bases.

The data were plotted in three different ways in order to smooth out all points and obtain the best line for plotting on a large-scale working chart. The three plots were: (1) the percentage of water to saturate mixtures of alcohol and acetate *vs.* the percentage of alcohol (weight per cent), (2) the specific gravity *vs.* the weight per cent of alcohol in the saturated mixtures, and (3) the specific gravity *vs.* the weight per cent of water in the saturated mixtures. In plotting the final chart for use, each point chosen had to check the other three charts to satisfy the correct line. Thus, there was a triple check on the accuracy of the data. All doubtful points were thrown out and the compositions rerun. The data for specific gravity *vs.* per cent butanol are presented as the saturation line in Figure 2. The compositions at saturation are shown on the triangular chart (Figure 3).

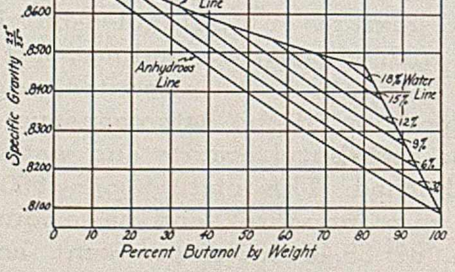

FIGURE 2. SPECIFIC GRAVITY *vs.* PER CENT BY WEIGHT OF BUTANOL FOR DIFFERENT WATER CONTENTS IN THE SINGLE-PHASE SYSTEM BUTANOL–BUTYL ACETATE–WATER

TABLE I. COMPOSITION AND SPECIFIC GRAVITY OF WATER-SATURATED MIXTURES OF BUTANOL, BUTYL ACETATE, AND WATER AT 25° C.

	Weight Per Cent			Mole Per Cent			
Run	BuOH	BuOAc	H_2O	BuOH	BuOAc	H_2O	Sp. Gr., 25/25
58	0.00	99.43	0.56	0.00	96.41	3.59	0.8787$_7$
1	0.00	99.71	0.28	0.00	98.22	1.78	0.8775$_4$
72	0.00	0.83	99.17	0.00	0.13	99.87	0.9987$_3$
73	0.00	0.94	99.06	0.00	0.15	99.85	0.9991$_5$
59	4.56	93.66	1.77	6.37	83.45	10.18	0.8759$_2$
70	7.32	0.00	92.67	1.89	0.00	98.11	0.9886$_6$
2	9.24	90.12	0.63	13.33	82.92	3.75	0.8722$_0$
13	13.37	85.32	1.31	11.85	80.21	7.94	0.8696$_3$
3	18.29	79.35	2.34	23.30	64.44	12.26	0.8670$_2$
14	22.35	73.92	33.71	27.72	58.45	13.83	0.8660$_6$
4	27.20	68.50	4.30	30.71	49.31	19.98	0.8639$_0$
25	28.82	65.61	5.55	30.83	44.74	24.43	0.8637$_1$
15	30.41	64.24	5.33	32.60	43.90	23.50	0.8637$_1$
5	35.45	58.06	6.47	35.75	37.35	26.87	0.8613$_2$
16	39.20	52.80	8.00	37.07	31.82	31.11	0.8593$_3$
6	43.20	47.80	9.00	39.03	27.53	33.44	0.8572$_7$
17	47.66	42.30	10.13	41.52	23.48	35.00	0.8560$_4$
24	51.46	37.52	11.00	42.67	19.82	37.51	0.8550$_3$
18	55.26	32.86	11.86	44.22	16.76	39.02	0.8536$_7$
8	59.41	27.84	12.74	45.86	13.69	40.45	0.8524$_4$
19	64.24	22.39	13.35	48.16	10.69	41.15	0.8506$_6$
22	66.90	18.75	14.35	48.53	8.66	42.81	0.8498$_2$
20	70.98	13.80	15.21	49.89	6.14	43.97	0.8478$_5$
10	74.23	9.10	16.66	50.74	3.96	45.30	0.8469$_8$
12	74.01	8.80	17.17	49.32	2.99	47.69	0.8477$_2$
21	77.30	4.40	18.30	49.76	1.80	48.44	0.8470$_0$
11	80.25	0.00	19.75	49.70	0.00	50.30	0.8465$_7$

TABLE II. WEIGHT PER CENT AND SPECIFIC GRAVITY FOR UNSATURATED MIXTURES OF BUTANOL, BUTYL ACETATE, AND WATER

	Weight Per Cent			
Run	BuOH	BuOAc	H_2O	Sp. Gr., 25/25
26	81.66	00.00	18.33	0.8429$_0$
68	82.05	00.00	17.95	0.8422$_5$
27	76.83	5.31	17.84	0.8458$_8$
62	85.48	00.00	14.51	0.8359$_3$
63	78.33	7.16	14.50	0.8406$_5$
64	69.44	16.44	14.11	0.8461$_4$
69	72.84	10.57	16.54	0.8468$_0$
65	85.62	00.00	14.37	0.8356$_4$
66	78.38	7.14	14.47	0.8405$_7$
67	71.01	14.25	14.73	0.8458$_5$
29	87.85	00.00	12.14	0.8318$_7$
30	82.53	5.29	12.17	0.8352$_7$
38	78.37	10.13	11.48	0.8368$_6$
31	77.32	10.53	12.14	0.8386$_4$
32	73.56	14.21	12.22	0.8412$_4$
33	66.80	21.01	12.17	0.8475$_8$
46	65.77	20.34	13.88	0.8356$_6$
34	61.48	26.01	12.50	0.8497$_6$
35	56.84	31.23	11.91	0.8521$_9$
52	90.70	00.00	9.29	0.8266$_8$
53	80.38	10.57	9.04	0.8328$_2$
54	69.69	21.11	9.18	0.8399$_6$
55	59.56	31.43	9.00	0.8464$_0$
57	49.52	41.04	9.43	0.8540$_5$
37	94.00	00.00	5.99	0.8203$_4$
39	72.62	21.27	6.10	0.8339$_5$
40	60.45	33.75	5.79	0.8375$_5$
41	52.45	41.64	5.90	0.8472$_5$
42	43.23	50.57	6.19	0.8541$_1$
43	32.60	61.19	6.19	0.8616$_7$
44	96.91	00.00	3.08	0.8148$_5$
45	86.11	10.71	3.16	0.8214$_6$
46	65.15	31.84	2.99	0.8344$_5$
47	59.07	38.16	2.76	0.8381$_0$
48	45.14	51.76	3.08	0.8482$_2$
49	35.25	61.70	3.04	0.8549$_1$
50	25.67	71.34	2.97	0.8618$_1$
51	16.23	80.92	2.83	0.8686$_3$

Next a series of mixtures containing a known amount of water, less than that required for saturation, were made up and their specific gravities determined at 25° C. These data are shown in Table II.

The data of Table I and II together with the specific gravity *vs.* weight per cent of alcohol on the dry basis are plotted in Figure 2. From this plot the lines of constant specific gravity were scaled off, and the points for plotting included in Table III. These data and the saturation lines are plotted on the isometric chart (Figure 3).

Near the water apex of the isometric chart the other boundary of the heterogeneous phase may be seen. The data for this line are plotted on a larger scale in Figure 4. The specific gravity data for this saturation line are plotted in Figure 5.

To use Figure 3 to determine the composition of any mixture of the three components, the specific gravity of the mixture is determined at 25° C.; then the sample is saturated with water by either of the methods described, and the gravity is again determined. A straight edge is laid from the water apex of the isometric chart to the point on the saturation line corresponding to the specific gravity at saturation. If this line is extended until it cuts the constant specific gravity corresponding to that of the original sample, the point of intersection gives the composition of the original sample. The proof of this method lies in the well-known theorem of geometry that, if a line is drawn from the apex of an equilateral triangle to the opposite base, it will divide the triangle so that the segments it cuts on any lines drawn parallel to that base will always be in the same proportion. The diagrams and the method were checked with known mixtures of the three components, and the compositions checked within the accuracy of reading the charts.

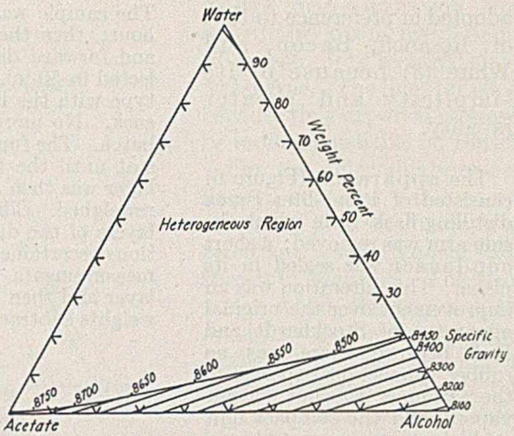

FIGURE 3. COMPOSITION AND SPECIFIC GRAVITY AT 25°/25° C. FOR MIXTURES OF BUTANOL–BUTYL ACETATE–WATER

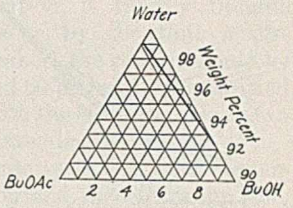

FIGURE 4. SATURATION LINE FOR SYSTEM BUTANOL–BUTYL ACETATE–WATER AT 25° C.

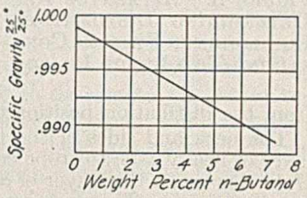

FIGURE 5. SPECIFIC GRAVITY OF WATER SATURATED WITH BUTANOL AND BUTYL ACETATE

Distillation Methods and Results

Othmer (*6, 7*) made no claim that his apparatus and method would work on a two-phase system; but it was thought that if sufficient agitation were maintained in the still pot by rapid ebullition and if the rate of distillation were fast enough to prevent the two layers from separating in the receiver, satisfactory results might be obtained. The first set of data determined was a liquid-vapor equilibrium curve for a series of saturated systems in which two phases were present in both the distillate and the residue at the boiling temperature. To do this, mixtures of alcohol and acetate were made up in the same way as for the binary system (*1*), and sufficient water was added to have two phases present at the boiling point.

A series of nine runs was made with the Othmer apparatus, and, when the results were computed, it was found that the water content of the residue was always greater than the water content of the distillate. This behavior was contrary to qualitative calculations made on the assumption that the system was that of a simple steam distillation, with the boiling point of the alcohol-acetate phase higher than that of the water phase.

The data obtained on the two-phase saturated systems seemed unsatisfactory, but it was thought that the apparatus might give satisfactory operation on a single-phase system with three components. Hence the water layer was removed from residue in the still body of the Othmer apparatus, and the single phase was distilled. As the distillate came over into the receiver and separated into two layers, the water layer was continually removed until the distillate was also a single layer; then the apparatus was allowed to come to equilibrium and samples were taken for analysis. The water content of the residues of these runs was so low that the compositions could not be accurately determined without resorting to saponification of the samples to determine the ester content as a check on the gravity analysis.

The water content of systems that had only a single phase in residue and distillate was so low in all cases that the determinations were inaccurate. The Othmer method was therefore abandoned, and that of Stockhardt and Hull (*10*) given a trial. On the several experiments carried out with known mixtures, gravity and saponification analyses were made on the equilibrium mixtures and found to agree very closely; hence the method was

TABLE III. CONSTANT GRAVITY LINES FOR SYSTEM BUTANOL–BUTYL ACETATE–WATER

Sp. Gr., 25/25	Weight Per Cent BuOH	BuOAc	H_2O
0.8100	97.20	2.80	0.00
	99.10	0.00	0.90[a]
0.8150	88.90	11.10	0.00
	96.15	0.85	3.00
	95.55	0.00	3.45[a]
0.8200	80.50	19.50	0.00
	88.00	9.00	3.00
	93.80	0.00	6.20[a]
0.8250	72.50	27.50	0.00
	79.70	17.30	3.00
	86.50	7.50	6.00
	91.35	0.00	8.65[a]
0.8300	64.60	35.40	0.00
	71.50	25.50	3.00
	78.45	15.55	6.00
	85.00	6.00	9.00
	88.70	0.00	11.30[a]
0.8350	57.00	43.00	0.00
	63.50	33.50	3.00
	70.75	23.25	6.00
	77.00	14.00	9.00
	82.75	5.25	12.00
	86.15	0.00	13.85[a]
0.8400	49.50	50.50	0.00
	56.20	40.80	3.00
	62.75	31.25	6.00
	69.25	21.75	9.00
	75.20	12.80	12.00
	81.00	4.00	15.00
	83.55	0.00	16.45[a]
0.8450	42.20	57.80	0.00
	49.15	47.85	3.00
	55.30	38.70	6.00
	61.75	29.25	9.00
	67.70	20.30	12.00
	74.00	11.00	15.00
	80.00	2.00	18.00
	81.00	0.00	19.00[a]
0.8500	35.00	65.00	0.00
	42.10	54.90	3.00
	48.15	45.85	6.00
	54.45	36.55	9.00
	60.00	28.00	12.00
	66.25	19.55	14.20[a]
0.8550	28.00	72.00	0.00
	35.20	61.80	3.00
	41.35	52.65	6.00
	47.25	43.75	9.00
	51.00	28.25	10.75[a]
0.8600	21.25	79.75	0.00
	28.10	68.90	3.00
	34.50	59.50	6.00
	37.20	55.20	7.60[a]
0.8650	14.65	85.35	0.00
	21.35	75.65	3.00
	24.50	71.25	4.25
0.8700	8.20	91.80	0.00
	13.30	84.90	1.80
0.8750	2.00	98.00	0.00
	4.25	95.00	0.75[a]

[a] Saturated.

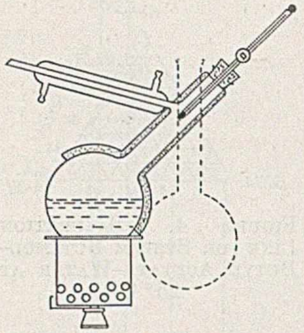

FIGURE 6. APPARATUS FOR DETERMINING DISTILLATION EQUILIBRIA IN SYSTEMS CONTAINING TWO LIQUID PHASES

adopted in preference to that of Rosanoff, Bacon, and White (*8*) because of its simplicity and greater rapidity.

The apparatus (Figure 6) consisted of a one-liter Pyrex distilling flask from which the side arm was removed; a short condenser was sealed in its place. This alteration was an improvement over the original apparatus of Stockhardt and Hull because there was no rubber connection exposed to the action of the hot solvent vapors, and the compact unit could be swung on a clamp from the distillation position to the reflux position very quickly.

The neck and sides of the flask were wrapped with a double layer of heavy asbestos rope cemented in place with water glass. Over this was a thin layer of asbestos cement such as is used on furnace piping. The apparatus was heated on a large electrical heater arranged with a short sheet-iron chimney so that the hot air rising from the heater passed up around the sides of the flask, keeping it nearly at the same temperature as the inside. Little or no condensation was ever noticed in the upper portion of the neck of the flask where it was most likely to occur. Boiling tubes had to be placed in the flask when mixtures of two liquid phases were distilled in order to prevent local superheating and subsequent violent bumping of the liquid which would carry over into the condenser and thus destroy the accuracy of the results.

This method of obtaining vapor-liquid equilibrium data depends upon distilling out a relatively small sample from a large amount of liquid and determining the composition of both the distillate and the residue. A known mixture of alcohol, acetate, and water was made up by weighing the separate components into a large tared Erlenmeyer flask. A 700 to 800-gram sample was taken each time. The volume of this sample was nearly a liter and would allow the distillation of four to five small fractions without seriously affecting the composition of the residue. The specific gravity of the sample was taken and recorded as a check on the weights and the chart. The sample was then placed in the apparatus with the condenser in the reflux position. The sample was gently boiled and allowed to reflux for half an hour; then the apparatus was placed in the distilling position, and forward distillation was started. The distillates were collected in 50-ml., tared, glass-stoppered funnels of the separatory type with the long bottom tube cut off directly under the stopcock. No more than five fractions were ever distilled out of a batch. The funnels were weighed and then placed in the thermostat until the two layers had separated at 25° C. The water layer was then removed, and the funnel was dried carefully and reweighed. The specific gravities of both the upper and lower layers of the distillate were next determined and their compositions ascertained from the charts (Figures 3 and 5). From these measurements the weights of the three components in each layer and then in the total distillate could be calculated. These weights subtracted from the original weights of each component present gave the amounts in the residue. The average weight and mole percentages for the run for both distillate and residue were then calculated for each component on both the wet and dry bases.

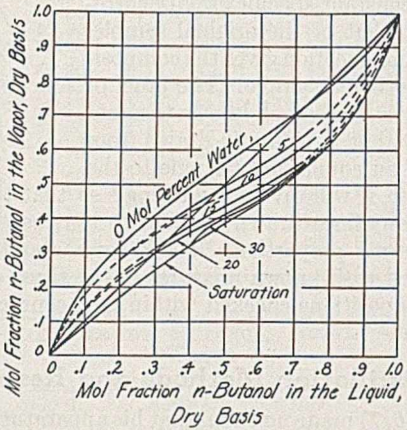

FIGURE 7. VAPOR-LIQUID EQUILIBRIA FOR SYSTEM BUTANOL–WATER–BUTYL ACETATE FOR VARIOUS CONSTANT PERCENTAGES OF WATER

The residue remaining in the distilling flask after the several samples had been distilled out was weighed, and its specific gravity determined. A portion was then saturated with water at 25° C. and the gravity again determined. The charts (Figures 2 and 3) were used to find out if the composition calculated from the last residue of the distillation checked with that actually there. As a further check on the accuracy, another portion of the residue was saponified for ester content. By this procedure any batch of samples had a triple check to determine its composition.

While making a material balance after each series of distillations, a discrepancy of about a gram in the 800-gram sample taken was found to be the usual difference. This loss was attributed to the fact that, when starting up a refluxing period, the air in the flask which was displaced by the vapor of the distillate would usually become saturated with the vapor and carry some of it out of the apparatus uncondensed.

TABLE IV. DATA AND CALCULATIONS FOR RUN 31

(Corrected barometric pressure, 761.8 mm.; average vapor temperature, 90.6° C.)

I. Initial Sample

	Weight Per Cent	Weight, Grams
BuOH	39.97	320.0
BuOAc	39.97	320.0
H_2O	20.05	160.5
Total sample		800.5

II. Distillate

Weight, grams:		Weight per cent (lower layer):		Weight per cent (upper layer):	
Funnel + sample	81.6535	BuOH	3.8	BuOH	33.00
Funnel empty	30.1300	BuOAc	0.4	BuOAc	60.55
Sample	51.5235	H_2O	95.8	H_2O	6.45
Funnel + upper layer	76.5222	Weight, grams (lower layer):		Weight, grams (upper layer):	
Upper layer	37.3922	BuOH	0.5369	BuOH	12.3394
Lower layer	14.1313	BuOAc	0.565	BuOAc	22.6409
Pycnometer + lower layer	5.7470	H_2O	13.5378	H_2O	2.4117
Pycnometer empty	3.7660	Pycnometer + upper layer	53.1076	Total BuOH	12.8763
Sample	1.9810	Pycnometer empty	31.5828	Total BuOAc	22.6974
Sp. gr., 25/25	0.9934_8	Sample	21.5248	Total H_2O	15.9495
		Sp. gr., 25/25	0.8617_6	Total sample	51.5232

	Wet Basis	Dry Basis
Weight per cent (total distillate):		
BuOH	24.99	36.20
BuOAc	44.05	63.80
H_2O	30.96	...
Mole per cent (total distillate):		
BuOH	13.86	42.00
BuOAc	15.57	58.0
H_2O	70.60	...

III. Residue

			Wet Basis	Dry Basis
Weight, grams (by difference):		Av. weight per cent:		
BuOH	307.1237	BuOH	40.49	50.41
BuOAc	297.3026	BuOAc	39.83	49.59
H_2O	144.5505	H_2O	19.68	...
Total residue	748.9768			
Weight per cent:		Mole per cent:		
BuOH	41.00	BuOH	27.58	61.40
BuOAc	39.69	BuOAc	17.29	38.60
H_2O	19.30	H_2O	55.12	...

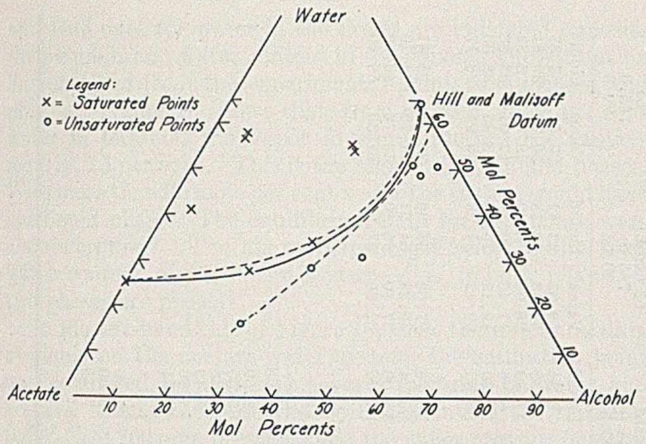

FIGURE 8. TERNARY PLOT FOR SOLUBILITY OF WATER IN MIXTURES OF BUTANOL AND BUTYL ACETATE AT THE BOILING POINT

This loss, however, was quite small and therefore negligible in the ensuing calculations of vapor and residue compositions. Table IV shows a sample of the data and calculations for a typical run. A summary of experimental results is presented in Table V.

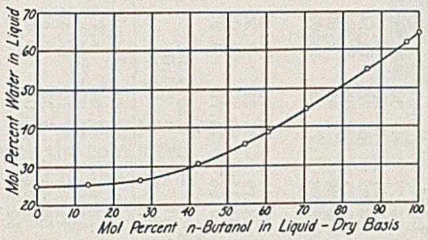

FIGURE 9. CURVE FOR SOLUBILITY OF WATER IN MIXTURES OF BUTANOL AND BUTYL ACETATE AT THE BOILING POINT

Correlation of Data

Consideration of the phase rule (*4*)

$$F = C - P + 2$$

where F = No. of degrees of freedom
C = No. of individual independent components
P = No. of separate phases coexisting at equilibrium

shows at once that in a system of three components, when there is only one liquid phase and a gas or vapor phase, there will be three degrees of freedom—namely, temperature, pressure, and the ratio of one of the components to the other two. If pressure is fixed at atmospheric, it is necessary to fix either the temperature and a composition or two compositions before the system is defined. It is convenient not to bring temperature into the correlation; hence it is necessary to use the concentration of two of the components to fix the system. To portray the equilibrium compositions in a system where two concentrations in one phase must be fixed requires the use of a series of space models, or their equivalent. An entirely satisfactory method for the representation of such data on phase surfaces has not been found, though it is possible to define the system.

For one method of correlation in the present investigation, the anhydrous vapor-liquid equilibrium curve for the system *n*-butanol–*n*-butyl acetate was drawn, together with the points determined for saturated systems recomputed to the dry basis (Figure 7). The diagram shows that all possible compositions from zero per cent water to saturation must lie between the band defined by the anhydrous and saturated curves. The data for 5, 10, etc., mole per cent water were next plotted on the diagram, and the lines of constant water content in the liquid were thus drawn in. The data points are not shown, but the experimental results are summarized in Table V. The lines of constant water content in Figure 7 represent interpolations from the data of Table V. The data spattered somewhat and in some cases did not extend from the mid-portion of the diagram very far in either direction; hence the uncertain portions were indicated by dotted lines. This uncertain area was not due to lack of attempts to obtain data in that region. The water proved to be such a volatile constituent that, if the residue contained water at less than saturation concentration, it rapidly became anhydrous upon distillation. Hence by the time a distillate sample of required size was taken, the residue would be water-free. The lines for 40, 50, and 60 per cent were omitted because they crowded so closely upon the saturation line as to be indistinguishable on the small-scale diagram.

For the determination of the intersection of the various lines of constant water composition and the saturation line, a ternary plot was made of compositions known to be saturated and several known to be unsaturated. These data are shown in Figure 8. The two dotted lines show the limits between which the true saturation line (at the boiling point) must lie. For pure butanol and water the datum of Hill and Malisoff (*5*) was used, and for the pure butyl acetate and water the datum was determined.

It is difficult to obtain saturation data for a system of this kind. In the experimental work to determine the water required to saturate pure acetate at the boiling point, a small, round-bottom flask was connected to a condenser with a small pipet fastened to it near the point of entrance to the flask. The flask was heated on a small hot plate so that the boiling, while not violent, was at least sufficient to agitate the contents of the flask. Supplementary to this the flask was rotated by hand as the water was added. Three separate 25-gram samples of the acetate were taken, and the amount of water required to saturate each one was determined by means of the criterion already discussed.

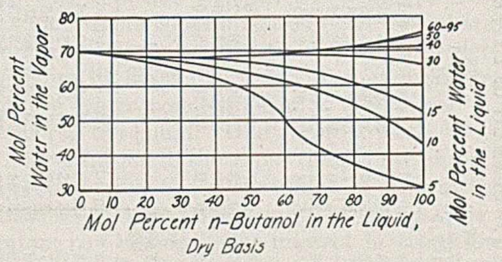

FIGURE 10. VAPOR-LIQUID EQUILIBRIA FOR SYSTEM BUTANOL–BUTYL ACETATE–WATER

The average percentage of water for the three runs was taken as the desired datum point for the saturation of pure acetate for Figure 8.

Points were taken from the smooth solid curve of Figure 8, and the butanol–butyl acetate content was computed to mole per cent on the dry basis. The mole per cent of butanol in the liquid on the dry basis was then plotted against the mole per cent of water in the liquid as shown in Figure 9. From this curve the terminal points for the various percentages of water at the saturation line of Figure 7 were picked off and marked on the diagram.

This method of computing the ternary composition to the dry basis—in other words, plotting as the ratio of the two important components—seems to be advantageous. The vapor-liquid equilibrium can thus be completely defined by two linear-coördinate plots. Equilibrium concentrations in two phases cannot be conveniently represented on ternary diagrams, and space models are not suitable for quantitative work.

Obviously Figure 7 does not completely define the liquid-vapor equilibrium for the entire system, for it does not give any information as to the water concentration in the vapor. Water concentrations in the vapor are plotted as ordinates in Figure 10. The abscissa is the same as for Figure 7.

Along the right-hand margin of Figure 10 the Stockhardt

Table V. Summary of Experimental Data

Run No.	24		25		26		27		28		29		30		31 (satd.)		32 (satd.)		33	
Cor. pressure, mm.	762.61		766.3		766.3		752.2		746.1		757.4		762.1		761.8		765.7		761.4	
Av. vapor temp., ° C.	94.5		94.0		101		107.5		93.6		99.4		109.6		90.6		90.75		90.8	
	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Wt. % BuOH	32.06	55.9	29.57	57.72	41.28	59.01	52.94	59.93	30.19	58.66	38.18	61.11	56.00	62.57	24.99	40.49	24.66	41.59	26.12	44.72
Wt. % BuOAc	39.07	38.71	39.18	39.69	38.06	38.69	34.13	38.84	38.88	36.75	37.51	36.62	40.10	36.38	44.05	39.83	44.29	39.53	43.18	47.20
Wt. % H_2O	28.87	5.38	31.25	3.59	20.66	2.34	12.93	1.17	30.93	4.58	24.37	2.27	3.90	1.03	30.96	19.68	31.05	18.88	30.69	8.09
Mole % BuOH	18.25	54.43	16.16	59.43	30.42	63.25	41.37	66.90	16.57	58.14	23.53	65.15	57.39	65.53	13.86	27.58	13.66	28.80	14.52	41.38
Mole % BuOAc	14.17	24.02	13.64	25.37	17.88	26.43	17.08	27.72	13.61	23.21	14.73	24.89	26.19	25.76	15.57	17.29	15.64	17.45	15.31	27.84
Mole % H_2O	67.58	21.55	70.20	15.20	51.70	10.32	41.55	5.38	69.82	18.65	61.74	9.97	16.42	4.70	70.60	55.12	70.70	53.75	70.17	30.78
Dry Basis																				
Wt. % BuOH	45.07	59.04	43.01	59.87	52.02	60.39	54.53	60.67	43.70	61.48	50.44	62.53	58.27	63.22	36.20	50.41	35.77	51.27	37.69	48.65
Wt. % BuOAc	54.93	40.91	56.99	40.13	47.98	39.61	45.47	39.33	56.30	38.52	49.56	37.47	41.73	36.78	63.80	49.59	69.23	48.73	62.31	51.35
Mole % BuOH	56.0	69.2	54.05	68.95	62.95	70.35	65.15	70.60	54.90	71.25	61.40	72.25	63.40	72.75	42.00	61.40	46.55	62.25	48.55	59.65
Mole % BuOAc	44.0	30.8	45.95	31.05	37.05	29.65	34.85	29.40	45.10	28.75	38.60	27.75	36.60	27.25	58.00	38.60	53.45	37.75	51.45	40.35

Run No.	34		35		36		37		38		39		40		41		42		43	
Cor. pressure, mm.	761.4		761.2		761.2		758.2		761.0		761.0		758.8		758.8		768.8		758.0	
Av. vapor temp., ° C.	91.0		91.8		91.9		92.2		91.2		92.3		92.5		92.4		92.5		94.5	
	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Wt. % BuOH	26.70	46.73	30.94	48.24	30.79	49.01	33.21	49.70	47.47	72.88	47.86	74.77	49.00	77.07	49.01	79.82	51.30	83.06	54.11	86.81
Wt. % BuOAc	41.93	47.73	40.95	48.23	40.66	48.57	41.12	44.88	15.19	7.75	14.56	7.21	13.20	6.13	13.57	5.97	12.44	5.20	11.83	4.34
Wt. % H_2O	30.47	5.54	28.11	3.52	28.55	2.42	25.67	1.42	37.34	19.38	37.58	18.02	37.76	16.80	37.42	14.21	36.26	11.74	34.06	8.80
Mole % BuOH	15.37	46.76	17.93	51.62	17.69	54.51	20.13	57.33	25.53	46.28	22.61	48.73	23.06	51.36	23.17	56.19	24.63	61.69	26.83	69.03
Mole % BuOAc	14.88	30.44	15.12	32.90	14.89	34.43	15.89	35.94	4.60	3.13	4.38	2.99	3.95	2.60	4.09	2.68	3.80	2.46	3.74	2.20
Mole % H_2O	69.75	22.79	66.95	15.48	67.42	11.06	63.98	6.73	72.87	50.59	73.00	48.28	72.99	46.03	72.74	41.13	71.57	35.85	69.43	28.77
Dry Basis																				
Wt. % BuOH	39.69	49.47	43.04	50.00	43.09	50.23	44.68	52.55	75.76	90.39	76.67	91.21	78.79	92.63	78.31	93.04	80.48	94.11	82.06	95.24
Wt. % BuOAc	60.31	50.53	56.96	50.00	56.91	49.77	55.32	47.45	24.24	9.61	23.33	8.79	21.21	7.37	21.69	6.96	19.52	5.89	17.94	4.76
Mole % BuOH	50.60	60.40	54.00	61.00	54.10	61.20	55.65	63.45	82.90	93.60	83.60	94.15	85.30	95.05	84.75	95.40	86.20	96.00	87.65	96.85
Mole % BuOAc	49.40	39.60	46.00	39.00	45.90	38.80	44.35	36.55	17.10	6.40	16.40	5.85	14.70	4.95	15.25	4.60	13.80	4.00	21.35	3.15

Run No.	44 (satd.)		45		46		47		48		49		50 (satd.		51 (satd.)		53 (satd.)		54	
Cor. pressure, mm.	754.1		754.1		760.3		762.3		762.3		762.3		764.0		764.0		745.0		745.0	
Av. vapor temp., ° C.	91.15		91.4		91.6		92		91.6		92.5		90.5		90.5		90.05		90.3	
	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Wt. % BuOH	35.79	60.36	36.79	62.35	37.55	64.56	38.27	67.09	38.99	70.09	43.05	73.45	7.04	8.71	6.96	8.84	19.63	32.42	20.52	33.37
Wt. % BuOAc	29.83	19.77	28.65	18.99	28.05	18.17	27.25	17.27	26.77	16.24	26.97	15.01	65.81	72.91	65.98	73.35	51.43	59.18	50.79	59.81
Wt. % H_2O	34.38	19.87	34.56	18.66	34.40	17.27	34.48	15.64	34.24	13.67	29.88	11.54	27.19	18.49	27.06	17.80	28.94	8.90	28.69	6.82
Mole % BuOH	18.25	39.03	18.66	41.25	19.07	43.88	19.39	47.12	19.81	51.30	23.46	56.46	4.38	6.64	4.34	6.86	11.45	30.38	12.01	33.53
Mole % BuOAc	9.69	8.15	9.26	8.00	9.08	7.87	8.80	7.73	8.67	7.57	9.36	7.07	26.08	35.43	26.24	36.30	19.13	35.34	18.95	38.30
Mole % H_2O	72.06	52.82	72.08	50.75	71.84	48.25	71.81	45.15	71.52	41.14	67.17	36.47	69.53	57.93	69.42	56.83	69.42	34.28	69.04	28.17
Dry Basis																				
Wt. % BuOH	54.84	75.33	56.22	76.65	57.28	78.04	58.41	79.73	59.29	81.18	61.48	83.03	9.66	10.67	9.54	10.76	27.62	35.39	28.78	35.81
Wt. % BuOAc	45.46	24.67	43.78	23.35	42.72	21.96	41.59	20.47	40.71	18.82	38.52	16.97	90.34	89.33	90.46	89.24	72.38	64.61	71.22	64.19
Mole % BuOH	65.25	82.50	66.60	83.60	67.55	84.60	68.55	85.80	69.40	86.85	83.45	88.40	14.50	15.70	14.30	16.00	37.40	46.10	38.70	46.60
Mole % BuOAc	34.75	17.50	33.4	16.40	33.45	15.40	31.45	14.20	30.60	13.15	16.55	11.60	85.50	84.30	85.70	84.00	62.60	53.90	61.30	53.40

Run No.	55		56		57		58 (satd.)		59		(Determinations spoiled)		61		62 (satd.)	
Cor. pressure, mm.	748.2		748.2		752.9		758.0		758				763.3		764.3	
Av. vapor temp., ° C.	91.2		92.7		95.5		90.25		97.7				120.3		90.5	
	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid			Vapor	Liquid	Vapor	Liquid
Wt. % BuOH	21.93	34.27	23.94	35.41	29.42	36.21	12.98	20.54	16.74	21.50			8.30	3.98	3.45	4.50
Wt. % BuOAc	49.60	60.60	49.47	61.61	48.87	62.66	59.90	72.96	59.59	75.25			91.65	95.73	70.35	85.55
Wt. % H_2O	28.46	5.03	26.58	2.98	21.71	1.13	27.11	6.49	23.67	3.26			0.05	0.30	26.19	9.98
Mole % BuOH	12.86	36.69	14.53	40.74	16.63	44.82	7.98	22.25	11.01	25.96			11.21	6.00	2.11	4.49
Mole % BuOAc	18.54	41.23	19.14	45.17	20.79	49.44	23.48	50.38	24.98	57.91			87.30	92.14	28.75	54.50
Mole % H_2O	68.60	22.07	66.33	14.09	59.58	5.74	68.54	27.38	64.01	16.13			0.29	1.86	69.04	41.01
Dry Basis																
Wt. % BuOH	30.66	36.19	32.61	36.50	37.58	36.62	17.81	21.96	21.93	22.22			8.30	3.99	4.67	5.00
Wt. % BuOAc	69.94	63.81	67.39	63.50	62.42	63.38	82.19	78.04	78.07	77.78			91.65	96.01	95.33	95.00
Mole % BuOH	40.75	47.00	43.00	47.40	48.50	47.50	25.25	30.50	30.42	30.78			12.50	6.00	6.90	7.75
Mole % BuOAc	59.25	53.00	57.00	52.60	51.50	52.50	74.75	69.50	69.58	69.22			87.50	94.00	93.10	92.25

and Hull data for water in the liquid are indicated opposite their equilibrium water content in the vapor. The saturation line obtained from the experimental points was located and plotted. Figure 10 shows that, from 60 to 95 mole per cent water in butanol, the vapor in equilibrium is the same—namely, 75 per cent. This is the region of two liquid phases. With more than 95 mole per cent water the system would have one liquid phase. The equilibrium data for this phase were not determined. The above percentages refer to the total water content of the entire system—i. e., in both phases, if two phases are present.

On the left-hand side of Figure 10, since there were no data available on the acetate-water system, the saturation point was computed by distilling several mixtures of water and acetate. From the observed boiling point of the mixtures (95.5° C. at 760 mm. pressure) and the vapor pressure of water at that temperature (*2*), the composition of the vapor could be calculated from the usual steam distillation equation. This computation gave the following results:

	Weight Per Cent	Mole Per Cent
n-Butyl acetate	72.90	29.44
Water	27.10	70.56

The acetate content of the samples was checked by a saponification analysis and found to agree closely with the computed value. Hence at zero per cent alcohol the water in the vapor was 70.5 per cent. This point marked the other end of the saturation line.

The position of the ends of the various iso-water lines were marked off on the saturation line from Figure 9 opposite their proper butanol contents, the remaining data points for the unsaturated systems were plotted, and the curves were drawn through these points from the Stockhardt and Hull data line to the saturation line.

This method of correlation pictures the system to the best advantage for the distillation mixtures of any compositions. The bunching of points near the saturation line made it desirable to determine more points of low water content. Several attempts were made to obtain data for very low water contents; but even starting with 800-gram batches and distilling out only a 10- or 12-gram sample, the water would nearly all be found in the distillate and thus destroy the accuracy of the determination.

Space models are not satisfactory for quantitative work, but they do help to visualize the system. Three such models were made up in clay on triangular bases of about 9 inches (22.9 cm.) on a side with the saturation line at the boiling point drawn upon each. The vertical component for each model was the percentage of butanol in the vapor, the percentage of butyl acetate in the vapor, and the percentage of water in the vapor, respectively. Photographs of these three models are given in Figure 11. The portion of the field for water contents greater than saturation is not shown. A two-dimensional drawing for the space model for butanol in the vapor as the vertical component is shown at the left in Figure 12. A two-dimensional diagram of the model for butyl acetate in the vapor is shown at the right in Figure 12.

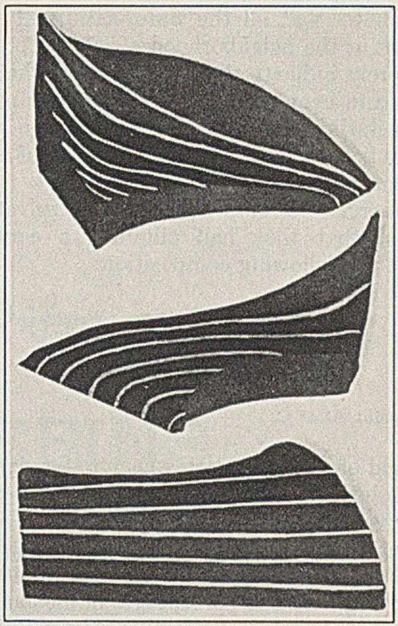

Figure 11. Triangular Space Models of Distillation Equilibria of System Butanol–Butyl Acetate–Water

The vertical distances show mole percentages in the vapor as follows: top, butanol; center, butyl acetate; bottom, water.

Ternary Constant-Boiling Mixture

Figure 7 shows that the saturation line does not cross the 45° diagonal. This observation would lead to the conclusion that there is no true ternary azeotrope for the system saturated with water. However, this does not preclude the existence of a ternary azeotrope for systems containing less water than that required for saturation. However, the experimentally determined curves (Figure 10) show that for water contents above 5 mole per cent the water concentration in the vapor is always greater than in the liquid. One run (61, Table V) showed a smaller concentration in the vapor than in the liquid, but this effect is probably due to the experimental error at these low concentrations (0.05 to 0.30 weight per cent). The present investigators had no particular interest in these low water concentrations and did not attempt to fill out the field completely. It may safely be concluded, however, that at all concentrations the water content of the vapor is higher than that of the liquid. This conclusion would preclude the possibility of any ternary azeotropic mixture.

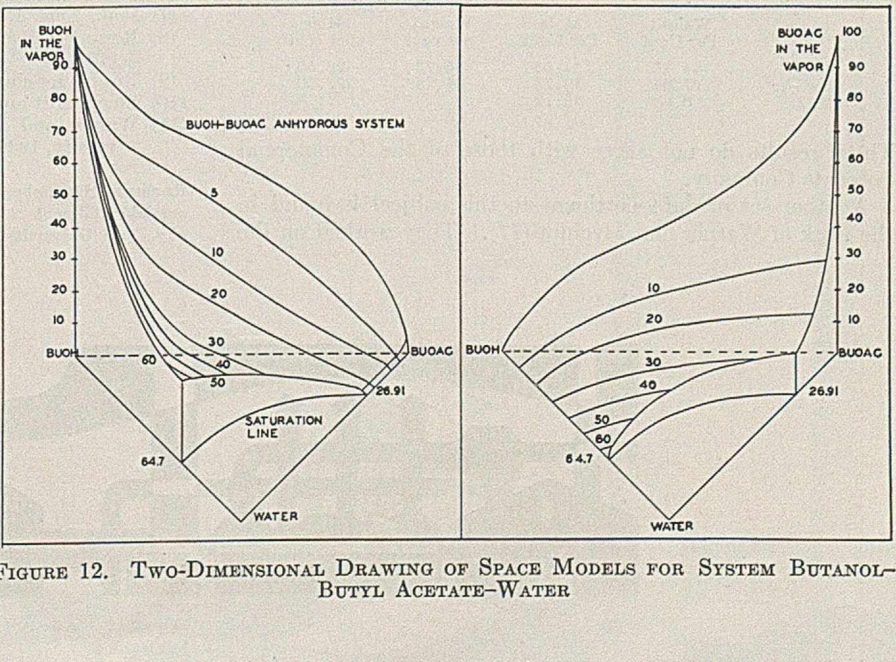

Figure 12. Two-Dimensional Drawing of Space Models for System Butanol–Butyl Acetate–Water

Table V shows that all the water-saturated systems had boiling points in the neighborhood of 90.5° C. These data, however, merely indicate that the action is that of a steam distillation; and even though the boiling temperature may be constant during the distillation of a large portion of a sample, there is no indication of the presence of an azeotropic mixture of constant composition.

The Commercial Solvents Company in a private communication stated that they had obtained a constant-boiling mixture with the following composition:

			Dry Basis	
	Weight Per Cent	Mole Per Cent	Weight per cent	Mole per cent
BuOH	29	15.94	42.03	53.00
BuOAc	40	14.01	57.97	47.00
H_2O	31	70.05	...	...

Boiling point, 91.4° C.

The method of determination was not stated; obviously it would be a solution saturated with water. The percentage of water in the vapor of the Commercial Solvents sample (70.05 mole per cent) is in keeping with the water in the vapor rising from saturated solutions as shown in Figure 10. However, according to Figure 7 the percentages of alcohol and acetate do not correspond to any azeotropic mixture. In a system containing an azeotrope of minimum boiling point, the composition may be approached by successive distillation of distillates. This is the action of a fractionating column; therefore, at the top of a long column, if a true azeotrope exists, the product should have approximately the same composition, no matter what the composition of the residue.

In order to check the figures given by the Commercial Solvents Company, the residues from all the equilibrium runs of this investigation were mixed in a large carboy, and enough water was added to saturate the mixture. Three liters of the upper layer were siphoned off and placed in the still pot of a 6-foot (1.5-meter) packed column. The column was operated under total reflux for 7 hours before forward distillation was begun. From this batch of more than 3 liters, about 53 grams of distillate were collected and the two layers were analyzed. This sample was then placed in a microfractionating column (*3*) and again operated under total reflux for 4 hours before the forward distillation was begun. Ten grams of sample were distilled out and analyzed. The boiling point was identical in both cases, and the difference in composition between the distillate and the residue in the microcolumn was only in the second decimal place. The results of the distillation are as follows:

			Dry Basis	
	Weight Per Cent	Mole Per Cent	Weight per cent	Mole per cent
BuOH	14.37	14.55	15.72	22.50
BuOAc	77.04	49.73	84.28	77.50
H_2O	8.58	35.72	...	...

These results do not agree with those of the Commercial Solvents Company.

Another set of data pertinent to this subject is found in the work of Warner and Mechlin (*11*). They worked on the separation efficiencies of packed and plate columns using the system *n*-butanol–*n*-butyl acetate–water as the experimental mixture in a sixteen-plate, bubble-cap column. They obtained a product boiling at 90.5° C., but unfortunately they did not analyze the water layer of the product. They did analyze a series of upper layers of distillates with the following results:

Run No.	I	II	III	IV
	Weight Per Cent			
BuOH	28.7	31.8	32.5	21.8
BuOAc	66.1	62.2	61.0	74.8
H_2O	5.2	6.0	6.5	3.4
	Mole Per Cent			
BuOH	31.1	33.0	33.1	26.1
BuOAc	45.7	41.3	39.7	57.2
H_2O	23.2	25.7	27.2	16.7
	Mole Per Cent, Dry Basis			
BuOH	40.5	44.5	45.5	31.3
BuOAc	59.5	55.5	54.5	68.7

This group of distillates shows considerable variation in composition. If there were a true azeotropic, the composition should be approximately the same for all runs. The compositions in this group vary widely from those given above for the distillation at the top of a microcolumn and also vary widely from the presumed azeotropic composition reported by the Commercial Solvents Corporation.

These experiments present good evidence that there is no true azeotropic mixture in the system butanol–butyl acetate–water. This evidence checks the conclusions drawn from a study of Figures 7 and 10. An apparent minimum boiling point in the neighborhood of 90.5° C. can be found and the percentage of water in the distillate is approximately constant at 70 mole per cent over a wide range of residue composition, but these phenomena are connected with distillation from two liquid phases and do not indicate an azeotropic system.

Acknowledgment

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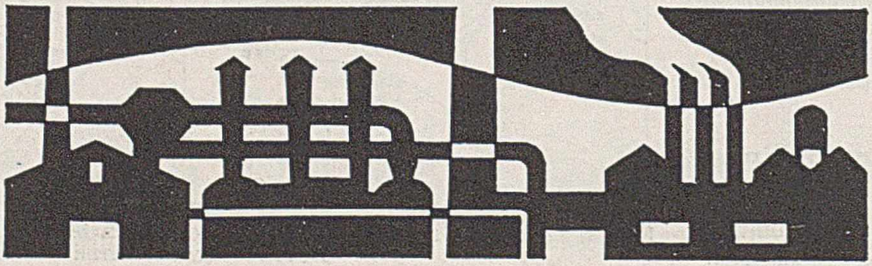

The pyrolysis of ethylene, propene, 2-butene, 1-butene, and isobutene was studied at 1100° and 1400° C. at a contact time of about 0.001 second. The yields of unsaturated hydrocarbon products are compared and the relative stability of the pure olefins established. Decomposition was the predominant reaction.

High-Temperature Pyrolysis of GASEOUS OLEFINS

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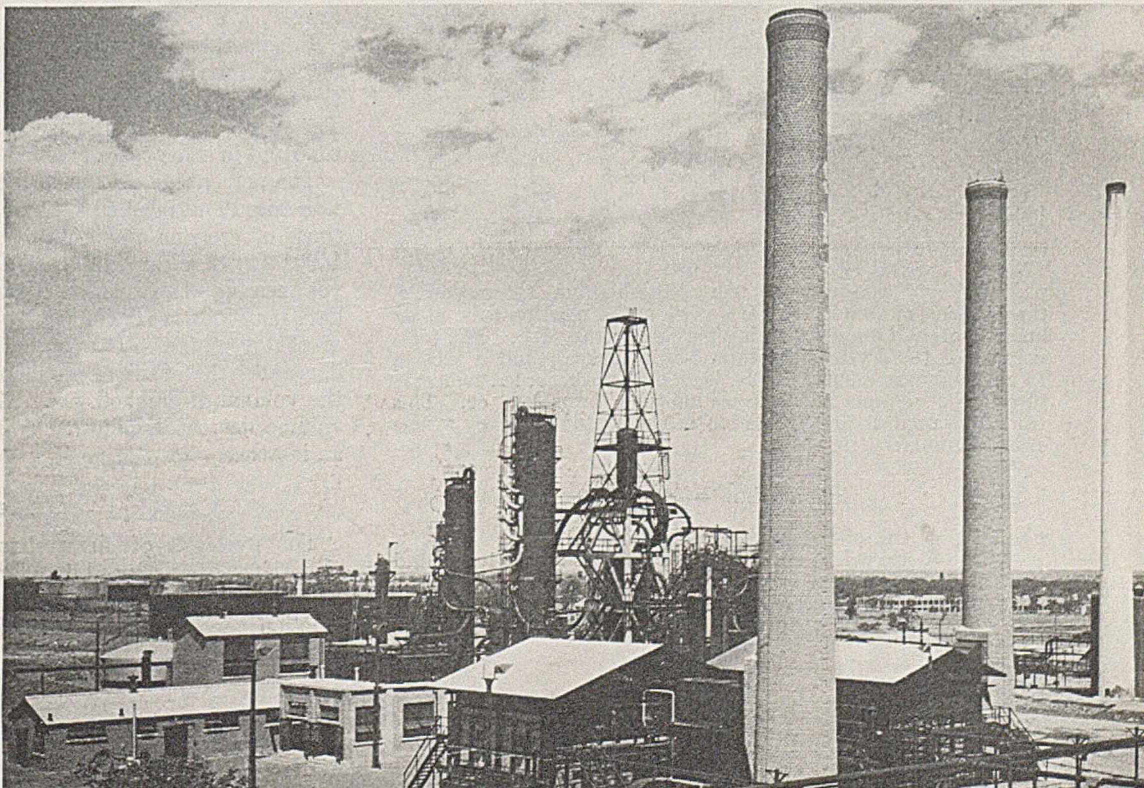
THE pyrolysis of olefinic hydrocarbons has been studied under many conditions of pressure and temperature. The object of these experiments was to derive the mechanism of the pyrolytic reactions and to determine suitable conditions for the production of desirable products. Much of the previous work was performed at relatively low temperatures and under atmospheric or higher pressures so that liquid products were formed (*2*). It was of interest, therefore, to choose temperature and pressure conditions which are capable of producing principally gaseous products.

High temperatures, low pressure, and short contact times were chosen in order to increase the formation of gaseous hydrocarbons during the pyrolysis of ethylene, propene, 1-butene, 2-butene, and isobutene. The temperatures used were 1100° and 1400° C., pressure of 50 mm., and contact time from about 0.0008 to 0.044 second. The results of this work offer a comparison of the yields of acetylene, ethylene, propene, butenes, and butadiene derived from ethylene, propene, and butenes, and their relative stability.

Apparatus and Procedure

The pure olefinic hydrocarbon was humidified in a water bubbler, passed through a pressure regulator, measured in a wet test meter, dried by calcium chloride, and, via a flowmeter and microscrew clamp control led into a Pythagoras (porcelain) tube of 3 mm. inside diameter. The latter, heated in a Burrell type B-6 high-temperature furnace, was suspended in the center of another porcelain tube 63 cm. long and 3.3 cm. inside diameter which extended through the Glowbar furnace. From the reaction tube the gases passed through an iron Liebig condenser into a trap, through a second microscrew clamp by means of which (together with the first one) the feed was regulated to the desired rate. The pressure which was measured at the exit of the reaction tube was adjusted to 50 mm. The cracked gas flowed into glycerol-filled Nelson pumps which maintained the desired pressure and, after humidification in a water bubbler, was measured in a wet test meter and salt water gas holder.

The temperature was measured by means of a calibrated



FIVE-THOUSAND-BARREL CRUDE OIL TOPPING AND TWO-COIL SELECTIVE CRACKING UNIT TO PRODUCE FINISHED GASOLINE, LOCATED IN CANADA

Courtesy, Universal Oil Products Company

TABLE I. PYROLYSIS OF ETHYLENE AT 1100° C.

Run. No.	165	167	163	166	171	168	169	170
Contact time, 10^{-3} sec.	0.7	0.9	2.2	4.1	6.1	10.0	14.0	44.0
Per cent expansion	−1.0	−2.0	−1.0	+3.0	+7.0	+18.0	+11.0	+40.0
Analysis, per cent:								
C_2H_2	5.9	6.7	7.2	8.4	8.9	9.3	11.2	15.2
C_2H_4	88.5	84.8	77.5	74.0	61.5	51.8	48.5	35.1
$C_3H_6 + C_4H_8$	0.9	2.5	3.2	2.5	2.5	2.5	3.0	1.7
C_4H_6	1.4	0.9	0.6	1.8	1.3	1.2	1.2	0.6
H_2	0.2	..	4.7	9.5	17.5	26.3	24.1	34.6
C_nH_{2n+2}	2.8	..	2.2	3.5	5.8	6.0	9.4	10.2
n in C_nH_{2n+2}	2.64	..	4.0	2.75	2.75	2.6	3.4	2.96
Yield, liters/100 liters of entering ethylene (volume per cent):								
C_2H_2	5.9	6.6	7.2	8.7	9.5	10.9	12.4	21.0
C_2H_4	88.0	83.5	77.0	76.0	65.8	61.0	53.8	48.0
$C_3H_6 + C_4H_8$	0.85	2.5	3.2	2.6	2.7	2.9	3.3	2.5
C_4H_6	1.4	0.9	0.6	1.9	1.4	1.4	1.3	0.8
H_2	0.2	..	4.7	9.8	18.2	31.0	26.7	48.4
C_nH_{2n+2}	2.8	..	2.2	3.6	6.2	7.1	10.4	14.2
Yield, moles/100 moles of reacting ethylene:								
C_2H_2	47.8	39.9	32.8	32.3	23.0	19.3	21.7	23.4
$C_3H_6 + C_4H_8$	7.0	14.9	13.8	9.6	6.5	5.2	5.8	2.6
C_4H_6	11.3	5.4	2.5	6.9	3.4	2.5	2.3	0.9
H_2	1.7	..	24.1	40.8	57.1	85.6	60.6	100.0
C_nH_{2n+2}	23.3	..	11.2	15.0	19.4	19.6	23.6	29.3

TABLE II. PYROLYSIS OF ETHYLENE AT 1400° C.

Run No.	176	179	178	180	177
Contact time, 10^{-3} sec.	0.8	1.6	2.3	4.1	8.4
Per cent expansion	27.0	56.0	54.0	64.0	63.0
Analysis, per cent:					
C_2H_2	18.1	33.9	49.8	33.2	28.8
C_2H_4	47.9	14.0	11.3	6.0	6.1
$C_3H_6 + C_4H_8$	0.0	0.0	0.0	0.0	0.0
CO_2	1.0	1.0	0.0	0.6	0.6
CO	0.4	0.8	2.3	3.6	5.2
H_2	28.0	45.9	29.4	52.6	54.0
C_nH_{2n+2}	4.6	4.5	7.2	4.0	5.3
n in C_nH_{2n+2}	1.99	1.45	1.9	1.78	1.64
Yield, liters/100 liters of entering ethylene (volume per cent):					
C_2H_2	23.0	52.7	76.6	54.3	46.9
C_2H_4	60.8	21.8	17.4	9.8	9.9
H_2	35.6	71.5	45.2	86.4	88.2
C_nH_{2n+2}	5.9	7.0	11.1	6.6	8.6
Yield, moles/100 moles of reacting ethylene:					
C_2H_2	59.0	67.4	92.5	60.2	52.1
H_2	91.0	91.5	54.7	95.6	98.0
CH_4	0.0	5.0	1.4	1.6	3.5
C_2H_6	15.1	4.0	12.0	5.7	6.1

TABLE III. PYROLYSIS OF PROPANE AT 1100° C.

Run No.	183	182	189	188	190
Contact time, 10^{-3} sec.	2.2	2.5	4.3	5.8	12.0
Per cent expansion	12.0	18.0	24.0	29.0	47.0
Analysis, per cent:					
C_2H_2	8.9	12.5	13.9	15.0	14.8
C_2H_4	10.5	13.1	17.1	18.9	19.4
$C_3H_6 + C_4H_8$	64.9	49.0	35.9	26.7	19.2
C_4H_6	0.7	1.8	2.0	2.2	1.9
CO_2	0.0	0.0	0.0	0.5	0.0
CO	2.2	0.3	1.0	1.1	1.6
H_2	4.1	9.4	12.4	15.1	17.4
$C_nH_{2n\pm2}$	8.8	13.9	17.7	20.5	25.7
n in C_nH_{2n+2}	1.39	1.27	1.07	1.23	2.03
Yield, liters/100 liters of entering propene (volume per cent):					
C_2H_2	9.9	14.7	17.2	19.3	21.8
C_2H_4	11.8	15.5	21.2	24.4	28.5
$C_3H_6 + C_4H_8$	72.6	57.8	44.4	34.4	28.2
C_4H_6	0.8	2.1	2.5	2.8	2.9
H_2	4.6	11.1	15.4	19.5	25.6
C_nH_{2n+2}	9.9	16.4	21.9	26.4	37.8
Yield, moles/100 moles of reacting propene:					
C_2H_2	36.4	34.9	31.0	29.4	30.5
C_2H_4	43.1	36.8	38.0	37.1	39.7
C_4H_6	2.9	5.0	4.5	4.3	4.0
H_2	16.8	26.3	27.7	29.7	35.6
CH_4	22.3	28.4	36.7	31.0	0.0
C_2H_6	14.1	10.4	2.7	9.2	52.7

platinum and platinum-(10 per cent)rhodium thermocouple, the junction of which was placed below the reaction tube at its linear center, the leads running parallel to the tube. The total volume of the Pythagoras tube was measured, and a section 15 cm. long was assumed to be heated to the recorded temperature. The volume of the "reaction zone" was 1.06 cc. This value was used in the calculation of the contact time by means of the formula:

$$\text{Contact time} = \frac{V_R}{V_A} \times t_{\text{sec.}}$$

where V_R = vol. of reaction zone (1.06 cc.)
V_A = av. vol. of entering and exit gases cor. to temp. and pressure of reaction zone, cc.
t = time necessary for measured vol. of entering gas to pass into reaction zone, sec.

Analysis of the cracked gas was made for acetylene by means of potassium iodomercurate (*6*, *7*), ethylene by bromine water, propene plus *n*-butenes in 87 per cent sulfuric acid (*6*), isobutene in 62 per cent sulfuric acid (*6*), and butadiene with maleic anhydride (*10*). Carbon dioxide, carbon monoxide, oxygen, hydrogen, and paraffins were determined by the usual methods.

The calculations are based upon the percentage of olefins in the cracked gas and are subject to certain errors—namely, the determination itself, polymerization to liquids which was observed in all experiments, reactions involving the percentages of unsaturated substances and coke formation.

Discussion of Results

The results in Tables I to X, inclusive, are presented in three ways. The first, analysis in per cent, is the observed composition of the cracked gas calculated to an oxygen- and nitrogen-free basis. The second is obtained by the formula:

$$(R)(A) + (A) = Y$$

where R = percentage expansion
A = analysis, per cent
Y = resultant yield, liters/100 liters of entering hydrocarbon (volume per cent)

The third method of presentation is based on the conversion to moles and a complete reaction of the entering hydrocarbon, and the results obtained are expressed as yields in moles per 100 moles of reacting hydrocarbon.

Interest in this work was centered upon the yields of unsaturated hydrocarbons obtained although liquids and carbon were observed in every experiment. The data show that the rate of decomposition increased more rapidly with the contact time for propene and the butenes than for ethylene, which shows the greater thermal resistance of the latter. In the pyrolysis of 1- and 2-butene at 1100° C., a greater yield of butadiene was obtained from the 2-butene, whereas isobutene gave about 54 per cent less butadiene and 50 per cent more acetylene than 2-butene. The total yield of acetylene and ethylene is about the same at similar contact times. There is no evidence of the isomerization of 1- or 2-butene to isobutene, possibly because of the greater instability of the latter, a result which was previously obtained at lower temperatures.

In general, the value of n for the paraffins (C_nH_{2n+2}) reaches a maximum and falls off, but there are some exceptions which may be explained by an error in determination. The paraffin and hydrogen yields increased with the contact time and in some cases reached a maximum.

The percentage expansion increased as the time of contact was raised and reached a maximum in every pyrolysis except those of propene and 1-butene at 1100° C. and ethylene at 1400° C. A clear explanation of this observation has not yet been found. However, it should be pointed out that these data may indicate some change or changes in the mechanism of the pyrolysis. The pyrolysis of ethylene at 1100° C. illustrates the effect of an increase in time of contact upon the volume of cracked gas. Thus, at the shortest time the volume decreases, followed by an increase, a decrease, and an increase.

Theory

The pyrolysis of olefins has been the subject of many researches (*3*) designed to clarify the reaction mechanism. These data show that under mild conditions there is a contraction; and as the conditions become more severe, a point is reached where there is no change in volume showing that the expansion which results from decomposition is equal to the contraction in volume from polymerization (*8*). If, however, the conditions are still more severe, decomposition will mask the polymerization and only the increase in volume will be observed. Such was the case in this work at 1100° and 1400° C. since an expansion was observed in all experiments except those of ethylene under the mildest conditions. Therefore, the true primary reactions were masked by the extensive decomposition. Furthermore, in order to obtain a satisfactory picture of olefin pyrolysis it seems necessary to investigate the polymer formation and finally the stability of the latter under the experimental conditions.

It might appear that the decomposition reaction would possibly precede the polymerization under the severe conditions used. The following considerations, however, show that this is not the case. Thus, if the activation energies of the carbon to carbon (C—C) bond and one of the bonds of the carbon to carbon double bond (C═C) are taken as Q_1 and Q_2, respectively, the relative rates of the two processes are given by the expression (*9*)

$$e^{\left(\frac{Q_1 - Q_2}{2T}\right)} : 1$$

where e = 2.718
T = the absolute temperature

If it is assumed that the activation energies of 72,000 and 39,000 calories (*1*) are accurate at T = 1373° K., and they are substituted for Q_1 and Q_2, respectively, it is found that the process involving the activation of the C—C bond can be neglected. If it is further assumed that the energy requirements of thermodynamics are satisfied, then the cracking of a C—C bond is negligible and the polymerization process is the primary reaction during the pyrolysis. Furthermore, an inspection of the formula shows that, as the absolute temperature is decreased, the relative rate of the polymerization activation is increased, provided the assumption of a difference in energy of activation of 33,000 calories holds.

The polymer obtained in the primary reaction would be unstable under the experimental conditions, partly decomposing to yield the observed gaseous products.

Pyrolysis of Ethylene at 1100° C.

When ethylene was pyrolyzed at 1100° C., 50 mm. pressure, and contact times varying from 0.0007 to 0.044 second, the yield of acetylene increased from 5.9 volume per cent at the former time to 21.0 per cent at the latter. The amount of ethylene in the off-gas fell from 88.0 volume per cent at 0.0007 second to 48.0 per cent at 0.044 second. The yields of propene + butenes, and butadiene were nearly constant at about 3.0 and 1.5 per cent, respectively. The results are given in Table I.

Pyrolysis of Ethylene at 1400° C.

As shown in Table II, the results of the pyrolysis of ethylene at 1400° C. and 50 mm. pressure differ greatly from those obtained at 1100° C. in that no propene + butenes or butadiene were found. The yield of acetylene reached a maximum of 76.6 volume per cent when the contact time was 0.0023 second.

Pyrolysis of Propene at 1100° C.

Propene was subjected to a temperature of 1100° C., 50 mm. pressure, and contact times varying from 0.0022 to 0.0120 second. Table III shows that the highest yields (in liters per 100 liters of entering propene) of acetylene (21.8), of ethylene (28.5), and of butadiene (2.9) were obtained when the contact time (0.0120 second) was the longest studied. The amount of propene + butenes in the off-gas dropped from 72.6 volume per cent at the shortest contact time (0.0022 second) to 28.2 per cent at the longest time (0.0120 second).

Pyrolysis of Propene at 1400° C.

In the pyrolysis at 1400° C. and 50 mm. pressure, the propene reacted entirely at the shortest contact time of 0.0009 second; the highest yield of ethylene (26.4 per cent) and of butadiene (4.2 per cent) was obtained under these conditions. The maximum yield of acetylene (59.3 per cent) was obtained when the contact time was 0.0022 second. Other yields at different contact times are found in Table IV, where the yield in liters per 100 liters of entering propene is equal to the moles per 100 moles of reacting propene because of the complete disappearance of the charge.

Pyrolysis of 1-Butene at 1100° C.

In pyrolyzing 1-butene at 1100° C. and 50 mm. pressure, the contact time was varied from 0.0019 to 0.013 second. Table V shows that the highest yield of acetylene (35.0 volume per cent) and of ethylene (42.6 per cent) was obtained when the contact time was 0.013 second. The amount of propene + butenes decreased from 30.4 volume per cent at the shortest contact time of 0.0019 second to 4.8 at the longest. The yield of butadiene reached a maximum of 17.4 volume per cent with the contact time at 0.0037 second, and there was no isobutene found in 63 per cent sulfuric acid.

TABLE IV. PYROLYSIS OF PROPENE AT 1400° C.

Run No.	200	196	195	203	197	198	204	199
Contact time, 10^{-3} sec.	0.9	1.0	1.2	1.4	1.6	2.2	3.0	3.8
Per cent expansion	89.0	93.0	109	116	111	129	122	152
Analysis, per cent:								
C_2H_2	25.3	26.1	26.1	24.5	25.7	25.9	25.4	22.2
C_2H_4	14.0	11.9	10.3	8.0	7.8	5.4	4.1	2.1
$C_3H_6 + C_4H_8$	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0
C_4H_6	2.2	2.0	1.4	0.8	1.0	0.0	0.0	0.0
CO_2	0.5	0.4	0.4	0.0	1.3	0.0	0.0	0.6
CO	1.2	1.0	1.0	0.4	0.5	1.0	1.6	1.5
H_2	20.1	25.0	41.5	47.5	45.1	51.6	57.3	65.6
C_nH_{2n+2}	36.7	33.6	19.3	18.3	18.6	16.1	11.6	8.0
n in C_nH_{2n+2}	1.41	1.03	2.23	1.41	1.6	1.31	1.35	1.06
Yield, liters/100 liters of entering propene (volume per cent), or moles/100 moles of reacting propene:								
C_2H_2	47.8	48.4	54.5	52.9	54.2	59.3	56.4	56.0
C_2H_4	26.4	22.9	21.5	17.3	16.4	12.4	9.1	5.3
C_4H_6	4.2	3.9	2.9	1.7	2.1	0.0	0.0	0.0
H_2	38.0	48.3	86.8	103.0	95.0	118.0	127.0	165.0
C_nH_{2n+2}	69.5	65.0	40.3	39.5	39.2	36.9	25.7	20.2
CH_4	41.0	63.0	...	23.3	15.6	25.5	16.7	19.0
C_2H_6	28.5	2.0	...	16.2	23.6	11.4	9.0	1.2

TABLE V. PYROLYSIS OF 1-BUTENE AT 1100° C.

Run No.	211	209	210	213
Contact time, 10^{-3} sec.	1.9	3.7	7.9	13.0
Per cent expansion	65.0	72.0	85.0	102
Analysis, per cent:				
C_2H_2	13.4	15.4	15.9	17.3
C_2H_4	18.5	18.5	20.6	21.1
$C_3H_6 + C_4H_8$	18.4	6.2	5.5	2.4
Iso-C_4H_8	0.0	0.0	0.0	0.0
C_4H_6	6.2	10.1	4.1	2.7
CO_2	0.0	0.0	0.7	0.0
CO	0.9	1.1	1.2	1.0
H_2	15.3	17.8	20.4	27.8
C_nH_{2n+2}	27.4	31.0	31.8	27.7
n in C_nH_{2n+2}	1.50	1.70	1.86	1.03
Yield, liters/100 liters of entering 1-butene (volume per cent):				
C_2H_2	22.1	26.5	29.4	35.0
C_2H_4	30.5	31.8	38.1	42.6
$C_3H_6 + C_4H_8$	30.4	10.7	10.1	4.8
C_4H_6	10.2	17.4	7.6	5.5
H_2	25.2	31.6	37.8	56.1
C_nH_{2n+2}	45.2	53.2	58.9	55.9
Yield, moles/100 moles of reacting 1-butene:				
C_2H_2	31.8	29.8	32.7	36.8
C_2H_4	43.7	35.7	42.4	44.7
C_4H_6	14.5	19.5	8.5	5.8
H_2	36.2	35.5	42.1	59.0
CH_4	32.4	17.8	9.14	56.9
C_2H_6	32.4	41.7	56.1	1.8

TABLE VI. PYROLYSIS OF 1-BUTENE AT 1400° C.

Run No.	217	214	215	216
Contact time, 10^{-3} sec.	0.9	3.6	5.9	9.8
Per cent expansion	151	161	132	156
Analysis, per cent:				
C_2H_2	25.7	22.1	18.4	19.8
C_2H_4	15.2	2.3	0.7	0.4
$C_3H_6 + C_4H_8$	1.7	0.0	0.0	0.0
CO_2	0.6	1.3	0.0	0.2
CO	1.5	4.5	7.5	6.2
H_2	34.4	60.2	66.2	70.8
C_nH_{2n+2}	20.9	9.6	7.2	2.7
n in C_nH_{2n+2}	1.45	1.02	2.7	2.2
Yield, liters/100 liters of entering 1-butene (volume per cent):				
C_2H_2	64.5	57.6	42.7	50.6
C_2H_4	38.2	6.0	1.6	1.0
$C_3H_6 + C_4H_8$	4.3	0.0	0.0	0.0
H_2	86.5	157.0	154.0	181.0
$C_nH_{2n\pm2}$	52.5	25.0	16.7	6.8
Yield, moles/100 moles of reacting 1-butene:				
C_2H_2	65.6	57.6	42.7	50.6
C_2H_4	38.9	6.0	1.6	1.0
H_2	88.0	157.0	154.0	181.0
CH_4	28.9	24.5	...	...
C_2H_6	23.6	0.5	...	...

TABLE VII. PYROLYSIS OF 2-BUTENE AT 1100° C.

Run No.	218	223	219	222	221
Contact time, 10^{-3} sec.	1.2	2.5	3.0	5.8	11.0
Per cent expansion	24.0	62.0	87.0	75.0	63.0
Analysis, per cent:					
C_2H_2	6.8	11.3	13.9	13.3	15.4
C_2H_4	5.6	12.5	16.8	18.6	18.5
$C_3H_6 + C_4H_8$	53.2	20.0	12.2	8.3	5.5
Iso-C_4H_8	0.0	0.0	0.0	0.0	0.0
C_4H_6	12.6	14.4	9.2	6.2	2.4
CO_2	0.5	0.5	0.6	0.2	0.7
CO	0.3	0.6	0.5	2.7	4.5
H_2	7.0	15.0	19.8	21.2	24.0
C_nH_{2n+2}	14.0	25.7	27.0	29.7	29.1
n in C_nH_{2n+2}	1.32	1.29	1.02	1.18	1.04
Yield, liters/100 liters of entering 2-butene (volume per cent):					
C_2H_2	8.4	18.3	26.0	23.3	25.0
C_2H_4	7.0	20.2	31.4	32.6	30.2
$C_3H_6 + C_4H_8$	66.0	32.4	22.8	14.5	9.0
C_4H_6	15.6	23.3	17.2	10.8	3.9
H_2	8.7	24.3	37.0	37.0	39.1
C_nH_{2n+2}	17.3	41.6	50.5	52.0	47.5
Yield, moles/100 moles of reacting 2-butene:					
C_2H_2	24.7	27.0	33.6	27.3	27.5
C_2H_4	20.6	29.8	40.7	38.1	33.2
C_4H_6	45.8	34.5	22.3	12.6	4.3
H_2	25.6	35.9	47.9	43.2	43.0
CH_4	34.6	43.7	65.4	49.8	52.2
C_2H_6	16.3	17.8	...	11.0	0.0

TABLE VIII. PYROLYSIS OF 2-BUTENE AT 1400° C.

Run No.	235	234	236	237
Contact time, 10^{-3} sec.	1.0	1.9	2.8	6.6
Per cent expansion	86.0	168	155	80.0
Analysis, per cent:				
C_2H_2	23.4	23.9	22.3	15.6
C_2H_4	5.0	3.7	2.1	0.0
$C_3H_6 + C_4H_8$	1.1	0.9	0.6	0.0
CO_2	0.0	1.1	0.6	0.7
CO	7.5	0.5	3.8	8.5
H_2	43.6	51.8	60.3	49.1
C_nH_{2n+2}	19.4	18.0	10.3	26.2
n in C_nH_{2n+2}	1.3	1.2	1.2	1.3
Yield, liters/100 liters of entering 2-butene (volume per cent), or moles/100 moles of reacting 2-butene:				
C_2H_2	43.5	64.1	56.8	28.1
C_2H_4	9.3	9.9	5.4	0.0
H_2	81.0	139.0	154.0	88.5
CH_4	25.2	38.6	21.0	33.0
C_2H_6	10.8	9.6	5.3	14.1

TABLE IX. PYROLYSIS OF ISOBUTENE AT 1100° C.

Run No.	228	226	225	230	231	227
Contact time, 10^{-3} sec.	1.3	2.8	4.0	4.9	7.1	11.0
Per cent expansion	18.0	95.0	128	96.0	70.0	72.0
Analysis, per cent:						
C_2H_2	7.8	16.6	16.5	20.6	18.6	17.6
C_2H_4	1.1	4.3	8.8	6.4	7.7	8.8
$C_3H_6 + C_4H_8$	16.1	11.6	9.2	8.4	6.1	11.6
C_4H_6	4.1	5.6	4.0	2.7	2.2	2.1
Iso-C_4H_8	46.1	14.5	3.4	2.1	1.1	0.0
CO_2	0.3	0.0	0.0	0.4	1.1	0.0
CO	1.2	0.7	3.5	0.7	3.5	4.2
H_2	5.2	11.2	14.4	20.1	16.9	21.1
C_nH_{2n+2}	18.1	34.5	40.0	38.6	42.8	35.0
n in C_nH_{2n+2}	1.27	1.41	1.33	1.2	1.08	1.66
Yield, liters/100 liters of entering isobutene (volume per cent):						
C_2H_2	9.2	32.4	37.6	40.3	31.6	30.2
C_2H_4	1.3	8.4	20.1	12.5	13.1	15.1
$C_3H_6 + C_4H_8$	19.0	22.6	21.0	16.4	10.3	19.1
C_4H_6	4.9	10.9	9.1	5.3	3.7	3.6
Iso-C_4H_8	54.4	28.3	7.8	4.1	1.9	0.0
H_2	6.1	21.8	32.8	39.4	28.7	36.3
C_nH_{2n+2}	21.4	67.2	91.2	75.6	72.9	60.1
Yield, moles/100 moles of reacting isobutene:						
C_2H_2	20.2	45.2	40.8	42.1	32.2	30.2
C_2H_4	2.9	11.7	21.8	13.1	13.4	15.1
$C_3H_6 + C_4H_8$	41.6	31.5	22.8	17.1	10.5	19.1
C_4H_6	10.7	15.2	9.9	5.5	3.8	3.6
H_2	13.4	30.4	35.6	41.1	29.3	36.3
CH_4	35.4	55.2	66.3	63.2	67.7	19.8
C_2H_6	12.6	38.3	32.7	15.8	5.9	40.3

TABLE X. PYROLYSIS OF ISOBUTENE AT 1400° C.

Run No.	232	233	238
Contact time, 10^{-3} sec.	0.8	1.8	3.1
Per cent expansion	95.0	181	138
Analysis, per cent:			
C_2H_2	19.8	20.6	20.2
C_2H_4	5.3	2.8	0.0
$C_3H_6 + C_4H_8$	1.2	0.4	0.0
Iso-C_4H_8	0.0	0.0	0.0
C_4H_6	0.3	0.0	0.0
CO_2	1.9	1.0	0.9
CO	5.5	1.6	5.1
H_2	39.3	55.0	62.7
C_nH_{2n+2}	26.6	18.5	11.2
n in C_nH_{2n+2}	1.4	1.15	1.25
Yield, liters/100 liters of entering isobutene (volume per cent), or moles/100 moles of reacting isobutene:			
C_2H_2	38.6	57.8	48.1
C_2H_4	10.3	7.9	0.0
$C_3H_6 + C_4H_8$	2.3	0.0	0.0
C_4H_6	0.6	0.0	0.0
H_2	74.6	154.0	149.0
CH_4	31.1	44.2	20.0
C_2H_6	20.7	7.8	6.6

TABLE XI. RELATIVE STABILITY AT 1100° C.

	1	2	3	4
Ethylene:				
Unreacted vol., per cent	77.0	76.0	65.8	53.8
Contact time, 10^{-3} sec.	2.2	4.1	6.1	14.0
Table I, expt. No.	163	166	171	169
Propene:				
Unreacted vol., per cent	72.6	44.4	34.4	28.2
Contact time, 10^{-3} sec.	2.2	4.3	5.8	12.0
Table III, expt. No.	183	189	188	190
1-Butene:				
Unreacted vol., per cent	30.4	10.7	10.1	4.8
Contact time, 10^{-3} sec.	1.9	3.7	7.9	13.0
Table V, expt. No.	211	209	210	213
2-Butene:				
Unreacted vol., per cent	32.4	22.8	14.5	9.0
Contact time, 10^{-3} sec.	2.5	3.0	5.8	11.0
Table VII, expt. No.	223	219	222	221
Isobutene:				
Unreacted vol., per cent	28.3	7.8	1.9	0.0
Contact time, 10^{-3} sec.	2.8	4.0	7.1	11.0
Table IX, expt. No.	226	225	231	227

Pyrolysis of 1-Butene at 1400° C.

In pyrolyzing 1-butene at 1400° C. and 50 mm. pressure, the contact time was varied from 0.0009 to 0.0098 second. The highest yields of acetylene (64.5 volume per cent) and ethylene (38.2 volume per cent) were obtained at the shortest contact time. The results are given in Table VI.

Pyrolysis of 2-Butene at 1100° C.

2-Butene was pyrolyzed at 1100° C., at a pressure of 50 mm., and for the contact time range of 0.0012 to 0.011 second. The results (Table VII) show that the highest yield of acetylene (26.0 volume per cent) was obtained at the contact time of 0.003 second, of ethylene (32.6) at 0.0058 second, and of butadiene (23.3) at 0.0025 second. Yields of other products are also recorded in Table VII; no isobutene was found.

Pyrolysis of 2-Butene at 1400° C.

When 2-butene was pyrolyzed at 1400° C., a pressure of 50 mm., and for the contact time range of 0.001 to 0.0066 second, the results were those recorded in Table VIII which gives the highest yields of unsaturated hydrocarbon as follows:

acetylene (64.1 volume per cent) at the contact time of 0.0019 second and ethylene (9.9 volume per cent) at the same time. In Table VIII the yield in liters per 100 liters of entering 2-butene is equal to the yield in moles per 100 moles of reacting 2-butene because for complete decomposition the results are on the same basis.

Pyrolysis of Isobutene at 1100° C.

The contact time range of 0.0013 to 0.011, a pressure of 50 mm., and the temperature of 1100° C. were the conditions used to obtain the results recorded in Table IX. The highest yields of unsaturated hydrocarbons obtained were: 40.3 volume per cent for acetylene, 20.1 for ethylene, and 10.9 for butadiene at contact times of 0.0049, 0.004, and 0.0028 second, respectively.

Pyrolysis of Isobutene at 1400° C.

The pyrolysis of isobutene at 1400° C. and 50 mm. pressure was performed for contact times of less than 0.0031 second because of the coking in the reaction tube. The results are recorded in Table X, and the highest yield of acetylene (57.8 volume per cent) was found at the contact time of 0.0018 second; of ethylene (10.3 volume per cent) at 0.0008 second; and of higher olefins (2.3 volume per cent) at 0.0008 second.

Relative Stability to Heat

The relative stability of ethylene, propene, 1-butene, 2-butene, and isobutene is obtained by a comparison of the amounts of unreacted olefins at a given temperature and contact time. The comparison is made at 1100° and 1400° C., but the former offers a wider range because complete decomposition is not approached until the longest contact times are reached while in some cases at 1400° C. complete decomposition is obtained at the shortest contact time.

The resistance to thermal reaction at 1100° C. is compared in Table XI which shows that ethylene is by far the most stable with propene relatively close at the shortest contact time. However, as the time is increased, propene shows much less resistance than ethylene. The butenes decrease in stability thus: 2-, 1-, and isobutene. Therefore, the complete order of decreasing stability is: ethylene, propene, 2-butene, 1-butene, and isobutene which is not the same as that found at 600–700° C. (*4*, *5*).

TABLE XII. RELATIVE STABILITY AT 1400° C.

	1	2	3
Ethylene:			
Unreacted vol., per cent	60.8	9.8	9.9
Contact time, 10^{-3} sec.	0.8	4.1	8.4
Table II, expt. No.	176	180	177
Propene:			
Unreacted vol., per cent	0.0	0.0	...
Contact time, 10^{-3} sec.	0.9	3.8	...
Table IV, expt. No.	200	199	...
1-Butene:			
Unreacted vol., per cent	4.3	0.0	0.0
Contact time, 10^{-3} sec.	0.9	3.6	9.8
Table VI, expt. No.	217	214	216
2-Butene:			
Unreacted vol., per cent	2.0	0.0	0.0
Contact time, 10^{-3} sec.	1.0	2.8	6.6
Table VIII, expt. No.	235	236	237
Isobutene:			
Unreacted vol., per cent	0.0	0.0	...
Contact time, 10^{-3} sec.	0.8	3.1	...
Table X, expt. No.	232	238	...

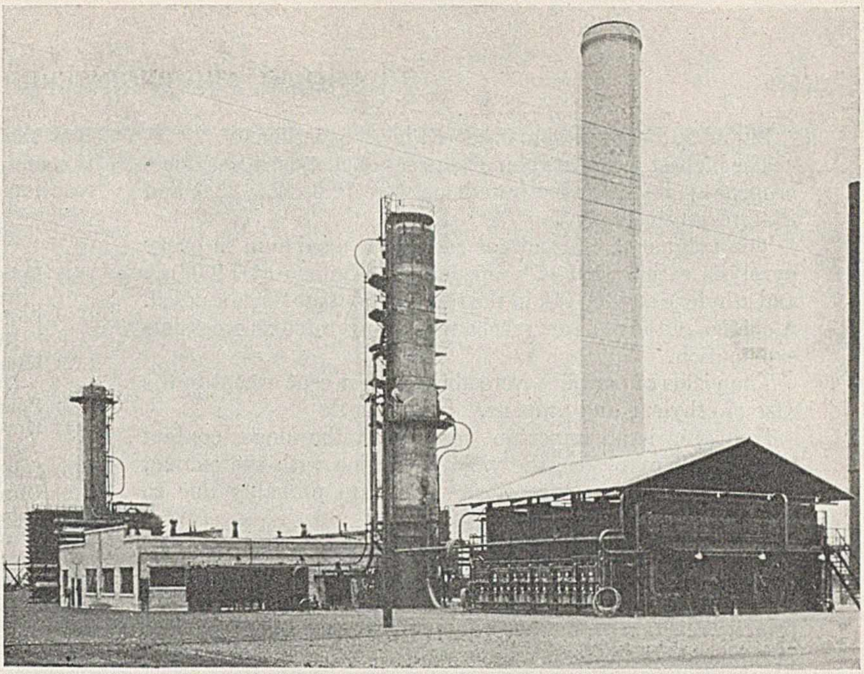


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Table XII shows that only ethylene is stable enough at 1400° C. in order to remain partly unreacted. In the case of 1- and 2-butene, the small volume percentages are accounted for by the absorption of other gases.

Summary and Conclusions

The five olefins—ethylene, propene, 1-butene, 2-butene, and isobutene—have been pyrolyzed at the temperatures of 1100° and 1400° C., a pressure of 50 mm., and contact times in the order of 0.001 second.

The highest yields from the five olefins, in liters per 100 liters of entering olefin, of unsaturated hydrocarbons obtained at 1100° C., 50 mm. pressure, and contact time of approximately 0.001 second, are as follows:

Product Obtained	Substance Pyrolyzed: Ethylene	Propene	1-Butene	2-Butene	Isobutene
C_2H_2:					
Vol. per cent	21.0	21.8	35.0	26.0	40.3
Contact time, 10^{-3} sec.	44.0	12.0	13.0	3.0	4.9
C_2H_4:					
Vol. per cent	..	28.5	42.6	32.6	20.1
Contact time, 10^{-3} sec.	..	12.0	13.0	5.8	4.0
$C_3H_6 + C_4H_8$					
Vol. per cent	3.0	..	..	..	22.6
Contact time, 10^{-3} sec.	[a]	..	..	..	2.8
C_4H_6:					
Vol. per cent	1.5	2.6	17.4	23.3	10.9
Contact time, 10^{-3} sec.	[b]	[c]	3.7	2.5	2.8

[a] 2.2 to 44.0. [b] 0.7 to 44.0. [c] 2.5 to 12.0.

The highest yields in volume per cent of acetylene and ethylene obtained at 1400° C., 50 mm. pressure, and for a contact time ranging from 0.0008 to 0.010 second were:

Products Obtained	Substances Pyrolyzed: Ethylene	Propene	1-Butene	2-Butene	Isobutene
C_2H_2:					
Vol. per cent	76.6	59.3	64.5	64.1	57.8
Contact time, 10^{-3} sec.	2.3	2.2	0.9	1.9	1.8
C_2H_4:					
Vol. per cent	..	26.4	38.2	9.9	10.3
Contact time, 10^{-3} sec.	..	0.9	0.9	1.9	0.8

There were no propene + butenes obtained in the pyrolyses at 1400° C., and butadiene was obtained only from propene; the maximum yield was 4.2 volume per cent at the contact time of 0.008 second.

Liquid and carbon were observed in all experiments.

The highest yields in volume per cent of acetylene, ethylene, propene + butenes, and butadiene were 76.6, 42.6, 22.6, and 23.3, respectively.

The volume of cracked gas reached a maximum in every pyrolysis except that of propene and 1-butene at 1100° C. and ethylene at 1400° C. in the range of contact times studied. A change in the reaction mechanism is suggested as a possible explanation.

The yields of paraffins were above 25 per cent except in the case of ethylene and propene.

Hydrogen is an important product at the longer contact times in all pyrolyses, the yield increasing with the contact time with but few exceptions which are probably due to experimental error.

The relative stability at 1100° C. decreases in the order: ethylene, propene, 2-butene, 1-butene, isobutene.

The severe conditions of pyrolysis completely masked the primary reaction products because of extensive decomposition. It is pointed out by experiment and theoretical considerations that the decomposition of olefins is preceded by polymerization and that the gaseous products are produced by secondary reaction.

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EFFECT OF HEAT ON NUTRITIVE VALUE OF SOY-BEAN OIL MEAL

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IN SPITE of the established place of soy-bean oil meal in animal feeding, no work has been reported on the effect of variation in the amount of heat used in the manufacturing process on its nutritive properties. Up to the present time, nutrition investigators have paid no particular attention to the history of the samples of soy-bean oil meal studied beyond determining the process by which they are manufactured. The fact that some of the results were at variance with others indicates that there were differences occurring among the samples used.

In previous studies on soy-bean oil meal by the authors, no particular advantage could be attributed to meals prepared by any of the manufacturing processes in common use, since the commercial meals studied were equally satisfactory in protein efficiency regardless of whether they were prepared by the expeller or by the hydraulic process (*10*), and since part or all the meat scrap in a practical chick ration could be replaced by solvent-process soy-bean oil meal with equal or superior growth (*11*). One sample of hydraulic-process meal, however, was slightly inferior in protein efficiency in these studies (*10*). This behavior was attributed tentatively to insufficient cooking, since this meal had a slightly raw, beany flavor and a light color. Probably, therefore, differences in the nutritive value of soy-bean oil meals were due to differences in the amount of heat treatment rather than to characteristics peculiar to the process.

That these differences may occur was shown by the work of Osborne and Mendel (*6*) and of Robison (*7*) who reported that feeding soy beans cooked at a high temperature improves the growth of rats and swine, respectively, over that obtained with raw beans. This work appears to substantiate the demand in the field for a well-cooked meal of brownish color and without any raw or beany flavor. On the other hand, an excess amount of heat might be harmful as indicated by the reports on the detrimental effect of heat on cereal proteins by Morgan (*5*) and on fish meal proteins by numerous investigators previously cited by the authors (*9*).

Because of the lack of definite information on the effect of heat treatment and in view of the increasing production of soy-bean oil meal, it appeared highly desirable to determine the effect of the amount of heat used in the manufacturing process on the nutritive value of the meal.

Experimental Methods

Since the nutritive value of common protein supplements has been shown to be due to quality of the proteins and to their content of growth-promoting vitamin G, the relative protein efficiency and the relative vitamin G content of the samples of soy beans and soy-bean oil meal were determined by methods described elsewhere in detail (*10*).

The relative protein efficiency is an expression of the utilization for the growth of White Leghorn chicks of the protein of a protein supplement when combined with an equal quantity of protein from yellow corn meal and wheat flour middlings. It was obtained by determining the percentage of protein stored during the seventh week of age, dividing the percentage storage by that of a standard diet in which casein was used as the protein supplement, and multiplying by 100.

In the vitamin G studies, day-old White Leghorn chicks were depleted of their natural reserve of vitamin G by placing

TABLE I. EFFECT OF MANUFACTURING PROCESS UPON RELATIVE PROTEIN EFFICIENCY

Sample No.	Soy-Bean Material	Drier		Conveyer		Prewarmer		Expeller		Relative Protein Efficiency	Relative Vitamin G Content
		Temp. ° *C.*	Time *Min.*	Temp. ° *C.*	Time *Min.*	Temp. ° *C.*	Time *Min.*	Temp. ° *C.*	Time *Min.*		
					Expeller Process						
1	Beans	.....	..	...	..	.....	..	.....	...	38[a]	2
2	Oil meal	100–112	8	82.90	7	90	13	105	2.0	47	2
3	Oil meal	100–112	8	82–90	7	100–112	13	112–125	1.5	80	1
								130	1.0		
4	Oil meal	100–112	8	82–90	7	100–112	13	140	1.5	84	2
								150	1.0		
					Hydraulic Process						
		Drier		Heater		Cooker		Press			
5	Beans	...	..	..	..	...	..	...	...	60[b]	3
6	Oil meal	60–80	60	60	10	82	90	75–65	50–60	80	2
7	Oil meal	60–80	60	60	10	105	90	75–65	50–60	88	3
8	Oil meal	60–80	60	60	10	121	90	80–68	50–60	82	3
					Solvent Process						
		Heater		Extractor		Drier		Aërator and Cooler			
9	Beans	..	..	..	..	..	..	...	...	57[b]	4
10	Oil meal	60	10	45	Continuous	98	15	78–45	10–20	92	3

[a] Ground several weeks before use. [b] Ground immediately before use.

them for 2 weeks on a ration deficient in this vitamin but complete in all other respects. They were then fed the basal ration to which 5 or 10 per cent of the material under study was added. The differences in gains during the following 4 weeks between the pens receiving the supplemented rations and a pen receiving the basal ration were compared to those obtained by feeding graded amounts of a standard dried pork liver. The relative vitamin G content was expressed in percentage with dried pork liver as 100, and was obtained by dividing the amount of standard pork liver which afforded a gain equivalent to that obtained on a supplemented ration by the percentage of supplement used and multiplying by 100.

Preparation of Soy-Bean Oil Meals

When the coöperation of various manufacturers of soy-bean oil meal was sought, the authors were informed of the study undertaken on the same subject by J. W. Hayward, of the Wisconsin Agricultural Experiment Station. At the suggestion of one of the manufacturers, Hayward kindly supplied the experimental samples used in these studies together with samples of the raw beans from which the meals were prepared. These samples were produced at commercial plants under his supervision and under controlled conditions by the expeller, hydraulic, and solvent processes. Samples were prepared by the first two processes at low, medium, and high temperatures. The medium temperatures are generally used commercially. Only one solvent-process sample was prepared, since the temperature could not be varied to any marked extent. The essential data on the preparation of the samples are included in Table I, and the analyses for moisture, protein, ether extract, and ash are given in Table II.

TABLE II. ANALYSIS OF SOY-BEAN OIL MEALS

Sample No.	Soy-Bean Material	Moisture %	Protein %	Ether Extract %	Ash %
		Expeller Process			
1	Beans	8.94	34.32	19.56	4.30
2	Oil meal	7.30	39.84	6.77	4.98
3	Oil meal	6.59	43.68	5.12	5.24
4	Oil meal	6.39	42.72	4.87	5.34
		Hydraulic Process			
5	Beans	7.18	36.75	18.20	4.06
6	Oil meal	10.65	43.43	4.84	5.00
7	Oil meal	5.59	45.76	5.09	5.47
8	Oil meal	6.00	45.58	4.97	5.56
		Solvent Process			
9	Beans	6.92	35.73	18.78	4.78
10	Oil meal	7.51	46.06	0.56	5.97

Soy-bean oil meals which are satisfactory as sources of high-quality protein for feeding poultry may be produced by the expeller, hydraulic, and solvent processes, by the application of a sufficient amount of heat. The optimum temperature found in this study for the expeller method was 140° to 150° C. for 2 minutes in the expeller, and for the hydraulic method was 105° C. for 90 minutes in the cooker. A solvent-process meal produced at 82° C. for 15 minutes (the usual commercial procedure) was excellent in protein efficiency.

The vitamin G content of the soy beans studied was low and was not affected to any measurable extent by the manufacturing processes. The color and flavor of the meals were not infallible criteria of their nutritive value, but a raw, beany flavor was indicative of an insufficient application of heat and a resulting inferior protein efficiency.

The soy beans used in the preparation of the various samples by each of the three processes consisted of the following varieties or mixtures of varieties:

Process	Sample No.	Variety
Expeller	1–4	Illini
Hydraulic	5–8	Manchu and Illini
Solvent	9–10	Illini, Manchu, some Black Ebony

Effects of Processes

No effect of the amount of heat treatment was apparent on the analysis of the meals. In the expeller-process meals, the protein content of low-temperature sample 2 was slightly reduced, because of a slightly higher moisture and fat content resulting from the low pressure exerted in the expeller. The very low fat content of the solvent-process meal was caused by the nature of the extraction process.

The biological results are presented in Table I. No significant differences in relative vitamin G content were found between the raw soy beans and the soy-bean oil meals, since all of the values were within the range of experimental error. The vitamin G content of all the samples was low, averaging about 3 per cent of that found in the standard liver (or about 15 per cent of that present in dried skim milk). This is in agreement with the values previously reported by the authors on other samples of soy-bean oil meal (*10*).

On the other hand, the effect of amount of heat on the relative protein efficiency was very marked, since a difference of 4 was previously shown to be significant (*10*). All the raw bean samples were found to be inferior to the meals. The low value of these soy beans is in agreement with unpublished data at this laboratory and with published results; the most outstanding were those of Tomhave and Mumford (*8*) with chicks, Osborne and Mendel (*6*) with rats, and Robison (*7*) with swine.

The low value found for soy-bean sample 1 may have been due to the oxidation of the fat during the time elapsed between grinding and feeding, since it was not fed until several weeks after grinding, whereas samples 5 and 9 were incorporated in the rations immediately after grinding. In some unpublished work, a value of 31 was also found for another sample of soy beans fed a number of weeks after grinding. Both of these samples were unpalatable to the birds.

Mitchell and Smuts (*4*) showed that cystine is a limiting factor in the biological value of soy-bean protein; Csonka and Jones (*1*) reported that the chief protein, glycinin, of soy beans is higher in cystine (but not in tryptophan or tyrosine) in the Manchu variety than in the Illini variety. Probably, however, the difference in cystine content was not responsible for the differences in protein efficiency obtained between raw soy-bean sample 1 and samples 5 and 9, since the basal ration used was well supplied with this amino acid by means of the proteins from corn and wheat (*3*). Furthermore, the cystine content of the glycinin from the Illini variety, 0.74 per cent, is more than double that generally accepted for casein, 0.33 per cent (*2*).

There were no consistent differences in protein efficiency between the soy-bean oil meals produced by the several processes; but within processes where controlled temperature variations were applied to the soy beans, significant differences were obtained in protein value. In the expeller method the highest protein efficiency was found for the meal subjected to a temperature of 140° to 150° C. in the expeller. This sample had a pronounced nutty flavor, a slightly roasted odor, and a brown color. The meal produced at about 125° C. was slightly inferior in protein efficiency. It possessed a mild nutty flavor, no roasted odor, and a light brown color. The meal produced at 105° C. with a water-cooled shaft was of little more value than the ground soy beans. This meal had a distinctly raw, beany flavor and a light yellow color.

In the hydraulic process a cooking temperature of 105° C. gave the highest protein efficiency. This meal had a cooked flavor and a light brown color. The meal produced at 121° C. was poorer; this temperature, therefore, is above that at which the product may be produced without some detrimental effect. This sample possessed a cooked flavor and a brown color. Even the temperature of 82° C. produced a meal of fair protein quality, although it was slightly raw and beany in flavor and light in color.

The relative protein efficiency of the solvent-process meal was good. Apparently the cooking effect in the two drying periods was sufficient even at the moderate temperatures used. This sample had no distinct flavor or odor and was light in color.

These results show that the main factor in the production of a soy-bean oil meal of high nutritive value is the amount of heat applied in the manufacturing process. It is a function of both the temperature and the length of its application. In the expeller process the very short time of exposure to heat was apparently compensated by the higher temperatures used. Probably the pressure within the expeller should be such as to raise the temperature as high as possible without scorching the meal or injuring the quality of the oil (around 140° C.). A good yield of oil is also thus attained. In the hydraulic process the low temperatures used were compensated by the longer time of exposure to heat. The optimum temperature found in these studies was 105° C. In the solvent process a low temperature for an even shorter period of time than in the hydraulic method appeared satisfactory for a reason not yet apparent. Possibly the solvent exerted some beneficial effect.

The color and flavor of the meals were generally in direct correlation with the amount of heat used in their production. A comparison of color and flavor with relative protein efficiency shows that the expeller-process meal, which possessed a brown color and a distinctly nutty flavor, was of high nutritive value. This was not true of the hydraulic meals, since the one subjected to the highest temperature was slightly inferior to the one produced at the next lower temperature. Nor is it true of the solvent process meal which was nearly as light in color as the ground beans and possessed no pronounced flavor, but was nevertheless of excellent protein efficiency. These results therefore demonstrate that the color and flavor of soy-bean oil meal may not offer infallible criteria of its nutritive value. It is probable, however, that a meal of raw, beany flavor is of inferior value because of insufficient heat treatment.

Upon comparing the relative protein efficiencies obtained in these studies with those previously reported (*10*), it is evident that in this respect properly prepared soy-bean oil meal is generally superior to meat scraps and only slightly inferior to most fish meals. Other unpublished experiments in this laboratory substantiate this evidence.

Acknowledgment

Acknowledgment is hereby made of the coöperation of the Grange League Federation Exchange, Inc., of Ithaca, N. Y., which made this investigation possible by establishing a temporary investigatorship at Cornell University.

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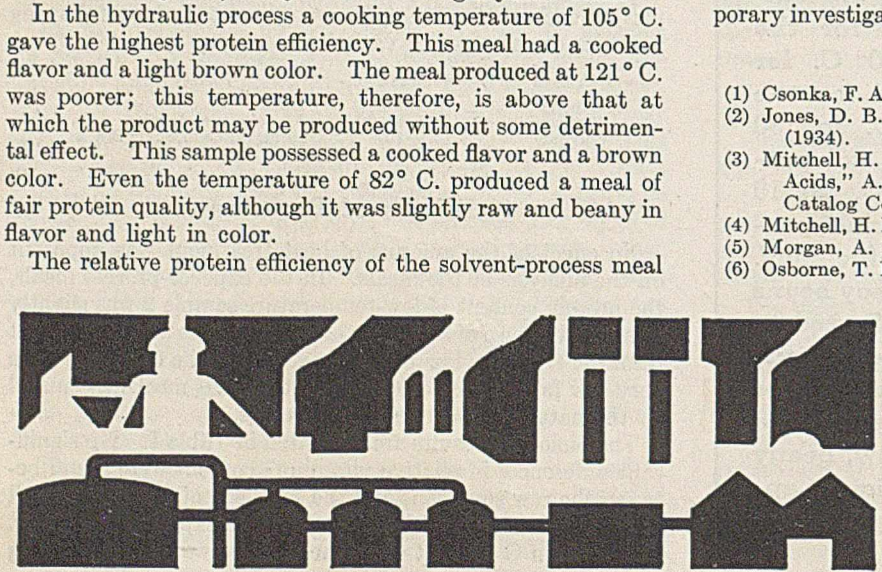

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Evaporation by Submerged Combustion

III. Sodium Sulfate Decahydrate[1]

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By the use of submerged combustion, 46.1 per cent of anhydrous sodium sulfate can be recovered from sodium sulfate decahydrate by heating to 90° C. The evaporation of a saturated solution of sodium sulfate can be carried out with no scale formation on the evaporator body. Scale formation which occurs on the burner, and crystal size and factors affecting it are discussed. A cycle of operations is proposed, and the thermal requirements of this cycle are compared with those for a tube evaporator.

WITH the decline in the production of hydrochloric acid from sodium chloride and sulfuric acid, the amount of by-product salt cake available for the chemical industry has decreased to such an extent that the demand for sodium sulfate must be met from other sources. This country has attempted to supply the deficiency by utilizing the natural deposits of sodium sulfate which occur in the western states (*13*). These deposits are of two kinds: Those in the Southwest are anhydrous sodium sulfate (thenardite); and those in the Northwest and Canada are sodium sulfate decahydrate (mirabilite). The deposits of thenardite have been worked to the greater extent, for they produce directly a material comparable to salt cake (*10*, *11*). The deposits of mirabilite have been worked only on a small scale owing to the necessity of dehydrating the decahydrate before shipping. Sodium sulfate decahydrate is composed of 44.1 per cent sodium sulfate and 55.9 per cent water; the need for dehydration is apparent.

The occurrence of large deposits of mirabilite in the State of Washington has led to the study of dehydration so that the product may be more cheaply shipped by rail to the coast where the sulfate pulp mills offer a market.

Dehydration of Sodium Sulfate Decahydrate

The dehydration of sodium sulfate decahydrate has been a rather difficult problem because of the character of the salt. At 32.4° C. the decahydrate melts, forming solid sodium sulfate and a saturated solution. Drying processes must operate below this transition temperature to avoid melting the salt. The first attempts were to expose the decahydrate to outdoor conditions. The hydrate was spread on trays placed in rows one above the other in a building with removable sides. This arrangement permitted the air to circulate freely over the trays and carry away the water. About two weeks were required to reduce the water content from 56 to 15 per cent. This remaining water was removed by heating the material on a shallow metal tray over a small stove (*2*). Production by this method was so slow and required such a large installation of drying sheds as to be commercially unfeasible. Controlled humidity drying also requires a large installation because the wet-bulb temperature must be kept below the transition temperature. Both of these processes produce a fine powdery dust which does not find a ready market. The operation of a rotary kiln drier above the transition temperature requires that a large fraction of the dehydrated product be mixed with the decahydrate feed so that, when the latter melts, the entire mass will have the consistency of sand and will not adhere to the sides of the kiln (*7*).

The success attained by evaporation methods on other salt solutions led to the use of multiple-effect evaporation for the recovery of anhydrous sodium sulfate. It is necessary that additional water be added to the decahydrate to form a saturated solution, or a natural brine can be employed direct. The operation of such an evaporator system was studied by Badger and Caldwell (*1*). Under ordinary operating conditions, crystal formation became so great in an hour that it was necessary to clean out the evaporator. By withdrawing the solution continuously from the evaporator, superheating, and flashing it under the tubes, seed crystals formed and the vigorous circulation obtained made it possible to operate for a 10.5-hour period followed by a 1.5-hour boil-out period in which the sodium sulfate scale was dissolved from the evaporator body and tubes. Spray evaporators, in which the saturated solution is sprayed countercurrent to a rising stream of hot air, work satisfactorily but produce a fine, light powder which is undesirable for many uses. The difficulties surrounding these various methods make it apparent that submerged combustion offers many advantages in the dehydration of sodium sulfate decahydrate.

Advantages of Submerged Combustion

Multiple-effect evaporation would be satisfactory were it not for the fact that sodium sulfate has an inverted solubility curve above 32.4° C. (Figure 1). This decrease in solubility of sodium sulfate with increase in temperature causes the salt to crystallize from its solution on surfaces which are at a temperature above that of the solution. With tube evaporators there must be considerable surface at a higher temperature so that heat may be conducted to the solution being

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[1] For Parts I and II, see literature citation *6*.

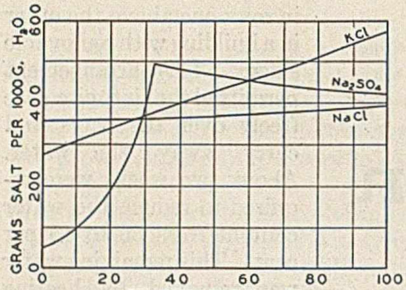

FIGURE 1. SOLUBILITY CURVES

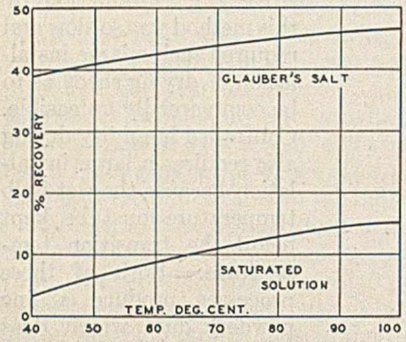

FIGURE 2. RECOVERY OF SODIUM SULFATE ON HEATING

evaporated. Thus we may expect the sodium sulfate to form rapidly a hard scale which will eventually cause the evaporator to be shut down. As was previously pointed out (*4*, *8*), submerged combustion does not give the opportunity for scale formation. Combustion takes place in a closed chamber beneath the surface of the liquid, and the hot products of combustion bubble up through the solution. Heat transfer takes place directly between the gas and liquid, so that there is no large metal surface on which sodium sulfate can crystallize. Even though some scale formation occurs on the burner, it is not necessary to shut down the entire apparatus; the burner is merely withdrawn and cleaned, while another burner may be inserted into the liquid.

The feed for the evaporator must be a solution of sodium sulfate, which is usually saturated, or a natural brine. For a submerged combustion system the solid decahydrate may be used as the feed. If a solution saturated with sodium sulfate at 32.4° C. (the point of greatest solubility) is heated, sodium sulfate will precipitate out as the temperature rises (Figure 2). If the solution is heated to 40° C., 2.8 per cent of the sodium sulfate in the solution saturated at 32.4° will be precipitated; if the temperature is raised to 100°, 15.2 per cent of the salt separates. Thus, by merely heating the solution above the transition temperature, solid sodium sulfate separates and may be recovered. In the usual operation the sodium sulfate solution is saturated at outdoor temperature. Thus, if the temperature is below 30° C., Figure 1 shows that there will be no precipitation of salt due to solubility effect, and it is usually necessary to evaporate water before the solution becomes saturated. If the solid decahydrate is heated, the recovery is much greater (Figure 2) than from a saturated solution. At 40° C., 38.9 per cent of the sodium sulfate in the decahydrate remains as solid; if the temperature is raised to 100°, 46.7 per cent of the salt can be recovered as solid. Such a recovery may be obtained by using the solid decahydrate as the feed and allowing it to drop into the saturated solution in the body of the evaporator. With a submerged combustion burner evaporating the solution at 90°, the use of decahydrate as the feed will give a precipitation of 46 per cent of the sodium sulfate and a saturated solution containing the other 54 per cent. Thus, submerged combustion allows the recovery of sodium sulfate by two methods: solubility-temperature effect, and evaporation of a saturated solution.

Submerged Combustion Evaporation

The equipment used for submerged combustion evaporation was described (*6*). The apparatus used in this work is shown in Figure 3.

Fifty pounds of decahydrate were placed in the evaporator and 13.5 pounds of hot water added to give a liquid layer into which the burner could be introduced. As the temperature of the solution increased, the decahydrate melted and the burner could be pushed down farther into the evaporator. After all decahydrate was melted, the solid sodium sulfate which had collected in the cone bottom was removed through the gate valve. The temperature of the solution rose to 89.7° C. where evaporation took place. At 10-minute intervals the gate valve was opened and the precipitated salt withdrawn. The liquid sludge that was removed was filtered immediately through a Büchner funnel and the filtrate returned to the evaporator. The filtered salt contained about 10 per cent water, although it is apparent that, by centrifuging the crystals, the moisture content could be reduced to 5 per cent. The run was discontinued after 2 hours and 10 minutes. Examination of the evaporator showed no scale on the body. The burner, however, showed a fusion of salt forming a hollow cone over the end and leaving a hole barely large enough for the escape of the products of combustion. This is easily removed by a blow from a hammer.

A more detailed investigation of this cone formation was undertaken. A modified burner was constructed so that changes in orifices could be made. Two such burners are shown in Figure 4. They were constructed from standard pipe fittings. *B* is a reducer 1 to 1/4 inch (2.5 to 0.64 cm.) in size, *D* a 1-inch (2.5-cm.) nipple 1 1/4 inches (3.2 cm.) long, and *H* a 1-inch cap. *A* is connected to the gas-air supply from the mixing chamber through a 1/8-inch (0.32-cm.) pipe to insure a high velocity to the gas mixture, thus preventing the flame from flashing back through the piping. *C* is a screen, such as the screen from the top of a laboratory Meeker burner or a number of layers of iron wire gauze. The screen separates the flame zone in *D* from the gas-air zone in *B* by increasing the velocity of the gas-air mixture and preventing the flame from flashing back of the screen. To *D* may be connected a cap, *H*, drilled to give any type orifice, as *I*. For the study of cone formation a 1/4-inch (0.64-cm.) hole was drilled in the cap.

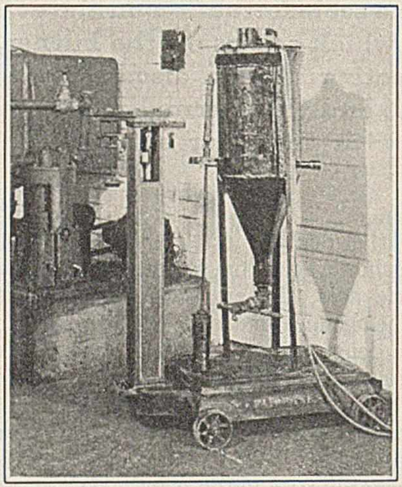

FIGURE 3. EQUIPMENT FOR LARGE-SCALE RUNS

One difficulty in studying the scale formation was that, once the burner was immersed in the solution, nothing could be seen of the scale and its formation until the burner had been removed from the solution. The gas and air flowmeters showed decreasing flows as the run progressed, although when the burner was removed from the solution only a small scale form could be seen on the outside of the orifice surrounding the flame zone. Since this scale was small and appeared to offer no resistance to the flow, it did not seem logical to attribute the decreasing flows to scale. However, to investigate this phase more fully, an evaporator was constructed with a Pyrex glass window. By placing the burner relatively close to the glass, sufficient light was given off by the flame to observe the scale forming. Observations of runs made in this manner showed that scale formed around the flame zone continuously once the solution became saturated. This scale form was red hot at all times when the burner was lighted. The shape and permanency of this scale form were matters of chance. If the velocity of the issuing gases changed slightly, or if the burner moved suddenly, or if the gas-air ratio changed slightly and thus caused a change in the flame issuing from the orifice, the scale form might blow off or change its shape. Although the scale forms never seemed to be solidly attached to the burner, they were strong enough to exert sufficient resistance to gas flow so that the flame would be extinguished in a half-hour run in a saturated solution. If the flame was extinguished while the burner was still in the solution, the scale form broke. This behavior was due to the sudden contraction of the red hot scale as the solution conducted the heat away from the scale very rapidly. This explained why no appreciable amount of scale was attached to the burner when the flame was extinguished while the burner was in the solution and then removed. When the burner was removed while the flame was still lighted, the heat of the flame on the scale melted it before it could be investigated. To obtain specimens of scale form, the burner was pulled out of the solution quickly and the gas-air supply was closed the instant the burner was out of the solution. Figure 5 shows a group of scale forms obtained. Those in the upper row were formed in solutions of sodium sulfate obtained from natural deposits. This salt contained some foreign material which caused the peculiar formation. Those in the lower row show scales formed from pure sodium sulfate.

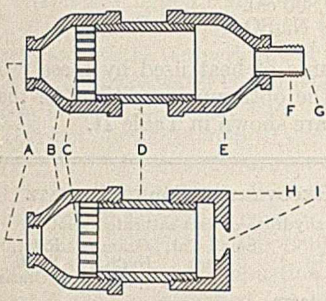

FIGURE 4. SMALL BURNERS

A mechanical device for removing the scale formed was one satisfactory solution of the problem. A simple rotating wiper moved across the path of the flame at frequent intervals. The wiper was not placed in direct contact with the face of the burner, but the scale was allowed to form and then be broken. The scale cone did not grow beyond the path of the revolving rod and was hollow, so that it did not interfere with the flame.

TABLE I. SCREEN ANALYSES OF SODIUM SULFATE CRYSTALS

Screen Size	Per Cent Retained on Screen				
	1[a]	2	3	4	5
Mesh					
On 28	0.2	5.4	0.3	3.4	1.6
35	0.8	4.5	2.2	4.6	2.9
48	3.4	6.6	10.2	10.3	9.9
65	14.1	5.8	9.2	24.7	14.1
100	50.0	13.4	39.0	15.6	30.2
150	22.6	15.4	28.5	15.7	19.6
200	6.3	19.7	8.2	14.3	10.9
Pass 200	2.7	29.4	2.5	11.3	10.7

[a] Sample 1, evaporation of a saturated solution with a quiet zone maintained in the cone of the evaporator when crystal growth could occur; sample 2, evaporation of a solution with violent agitation; sample 3, evaporation with 200 grams decahydrate fed into the solution every half-minute; sample 4, as in 3 but feed increased to 2–4 kg. every 5 minutes; sample 5, commercial salt cake used by a local kraft pulp mill.

A nozzle orifice and high gas velocity were the most satisfactory solution to the scale problem. The drilled cap was replaced by a reducer, *E* (Figure 4), fitted with a $^1/_4$-inch (0.64-cm.) close nipple, *F*. This nozzle not only allows a high gas velocity but it has only a very thin edge to which the cone may adhere. The cone would form to a length of about 2 inches (5 cm.) and then blow off. Fluctuations shown on the pressure gage on the gas-air mixing chamber showed when and how the cone was growing. By varying the gas-air ratio and pressure, practically no fluctuation in the pressure gage was found, indicating either no scale formation or no change in nozzle opening. On removing the burner, a thin scale formation was found on the rim at the edge of the close nipple. During the remainder of the run the scale varied from $^1/_4$ inch (0.64 cm.) to $^3/_4$ inch (1.92 cm.) in length. Under these conditions it was found that the sodium sulfate was being melted on the inside of the cone and being blown out. This effect was considerably different from that of the run at lower heating rates, where scale in the cone reached a thickness of $^1/_{16}$ inch (1.6 mm.) or greater. The flame temperature calculated for this particular gas-air ratio corresponds to the highest available with this city gas and air. Thus, a sharp-nozzle orifice, high rate of flow of hot gas, and high flame temperature successfully prevent scale formation when the gases are projected into the solution.

Crystal Formation

The product obtained is crystalline. Screen analyses of the product under various conditions of operation are given in Table I.

A microscopic examination of the various crystals formed showed individual crystals in all except sample 2. The larger crystals here consisted of many very small crystals cemented together.

Thus, variation of crystal size can be effected by control of operating conditions. By providing maximum agitation of the solution, the product formed predominates in crystals of small sizes. With less agitation where a quiet zone is provided and where the crystals have opportunity to grow, the resulting product has a greater percentage of large crystals. With the intermittent feed, variation in crystal size is affected by the amount of feed in unit time, but in general, the crystals seem to be larger than in the case of evaporation only.

Submerged Combustion Cycle

With a submerged combustion evaporator using sodium sulfate decahydrate as the feed, a cycle of operations may be constructed. Figure 6 shows such a cycle:

Decahydrate, *A*, is introduced into the evaporator body, *B*, where it comes into contact with a saturated solution of sodium sulfate at 90° C., the boiling point with submerged combustion. The decahydrate is heated to the transition temperature and melts, depositing sodium sulfate, and the saturated solution is heated to 90° C., depositing more sodium sulfate which is removed at *C* to be centrifuged and completely dried. The saturated solution formed when decahydrate melts may be treated in two ways. The water may be evaporated, leaving the salt, or the solution may be run to a cooling pond, *D*, where it cools to outdoor temperature. This latter process will result in the deposition of more decahydrate which may be removed and reintroduced into the evaporator, *E*. The mother liquor from the crystallization is discarded, *F*, or placed in other ponds for solar evaporation for recovery of all salt as decahydrate. Assuming a gram

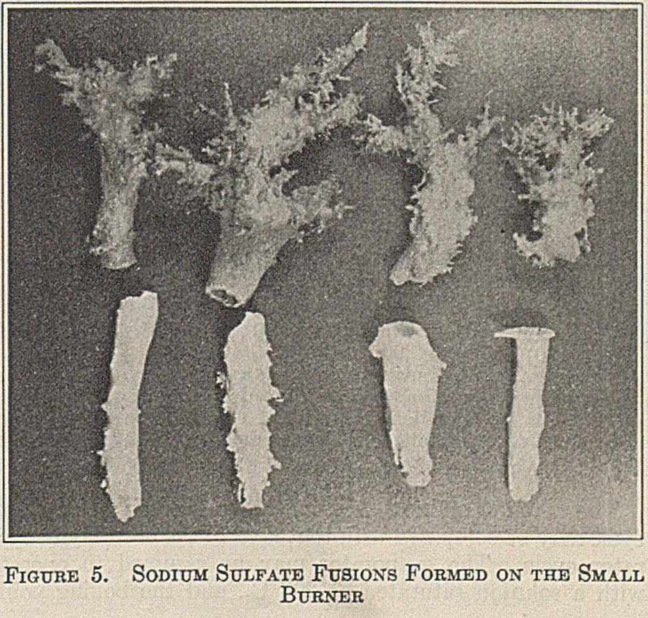

FIGURE 5. SODIUM SULFATE FUSIONS FORMED ON THE SMALL BURNER

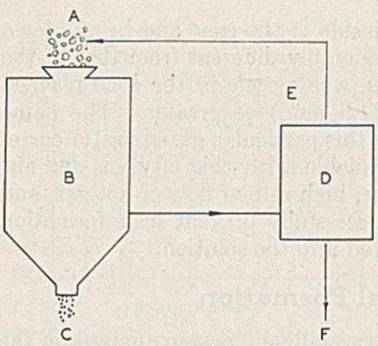

FIGURE 6. CYCLE FOR RECOVERY OF SODIUM SULFATE FROM SODIUM SULFATE DECAHYDRATE

mole of sodium sulfate decahydrate (142 grams sodium sulfate and 180 grams water) is introduced at *A*, the melting and solubility effect at 90° C. will cause 46.1 per cent (65.5 grams) of the sodium sulfate to precipitate in *B* and be removed at *C*. The saturated solution (76.5 grams sodium sulfate and 180 grams water) removed to *D* contains 53.9 per cent of the sodium sulfate introduced. If we assume the outdoor temperature of the crystallizing pond, *D*, to be 20° C., there will be precipitated 125.0 grams sodium sulfate decahydrate (55.1 grams sodium sulfate), or 38.8 per cent of the sodium sulfate introduced can be recycled, *E*. The mother liquor discarded, *F*, from the crystallizing pond contains 110.1 grams water and 21.4 grams sodium sulfate, or 15.1 per cent of that introduced.

Thermal Requirements of the Cycle

The amount of heat necessary to carry out the cycle may be calculated. New thermal data are reported in another paper (*5*). The values will allow the calculation of optimum conditions for the cycle and give a comparison with the usual evaporation process:

Reference temperature: 20° C.
Basis: 1 gram mole $Na_2SO_4 \cdot 10H_2O$ (Na_2SO_4 = 142 grams, $10H_2O$ = 180 grams)

1. Heat required to raise $Na_2SO_4 \cdot 10H_2O$ to the transition temperature:
   Specific heat $Na_2SO_4 \cdot 10H_2O$ = 119.8 cal./mole
   $(119.8)(32.4 - 20) = 1490$ cal.

No experimental data are available for the specific heat of the decahydrate so Kopp's rule was employed.

2. Heat of transition = 18,700 cal./gram mole (*5*)
3. Heat required to raise saturated solution from 32.4° to 90° C.:
   Average weight of solution = 265 grams
   $(90 - 32.4)(265)(0.783) = 11,930$ cal.

Because of the inverted solubility curve, the weight of saturated solution is not constant. A graphical integration shows the average weight to be 265 grams over the temperature range 32.4° to 90° C.

The mean heat capacity of the saturated solution over the temperature range 32.4° to 90° C. is found by graphical integration of the heat capacity curve of Kobe and Anderson (*5*) to be 0.783 cal./gram.

4. Heat required to raise the precipitated salt from 32.4° to 90° C.:
   Average weight of Na_2SO_4 = 60.2 grams
   Specific heat of Na_2SO_4 = 0.21
   $(90 - 32.4)(60.2)(0.21) = 730$ cal.

A graphical integration of the Na_2SO_4 solubility curve shows an average of 60.2 grams present. The average specific heat over this range is taken to be 0.21 (*3*).

Heat required for Na_2SO_4 by temperature solubility effect equals only:

$$1490 + 18,700 + 11,930 + 730 = 32,850 \text{ cal.}$$

This precipitates 65.5 grams Na_2SO_4, leaving 256.5 grams saturated solution (76.5 grams Na_2SO_4, 180 grams H_2O).

5. Evaporation of the water in the solution:
   Latent heat of evaporation of 90° C. = 555 cal./gram H_2O
   $(180)(555) = 99,900$ cal.

The latent heat of evaporation was calculated from the slope of the Dühring line for water-saturated solution vapor pressures (*12*). This includes both the heat of vaporization of the water and the heat of precipitation of the salt from the saturated solution.

The amount of heat used in the submerged combustion cycle may be compared with that used in the ordinary evaporator cycle. The evaporator may be assumed to operate with a solution saturated at 20° C., and the boiling point and latent heat of evaporation may be assumed to be the same as for a solution saturated at its boiling point (102.8° C.):

Reference temperature: 20° C.
Basis: 1 gram mole Na_2SO_4 in a saturated solution (142 grams Na_2SO_4 + 747 grams H_2O = 889 grams solution)

6. Heat required to heat solution from 20° to 102.8° C.:
   Specific heat of solution saturated at 20° C. = 0.84 (*9*)
   $(102.8 - 20)(889)(0.84) = 61,800$ cal.
7. Evaporation of the water in the solution:
   Latent heat of evaporation at 102.8° = 551 cal./gram H_2O
   $(747)(551) = 412,000$ cal.
   Total heat required:
   $61,800 + 412,000 = 473,800$ cal.
   This precipitates 142 grams Na_2SO_4.

A comparison of the amounts of heat used by these two systems of evaporation and the optimum conditions for the submerged combustion cycle are shown in Table II.

TABLE II. HEAT USED IN RECOVERY OF SODIUM SULFATE

(Basis: 142 grams Na_2SO_4 as decahydrate or as a saturated solution)

Process	Small Cal. Heat Used	Grams Na_2SO_4 Pptd.	Ratio, Small Cal./Grams
Heating $Na_2SO_4 \cdot 10H_2O$ to transition temp., 1 + 2	20,190	52.5	385
Heating $Na_2SO_4 \cdot 10H_2O$ to b. p. (90° C.), 1 + 2 + 3 + 4	32,850	65.5	502
Heating $Na_2SO_4 \cdot 10H_2O$ to b. p. (90° C.) and evaporating water, 1 + 2 + 3 + 4 + 5	132,750	142	934
Heating soln. satd. at 20° C. to b. p. (102.8° C.) and evaporating, 6 + 7	473,800	142	3338

The optimum condition for the operation of the submerged combustion cycle would be to heat the decahydrate crystals only to the transition temperature and supply the heat of melting. The difficulty of doing this is apparent. In order to have heat transfer from the saturated solution to the decahydrate crystal, it is necessary that the solution be at a temperature enough above the transition point so that the necessary heat will be transferred to the crystal as it drops through the solution. This temperature will be a function of the crystal size, and it is apparent that the heat required will decrease as the temperature is the lowest at which sufficient heat transfer can be obtained. When heating by submerged combustion, some evaporation must take place. The figures in Table II do not take this into consideration.

The evaporation process (6 + 7) shows that, even if a triple-effect evaporator were used and its theoretical steam economy of 3 assumed, the amount of heat required would still exceed that for the submerged combustion evaporation starting from decahydrate as feed. It would be possible to combine the advantages of both processes by using submerged combustion for the difficult task of melting the crystal and heating the solution to the boiling point. The saturated solution may then be transferred to a multiple-effect evaporator where its steam economy may be

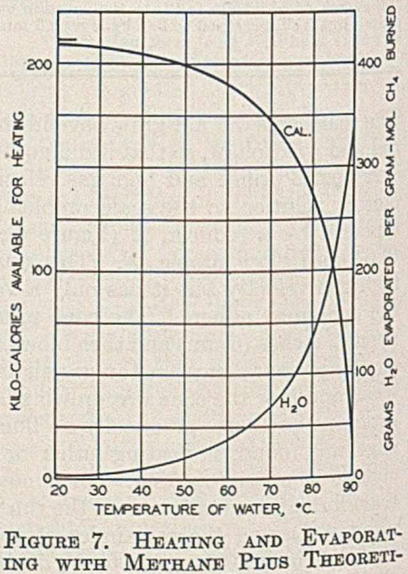

FIGURE 7. HEATING AND EVAPORATING WITH METHANE PLUS THEORETICAL AIR FOR COMBUSTION

used to reduce the heat required for the evaporation process. In such a combination the relatively simple submerged combustion melting tank produces 46.1 per cent of the sodium sulfate whereas the multiple-effect system produces the remaining 53.9 per cent. Calculation shows that the heat requirement of a triple-effect evaporator working on this saturated solution is about the same as the submerged combustion melting tank, per gram of sodium sulfate produced.

Submerged Combustion for Heating

When submerged combustion heating is used, evaporation is always taking place as the products of combustion leave saturated at the temperature of the liquid. At lower temperatures very little water is carried out with the gas; in fact, water may be given up to the solution by the water of combustion. This fact allows submerged combustion heating to utilize the gross heating value of the gas or permits an efficiency of over 100 per cent based on the net heating value of the gas, a value which astounded early workers and cast some discredit on their calculations. The boiling point of the liquid is that at which the heat of combustion is equal to the heat of evaporation of the water carried out at that temperature, plus any other thermal effects.

If the combustion reaction in which methane is burned with the theoretical amount of air in water is considered, the fraction of the heat available for heating purposes may be calculated. The results are shown graphically in Figure 7; below 50° C. more than the net heating value of the methane is available for heating purposes. As the temperature of the water rises, more of the heat is used for evaporation and less is available for heating. The amount of water evaporated by this combustion reaction increases rapidly with temperature. For sodium sulfate recovery, the optimum temperature of operation is the lowest possible, for here the greatest proportion of the heat available is used for heating the solution. The heat used for evaporation is not wasted, since sodium sulfate is deposited from the saturated solution, but the heat is used in a less efficient manner than in the heating cycle.

Discussion of Results

The submerged combustion cycle shown in Figure 6 was designed primarily to operate on natural Glauber's salt where the cost of the raw material is small, ample outside storage space is available, and large crystallizing ponds may be constructed to care for the liquor from the evaporators. Evaporation either by submerged combustion or tube evaporators may be used on this liquor so that recrystallization is avoided. However, it has been definitely shown that the heat requirement per unit of sodium sulfate precipitated is lowest when the decahydrate crystal is melted, so that, whenever these crystals are available, a melting process should be used rather than a solution process to produce a saturated solution. Submerged combustion offers a ready solution to the technical difficulty of melting these crystals.

Previous runs made for the submerged combustion of water and sulfite waste liquor (*6*) showed thermal recoveries of 92 to 96 per cent. The runs on sodium sulfate solutions gave thermal equilibrium between the liquid and the gases leaving, so that efficiencies should remain equally high if the evaporator body is insulated. Gaseous fuel was used in this work since the necessary equipment was already available; however, fuel oil can also be adapted to submerged combustion.

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IV. Potassium Chloride from Sylvinite

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THE discovery of large deposits of potassium salts in the Permian basin of Texas and New Mexico has founded a new industry in these states. Potassium chloride is produced by refining sylvinite, the approximate composition of which is 42.7 per cent potassium chloride, 56.6 per cent sodium chloride, and 0.7 per cent insoluble matter.

The refining of sylvinite was discussed by Ward (*4*) and a flow sheet was given (*2*). The method is essentially that of Blasdale (*1*). A solution saturated with sodium chloride and potassium chloride at 20° C. is placed in contact with the sylvinite and the temperature raised to the boiling point (108° C.) by admitting live steam to the digesters.

The numerous advantages of submerged combustion heating for many chemical processes (*3*) show that it might be possible to use this efficient form of heating in place of steam in the digesters. The solubility curves of sodium and potassium chlorides are typical of salts having, respectively, flat and rapidly rising solubilities, and their behavior may then be compared with sodium sulfate and its inverted solubility curves (Figure 1, Part III).

Submerged combustion heat may be successfully applied to the recovery of potassium chloride from sylvinite. Conditions of operation for salts with flat and rising solubility curves are given and shown to be different from those with inverted solubilities.

Evaporation of Salt Solutions

The previous work with sodium sulfate showed the difficulty encountered with a salt having an inverted solubility curve. In order to determine the evaporation characteristics of salts with other types of solubility curves, saturated solutions of sodium chloride and potassium chloride were evaporated. It was at first believed that sodium chloride with its flat solubility curve might behave similarly to sodium sulfate. A burner with a high-velocity nozzle formed by a $^1/_4$-inch (0.64-cm.) close nipple (upper part of Figure 4, Part III) soon plugged with a hard scale about $^1/_8$ inch (0.32 cm.) inside the burner nozzle. The scale was not more than $^1/_{32}$ inch (0.8 mm.) thick and had built out from the circular opening. This type of nozzle was replaced by a cap, *H*, drilled to give a sharp-edged orifice, *I* (Figure 4, lower part). This burner was found to give continuous operation; however, the pressure in the mixing chamber fluctuated continually, indicating that scale was forming at the orifice and being blown off.

Potassium chloride has a rising solubility curve. Conditions for evaporation were found to be identical with those of sodium chloride. Pressure fluctuations covered the same range but were a little more rapid, undoubtedly because of the more concentrated solution.

Potassium Chloride from Sylvinite

A saturated solution of sylvinite at room temperature was made as the original leaching liquor. This was placed in a cone-bottom evaporator (Figure 3, Part III), the lighted burner placed in the solution, and the calculated amount of sylvinite added to saturate the solution with potassium chloride. The agitation of the hot gases from the burner bubbling through the solution was sufficient to keep the sylvinite crystals suspended in the solution. The solution came to a boiling point of 90° C.; because of the partial pressure of the products of combustion, the boiling point was below 100° C. After a short time at the boiling point the burner was removed, the sodium chloride crystals were allowed to settle, and the solution was removed to a crystallizing tank. A pale pink mass of crystals of potassium chloride separated out as the solution cooled.

Two modifications can be made in the process (*2*) when submerged combustion heating is used. The submerged combustion of natural gas replaces steam for the heating. The steam digester has a liquor circulating pump, which will be unnecessary with submerged combustion heating. The burners can be placed directly in the digester and thus give excellent agitation of liquor, or they can be placed in a side tube connecting the bottom and top of the digester. The release of the products of combustion will give the same effect as an air lift and circulate the liquor in the digester.

The yield of potassium chloride per unit of solution will not be as great with submerged combustion heating as with steam heat. With the latter the boiling point of the solution is 108° C.; with the former it is reduced to 90° C. Reference to the solubility isotherms of Blasdale (*1*) shows that this will decrease the amount of potassium chloride in solution from 37 pounds potassium chloride per 100 pounds water at 108° C. to 32.5 pounds potassium chloride per 100 pounds water at 90° C. If the solution is cooled to 20° C., the recovery in the latter case is only 80 per cent of the former. This indicates that the capacity of the plant is theoretically reduced by 20 per cent when submerged combustion is used. Actual reduction in capacity cannot be predicted, since certain features of submerged combustion might offset the lowered solubility by giving greater rate of solution.

Acknowledgment

The writers wish to thank the U. S. Potash Company for supplying the sylvinite used in this investigation.

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V. Sodium Carbonate Decahydrate

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THE natural deposits of sodium carbonate in the western states differ, as do the deposits of sodium sulfate, from those in the southern and northern parts. The California deposits are trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) which may readily be calcined to give sodium carbonate. The Oregon and Washington deposits are sodium carbonate decahydrate. This hydrate contains 63 per cent water and must be dehydrated before shipping. The methods are almost the same as those used for sodium sulfate, since both salts are so similar in their physical properties. Both have transition temperatures at 32° to 35° C., and both have inverted solubility curves above the transition temperature, although the stable phase for sodium carbonate is the monohydrate whereas the sodium sulfate is anhydrous.

Submerged Combustion Cycle

In order to study the dehydration of sodium carbonate decahydrate by the cycle of operations proposed for sodium sulfate decahydrate (Part III), similar calculations were made. When sodium carbonate decahydrate is melted, sodium carbonate monohydrate and saturated solution are formed. When the $Na_2CO_3 \cdot 10H_2O$ is introduced into a saturated solution at 40°, 18.6 per cent of the sodium carbonate precipitates as $Na_2CO_3 \cdot H_2O$, and if the temperature is increased to 90° C., 25 per cent of the sodium carbonate precipitates. This is much smaller than the corresponding values for sodium sulfate from $Na_2SO_4 \cdot 10H_2O$.

If one gram mole $Na_2CO_3 \cdot 10H_2O$ is introduced at *A* (Figure 6, Part III) into a saturated solution at 90° C., 25 per cent of the sodium carbonate will precipitate as the monohydrate (31 grams) leaving 75 per cent of the sodium carbonate in solution (79.5 grams sodium carbonate and 175.5 grams water). When this is pumped to the outdoor crystallizing pond at an assumed temperature of 20° C., 61.3 per cent of the sodium carbonate crystallizes as the decahydrate (175 grams), leaving 13.7 per cent to be discarded (14.5 grams sodium carbonate and 65 grams water). Compared to sodium sulfate decahydrate, the sodium carbonate decahydrate gives a smaller recovery in the cycle, but less salt is discarded from the crystallizing pond so that more decahydrate is recycled.

The data in the literature are insufficient to calculate a thermal comparison with the evaporation method, although the same general conclusions for sodium sulfate decahydrate hold for sodium carbonate decahydrate.

The type of burner used for sodium sulfate solutions (Figure 4, upper part) was found to operate most satisfactorily. The salt that precipitated on the burner formed a chalklike mass and did not cake hard as did the sodium sulfate. Cone formation was very small and crumbly, and a large-size cone could not be formed with this type of nozzle. The formation was not even of sufficient strength to cause fluctuations in the gas-air pressure gage.

The explanation is that the monohydrate first precipitated is dehydrated by higher temperature of the flame and leaves a crumbly mass easily blown off. The sodium carbonate does not fuse as does the sodium sulfate, for sodium carbonate taken off the burner combustion chamber dissolved readily, which is not the case for the sodium sulfate burner scale.

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Enzyme Activity in FROZEN VEGETABLES

The catalase content of peas and spinach varies with the temperature of scalding. In a series of samples blanched at constant time, it is greater in those blanched at 40° C. than in those at 20° and 50°. The quality of the product is slightly affected in proportion to the catalase activity, but it is necessary to heat to higher temperatures than those required to inactivate the enzyme in order to secure a product of good quality.

The acetaldehyde content of peas is apparently related to the catalase activity as the two curves are decidedly similar. The acetaldehyde content of spinach remains constant and is not related to the enzyme content.

A satisfactory product has been obtained by scalding peas for 2 minutes at 80° to 90° C. They have retained their good quality for over 2 years in freezing storage.

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THAT changes occur in the flavor of most vegetables during freezing storage is common experience (*2–6, 8, 10, 12–18, 20*). The changes in flavor have been ascribed to the activity of enzymes which were not entirely inhibited by low temperatures and ice formation. Kohman (*13*) in 1928 pointed out that "cooking vegetables merely enough for serving" preserves the flavor of vegetables in freezing storage. Barker (*2*) in 1930[1] also recommended partial cooking; peas were cooked for about 8 minutes in water. Joslyn and Cruess (*10*) in 1929 favored blanching for a short period and Joslyn (*9*) pointed out that the destruction of the enzymes by heat should be carried out under conditions which would result in the minimum of injury to flavor and texture. It is well known that prolonged blanching is detrimental to flavor (*7, 11, 16*). Although today the preliminary blanching of the raw product to destroy the enzymes present prior to freezing is an accepted practice, Magoon (*16*), in 1931, questioned the reliability of the process.

To establish the process of blanching and chilling prior to freezing on a sound basis, it is necessary to know the nature of the enzymes or other agencies involved and the type of changes brought about in the product. Kohman (*15*) believes that the changes in flavor are brought about by a process of anaërobic respiration and more directly by respiratory enzymes. Barker (*2*) speaks of the process as autolysis. Tressler (*20*) believes that the reactions are both oxidative and hydrolytic in nature and implies that enzymes such as catalase and tyrosinase are involved.[2] Diehl et al. (*6*) found that the catalase activity in Alderman peas served as an index for adequate blanching. Peas blanched at sufficiently high temperatures and for a sufficiently long time to destroy catalase remained unaltered in flavor when stored for several months at −6.5° C. (20° F.) or lower. Peas showing positive catalase activity developed haylike flavors and odors with attendant changes in color. Joslyn and Marsh (*12*) found that peroxidase activity was not involved in changes in flavor; the inactivation temperature (and time) for peroxidase was considerably higher than the temperature necessary to inactivate the more thermolabile enzymes responsible for flavor changes.

Because of the close relationship between respiratory enzymes and catalase, it is possible that catalase activity may serve as an index of the activity of these enzymes.

It is well known that acetaldehyde is formed in appreciable amounts during anaërobic respiration; therefore acetaldehyde content should serve as an index of respiratory activity. To determine whether respiratory enzymes are involved and to test their relation to catalase activity, the acetaldehyde content and catalase activity of California garden peas and spinach, blanched at various temperatures for various lengths of time and stored at 0° F. (−17.8° C.) for over 2 years were determined, and the results are reported in this paper.

Preparation and Storage of Material

Locally grown Telephone variety peas were shelled by hand, and, after mixing and washing, aliquots were treated (blanched) in water for 2 minutes at 20°, 40°, 50°, 60°, 65°, 67.5°, 70°, 72.5°, 75°, 77.5°, 80°, 85°, 90°, 95°, and 100° C., respectively. The peas were immersed in a 12-gallon (45-liter) water bath in loosely tied cheesecloth bags containing approximately 3 pounds (1.4 kg.) of peas.

Each successive lot was blanched in the same water. After blanching, the peas were rapidly cooled in running cold water, packed into 8-ounce (237-ml.) tin cans, sealed, and stored at −17° C. Peas were also blanched in water for various lengths of time from 30 seconds to 60 minutes at 55°, 65°, and 75° C.; and in boiling water and in flowing steam for 15 and 30 seconds, and 1, 2, and 5 minutes, respectively.

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[1] Subsequently he reported that as little as 1 minute of blanching of peas prior to storage at −10° C. gave promising results [see T. N. Morris and J. Barker, Brit. Dept. Sci. Ind. Research, *Rept. Director Food Investigation*, 1933, 77–80 (1934)].

[2] In a private communication he pointed out that little scum forms and no foaming occurs during the cooking of properly blanched peas; during the cooking of underblanched peas, much foaming occurs and much scum forms.

Table I. Effect of Temperature of Blanching on Catalase Content

Temp., ° C.	Catalase Factor Peas	Catalase Factor Spinach
20	0.03468	0.02600
40	0.03905	0.03526
50	0.01877	0.02627
60	0.01163	0.00940
65–100	0.00000	0.00000

Table II. Effect of Period of Blanching on Catalase Content

Time	Catalase Factor 55° C.	65° C.	75° C.	100° C. (H_2O)	100° C. (steam)
Min.					
			Peas		
0.25	...	...	...	0.00000	0.01630
0.5	...	0.00930	0.00000		0.00000
1	0.01697	0.00455			0.00000
2	0.01466	0.00000			
4	0.01318	0.00000			
8	0.02480				
12	0.02000				
16	0.01732				
20	0.01480				
60	0.00000				
			Spinach		
0.25	...	...	...	0.00000	0.00778
0.5	0.03220	0.03368	0.02790		0.00000
1	0.04080	0.01521	0.02220		
2	0.03718	0.00180	0.00650		
4	0.02557	0.00000	0.00000		
8	0.01875				
20	0.01632				

In this set of tests the quantities of peas needed for the samples were tied in separate cheesecloth bags. All the bags that were to be held at a constant temperature were then immersed in a 12-gallon water bath; at definite prearranged intervals a bag of peas was removed, cooled in running water, packed, sealed, and stored. The water in the bath was changed for each succeeding temperature interval. In addition, in order to remove air from intercellular spaces and to destroy organic peroxides, samples of peas were impregnated in water, 3 per cent salt solution, 1 per cent hydrochloric acid solution, and 1 per cent tartaric acid solution by a process of vacuumization followed by release with air which was repeated for several cycles. The peas were under the various solutions mentioned when air replaced the vacuum. The spinach, after trimming and washing, was treated in like manner. The material was held at about −17° C. for over 2 years before examination.

Analytical Methods

Catalase. The catalase was determined by a slightly modified Balls and Hale procedure (*1*), which is itself a modification of the German method of Stern (*19*). Four grams of material were used instead of 2 grams, the catalase activity was measured at 20° C. instead of 0° C., and 4 *N* sulfuric acid was used instead of 2 *N*. Precautions were taken to avoid loss of iodine by volatilization. In other respects the method was that described by Balls and Hale, and the results are reported in terms of the catalase factor, K_f or k units per gram of fresh material.

Acetaldehyde Determination. Acetaldehyde was determined by the iodometric bisulfite procedure. A can of peas or spinach removed from freezing storage was finely ground cold, in a food chopper, and 50 grams of the ground sample were then steam-distilled. (It was necessary to use 5 to 10 cc. of crystal oil to prevent excessive foaming during the distillation.) The distillate was collected in a 500-cc. Erlenmeyer flask, and distillation was continued until 300 cc. of distillate had been collected. The receiving flask was kept in an ice bath during the distillation to prevent vaporization losses. As soon as 300 cc. of the distillate had been collected, the flask was removed from the ice bath and enough ethyl alcohol added to bring the total percentage to 10 per cent by volume. Then 10 cc. of 0.1 *N* potassium acid sulfite were added. The flask was then tightly stoppered and allowed to stand for exactly 30 minutes. At the end of 30 minutes 10 cc. of 0.1 *N* iodine were added, and the sample was titrated at once with 0.1 *N* thiosulfate, using starch indicator. A blank determination was made in the same manner using 300 cc. of distilled water in place of the distillate. The difference between the amount of thiosulfate used by the blank and the amount used by the distillate is the amount equivalent to the acetaldehyde present in the distillate. This method is subject to the criticism that other volatile sulfite-fixing and iodine-reducing matters may be involved. However, the method is commonly used for this purpose.

Only one series of spinach samples was tested for acetaldehyde content because it was found that the aldehyde content of spinach remained constant throughout the series. However, the complete series of peas was analyzed.

Organoleptic Observations

Samples of the canned frozen material were removed from freezing storage, allowed to thaw for several hours, opened boiled in 2 per cent sodium chloride solution for 10 minutes, and observed for color, odor, texture, and flavor before and after cooking. In the samples of peas blanched at a constant time of 2 minutes, decided color change occurred in the sample blanched at 70° C. Samples blanched below this temperature were a dull olive green color, those blanched at higher temperatures were the bright grass green characteristic of properly blanched peas. On cooking, the 70° and 75° C. samples turned to olive green whereas the sample blanched at 77.5° C. and above retained the green color. Texture changes occurred in the sample blanched at 90° C. Samples blanched below this temperature were of crisp texture and remained so on cooking. The 90°, 95°, and 100° C. samples had tough

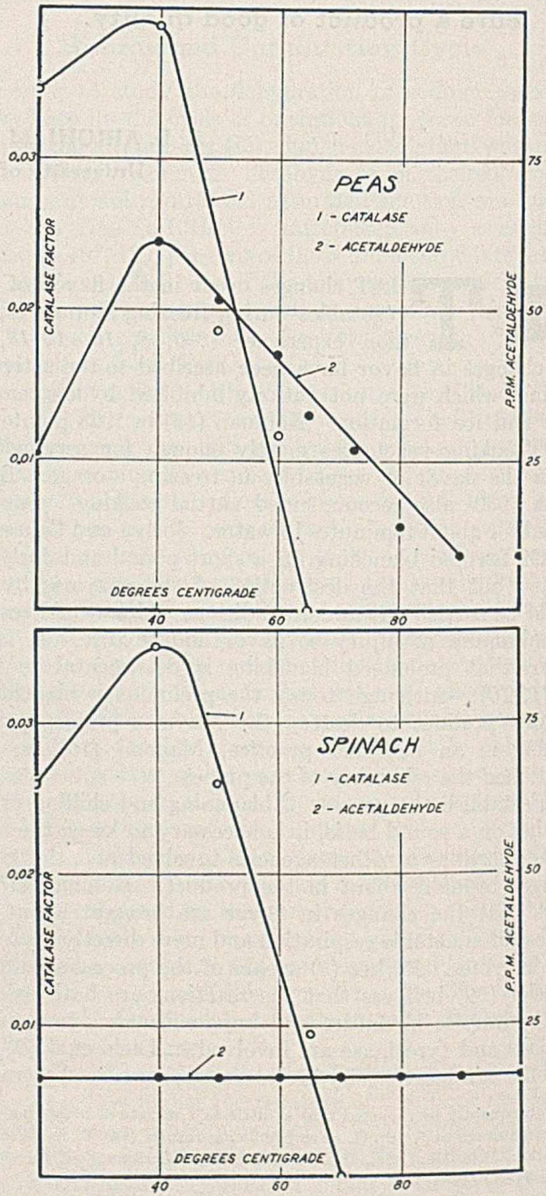

Figure 1. Catalase Activity and Acetaldehyde Content of Peas and Spinach Blanched at Various Temperatures

skins, and the cotyledons were of mushy texture, mushiness increasing with temperature. The skins separated from the cotyledons on cooking. Noticeable differences in flavor and odor occurred in the ranges of temperatures from 20° to 77.5° C., 80° to 85° C., and 90° to 100° C. Before and after cooking, the odor and flavor of the samples blanched in the temperature range of 20° to 77.5° C. were decidedly haylike and disagreeable. It was more pronounced in the sample blanched at 40° C. than in the unblanched sample at 20° C., and decreased in intensity as the temperature of blanching increased. The samples blanched at 80° and 85° C. had a clean, fresh pea odor and flavor comparable in all respects to those of the fresh product. In the cooked 90°, 95°, and 100° C. samples it was possible to detect an off-odor and off-flavor not usually associated with cooked peas; these effects increased in amount as the temperature increased.

Samples of peas blanched for various periods of time at 55°, 65°, and 75° C. were all found undesirable in color, odor, and flavor. Samples blanched for periods of time longer than 10 minutes at these temperatures were also decidedly mushy in texture on cooking.

The samples of spinach blanched at various temperatures for constant time were similar in behavior to peas in regard to the effect of temperature of blanching on color, odor, and flavor, but to a less marked degree and over broader temperature ranges. The samples blanched from 20° to 85° C. were of poor color, odor, and flavor. Those blanched above 85° C. were satisfactory in color and flavor and were equal to freshly cooked spinach in all respects.

Discussion of Data

The catalase activity of peas and spinach scalded at various temperatures for 2 minutes is shown in Table I, at various temperatures for different periods of time in Table II, and impregnated with various agents in Table III. The samples of peas blanched at 40° C. contained more catalase than those blanched at either 20° or 50° C. This behavior is in keeping with the organoleptic observations which also showed that this sample was inferior to the others. Impregnation with water did not inhibit catalase but sodium chloride seemed to reduce the activity of the enzyme. Hydrochloric and tartaric acids completely inactivated it; however, the vegetables impregnated with hydrochloric and tartaric acids were so badly disintegrated by these agents that they were not fit for use. The results obtained with spinach were similar to those obtained with peas.

The acetaldehyde content, in mg. per kg. of peas and spinach, is shown in Tables IV and V. The trend for acetaldehyde content in peas corresponded rather closely to that for catalase activity, but in spinach the acetaldehyde remained constant throughout the series (Figure 1). The acetaldehyde content of peas is apparently a good indication of quality, since it was found that the amount of acetaldehyde decreases as the quality of the samples improves. However, in the case of spinach, acetaldehyde cannot be used as an index of quality because it remains constant.

Apparently the acetaldehyde found was formed as a result of enzyme activity during freezing storage, for the freshly shelled peas had practically no acetaldehyde and neither did fresh peas directly after blanching. The results on unfrozen peas were obtained on another lot.

Table VI shows the relation of quality of samples to the amounts of acetaldehyde and catalase present. Table VI shows that the catalase content is not a reliable index of quality although it decreases as the quality of the samples becomes better. However, in order to inactivate the agencies producing off-flavor, it is necessary to scald at temperatures considerably higher or for longer times than those necessary to inactivate the catalase. There is a decrease in the amount of acetaldehyde in peas as the quality of the samples becomes better. In the last three samples the mushiness and poor flavor are undoubtedly due to overblanching.

TABLE III. EFFECT OF DEAËRATION IMPREGNATION ON CATALASE CONTENT

Impregnating Agent	Catalase Factor: Peas	Catalase Factor: Spinach
H_2O	0.03050	0.02780
NaCl, 3%	0.01370	0.09800
HCl, 1%	0.00000	0.00000
Tartaric acid	0.00000	0.00000

TABLE IV. EFFECT OF TEMPERATURE OF BLANCHING ON ACETALDEHYDE CONTENT OF PEAS AND SPINACH

Temp. ° C.	Acetaldehyde Peas P. p. m.	Acetaldehyde Spinach P. p. m.	Temp. ° C.	Acetaldehyde Peas P. p. m.	Acetaldehyde Spinach P. p. m.
20	26.4	17.6	75	..	17.6
40	61.6	17.6	80	18.1	17.6
50	52.8	17.6	85	..	17.6
60	44.0	17.6	90	8.8	17.6
65	35.2	17.6	95	..	17.6
70	..	17.6	100	8.8	17.6
72.5	26.4	..	..	..	..

TABLE V. EFFECT OF LENGTH OF BLANCHING PERIOD ON ACETALDEHYDE CONTENT OF PEAS

Time Min.	Acetaldehyde Content: 55° C. P. p. m.	65° C. P. p. m.	75° C. P. p. m.	100° C. (H_2O) P. p. m.	100° C. (steam) P. p. m.
0.25	..	..	..	70.4	61.6
0.5	..	26.4	35.2	61.6	26.4
1	44.0	52.8	61.6	44.0	17.6
2	61.5	44.0	44.0	35.2	8.8
4	52.8	44.0	35.2	..	..
5	..	..	..	17.6	0.00
6	..	39.6	24.6		
8	44.0	35.2	17.6		
10	..	26.4	4.4		
12	26.4	..	..		
15	..	17.6	0.0		
16	26.4				
20	17.6				
60	0.0				

TABLE VI. EFFECT OF ACETALDEHYDE AND CATALASE CONTENTS ON QUALITY OF PEAS

Temp. ° C.	Color	Texture	Remarks	Catalase Factor	Acetaldehyde P. p. m.
20	Olive green	Solid	Poor flavor	0.03468	26.4
40	Olive green	Solid	Worse flavor	0.03905	61.6
50	Olive green	Solid	Poor flavor	0.01877	52.8
60	Olive green	Tough	Poor flavor	0.01163	44.0
65	Olive green	Tough	Poor flavor	0.00000	35.2
67.5	Olive green	Tough	Poor flavor	....	..
70	Better	Firm	Poor flavor	....	..
72.5	Better	Firm	Poor flavor	....	26.4
75	Better	Firm	Fair flavor	....	..
77.5	Greener	Firm	Good flavor, slightly off	....	..
80	Good color	Firm	Good flavor	....	18.1
85	Good color	Firm	Good flavor	....	..
90	Good color	Slightly mushy	Good flavor	....	8.8
95	Good color	Mushy	Fair flavor	....	..
100	Good color	Very mushy	Poor flavor	....	8.8

Figure 1 shows that the acetaldehyde and the catalase contents of peas follow a curve of the same general type. The curve for catalase activity of spinach is similar to that of peas.

The results for catalase activity determined by rate of oxygen evolution from hydrogen peroxide, as followed manometrically in a Warburg apparatus, were closely similar to those obtained by the iodometric procedure.

While making the preliminary determination of acetaldehyde, it was noted that determinations made on the same sample before and after it had been allowed to stand for several hours did not agree. The latter determination was invariably higher in samples blanched at low temperatures. To determine the extent of this increase, three lots of frozen peas, which had been blanched for 2 minutes at 20°, 65°, and 77.5° C., respectively, were defrosted and brought to room temperature in a water bath, ground, and their acetaldehyde contents were determined immediately and after various intervals of time. The data obtained are as follows:

Time of Storage at Room Temp., Hours	Acetaldehyde Content of Peas Previously Treated in Water, Mg./Kg.		
	20° C.	65° C.	77.5° C.
0	26.4	17.6	17.6
3.25	127.6	..	..
4.50	145.2	..	..
5.0	...	44.0	26.4
9.33	127.6	..	..
10.25	...	44.0	26.4
13.0	...	44.0	26.4

The acetaldehyde content of samples of peas which were active in catalase increased on standing after defrosting. The increase was less in samples with the lower catalase activity.

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SULFITE TURPENTINE

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SULFITE turpentine is a by-product obtained from the pulping of spruce by the sulfite process. From 0.36 to 1.0 gallon of this by-product is obtained per ton of pulp, depending upon the conditions of pulping and the quality of the wood, with an annual supply of 1.5 to 2 million gallons from the mills of the United States and Canada (*8*). Most of this is not recovered on account of lack of any appreciable demand for *p*-cymene, the main constituent, at the price required to obtain *p*-cymene of a fair degree of purity from recovered sulfite turpentine. The purification of *p*-cymene is so tedious and expensive that Bert (*5*) claims that his synthetic process will produce *p*-cymene at least at the same price as *p*-cymene obtained from sulfite turpentine. This is important only to countries where sulfite turpentine is not available from domestic sources. Even then, some of the existing demand for *p*-cymene may be supplied by dehydrogenation of monocyclic terpenes as reported in the patent literature (*19*). These terpenes are themselves by-products in some industries, such as in deterpenation of essential oils or in the manufacture of synthetic camphor.

Various suggestions have been made to utilize sulfite turpentine. A fraction within close range of the boiling point of *p*-cymene (175° to 176° C.) may be used as a high-boiling solvent. According to Groggins (*10*) *p*-cymene is a solvent for many gums. Pure *p*-cymene may be used in certain organic syntheses. Wheeler and his co-workers (*22*, *23*, *24*) studied the nitro derivatives of *p*-cymene and prepared various dyes from aminocymene. Nitrocymene can be partially reduced to cymyl hydroxyl amine which can be made to rearrange to form aminothymol. Aminothymol is then diazotized and finally converted to thymol. In the electrolytic reduction of nitrocymene in acid solution by either the Cole (*7*) or the Austerweil (*3*) process, the rearrangement of cymyl hydroxyl amine takes place by itself. In chemical reduction with aluminum amalgam (*4*), cymyl hydroxyl amine is subsequently rearranged by warming its dilute acid extraction for half an hour at 60° C. or by boiling a few minutes. Thymol is converted by catalytic hydrogenation into menthol which is identical in all respects with the natural product except in its lack of optical activity. The annual world consumption of menthol is about 300 tons (*3*). Thymol and menthol, therefore, represent a potential outlet for *p*-cymene depending on whether thymol can be prepared at a price competitive with the price of thymol prepared by other methods. Thymol is prepared synthetically, according to various patents, by condensing *m*-cresol, in the presence of an inorganic acid, with propylene, with isopropyl alcohol, with isopropyl bromide, and with acetone-hydrogen mixture. It can also be prepared from the condensation product of *m*-cresol with acetone. This condensation product is decomposed and then partially hydrogenated. In the absence of cost data, the fact that most of these synthetic processes are patented by companies with headquarters in Germany (Rheinische Kampfer-Fabrik Ges.; Schering-Kahlbaum A.-G.; Chemische Fabrik auf Actien vorm. E. Schering), where sulfite turpentine is not a domestic by-product, suggests that the preparation of thymol starting with *p*-cymene may be successful in countries where it can be obtained in large quantities from sulfite turpentine. With this possibility in mind as one step towards the utilization of sulfite turpentine, pure *p*-cymene was prepared from it for nitration purposes. In the course of this preparation and nitration, certain observations were made, and therefore it

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is the main object of this paper to present them as the first contribution in a series.

Purification of *p*-Cymene

Sulfite turpentine, besides being saturated with sulfur dioxide, is a mixture of *p*-cymene (about 75 to 85 per cent) and various organic substances, mostly terpenes. Boedker (*6*) reports the presence, in addition to *p*-cymene, of terpenes, small amounts of fatty acids, resins, and methyl furfurals. Routala and Pohjola (*17*) give the following composition for sulfite turpentine: 74 to 84 per cent *p*-cymene, 5 per cent terpenes, 10 to 12 per cent sesquiterpenes, in some cases 4 to 5 per cent diterpenes, 2 per cent borneol, dicymene, and fatty and resin acids. After removing sulfur dioxide, a fraction of suitable boiling range may be taken either for use as a solvent or for the preparation of pure *p*-cymene. Pure *p*-cymene boils at 175° to 176° C. while the objectionable malodorous impurities boil below 173° C.; therefore, they can be separated by simple fractionation. Impure *p*-cymene darkens on standing and darkens more easily the wider the boiling range of the fraction. For purification purposes it is desirable to take a narrower range. Fractional distillation, or refluxing over metallic sodium are not alone sufficient to prepare pure *p*-cymene, and therefore Schorger (*18*) recommends treatment with concentrated sulfuric acid previous to fractional distillation over metallic sodium. Wheeler and Smithey (*24*) and Austerweil and Lemay (*4*) also find that such treatment, preceding distillation over metallic sodium, is the only way of purifying *p*-cymene. The purity of the product is tested with concentrated sulfuric acid as recommended by Schorger (*18*). According to this test, pure *p*-cymene will not color concentrated sulfuric acid. Wheeler (*21*) could not confirm the test of Schorger. Karvonen (*12*) and Boedker (*6*), on the other hand, agree with Schorger; Karvonen explains the negative results of Wheeler as due to impurities in *p*-cymene, and Boedker states that impure sulfuric acid becomes colored even with pure *p*-cymene.

Experimental Procedure

The sulfite turpentine used in this study was obtained from the Hammermill Paper Company, Philadelphia. It was saturated with sulfur dioxide. According to Wheeler (*21*), sulfur dioxide is best removed by drawing air through the liquid, allowing 10 hours for 5 gallons. This is a slow process, and therefore it was considered desirable to use sodium hydroxide solution. The removal of sulfur dioxide was very rapid when about 30 per cent solution of sodium hydroxide was used. One extraction was often sufficient to remove all of the sulfur dioxide. After this treatment, the remaining liquid was fractionated, preferably *in vacuo*, to obtain two fractions. The low-boiling fraction (55° to 62° C. at 10 mm.) consisted mainly of *p*-cymene. The high-boiling fraction was not a constant-boiling liquid. Its color changed from yellow to greenish yellow as the temperatures of the distillation rose. This separation was fairly sharp when an oil bath was used and the temperature was maintained at a point required for the distillation of the low-boiling fraction. The cut was made at the time when the thermometer began to fall. For further distillation to obtain the high-boiling fraction it was convenient to use lower pressure. The temperature rose fairly rapidly to 75° C. at 3 mm. and then slowly as the distillation was continued. The distillation was not carried beyond 100° C., although half of the fraction still remained in the flask. The low-boiling fraction represented about 75 per cent of the total. Pure *p*-cymene was obtained from it by treating with concentrated sulfuric acid (specific gravity, 1.84), washing, drying, and fractionating (boiling point = 174.6° C. at 747 mm.; n_D^{20} = 1.4902). The refractive index of pure *p*-cymene obtained from Finnish sulfite turpentine is given by Karvonen (*12*) as n_D^{20} = 1.49051, and from American sources as n_D^{20} = 1.4908 by Schorger (*18*). The use of metallic sodium, after the acid treatment, either for refluxing or for fractionating, did not seem necessary because the same physical constants were obtained.

In case the acid treatment of the low-boiling fraction was omitted, or if the number of acid treatments was not sufficient to remove all of the impurities, and it was refluxed and fractionated over metallic sodium, the residue left in the distilling flask set into a gel upon cooling. Impure *p*-cymene (low-boiling fraction) was treated a few times with concentrated sulfuric acid, washed, dried, and then refluxed for about 10 hours over metallic sodium and fractionated. The residue in the flask set into a soft gel, indicating that the impure *p*-cymene had not been treated a sufficient number of times to remove all the impurities. The residue was not investigated until several days afterwards. The sodium had all disappeared, and the residue itself had become a stiffer gel. When shaken with water, the gel changed into an oily liquid; it was separated from the aqueous alkaline layer, washed, dried, and fractionated at 4 mm. pressure. The first fraction distilled at about 34° C.; it consisted of *p*-cymene. From 34° to 55° C. at 4 mm. pressure a colorless liquid was obtained, and at 55° C. a colorless product solidified in the condenser. This latter was dried on a piece of porous plate. It had a camphorlike odor and was very soluble in all the common organic solvents. After crystallizing once from carbon tetrachloride, it melted and sublimed at 201° C. The melting point after purification by sublimation was 202° C. Its analysis was: carbon, 77.57 per cent; hydrogen, 11.58. From the composition and physical properties the compound is borneol which has the composition: carbon, 77.80 per cent; hydrogen, 11.75, as calculated. The fraction following borneol distilled mostly between 90° and 100° C. at 4 mm. pressure. It had a yellowish green color and an unpleasant odor.

The aqueous alkaline fraction was neutralized. It turned cloudy, but no precipitate was formed. It was extracted with ether, the ether was evaporated, and a small amount of a viscous liquid was obtained which had an unpleasant odor.

Boedker (*6*) obtained different results under somewhat different conditions. When he kept impure *p*-cymene in the cold over metallic sodium overnight and then fractionated, he was able to isolate from the residue which solidified on cooling two products: dicymyl ($C_{20}H_{26}$) (boiling point, 200° C. at 15 mm.; melting point, 157° C.) and cuminic acid (melting point, 117° C.). Boedker considered that the formation of these two compounds is due to the atmospheric oxidation of *p*-cymene. Oxidation of *p*-cymene to cuminic acid by shaking with sodium hydroxide had already been reported by Nencki (*14*). Boedker, however, was not able to oxidize pure *p*-cymene in the presence of 10 per cent sodium hydroxide, even by bubbling oxygen, and therefore he concluded that the impurities associated with *p*-cymene in sulfite turpentine act as catalyst. It is more probable that not *p*-cymene, but certain terpenic impurities are oxidized to cuminic acid, and probably Nencki's *p*-cymene was not pure. Thus when impure *p*-cymene was treated several times with concentrated sulfuric acid to make sure that all of the impurities were removed, then refluxed over metallic sodium for several hours, decanted, and fractionated, the only product obtained was *p*-cymene. The methyl group of certain monocyclic terpenes can be oxidized. Thus Schwenk and Borgwardt (*19*) showed that alpha-phellandrene can be oxidized to cuminaldehyde with selenium dioxide as the oxidizing agent. The disagreement with Boedker's results is due to the difference in the composition of the sulfite turpentine. As already stated, the yield and the composition of sulfite turpentine depend upon the conditions of pulping and upon the quality of the wood.

Routala and Pohjola (*17*) reported the presence of borneol in sulfite turpentine in some cases. It was not possible to isolate any borneol by fractional distillation from impure *p*-cymene (boiling at 173° to 182° C.) which had not been treated with metallic sodium. It is difficult to state with any degree of assurance, but probably borneol also is formed by the oxidation of some of the impurities.

The gel formation of the impurities associated with *p*-cymene in sulfite turpentine can be brought about by special treatment with alkali. When sulfite turpentine, from which sulfur dioxide had been removed, was treated once more with sodium hydroxide (commercial grade, small flakes) added in the solid form, followed by the addition of a small amount of water (not enough to dissolve the alkali), and shaken vigorously, the heat evolved by the action of water on the alkali caused the formation of a stable foam which imparts viscous character to the liquid. As a result of this treatment the liquid began to set to a gel within an hour, becoming stiffer and stiffer on longer standing. This did not happen when the alkali was used in the form of a solution. In case the liquid did not foam in the presence of solid alkali, warming was found helpful. The liquid phase (mainly *p*-cymene, boiling range, 172° to 182° C.) was separated by vacuum distillation. The solid residue was shaken with water. It changed into an oily liquid and was separated from the aqueous alkaline layer. The liquid was fractionated afterwards, and it was possible by slow fractionation to isolate a solid substance (borneol) identical with that obtained from the residue of fractionation over metallic sodium as indicated by the mixed melting point test. The fractionation was done at 8 mm. pressure. The first fraction was mostly *p*-cymene; next came the borneol. The rest, constituting the main part, boiled over a wide range. It was an oily substance with an unpleasant odor and with a color changing from yellow to greenish yellow as the boiling point increased.

The aqueous alkaline fraction was clear, and, therefore, at least in appearance, it did not suggest the presence of an emulsion. When it was neutralized with an acid, a viscous oil separated. It was washed free of acid, dried, and fractionated. At a pressure of 5 mm. it began to distill at 87° C. but had no definite boiling point. The lower boiling fractions, yellow in color and with an unpleasant odor, were neither soluble in alkali nor did they form a stable emulsion. This behavior indicates that the original mixture contains substances capable of forming with the alkali soaps which in turn produce a stable emulsion. When the original mixture was shaken with a dilute alkali solution, the resulting product was clear when a sufficient amount of alkali solution was used, and upon shaking it formed a soap lather which was stable for several minutes.

The results obtained by treating the impurities with metallic sodium or with sodium hydroxide appear to be identical. Evidence supports the existence of atmospheric oxidation. It is difficult to know whether any other type of reaction takes place as a result of these two treatments. Further study of the noncymene fraction is necessary. Previous investigators, in their efforts to find outlets for sulfite turpentine, have devoted their attention only to *p*-cymene, about 70 to 75 per cent of the total sulfite turpentine. The remaining fraction may contain valuable substances which may contribute to the economic disposal of sulfite turpentine.

Nitration of *p*-Cymene

Nitration of *p*-cymene is one of the reactions which has been studied by various investigators. Its importance is conceivable because nitrocymene is an intermediate of various products; one which attracted the writers' attention was thymol. The electrolytic reduction of nitrocymene to obtain aminothymol, an intermediate of thymol, will be reported in the future. The present notes represent certain observations made while preparing nitrocymene for the electrolysis.

p-Cymene is nitrated according to Andrews' method (*1*), slightly modified by Wheeler and Smithey (*24*). This modification consists in adding to *p*-cymene, in addition to concentrated sulfuric acid as solvent, 15 ml. of glacial acetic acid per 100 grams of *p*-cymene, in order to prevent the solidification of the reaction products before the completion of the nitration. Austerweil (*3*) recommends the use of a temperature of +2° to +4° C. instead of 0° C. as does Andrews. Recently Inoue and Horiguchi (*11*) stated that better results are obtained in using nitric acid of specific gravity 1.385 (d_{15}) instead of 1.42. The nitration is performed at 0° to 10° C.

Andrews (*2*) does not consider purification of *p*-cymene necessary for nitration; he says the terpenes remain for the most part unchanged during the nitration and may be readily separated subsequently. Fittica (*9*) and Wheeler and Smithey (*24*), on the contrary, recommended the removal of impurities. *p*-Cymene was therefore carefully purified (boiling point = 174.6° C. at 747 mm.; $n^{20}_{D} = 1.4902$), and nitrated according to the methods already described.

The yields of nitrocymene obtained by Andrews and by Inoue and Horiguchi were 85 and 80.7 per cent, respectively. The highest yields obtained by the present writers were 55 to 60 per cent. This discrepancy is due to the fact that an appreciable amount of *p*-cymene is converted into other products because of side reactions, as a result of which *p*-tolylmethyl ketone (about 15 per cent), some *p*-nitrotoluene (about 1 to 2 per cent), and tar (about 16 per cent) are formed. It was possible to identify in this tarry residue of distillation the presence of *p*-toluic acid, and 2-, 5-, and 2,6-dinitrocymene in very small amounts.

It is difficult to explain the difference in the yields obtained by the present writers and by the investigators mentioned. The nitration was carried out in a flat-bottom 5-pound reagent bottle using 268 grams *p*-cymene for each nitration. In spite of the addition of glacial acetic acid, the nitration mixture thickened when about 60 per cent of the nitrating acid was added. Stirring became difficult with such a viscous mass; nevertheless the temperature was easily maintained at 0° to −5° C. Apparently much closer definition of conditions of nitration is necessary if yields as high as 80 per cent are to be obtained. Another investigator, Kuan (*13*), using nearly the same conditions as Inoue and Horiguchi, could obtain only 60 per cent nitrocymene.

The formation of *p*-nitrotoluene as a by-product in the nitration of *p*-cymene was not reported by any one of the investigators cited or by others preceding them. On the other hand, when Wheeler and Harris (*23*) nitrated *p*-cymene with fuming nitric acid in order to prepare 2,6-dinitrocymene, they obtained also some nitrotoluene and an appreciable amount of dinitrotoluene as a by-product. Puranen (*15*), likewise using fuming nitric acid in a mixture of glacial acetic acid and acetic anhydride, obtained *p*-nitrotoluene and dinitrotoluene as by-products with dinitrocymene. The conditions used by these investigators are distinctly different from those used in preparing mononitrocymene.

TABLE I. BOILING POINTS OF COMPOUNDS

Pressure *Mm.*	*p*-Tolyl Methyl Ketone ° *C.*	*p*-Nitrotoluene ° *C.*	Nitrocymene ° *C.*	*p*-Toluidine (*16*) ° *C.*	Cymidine ° *C.*
2	68.6	...	97.6	..	87
3	75.4	86	104.3	..	...
4	...	...	...	66.5	96
5	84.5	93.4	112	70.2	...
6	...	...	...	73.7	104.3
8	93.1	103.5	121.5	78.4	108.5
10	97.5	108	126.2	82.4	112.2
13	102.1	112	131.4	..	...
20	111	120.8	141	..	...

The effect of *p*-nitrotoluene as an impurity upon the electrolysis of nitrocymene will be reported separately. The formation of *p*-nitrotoluene, therefore, presents a difficult problem in the purification of nitrocymene on account of the closeness of the boiling points. The nitration mixture consists mainly of unchanged *p*-cymene (boiling point, 175° C.), *p*-tolyl methyl ketone (boiling point, 217° C.), *p*-nitrotoluene (boiling point, 238° C.), and nitrocymene (decomposes). The fractionation of the mixture showed the need of determining the boiling points at reduced pressures of the last three compounds (Table I). The difference between the boiling points of *p*-nitrotoluene and nitrocymene is only 19° to 20° C. In spite of very slow fractionation, it was not possible to make a sharp separation. The distillation immediately following *p*-nitrotoluene still contains some *p*-nitrotoluene as indicated by the decrease of the refractive index (the addition of nitrotoluene to nitrocymene raises the refractive index of the latter) of successive samples of distillate until they are constant at $n^{20}_{D} = 1.5282$. Toward the end of the distillation the refractive index of nitrocymene rises slightly because of impurities. These impurities are found in the tarry residue. The control of fractionation to obtain pure nitrocymene by the boiling point alone is not sufficient, and therefore the refractive index should also be used. About the first 10 per cent of the total yield of nitrocymene is thus contaminated with *p*-nitrotoluene, even after using very slow fractionation. This mixture of nitrocompounds may be reduced, and the resulting amines fractionated at a reduced pressure. The difference between the boiling points of *p*-toluidine and cymidine is 30° C. (Table I). Separation may be effected also by fractional crystallization as sulfate, cymidine forming the less soluble monosulfate ($2C_{10}H_{13}NH_2 \cdot H_2SO_4 \cdot H_2O$) in flaky, colorless crystals. The monosulfate was readily obtained when the solution in sulfuric acid was slowly and gradually neutralized in the presence of ice. The refractive index of cymidine is $n^{20}_D = 1.5395$.

Acknowledgment

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Phase Equilibria in Hydrocarbon Systems

XIII. Joule-Thomson Coefficients of Propane[1]

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In determining the thermal properties of hydrocarbons in the gaseous region, the Joule-Thomson coefficient is a powerful tool when known as a function of the state. The purpose of the present paper is to describe an apparatus developed to measure this property, to report upon the data obtained for propane, and to outline the usefulness of this measurement in thermal calculations.

THE Joule-Thomson coefficient is defined as the change in temperature with very small change in pressure at constant heat content:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_P} \qquad (1)$$

It may be used to advantage in (1) calculating changes in specific heat at constant pressure of the superheated gas at low pressures, (2) obtaining the partial differential of H with respect to P at constant T at low pressures, (3) calculating the specific heat in the region of the critical state, and (4) constructing throttling curves.

Previous experimenters (*1*) have used throttling experiments to determine the Joule-Thomson coefficient, since the slope of a throttling curve is directly $(\partial T/\partial P)_H$. This method used very large pressure and temperature changes which, when the derivative μ changes rapidly with pressure or temperature, leads to inaccurate results. It is thus unsuited for use with most hydrocarbons in the limits of pressure and temperature which are encountered in petroleum formations and for which the present apparatus was designed. The apparatus developed utilized a small, automatically maintained constant-pressure drop across a radial-flow porous plug at a given temperature and pressure; the fall in temperature of the gas in passing the porous plug was measured. A flow-sheet diagram of the apparatus is shown in Figure 1:

A cam pump delivered gas to a header, one valve of which, *A*, allowed a given amount of gas to by-pass to the pump intake, thus aiding in adjusting the pressure drop across the porous

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[1] Previous papers in this series appeared during 1934 and 1935, and in January, February, and April, 1936.

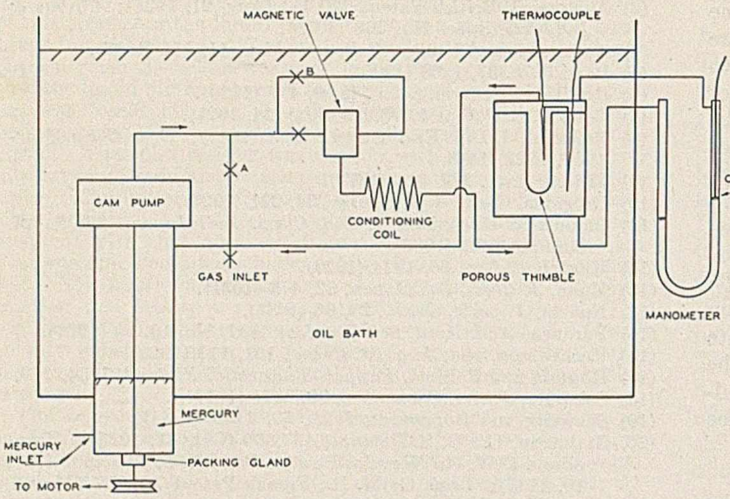

FIGURE 1. DIAGRAM OF APPARATUS

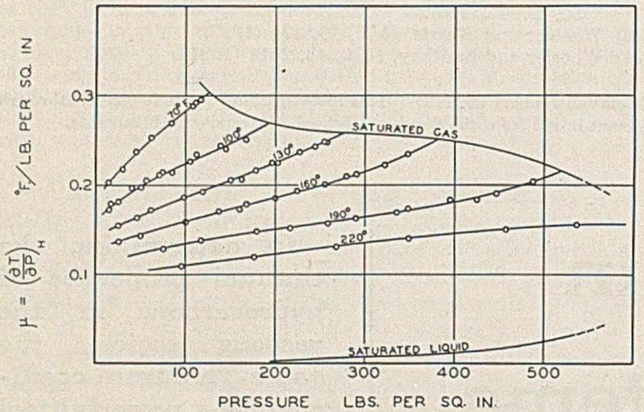

FIGURE 2. EXPERIMENTAL VALUES OF JOULE-THOMSON COEFFICIENT OF PROPANE GAS

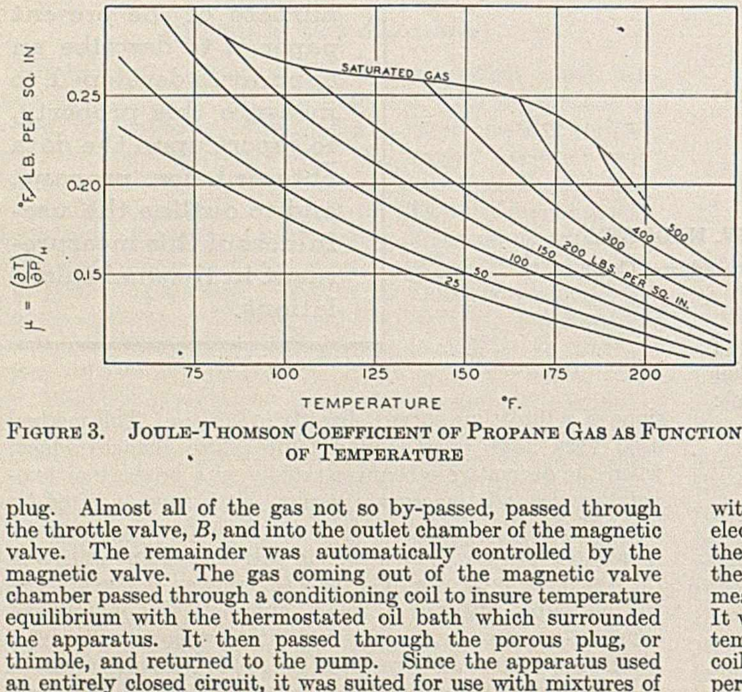

FIGURE 3. JOULE-THOMSON COEFFICIENT OF PROPANE GAS AS FUNCTION OF TEMPERATURE

plug. Almost all of the gas not so by-passed, passed through the throttle valve, *B*, and into the outlet chamber of the magnetic valve. The remainder was automatically controlled by the magnetic valve. The gas coming out of the magnetic valve chamber passed through a conditioning coil to insure temperature equilibrium with the thermostated oil bath which surrounded the apparatus. It then passed through the porous plug, or thimble, and returned to the pump. Since the apparatus used an entirely closed circuit, it was suited for use with mixtures of known composition over the desired ranges of pressure and temperature.

The pressure existing in the system was measured by means of fluid pressure scales. The oil-filled tubing from the pressure scale was connected to the system through a mercury trap (*3*). The pressures reported, however, were the average of the entrance and exit pressures at the thimble, having an absolute accuracy of at least 0.5 per cent of the pressure reading. Mercury at pressures up to 3000 pounds per square inch could be added to the space below the pump to increase the pressure on the confined gas. The automatically maintained temperature of the oil bath was determined by a calibrated thermometer. It is believed that the maximum temperature variation throughout the bath was 0.02° F., with a localized variation with time at the control heater of 0.005° F.

The cam pump, *A* (Figure 1), was constructed of cold-rolled steel. The stationary contact surfaces were inserts of a special alloyed cast iron. The sliding vanes in the rotor were of hardened tool steel. The rotor was of cold-rolled steel, chromium-plated. Ball bearings at the base of the rotor took up side thrust. Bearing surfaces were lubricated with a very light film of petroleum jelly. The pump was driven by a vertical shaft which passed through a packing gland below the oil bath. The pump was driven at nearly constant speed by a belt-connected induction motor. Variable demands upon the pump due to changes in pressure and temperature were adjusted by means of the by-pass valve, *A*. In operation, this valve was adjusted until just slightly less gas than was necessary to maintain the pressure drop across the porous plug was flowing through the throttle valve, whereupon the operation of the magnetic valve maintained the desired pressure drop.

The magnetic valve consisted of an iron core sliding vertically in a monel metal tube under the influence of a solenoid coil which surrounded it. A spring served to return the iron core to its original position when the current was broken. The magnetic valve was controlled through a relay by the high-pressure manometer which was constructed of 1-inch Shelby tubing surrounded by a steam jacket to maintain constant temperature. An insulated iron rod in one leg of the manometer made contact with the mercury surface and completed the relay circuit when the pressure was at the desired value. The pressure drop at which the manometer operated could be changed by adding or withdrawing mercury. The pressure drop was calibrated at atmospheric pressure by using an auxiliary mercury-in-glass manometer and measuring the difference in levels with a vertical interval cathetometer. For calibration the manometers were connected together and air was slowly withdrawn from the contact side of the manometers until the signal lamp on the relay flashed. Another reading was secured by adding air until the lamp flashed again. The reproducible accuracy of this pressure drop measurement was 0.3 per cent. The pressure drop used varied from 0.9 to 1.3 pounds per square inch, as compared to values of 15 to 100 pounds previously used in similar work.

The porous plug was constructed of a fine-grained alundum extraction thimble. The gas entered the bottom of the porous plug chamber, and flowed up around a radiation shield, past three thermocouple junctions, and then downward to pass into the porous plug. After passing through the lower part of the plug (the upper third being covered with an impervious coating), the gas passed three more thermocouple junctions before leaving the thimble. Pressure lines leading to the high-pressure manometer were connected to the high- and low-pressure sides of the porous plug. The three-junction copper-constantan thermocouples, made of No. 36 wire, were strung on a drilled Bakelite mounting. This arrangement served also to integrate minute fluctuations in temperature. The thermocouple wire was separately calibrated at various temperatures used. A high-sensitivity, low-resistance galvanometer in connection with a calibrated potentiometer (*4*) was used to measure the electromotive force; this value, combined with the calibration of the thermocouple at the average temperatures encountered, gave the temperature changes. The temperature change could be measured to the same accuracy as the pressure drop (0.3 per cent). It was essential that the gas entering the plug be at a uniform temperature, and for this reason the gas traversed a conditioning coil of medium-sized tubing to bring it to the average temperature of the oil bath. The heaters in the oil bath were necessarily adjusted so that fluctuations in the bath temperature were at a minimum. A signal lamp connected to the relay operating the control heater showed, by the frequency of its operation (5 to 10 seconds), that sensitive temperature control was being maintained. A thermocouple, mounted near the conditioning coil showed that, under this condition of operation, temperature fluctuations over short intervals of time were about 0.001° F.

Tests of the Apparatus

The Joule-Thomson coefficients of carbon dioxide, which were investigated by Burnett (*1*), were determined on this apparatus to check the reliability of the instrument. The agreement obtained was reasonable, especially at higher pressures. It is worthy of note that several different settings of the differential pressure manometer gave the same Joule-Thomson coefficient. A maximum was obtained in isothermal curves of μ *vs.* pressure at 200 to 300 pounds per square inch; the values then decreased as the pressure decreased. This trend extends into a region where experimental inaccuracies leave uncertainty as to what values the Joule-Thomson coefficient and $(\partial H/\partial P)_T$ approach as the pressure approaches zero. Values of μ given by Burnett continue to increase as the pressure decreases.

The Joule-Thomson coefficients obtained with the present apparatus would be too low if heat were transferred from one surface of the porous plug to the other faster than the gas flowing through could maintain the temperature difference. This effect would be more noticeable at low pressures where the volumetric thermal capacity was smaller. A test was made to indicate the amount of this thermal leakage. With the pump running and the plug at equilibrium at about 30 pounds per square inch pressure of propane, the pump was stopped and readings were made of the temperature difference existing in the stationary gas on each side of the porous plug. Less than 10 seconds after the pump was stopped, the temperature difference dropped off to less than half of its equilibrium value, owing to the adiabatic expansion of the gas on the high-pressure side. Inside of 2 minutes the temperature difference had risen to its previous value; then it decreased slowly. The decrease was so slow that at the end of 45 minutes the temperature difference was still more than half the value before the pump was stopped.

When the pump was started some time was required for the apparatus to reach equilibrium. Over the period of about one-half hour a gradual shift could be observed in the temperature difference obtained. At lower pressures, because of lower volumetric thermal capacity, this period of reaching equilibrium became longer.

Some fluctuations were noticed in the readings obtained. The galvanometer needle, when connected to the thermocouple, at times oscillated slowly back and forth, especially if the magnetic valve was controlling any considerable proportion of the gas flowing. This oscillation is to be explained in the slight pulsations of the pump and the magnetic valve, causing adiabatic compressions and expansions. The oscillations are regular and have a reproducible center. By proper adjustment of the valves it was possible to decrease the oscillation to a barely noticeable amount, which was about 2 per cent of the temperature difference being measured. Violent fluctuations of the temperature difference were noticed when the pressure was brought very close to saturation, showing the presence of a small amount of liquid spray.

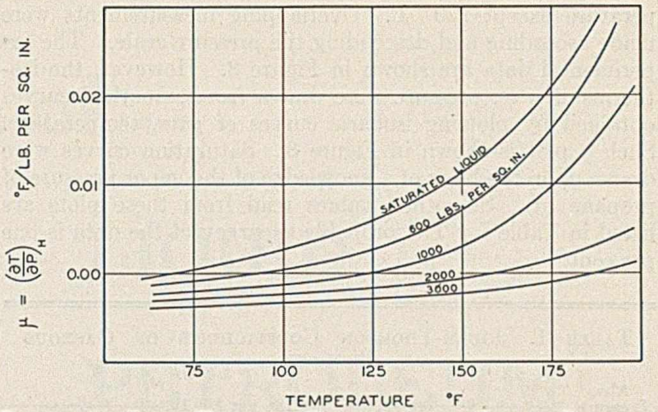

FIGURE 4. JOULE-THOMSON COEFFICIENT OF LIQUID PROPANE AS FUNCTION OF TEMPERATURE

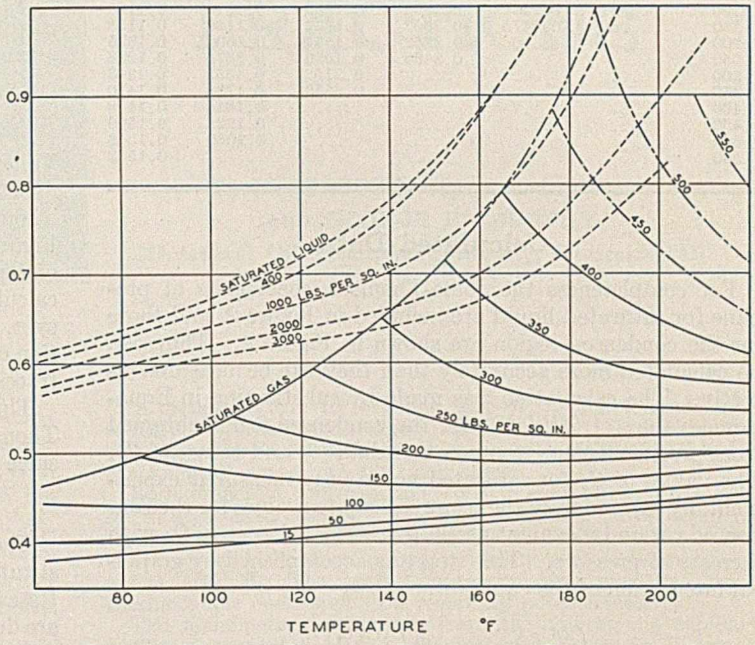

FIGURE 5. SPECIFIC HEAT AT CONSTANT PRESSURE OF GASEOUS AND LIQUID PROPANE

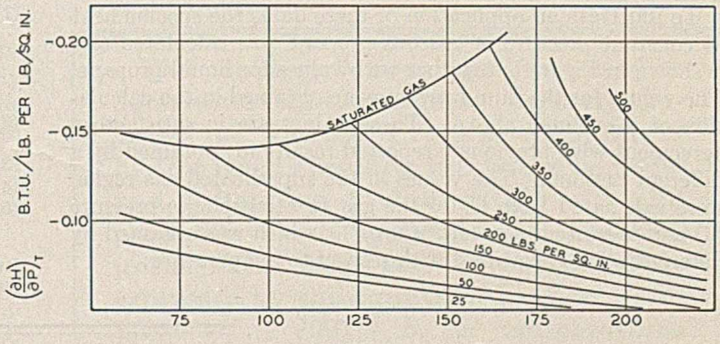

FIGURE 6. VALUES OF $(\partial H/\partial P)_T$ FOR GASEOUS PROPANE

Materials

The propane used in this study was obtained from the Philgas Company, Bartlesville, Okla. Their analysis showed it to be pure propane, containing neither ethane nor isobutane in appreciable amounts. The same material was used in previous studies (*5*) of thermodynamic properties. Carbon dioxide used for testing was the commercial product.

Experimental Results

The Joule-Thomson coefficients of propane gas were measured at six temperatures and at pressures up to 550 pounds per square inch. Several samples were used for each temperature except 220° F. Overlapping measurements were made ascending and descending the pressure scale. The experimental data are shown in Figure 2. However, the isotherms of μ *vs.* pressure were drawn from smoothed curves obtained by plotting isobaric curves of μ *vs.* temperature. Such a plot is shown in Figure 3. Saturation curves were drawn upon the basis of a knowledge of the vapor pressure of propane (*5*). Smoothed values read from these plots are listed in Table I. The probable accuracy of the data is one per cent.

TABLE I. JOULE-THOMSON COEFFICIENTS OF GASEOUS PROPANE

Abs. Pressure, Lb./Sq. In.	μ, ° F. per Lb. per Sq. In. 70° F.	100° F.	130° F.	160° F.	190° F.	220° F.
Satd. gas	0.3040	0.2677	0.2589	0.2518	0.217	....
25	0.2150	0.1824	0.1542	0.1339	0.116	0.100
50	0.2409	0.1995	0.1658	0.1433	0.1232	0.1040
100	0.2831	0.2242	0.1862	0.1589	0.1340	0.1100
150	....	0.2475	0.2052	0.1732	0.1436	0.1158
200	....	....	0.2252	0.1853	0.1506	0.1225
250	....	....	0.2468	0.1986	0.1575	0.1288
300	....	....	....	0.2152	0.1653	0.1343
350	....	....	....	0.2353	0.1735	0.1410
400	....	....	....	....	0.1818	0.1458
450	....	....	....	....	0.1925	0.1500
500	....	....	....	....	0.2080	0.1540
550	....	....	....	....	....	0.1557

Calculated Data

For completeness the Joule-Thomson coefficients of propane for saturated liquid are included in Figure 2, and those for the condensed region are shown in Figure 4. They can be calculated more accurately than they can be measured directly. The calculation was made by substituting in Equation 1 values of $(\partial H/\partial P)_T$ for the condensed region obtained from pressure-volume-temperature data (*5*) and values of C_P. The values of C_P for saturated liquid were measured experimentally (*4*), and from these were calculated values for the condensed region by evaluating the isothermal change in C_P with increase of pressure. This step was accomplished by graphical integration of the equation:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{2}$$

The latter term is obtainable from the P-V-T measurements.

To illustrate an application of these data, the specific heat at constant pressure of gaseous propane was calculated and is shown in Figure 5, together with values for liquid propane. The values for the liquid region were obtained in the calculation of μ outlined above. These values are in satisfactory agreement with previously reported results (*5*) obtained by a different method. The values in the superheated gas region were calculated from C_P of the gas at atmospheric pressure (*4*) and the integration of $(\partial C_P/\partial P)_T$, which was obtained by differentiating Equation 1 with respect to temperature:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial\left(\frac{\partial H}{\partial P}\right)_T}{\partial T}\right)_P = -\mu\left(\frac{\partial C_P}{\partial T}\right)_P - C_P\left(\frac{\partial \mu}{\partial T}\right)_P \tag{3}$$

In evaluating Equation 3, μ and $(\partial\mu/\partial T)_P$ were known throughout the pressure and temperature ranges, while C_P and $(\partial C_P/\partial T)_P$ were known only at atmospheric pressure but throughout the temperature range. Values of C_P for high pressures were obtained by progressive approximative integration of the equation. The agreement of these values of specific heat when compared with previous tentative values (*2*) was unsatisfactory near saturation, indicating the possible presence of traces of oil in the apparatus during the P-V-T work, which would affect the results strongly in this region. The agreement obtained by the calculation of $-T(\partial^2V/\partial T^2)_P$ for the gas from P-V-T data and comparison with the values of $(\partial C_P/\partial P)_T$ obtained above was considered satisfactory.

A further application of the Joule-Thomson data lies in the calculation of $(\partial H/\partial P)_T$ for the superheated gas region. Rearranging Equation 1,

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu C_P \tag{4}$$

Values calculated by Equation 4, which are substantially independent of P-V-T data and depend only upon Joule-Thomson and specific heat measurements, are shown in Figure 6. Changes in heat content calculated by integration of the curves in Figure 6 are in good agreement with those calculated from P-V-T data, except near saturation. However, high accuracy is required in P-V-T data in the calculation of $(\partial H/\partial P)_T$ and is markedly affected near saturation by traces of oil in the apparatus.

Throttling curves may also be constructed by use of Joule-Thomson data, but this calculation has not been made here since such curves have already been published (*2*).

Acknowledgment

The financial assistance of the American Petroleum Institute in this work, carried out as a part of the work of its Research Project 37, is gratefully acknowledged. Thanks are due D. S. Clark for suggestions regarding the design of the cam pump and for the special cast iron used therein.

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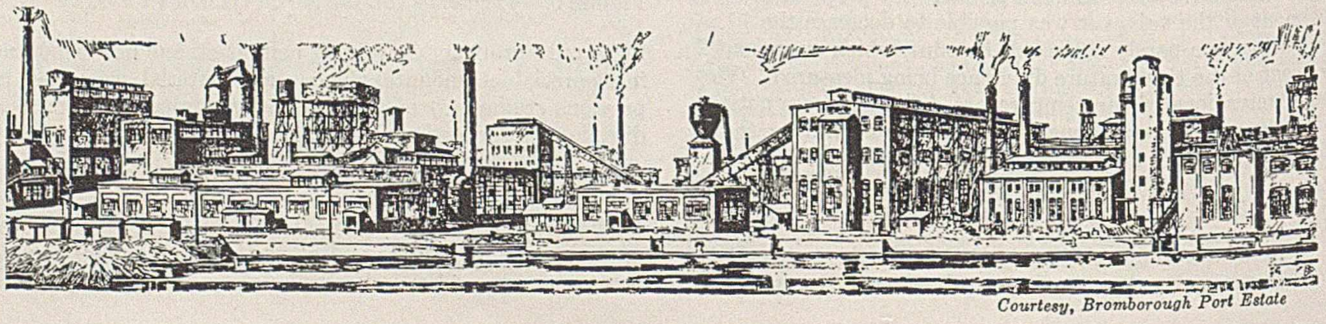
RECEIVED October 4, 1935.



Courtesy, Bromborough Port Estate

HIGH-TEMPERATURE VISCOSITIES OF . . . LIQUID PETROLEUM FRACTIONS

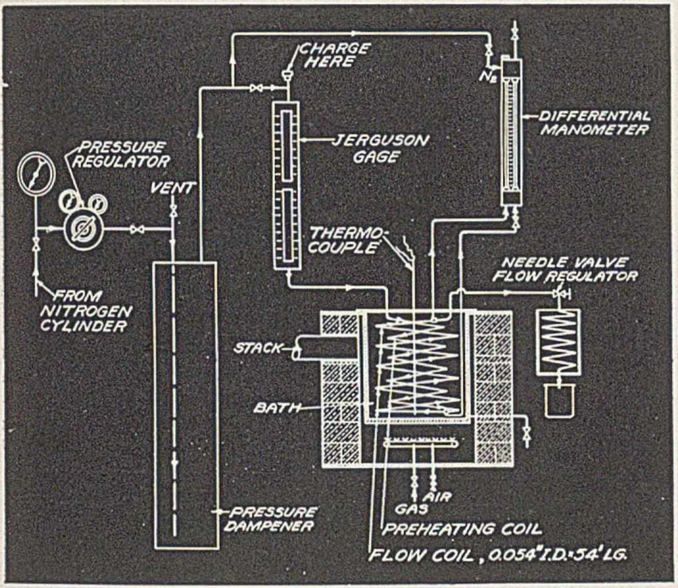


FIGURE 1. HIGH-TEMPERATURE VISCOMETER

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IN OPTIMUM design of petroleum refining equipment, calculations of heat transfer coefficients and pressure drops are of considerable importance. It is frequently necessary to know the viscosity of the oil at temperatures ranging up to 1000° F. The literature contains very few data on liquid hydrocarbon viscosities above 300° F., and the proposed methods for extrapolating to obtain the values at high temperatures appear uncertain.

The purpose of the work here described was to determine the viscosities of various hydrocarbon materials at high temperatures and develop a reliable method of general correlation. The viscosity determinations were made upon a series of liquid hydrocarbons ranging from the pure compounds, benzene and *n*-heptane, to lubricating oils and highly cracked compounds from commercial cracking units. The range of temperatures used was from 100° to 800° F. with pressures varying from atmospheric to 500 pounds per square inch.

Apparatus and Procedure

The viscosity measurements were based on Poiseuille's law stating that the pressure drop of a liquid passing in streamline flow through a capillary tube is proportional to the product of the absolute viscosity and rate of flow. In order to insure streamline flow conditions at high temperatures and pressures where the densities are high and the viscosities low, it is necessary that a very long capillary of small diameter be used to permit measurable rates.

Figure 1 shows the principal features of the apparatus:

> It consisted chiefly of a coiled 54-foot length of steel tubing, $^1/_8$ inch outside diameter and approximately 0.054 inch inside diameter. To the ends of this coil were attached two tees which had connections leading to a differential manometer. The outlet end of the coil was fitted to a fine needle valve with a $^1/_{16}$-inch opening in its seat; the other end was joined by a union to a preheating coil 10 feet long, also of $^1/_8$-inch tubing but of slightly larger inside diameter. The inlet end of the heating coil was connected to a Jerguson gage which, calibrated in cubic centimeters, served as a charging vessel.
>
> Both preheater and capillary coils were immersed in a bath set in a gas-fired furnace. The bath contained oil for temperatures up to 450° F. and a fused salt of approximately 50 per cent each by weight of sodium and potassium nitrates for temperatures above 450° F. The bath temperature was measured by a thermocouple connected to a recording potentiometer.
>
> The manometer connections from the end of the capillary coil were connected to the manometer as shown in Figure 1. The fluids in the manometer were the oil flowing in the tube and nitrogen gas above it.

The capillary tube method was used to determine the kinematic viscosity between 100° and 800° F. of a series of liquid hydrocarbons ranging from pure benzene and *n*-heptane to lubricating oils and products from commercial cracking units. The data can be satisfactorily expressed by the equation, log (log μ/s + 1.7 = $a(t + 100) + b$, for temperatures above 210° F.

On the basis of this equation a high-temperature viscosity chart was developed. A nomograph was developed permitting the estimation of the viscosity-temperature curve of a liquid from laboratory inspection data. Pressures up to 500 pounds per square inch had little effect on the kinematic viscosity in the range of the determinations.

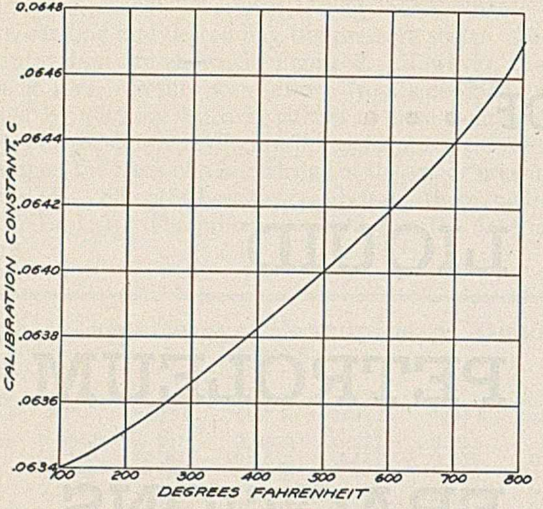

Figure 2. Variation of Calibration Constant with Temperature

A nitrogen cylinder equipped with a pressure regulator kept the desired pressure upon the charging vessel. An empty tank was inserted in the line to the nitrogen gas tank to take up the small pressure fluctuations from the regulator.

The coil was calibrated with a liquid of known viscosity (chemically pure benzene) after which runs on the various stocks were made. After every five to eight runs the calibration of the coil was checked.

A typical run was conducted as follows:

The bath was brought up to and held constant at the desired temperature. A sample of oil to be run was filtered and charged into the Jerguson gage, and the desired pressure was put on the system. A small portion of oil was allowed to flow out of the manometer after which the manometer levels were adjusted at a suitable zero, with no oil flowing through the coil, by introducing compressed nitrogen to the top of the manometer. The run was started by opening the needle valve to give the desired differential pressure and observing the liquid level in the Jerguson gage and the time. The manometer was read every minute, and the reading kept constant by adjusting the needle valve. The time was recorded for every 5 cc. of oil, and at least 30 cc. of oil were used in each run. The temperature of the room and pressure in the system were recorded, the latter being held constant by the pressure regulator.

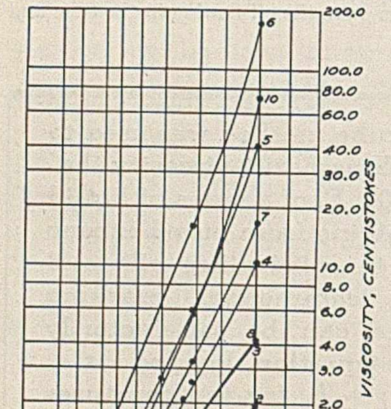

Figure 3. Plot of Log μ/s vs. Log t° F.

Rates of flow up to 2.0 cc. per minute of cold oil were used, maintaining differential manometer readings of from 4 to 10 inches. At high temperatures the pressure drop was kept low to insure streamline flow. At none of the conditions investigated was there indication of deviation from streamline flow as evidenced by a change of apparent viscosity with change in rate.

After the run the flow valve was closed, and the manometer was allowed to approach no flow equilibrium. If it did not balance, there was evidence of a leak, and the run was discarded. The coil was emptied immediately to prevent any oil from coking or cracking. Before a different stock was run, the coil was cleaned by passing solvent naphtha, then motor benzene, and finally c. p. benzene through the coil, followed by nitrogen gas. Check runs were made at different rates of flow at the same temperature.

At no time during any run was cracking indicated by gas at the outlet or vaporization in the tube which would have caused the manometer to be erratic. If there was cracking and the gas had been held in solution, it is assumed that the amount formed did not affect the measurements within the precision of the determination. Furthermore, the oil was in the coil such a short time that appreciable cracking at the temperatures employed was improbable.

For temperatures between 100° and 210° F., and also as a check on the 200° F. determination of the high-temperature viscometer, the viscosities were determined in the laboratory by means of modified Ostwald pipets.

After the apparatus was calibrated with pure liquids of known viscosities at a variety of conditions of flow and temperature to verify the principle of the measurements, viscosity measurements were made on the stocks listed in Table I over the temperature ranges indicated. The detailed inspections of these stocks are shown in Table II. In these runs the pressure was held at approximately 50 pounds per square inch greater than that estimated as necessary to prevent vaporization. A few runs were made on stocks 5 to 9, to determine the effect of varying pressure.

Table I. Temperature Range of Viscosity Measurements

	Stock	Temp. Range ° F.
1.	300–400° F., Midcontinent naphtha	100–685
2.	400–500° F., Midcontinent kerosene	100–600
3.	500–600° F., Midcontinent gas oil	100–700
4.	600–700° F., Midcontinent gas oil	100–700
5.	Pennsylvania lube oil, S. A. E. No. 10	100–710
6.	Pennsylvania lube oil, S. A. E. No. 50	100–710
7.	Heat-exchanger condensate from Midcontinent topped crude	100–710
8.	Recycle stock from Midcontinent topped crude	100–700
9.	Combined feed from Midcontinent topped crude	100–800
10.	Residuum from cracking Midcontinent gas oil	100–665
11.	c. p. benzene (C_6H_6)	100–500
12.	*n*-Heptane (*n*-C_7H_{16})	100–500

Discussion of Results

The basic equation for calculating the viscosity is Poiseuille's law which, for liquids flowing through capillary tubes in streamline flow, is as follows:

$$\Delta P = \frac{kLV\mu}{gd^2} \tag{1}$$

where ΔP = pressure drop through tube
L = length of tube
d = inside diam. of tube
V = linear velocity of liquid flowing through tube
μ = abs. viscosity of liquid
g = acceleration due to gravity

By considering a tube of definite length and inside diameter and rate of flow, the following equation is obtained to apply to the test apparatus:

$$\mu/s = \frac{C\Delta h(s_c - d_g)}{s_c u} \tag{2}$$

where μ/s = kinematic viscosity, centistokes
C = calibration constant of tube
Δh = liquid differential of manometer, inches of fluid flowing at room temp.
s_c = sp. gr. of liquid flowing at room temp.
d_g = density of gas (nitrogen) in manometer at room temp. and system pressure, grams/cc.
u = rate of flow from charger at room temp., cc./min.

In order to evaluate the calibration constant, C, of Equation 2, runs were made with liquids of known viscosity. Chemically pure benzene was most satisfactory. This calibration constant is a function of the coil's length and inside diameter and changes due to expansion of the coil with temperature.

Table II. Boiling Range of Stocks (in ° F.)

Stock:[a]	1	2	3	4	5	6	7	8	9	10	11	12
Characterization factor *K*	11.8	11.8	11.8	11.8	12.3	12.5	11.2	10.7	10.8	10.2	9.8	12.5
Gravity, ° A. P. I.	47.2	40.4	35.3	30.4	30.3	28.0	19.5	22.2	19.6	5.4	29.6	75.5
Pressure, mm.	750	750	750		Vacuum Engler			750	Vacuum Engler			
Sp. gr.											0.878	0.6837
B. P., ° F.											176	209
Initial B. P.	296	414	504	595	276	735	390	396	400	667		
5% over	319	425	520	612	737	762	494	...	452	693		
10%	329	429	523	622	747	770	565	458	471	697		
20%	340	432	529	632	760	812	612	485	500	703		
30%	348	436	533	640	765	830	650	505	514	710		
40%	354	440	537	643	765	857	680	525	545	719		
50%	360	444	544	646	767	880	697	547	579	727		
60%	364	449	549	650	777	940	755	573	618	736		
70%	369	453	554	662	790	977	795	603	663	750		
80%	374	460	561	672	802	1040	827	638	732	768		
90%	381	470	573	685	830	1055 (85%)	887	700	821	798		
95%	388	480	585	713	872		915		895			
End point	411	496	589	738	910					829		

[a] Table I describes the stocks.

From the coefficient of expansion of the metal the ratio of length to the fourth power of the inside diameter was calculated for the different temperatures. The resulting relationship between calibration constant and temperature is plotted in Figure 2.

The viscosity results obtained are plotted in Figure 3 with log kinematic viscosity *vs.* log temperature in ° F. The numbers of the curves correspond to the numbers in Tables I and II. The dotted portion of the lines were extrapolated for viscosity values to the estimated critical points (*9*). The data between 100° and 210° F. are laboratory determinations with the modified Ostwald pipets. Figure 3 shows that the lines in the range from 200° to 300° F. are continuous and the change in slope is uniform, indicating satisfactory agreement between the Ostwald and high-temperature viscometers.

Curves 1, 2, 3, and 4 of Figure 3 represent narrow-boiling-range cuts from a Midcontinent crude. Herschel (*7*) pointed out that a series of cuts such as those plotted in Figure 3 give straight lines meeting at a common point at a relatively low temperature. These data indicate that this relationship is linear only over a relatively narrow range. The curves are not straight and show no indication of intersecting in the range investigated. A similar conclusion was reached by Fortsch and Wilson (*4*).

Comparison of curve 8, a cracked stock, and curve 3, an uncracked stock, shows that, although the two stocks have practically the same viscosity at low temperatures, the lines diverge at higher temperatures, curve 8 having a steeper slope. This effect shows that the cracked stock has a greater temperature coefficient of viscosity; it is more noticeable when a cracked residuum, curve 10, and a highly refined Pennsylvania lube oil, curve 5, are compared. However, the difference in this slope is minimized at temperatures above 210° F. where the lines tend to become more uniform.

Several measurements were made at pressures varying from 200 to 500 pounds per square inch at 700° F. on stock 9. A similar series of measurements at different pressures were made on stock 5 at 520° F. In both cases the effect of pressure on the kinematic viscosity was less than the probable error of the measurements.

In general, it may be concluded that pressure, up to 500 pounds per square inch, has little effect on the kinematic viscosities of liquid hydrocarbons at temperatures not too close to the critical. There is probably a considerable increase in absolute viscosity with increase in pressure at high temperatures. However, this effect is compensated by the corresponding increase in density, leaving the kinematic viscosity little affected.

General Correlation

For convenience in interpolation and accuracy of extrapolation it is desirable to develop a method of plotting to give straight-line relationships between temperature and viscosity. Numerous equations and empirical methods have been proposed for this purpose (*1, 3, 5, 6, 8*). However, none of these methods was entirely satisfactory when applied to the wide ranges of stocks and conditions here investigated.

Figure 4 is such an empirical chart; its ordinates are a function of the kinematic viscosity in centistokes and of Saybolt viscosity in seconds, and its abscissa is a function of temperature in ° F. The scales were derived by first plotting the data by the method of Coats and Brown (*2*) for vapor pressure. A rectangular chart was derived from this plot by

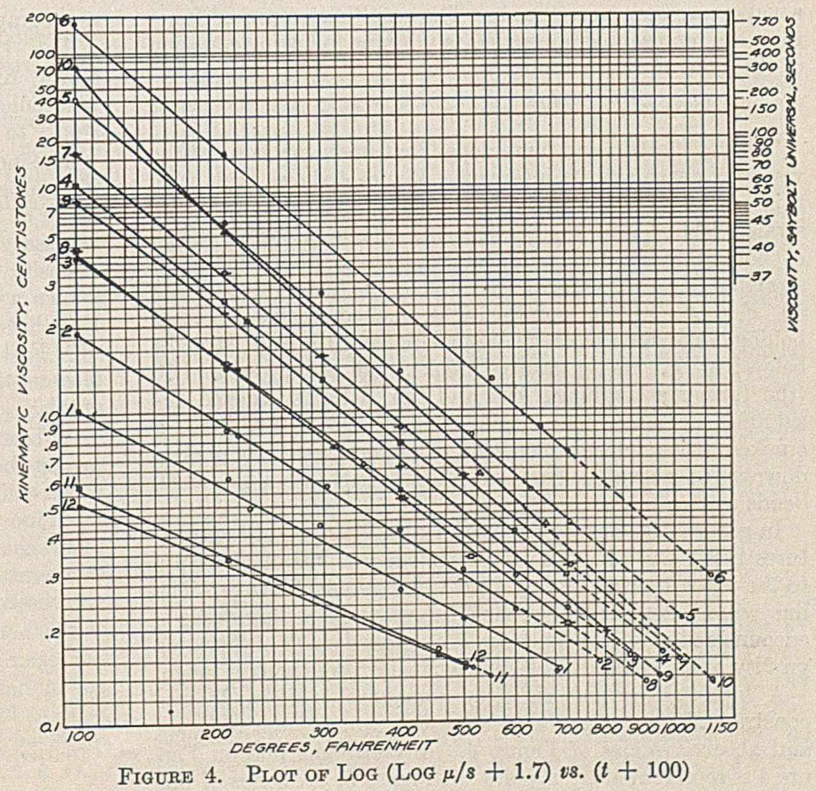

Figure 4. Plot of Log (Log $\mu/s + 1.7$) *vs.* ($t + 100$)

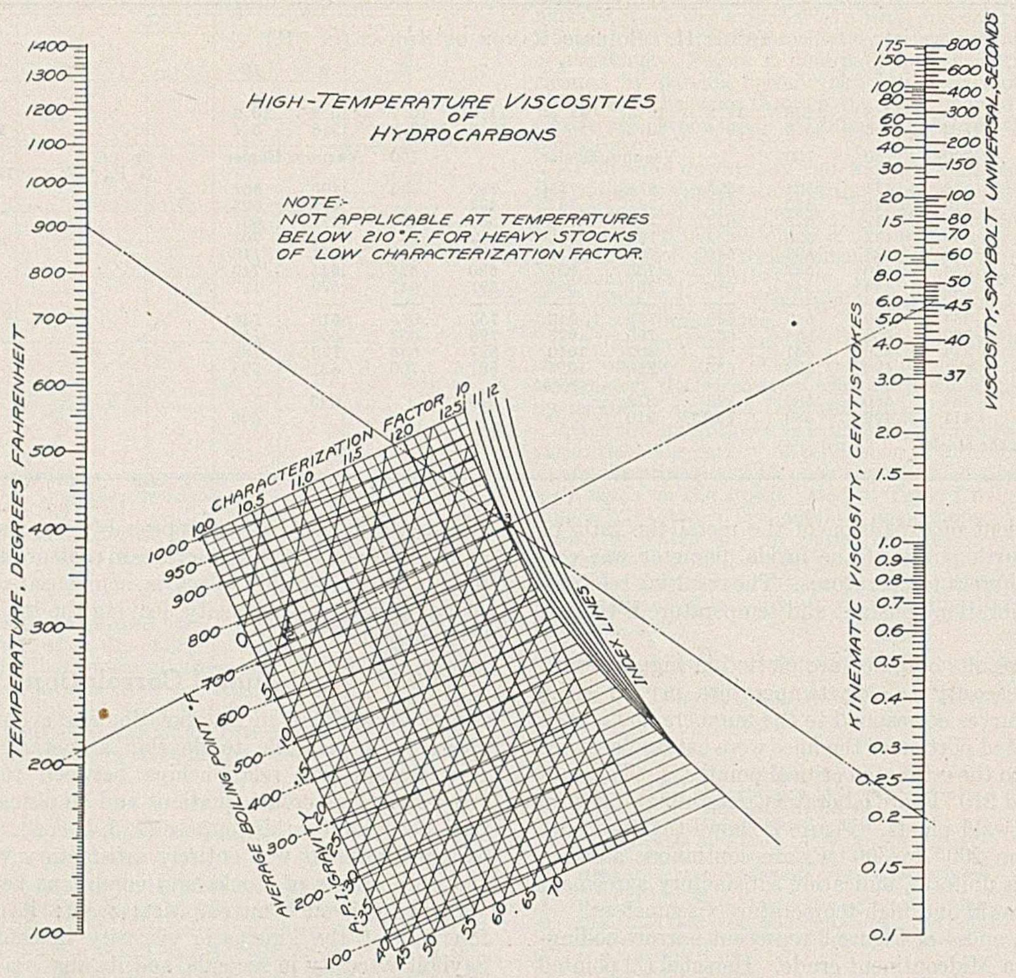

FIGURE 5. HIGH-TEMPERATURE VISCOSITY NOMOGRAPH

the method described by Watson and Wirth (*11*) in developing a vapor pressure nomograph. The resulting empirical functions are represented approximately by the following equation of the general form adopted by the A. S. T. M.:

$$\log(\log \mu/s + 1.7) = a \log(t + 100) + b \qquad (3)$$

The constants a and b are dependent upon the slope of the viscosity curve and its intercept. Figure 4 shows that, with this method of plotting, all the experimental curves are straight above 210° F. Straight-run stocks of normal width of boiling range and pure compounds are represented by straight lines throughout the range of temperature from 50° F. to the critical point. Light cracked stocks of normal boiling range, such as a recycle stock (curve 8), are also straight below 210° F. Heavy cracked stocks, such as curves 9 and 10 (the former a combined feed and the latter a cracked residuum), deviate from a straight line. Curve 9 which is a cracked stock but of relatively wide boiling range, bends downward; curve 10, a cracked stock of narrow boiling range, bends upward.

In general, the curves representing heavy stocks at temperatures below 210° F. will vary from one extreme of curvature to the other, depending upon the width of boiling range. The line will be straight if just the right width of boiling range is encountered as shown by curve 7, a cracked stock of the same gravity as curve 9 but of a somewhat narrower boiling range.

A high-temperature viscosity nomograph (Figure 5) was constructed by making the scales the same as the ordinate and abscissa scales of Figure 4. Any straight line on Figure 4 is represented by a point on Figure 5. A series of oils of the same type is represented by a number of points on the nomograph, and an index line is the locus of these points.

The Universal Oil Products (U. O. P.) characterization factor, K (*9*, *10*), classifies the different types of oils as to paraffinicity varying in values of 12.5 for purely paraffinic stocks to 10.0 or less for highly cracked aromatic stocks.

The index lines of Figure 5 are the loci of stocks of different K groups. To find the viscosity at any temperature in the range of straight-line relationship from the nomograph, it is necessary to know only the characterization factor and the viscosity at one temperature. Heavy stocks require the known viscosity to be at any temperature above 210° F. If values of viscosity for heavy stocks are needed below 210° F., they should be determined in the laboratory to supplement the high-temperature data estimated from the nomograph.

A correlation between U. O. P. characterization factor, average boiling point, A. P. I. gravity, and viscosity at 210° F. was recently presented by Watson, Nelson, and Murphy (*10*). By imposing this relationship on the nomograph as an auxiliary chart, it is possible to estimate the viscosity at any temperature if only any two of the above physical properties are known.

The nomograph and auxiliary chart are used in the following example: A residuum from cracking a Midcontinent gas oil has the following properties:

Gravity, ° A. P. I.	5.4	Viscosity at 210° F.	5.7
Av. B. P., ° F.	730	Viscosity at 122° F.	28.0
		Viscosity at 100° F.	72.5

The characterization factor and the point representing this stock on the rectangular portion of Figure 5 may be located from either the viscosity at 210° F. and the gravity, or from the gravity and boiling point. Two slightly different points, 1 and 2, result. For estimation of viscosities it is preferable to use the index point based on a viscosity measurement. This fixes the characterization factor at 10.32 and the index point at 3. The viscosity at 900° F. is then estimated by projecting a line from 900 on the temperature scale through the index point to the viscosity scale where it intersects at a value of 0.2 centistoke.

From Figures 4 and 5 the viscosity of any liquid stock at temperatures up to the critical may be estimated from ordinary laboratory inspection data. Pressure up to 500 pounds per square inch has little effect on these relationships. A complete viscosity-temperature curve for a heavy stock requires combination of the high-temperature data estimated from Figure 5 with actual laboratory measurements at temperatures below 210° F. The complete curve thus derived may or may not be a straight line below 210° F. when plotted on Figure 4, depending on the width of boiling range and other factors such as wax content.

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Germicidal Properties of Phenolic Compounds

sec-Amyltricresol, *o*-Hydroxyphenylmercuric Chloride, and a Mixture of the Two

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THE research presented in this paper was undertaken to determine the germicidal efficacy, under various conditions, of different solutions of *sec*-amyltricresol, *o*-hydroxyphenylmercuric chloride and a mixture, known as Mercresin, of the two chemicals. Information was also sought as to how solutions of these chemicals compared with some market mercurials and a phenol derivative in germicidal action.

Experimental Procedure

Food and Drug Administration methods (*2*) were followed. Preliminary work with mercurials showed that the apparent phenol coefficients obtained were often higher than the true ones, as the quantity of chemical carried from the medication tube to the broth subculture tube in the 4-mm. loopful required by the F. D. A. method was large enough to cause bacteriostasis. For this reason a second tube of sterile broth was always inoculated with four to seven 4-mm. loopfuls of material from the tube which had been inoculated directly from the medication tube. In a large part of the work a standard quantity of seven loopfuls was secondarily transferred. The secondary transfers were completed at once after each test in order to secure greater accuracy.

Although the F. D. A. method requires results to be based on the 48-hour observation, incubations over longer periods of time were frequently made to ascertain what part bacteriostatic action played.

Test Organisms

Staphylococcus aureus Rosenbach (*1*) (Government strain No. 209) and *Eberthella typhosa* (Zopf) Weldin (Hopkins strain) were secured from the Food and Drug Administration at Washington. Cultures of the same two organisms were also obtained from the Boston Biochemical Laboratory. The Health Department of Massachusetts at Boston furnished a culture of a hemolytic streptococcus. *Corynebacterium diphtheriae* (Flügge) Lehmann and Neumann was received from the Harvard Medical School, and *Sarcina ventriculi* Goodsir from Brown University. *Staphylococcus aureus* Rosenbach, *Escherichia coli* (Migula) Castellani and Chalmers, *Pseudomonas aeruginosa* (Shroeter) Migula, *Serratia pyoseptica* (Fortineau) Bergey et al, *Proteus vulgaris* Hauser, *Staphylococcus citreus* (Migula) Bergey et al., and *Streptococcus lactis* (Lister) Löhnis were taken from the stock collection of the Department of Biology and Public Health at the Massachusetts Institute of Technology.

sec-Amyltricresol (Pentacresol)

sec-Amyltricresol was dissolved to the extent of 1 per cent in a 2 per cent soap solution (a potassium soap prepared from two parts of coconut oil and 2 parts of castor oil); and the germicidal efficacy of the soap solution of the chemical was determined, using first *Staph. aureus* (Government 209) as the test organism at 20° C. A phenol coefficient of 1 was obtained. Its efficacy against *E. coli* was next determined. The test organism was destroyed by the undiluted 1 per cent stock solution of Pentacresol in 45 but not 30 minutes. Specific action towards *Staph. aureus*, a Gram-positive organism, was thus indicated. Since *E. coli* is a Gram-negative organism, other Gram-negative and Gram-positive bacteria were used in further tests.

TABLE I. GERMICIDAL ACTION OF PENTACRESOL

Test Organism	Phenol Coefficient: 1% solution	Phenol Coefficient: Full-strength chemical	Temperature ° C.	Gram Reaction
1% in 2% Soap Solution				
Staph. aureus (Gov. 209)	1	100	20	+
Staphylococcus aureus (Sherman)	1	100	20	+
Staph. citreus	2.5	250	20	+
Sarcina ventriculi	2	200	20	+
Streptococcus lactis	2	200	20	+
E. typhosa (Hopkins)	0.07+	7+	37	–
1% in 50% Alcohol–10% Acetone Solution				
A hemolytic streptococcus[a]	1+	100+	37	+
C. diphtheriae[a]	0.4+[b]	40+	37	+
E. typhosa (Hopkins)	0.14	14	37	–

[a] Grown and subcultured in beef infusion broth (final pH, 7.6).

[b] Did not survive for 5 minutes in a 1:60 dilution, the highest dilution run.

Staph. citreus, *Sarcina ventriculi*, and *Streptococcus lactis*, all Gram-positive bacteria, were easily destroyed by Pentacresol in high dilution; phenol coefficients of 2.5, 2, and 2, respectively, were obtained in tests conducted at 20° C. On the other hand, *Ps. aeruginosa*, *Ser. pyoseptica*, and *Proteus vulgaris*, Gram-negative bacteria, were much more resistant to this solution; the test organisms survived in the undiluted 1 per cent solution for more than 15 minutes.

There were three possible causes for the specificity thus shown by the soap solution of the chemical. Either the Pentacresol, the soap solution, or the solution of the two, was specific in its action.

To determine whether the Pentacresol was the cause of specificity and to eliminate any possible contributing action of the soap, a 1 per cent solution was prepared in 50 per cent alcohol and 10 per cent acetone. Dilutions of 1:2, 1:3, 1:4, 1:5, 1:10, 1:20, and 1:60 (which correspond to 50, 33.3, 25, 20, 10, 5, and 1.67 per cent of the 1 per cent tincture, respectively) were prepared from this stock solution. At the same time dilutions were made up from 5 per cent phenol for the purpose of showing, in the subsequent tests, that the resistance of each test organism employed was at least equal to that demonstrated in the foregoing tests with the soap solution of Pentacresol (which proved to be the case). The following organisms were then used in germicidal tests at 20° C.: *Staph. aureus*, *Streptococcus lactis*, *E. coli*, *Ps. aeruginosa*, and *Proteus vulgaris*.

Results of the tests showed that the alcohol-acetone solution of Pentacresol was specific in its action towards Gram-positive bacteria, but that it was decidedly more effective towards Gram-negative bacteria than the soap solution of the chemical. The two Gram-positive bacteria, *Staph. aureus* and *Streptococcus lactis*, were destroyed in less than 5 minutes in the 1:20 dilution. *E. coli* and *Proteus vulgaris* were destroyed in less than 5 minutes, and *Ps. aeruginosa* in less than 10 minutes, in the 1:2 dilution of the tincture, but all three of these Gram-negative bacteria survived for at least 15 minutes in the 1:4 dilution.

In order to ascertain what germicidal action could be attributed to the alcohol and acetone present in the stock solution of the 1 per cent Pentacresol, solutions containing varying percentages of 95 per cent alcohol and acetone were prepared, and germicidal tests were made. The solvents present in the stock solution were sufficiently germicidal to destroy each of the test organisms employed in the above tests in less than 5 minutes. But the solvents present in the various dilutions prepared from the stock solution of Pentacresol (1:2, 1:3, 1:4, etc.) failed in all cases to destroy any of the test organisms in 15 minutes.

Staph. aureus (Government 209), *Streptococcus lactis*, *E. coli*, *Ps. aeruginosa*, *Ser. pyoseptica*, and *Proteus vulgaris* were subjected to the action of the 2 per cent soap (which contained no Pentacresol) at 20° C. The bacteria survived for 45 minutes, the duration of the test, in all cases. The soap showed no germicidal properties and thus apparently contributed nothing to the specificity demonstrated by the solutions of Pentacresol.

The results of germicidal tests with some of the common pathogens (Table I) showed that Pentacresol was specific not only for Gram-positive cocci but for Gram-positive rods as well.

Table I shows that Pentacresol was highly efficacious as a germicide against Gram-positive bacteria, pathogenic and nonpathogenic. It also demonstrates the superiority of the tincture over the soap solution where *E. typhosa* was concerned.

Germicidal Action of Pentacresol in Presence of Organic Matter

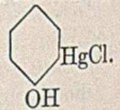
Germicidal tests were carried out according to F. D. A. methods (*2*) with the 1 per cent tincture of Pentacresol in the presence of 20 per cent sterile horse-blood serum with *Staph. aureus* (Government 209) and *E. coli* as test organisms at 30° C. Comparative tests were conducted at the same time with three of the leading market mercurials (tinctures), mercuric chloride excluded, a phenol derivative, solutions of *o*-hydroxyphenylmercuric chloride (the Mercarbolides), and Mercresin.

When *Staph. aureus* was used as the test organism in the presence of 20 per cent serum, the phenol coefficient of the 1 per cent tincture of Pentacresol was 0.16, or nearly three times that of the most effective mercurial (mercurial A) and over eight times that of the phenol derivative.

Although there was a reduction in germicidal efficacy due to the presence of blood serum when *Staph. aureus* was employed, there was practically no reduction when *E. coli* was used as the test organism; a phenol coefficient of 0.05 was obtained. This value was just one-half that of the most effective mercurial (mercurial A), but was greater than that of market mercurial C and far superior to that of the phenol derivative.

The Mercarbolides

"Mercarbolide" is the name given a preparation containing 0.1 per cent *o*-hydroxyphenylmercuric chloride,



Three solutions of this mercurial were investigated—an aqueous solution, an aqueous glycerol–sodium chloride solution, and an aqueous alcohol–acetone–sodium chloride solution. Analyses of these solutions are given in Table II.

Table II and other data not presented here demonstrate several facts. The apparent phenol coefficients of the three solutions of Mercarbolide were four to ten times as great as the true coefficients when *Staph. aureus* was employed as the test organism; the difference was due to bacteriostasis. The aqueous glycerol–sodium chloride solution did not destroy *Staph. aureus* in the usual 5-minute period, but the solution possessed bacteriostatic properties in the lower dilutions which, over a period of time, were equivalent to bactericidal action. Phenol coefficients obtained with *E. typhosa* were eighteen to one hundred times greater than corresponding coefficients secured with *Staph. aureus*. Secondary subcul-

TABLE II. GERMICIDAL ACTION OF MERCARBOLIDE

Mercarbolide Solution[a]	Test Organism	Phenol Coefficient: Apparent	Phenol Coefficient: True[b] A	Phenol Coefficient: True[b] B	Dilution	Test Organism: Destroyed	Test Organism: Not destroyed	Temperature
						Min.	*Min.*	° *C.*
Aqueous	*Staph. aureus* (Gov. 209)	0.17+	0.038	38	..	..	..	37
	Same	....	....	....	1:1	..	15	20
	E. typhosa (Hopkins)	...	0.67 or greater	670 or greater	..	..	..	37
Aqueous, glycerol (10%)–NaCl (0.9%)	*Staph. aureus* (Gov. 209)	0.13+	0.013	13	1:1	10	5	37
	Same	0.07	0.011	11	1:1	15	10	30
	E. coli	0.2+	0.16±	160	1:14	10	5	30
	E. typhosa	....	1.4±	1400	..	..	..	37
Tincture, alcohol (50%)–acetone (10%)–NaCl (0.9%)	*Staph. aureus* (Gov. 209)	0.14+	0.038	38	..	..	..	37
	Same	....	0.038	38	1:3	10	5	30
	E. coli	0.1+	0.086	86	..	..	..	30
	E. typhosa	....	1.13	1130+	..	..	..	30

[a] Each stock solution contained 0.1% *o*-hydroxyphenylmercuric chloride besides the constituents listed.

[b] The coefficients recorded in column *A* are based on the 1:1000 solution (0.1%) of *o*-hydroxyphenylmercuric chloride; those in column *B*, on the original *o*-hydroxyphenylmercuric chloride.

ture tubes, though used in the germicidal tests with *E. typhosa*, were found to be unnecessary because of the high dilutions in which Mercarbolide was lethal to this organism.

A comparison of the results shown in Table II indicates that the tincture was superior to the aqueous glycerol–sodium chloride solution and equal to the aqueous solution in respect to germicidal action against *Staph. aureus* at 37° C. However, the aqueous glycerol–sodium chloride solution appeared to be best in germicidal efficacy towards *E. coli* and *E. typhosa*.

The germicidal efficacy of the Mercarbolides varied directly with that of phenol as the medication temperature was changed and when *Staph. aureus* was employed.

Bacteriostatic action in the subculture tubes, inoculated from the lower dilutions of *o*-hydroxyphenylmercuric chloride during tests, corresponded to bactericidal action, for there was enough of the chemical present to prevent growth until the reproductive mechanism of the test organism was permanently disabled. This fact was proved by the absence of growth in secondary subcultures made after a few hours.

Germicidal Action of Mercarbolide in Presence of Organic Matter

Germicidal tests were performed according to F. D. A. methods with the exception that 20 per cent sterile horse-blood serum was present in the final chemical dilutions. A comparison of the germicidal action in the presence of organic matter was made with the chemicals listed in Table IV.

When *Staph. aureus* (Government 209) was employed as the test organism at 30° C., there was practically no reduction in the germicidal efficacy of Mercarbolide tincture due to the blood serum. Mercarbolide tincture was superior to mercurials B and C, aqueous solution of Mercarbolide, and the phenol derivative. Although the coefficient obtained with *E. coli* in the presence of organic matter was greater than that with *Staph. aureus*, there was a reduction in efficacy due to the serum. Mercarbolide tincture showed greater germicidal action than mercurial C, aqueous Mercarbolide solution, and the phenol derivative, and nearly as much as the 1 per cent tincture of Pentacresol toward *E. coli* at 30° C.

Mercresin

Mercresin is a solution of 0.1 per cent *o*-hydroxyphenylmercuric chloride and 0.1 per cent *sec*-amyltricresol in 50 per cent alcohol, 10 per cent acetone, and water.

The data in Tables I, II, and III demonstrate clearly that Mercresin combines in many respects the advantages of both Mercarbolide and Pentacresol: the strong action of the former against such Gram-negative organisms as *E. typhosa* and *E. coli*, and of the latter against Gram-positive organisms such as the hemolytic streptococcus and *Staph. aureus*.

When *Staph. aureus* was employed as the test organism, the germicidal efficacy of Mercresin varied directly with that of phenol as the temperature was changed.

Effect of Exposure Period on Germicidal Action of Mercresin

Tests to determine the effect of aqueous dilutions of Mercresin on *Staph. aureus* (Government 209) were carried out according to F. D. A. methods at 37° C., varying the periods of exposure from a few seconds to several hours. The time recorded for the short exposures was that elapsing between the instant when the first drop of culture struck the chemical solution in the medication tube and the instant when the 4-mm. loopful of material from the medication tube was deposited into sterile Reddish broth. The average results of the tests involving the lower dilutions are shown in Figure 1. The test organism was destroyed in less than 15 seconds by a 1:5 dilution, in less than 1 minute by all dilutions up to and including 1:10, in 5 minutes or less by all dilutions up to and including 1:16. A prolongation of the curve (indicated by the dotted line) demonstrated that Mercresin was practically instantaneous in its action against *Staph. aureus*. Other tests showed that *Staph. aureus* was destroyed in less than 15 seconds by a 1:5 dilution of Mercresin at 30° C. and in less than 4 hours by a 1:60 dilution at 37° C.

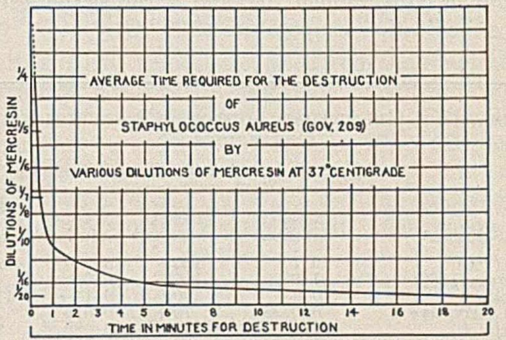


FIGURE 1

Germicidal Action of Mercresin in Presence of Organic Matter

Regular germicidal tests were carried out at 30° C., with the exception that normal horse serum, without preservative,

TABLE III. GERMICIDAL ACTION OF MERCRESIN

Test Organism	Phenol Coefficient 37° C.	Phenol Coefficient 30° C.	Test Organism	Phenol Coefficient at 20° C. True	Phenol Coefficient at 20° C. Apparent[a]
Staph. aureus (Gov. 209)	0.21	0.2	*Staph. aureus*	0.2	...
E. typhosa (Hopkins)	0.28	0.35	*Ps. aeruginosa*	...	0.5
A hemolytic streptococcus[b]	0.3	....	*Ser. pyoseptica*	...	0.38
C. diphtheriae[b]	0.18	....	*B. hoffmanni*	...	0.18+
E. coli	..	0.11+	*E. coli*	...	0.23

[a] Values obtained by the F. D. A. method when no secondary subcultures were made.

[b] Grown and subcultured in beef infusion broth (final pH, 7.6).

was substituted for some of the water in preparing dilutions of Mercresin and the other chemical solutions.

Staph. aureus (Government 209) was destroyed in less than 5 minutes in the presence of 50 per cent horse serum (five times the quantity of serum advocated by F. D. A. methods, (*2*). Using the same test organism, the average phenol coefficient of Mercresin in the presence of 20 per cent serum was 0.055.

A comparison of Mercresin with eight other chemical solutions[1] demonstrated the following descending order of germicidal efficacy in the presence of 20 per cent serum, when *Staph. aureus* (Government 209) was used as the test organism at 30° C.: iodine (7 per cent), Pentacresol (1 per cent), Mercresin and mercurial A (of nearly equal value), Mercarbolide, mercurial B, mercurial C, the phenol derivative, and aqueous Mercarbolide.

When *E. coli* was used, the descending order was: iodine, mercurial A, mercurial B, Mercresin, Pentacresol, Mercarbolide, mercurial C, aqueous Mercarbolide (glycerol–sodium chloride solution), and the phenol derivative.

Table III shows that *E. coli* was the most resistant to Mercresin of any of the eight test organisms employed. Yet the phenol coefficient of Mercresin, using *E. coli* as the test organism at 30° C. in the presence of 20 per cent serum, was 0.054.

Germicidal Activity of Some Antiseptics and Germicides

Germicidal tests were performed with the chemical solutions listed in Table IV, according to F. D. A. methods, using *Staph. aureus* (Government 209) and *E. coli* as the test organisms at a medication temperature of 30° C.

TABLE IV. GERMICIDAL ACTION OF ANTISEPTICS AND GERMICIDES

	Average Phenol Coefficient			
	Staph. aureus		*E. coli*	
Solution[a]	Market solution	Full-strength chemical[b]	Market solution	Full-strength chemical[b]
Iodine (7%)	10.7	153 −	8.9+	127
Pentacresol (1%)	1.0	100	0.05	5
Mercresin	0.2+	200+	0.11+	111+
Phenol derivative	0.07+	70+	0.075	75
Mercurial A	0.047±	9.4	0.089	17.8
Mercarbolide	0.038	38	0.086	86
Mercurial B	0.034	1.7	0.067	3.35
Mercurial C	0.025	25	0.039	39
Aqueous Mercarbolide	Survival for 10 min.	...	0.16	160

[a] All the solutions were tinctures except the phenol derivative and aqueous Mercarbolide.

[b] Phenol coefficients calculated on the basis of the dry chemical.

Using phenol coefficients as the basis for comparing the germicidal activity of the market solutions of the chemicals listed in Table IV, the descending order of germicidal efficacy was as follows when *Staph. aureus* (Government 209) was employed as the test organism: iodine, Pentacresol, Mercresin, the phenol derivative, mercurial A, Mercarbolide, mercurial B, mercurial C, and aqueous Mercarbolide.

The descending order with *E. coli* was: iodine, Mercresin, aqueous Mercarbolide, mercurial A, Mercarbolide, the phenol derivative, mercurial B, Pentacresol, and mercurial C.

Mercresin was superior to all the other market chemical solutions tested, except iodine (7 per cent) and Pentacresol in respect to *Staph. aureus*, and except iodine and aqueous Mercarbolide in regard to *E. coli*.

Mercarbolide tincture was superior as a germicide to mercurials B and C, and nearly as effective as mercurial A against both *Staph. aureus* and *E. coli*.

Summary and Conclusions

sec-AMYLTRICRESOL. Pentacresol (1 per cent in 2 per cent soap solution) at 20° C. demonstrated high germicidal action towards Gram-positive bacteria such as the hemolytic streptococcus, but was low in efficacy against Gram-negative bacteria such as *E. coli*. A 1 per cent solution of the chemical in 50 per cent alcohol and 10 per cent acetone served as a much more effective stock solution. Dilutions of the tincture, high enough to rule out the bactericidal action of the solvents, were germicidal towards Gram-negative bacteria and readily destroyed *E. typhosa*. In the presence of 20 per cent horse serum, Pentacresol (1 per cent) was more effective as a germicide against *Staph. aureus* than the six mercurials and the phenol derivative with which it was compared.

o-HYDROXYPHENYLMERCURIC CHLORIDE. Mercarbolide tincture, in contrast to Pentacresol, was most effective in germicidal action towards Gram-negative bacteria, the phenol coefficient with *E. typhosa* being over 1100 on the basis of the dry chemical. The different solutions of Mercarbolides demonstrated marked bacteriostatic action towards *Staph. aureus*. In the presence of 20 per cent serum, Mercarbolide tincture was reduced in efficacy only slightly, if any, when *Staph. aureus* was employed as the test organism. There was some reduction in efficacy when *E. coli* was used. Aqueous Mercarbolide solution showed higher germicidal action than the tincture towards *E. typhosa* and *E. coli*, but was not as effective as a bactericide against *Staph. aureus*.

MERCRESIN. This chemical was fairly uniform in its germicidal activity towards all the Gram-positive and Gram-negative pathogens and nonpathogens examined at 20°, 30°, and 37° C. Germicidal action was especially pronounced towards the hemolytic streptococcus and *E. typhosa*. Bacteriostasis was demonstrated to such a degree that secondary transfers were necessary in most cases to obtain true germicidal values. Short-time exposure tests showed Mercresin to be extremely rapid (almost instantaneous) in germicidal action against *Staph. aureus*. In the presence of 20 per cent horse-blood serum and using *Staph. aureus* as the test organism at 30° C., Mercresin was superior in germicidal efficacy to all the market mercurials examined except one, to which it was equal in value. Mercresin has shown no signs of deterioration over long periods of time.

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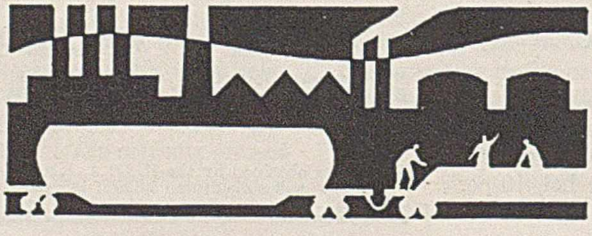
RECEIVED February 4, 1936. Contribution No. 68 from the Department of Biology and Public Health, Massachusetts Institute of Technology. The work was supported by a fellowship from the Upjohn Company.



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[1] All the solutions compared were tinctures, with the exception of aqueous Mercarbolide and the phenol derivative.

HYDROCARBON VAPOR PRESSURES

The saturated vapor pressures of all hydrocarbons with molecular weights over 30, whose data are available, can be correlated by three equations, if boiling point and critical temperature and pressure are known; and the latter can be calculated for the normal paraffin series.

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THE general equation chosen is

$$\log_{10} P = A(t - b)/T = A(1 - B/T) \quad (1)$$

where P = pressure, t, b = temp. and boiling point, ° C., T, B = the same, ° K. (0° C. = 273.16° K.). A varies through a relatively short range. The equation can be derived from an approximate integration of the Clapeyron equation and has been used extensively. Thiesen (*14*) used a formula for steam pressures which is equivalent to Equation 1 with $A = 5.409 + f(t - b)$. A formula equivalent to Equation 1 is used in International Critical Tables (*6*) with A constant for low pressures. The evidence indicates that A varies uniformly from the triple point to the critical point but is approximately constant for the vapor pressure of solids in the crystalline state. Cragoe (*4*) plots curves of A (Φ) against T/B for a number of substances.

Since normal boiling point is arbitrarily selected, whereas critical temperature is a natural datum point, it was thought best to utilize the theorem of corresponding states and plot A against reduced temperature, T/T_c, where T_c is the critical temperature in ° K. Then the obvious values to correlate for different members of a series would be A at the critical temperature, or A_c, and the values to correlate for each member of the series would be A/A_c. Log A_c was found to be preferable as the substance characteristic, since it proved to be linear with molecular weight for the normal paraffin series, the first to be considered. Accordingly, log (A/A_c) was plotted against $T_R(T/T_c)$ for propane, using the data named on Figure 1 and for pentane to octane, using Young's data (*17*). Each of these curves was found to be parabolic with log (A/A_c) = 0 at T_R = 1 and at T_R = 0.85. The fact that all the curves crossed the zero line at 0.85, as closely as could be detected, was particularly significant and indicated the equation,

$$\log_{10}(A/A_c) = E(1 - T_R)(F - T_R) \quad (2)$$

where F = 0.85 for the scope noted

The evaluation of E was effected by taking temperatures at which p = 15 mm. mercury and plotting log (B/T_{15}) against B. This proved to be linear even up to heptadecane. Using these values of T_{15}, two concordant equations were obtained for E and A_c which satisfied Equation 2:

$$E = 0.0008B - 0.04895 \quad (3)$$
$$\log_{10} A_c = 0.61076 + 0.0005m \quad (4)$$

Another equation which helped to correlate the critical points was:

$$\log_{10}(mP_c/C) = 0.766484 - 0.0000842m - 0.030506 \log_{10}m \quad (5)$$

where m = approx. mol. weight (whole numbers)
P_c = critical pressure, atm.
C = critical temp., ° K.

These equations fix P_c and C, which were calculated by trial and error.

The equation for normal boiling points was derived in a previous survey (*2*):

$$\log_{10}B = 1.07575 + 0.949128 \log_{10}m - 0.101 \log_{10}{}^2m \quad (6)$$

TABLE I lists values calculated from these equations for the series propane to n-octane; important observed values are also included for comparison. Table II gives values of A for T_R = 0.4, 0.5, 0.6, 0.7, 0.78, 0.925, and 1.0, calculated from Equations 2 and 3. These points are used in plotting the curves in Figures 1 to 6. The observed points were calculated from the data noted. The agreement is

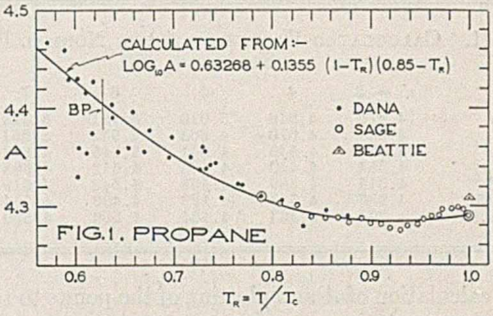

FIG. 1. PROPANE

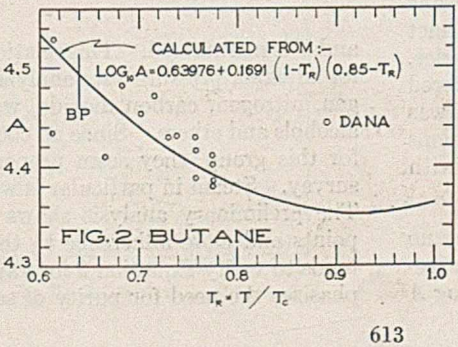

FIG. 2. BUTANE

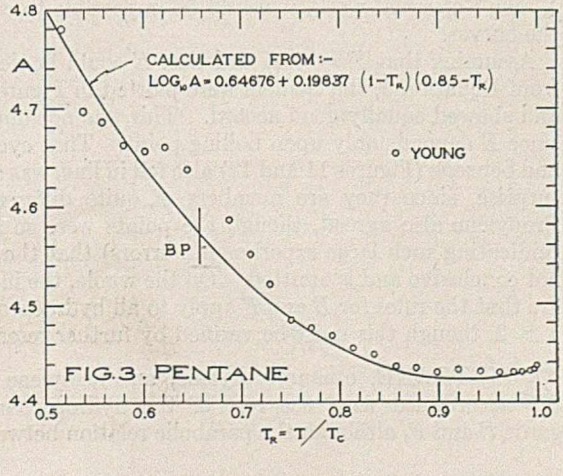

FIG. 3. PENTANE

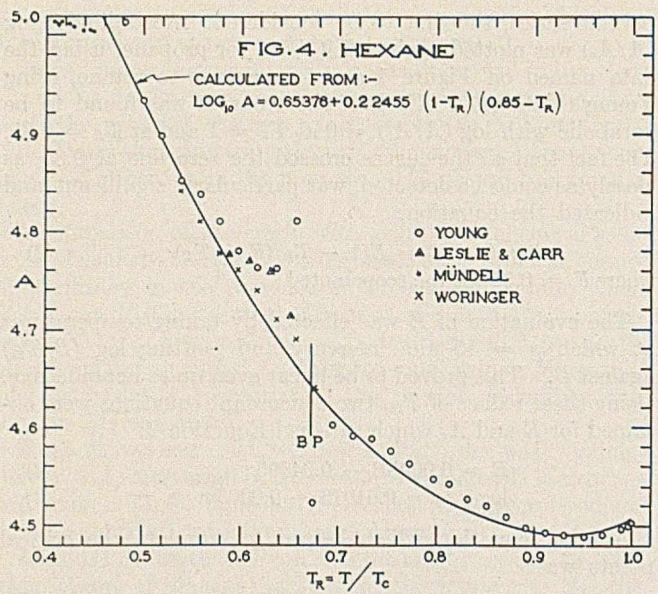
FIG. 4. HEXANE

particularly good, when compared with plots of older data where the points would fall entirely off the charts as drawn or were so scattered that not even the shape of the curves could be determined.

Table I. Principal Constants for Normal Paraffin Series

n =	3	4	5	6	7	8
Calcd. B, ° K.	230.57	272.51	309.16	341.87	371.54	398.75
Calcd. C, ° K.	373.27	426.34	470.24	507.64	540.20	569.00
Obsvd. C, ° K.	373.27[a]	426.36[b]	470.36[c]	507.96[c]	540.01[c]	569.36[c]
Calcd. P_c, atm.	43.77	37.51	33.02	29.60	26.89	24.68
Obsvd. P_c, atm.	43.78[a]	37.5[d]	33.04[c]	29.64[c]	26.90[c]	24.70[c]
Calcd. $\log_{10} A_c$	0.63276	0.63976	0.64676	0.65376	0.66076	0.66776
Obsvd. $\log_{10} A_c$	0.63268[a]	.....	0.64704[c]	0.65371[c]	0.66105[c]	0.66720[c]
Calcd. mP_c/C	0.71264	0.70780	0.70376	0.70023	0.69705	0.69414
Obsvd. mP_c/C	0.71264[a]	.....	0.70376[c]	0.70023[c]	0.69705[c]	0.69324[c]
Calcd. E	0.13551	0.16907	0.19837	0.22455	0.24828	0.27005

[a] Sage (*12*). [b] Seibert (*13*). [c] Young (*17*). [d] Kuenen (according to Grimard) (*7*).

Table II. Calculated Values of A for Normal Paraffin Series

T_R	n = 3	4	5	6	7	8
0.4	4.670	4.846	5.016	5.181	5.343	5.504
0.5	4.534	4.670	4.803	4.932	5.061	5.188
0.6	4.429	4.536	4.641	4.745	4.848	4.952
0.7	4.354	4.440	4.526	4.612	4.698	4.785
0.78	4.314	4.389	4.465	4.542	4.619	4.698
0.925	4.285	4.353	4.422	4.493	4.564	4.637
0.85, 1.0	4.293	4.363	4.434	4.506	4.579	4.653

This calculation of A and plotting of the points to the sensitive scales used, is a severe test of accuracy. Without Young's classical work, it would be impossible to coördinate the curves.

Assuming that $F = 0.85$ and that E could be determined from Equation 3, the isomers were plotted in Figures 7 to 10 and showed equally good accord. This was not unexpected, since E depends only upon boiling point. That cyclohexane and benzene (Figures 11 and 12) also fell in line, was a distinct surprise, since they are members of quite different series. Propylene also agreed, though the points were so scattered (indicating such large experimental errors) that the plot was not conclusive and is omitted. On the whole, the indications are that the rules for E and F apply to all hydrocarbons with $n > 2$, though this must be verified by further research.

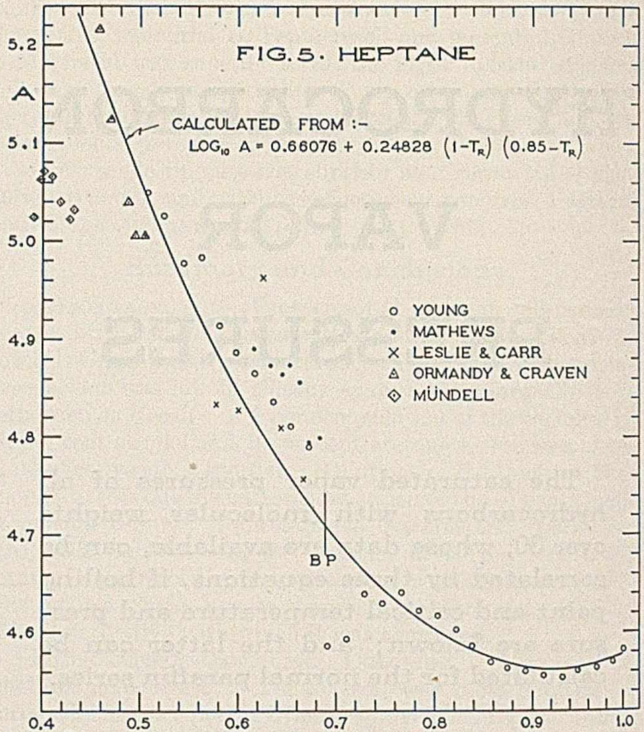
FIG. 5. HEPTANE

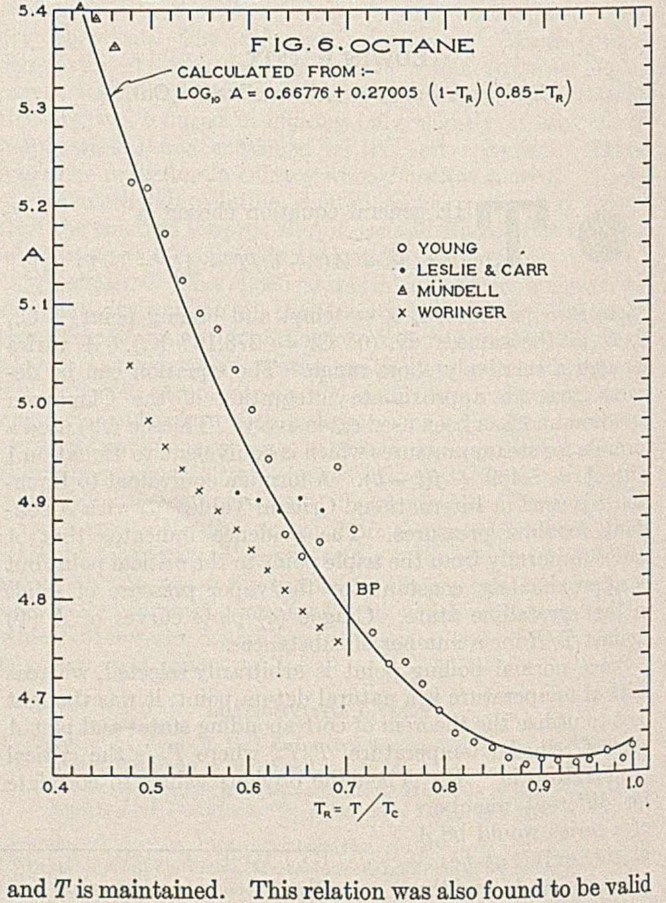
FIG. 6. OCTANE

METHANE, ethane, ethylene, and acetylene show no accordance with the rest of the hydrocarbons as regards E and F, although the parabolic relation between log A and T is maintained. This relation was also found to be valid for all vapor pressure data analyzed, including hydrogen, oxygen, nitrogen, carbon dioxide, water, ammonia, and several alcohols and ethers. Since no coördination has yet developed for this group, they seem properly to belong to a separate survey. Steam in particular is well worth a separate survey. The preliminary analysis shows such smooth alignment of points and close adherence to the parabolic relation that it tends to verify Equation 2 for vapors in general. It also emphasizes the need for purity of sample. The data on steam seem to show almost a higher order of precision. Part of this is no doubt due to its industrial importance and the amount of labor involved in its investigation, but part is also due to the ease with which pure samples can be obtained. Impurity of sample has so far been the greatest handicap to securing concordant vapor pressure data for the hydrocarbons.

The importance of purity is also emphasized by the findings in regard to boiling points (*2*). The latter were correlated to 0.01° C. from propane to

TABLE III. CALCULATIONS FOR MISCELLANEOUS HYDROCARBONS

	Isobutane	Isopentane	Diisopropyl	Diisobutyl	Cyclohexane	Benzene
Obsvd. *B*, ° K.	261.08[a]	301.01[c]	331.25[c]	382.37[c]	353.98[c]	353.37[c]
Obsvd. *C*, ° K.	406.86[b]	460.96[c]	500.51[c]	549.96[c]	553.11[c]	561.66[c]
Obsvd. P_c	36.54 atm.[b]	25018 mm.[c]	23360 mm.[c]	18660 mm.[c]	30260 mm.[c]	36395 mm.[c]
Calcd. $\log_{10} A_c$	0.63578	0.64079	0.64335	0.65913	0.64781	0.65620
Calcd. *E*	0.15990	0.19185	0.21605	0.25695	0.23423	0.23375
Calcd. *A*:						
$T_R = 0.4$	.....	.....	.....	5.352	5.141	5.240
$T_R = 0.5$	4.611	4.725	4.791	5.060	4.884	4.979
$T_R = 0.6$	4.485	4.571	4.623	4.840	4.691	4.782
$T_R = 0.7$	4.395	4.461	4.496	4.685	4.554	4.642
$T_R = 0.78$	4.347	4.403	4.433	4.604	4.481	4.569
$T_R = 0.925$	4.314	4.362	4.387	4.547	4.431	4.517
$T_R = 0.85$ & 1.0	4.323	4.373	4.399	4.562	4.444	4.531

[a] Dana (*5*). [b] Seibert (*13*). [c] Young (*17*).

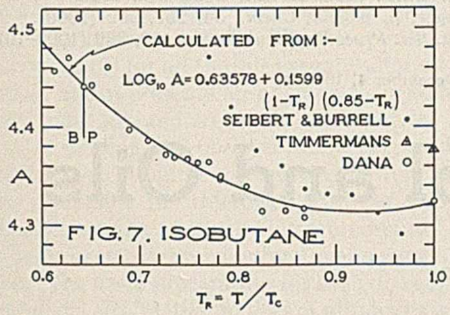

FIG. 7. ISOBUTANE

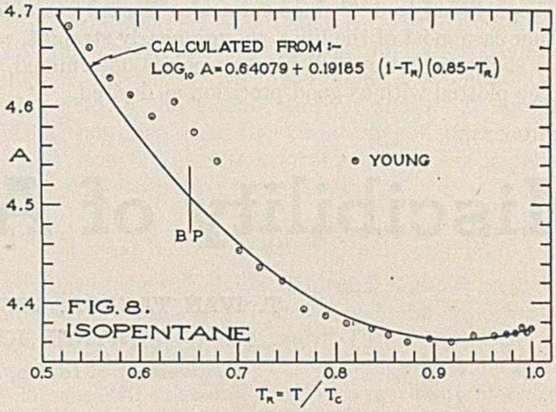

FIG. 8. ISOPENTANE

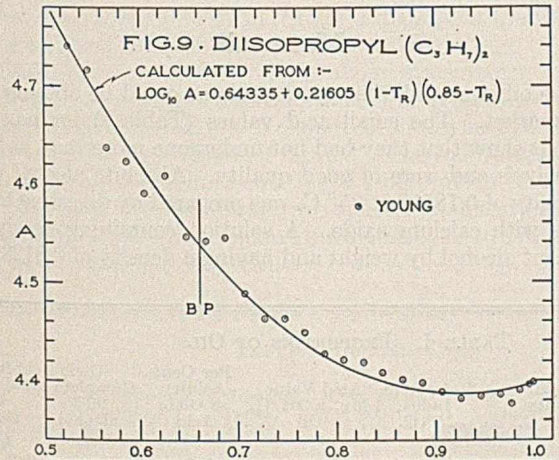

FIG. 9. DIISOPROPYL $(C_3H_7)_2$

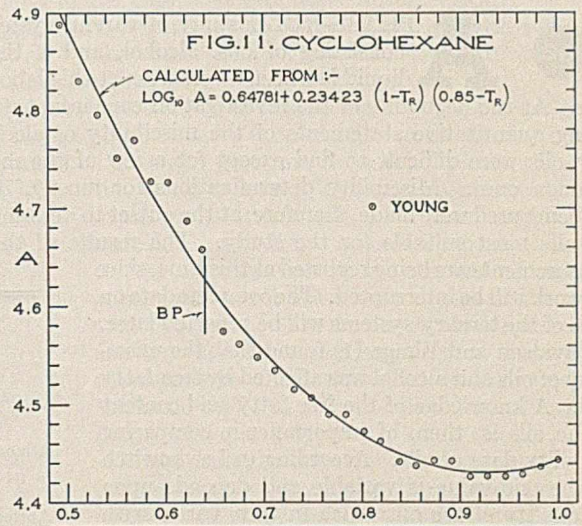

FIG. 11. CYCLOHEXANE

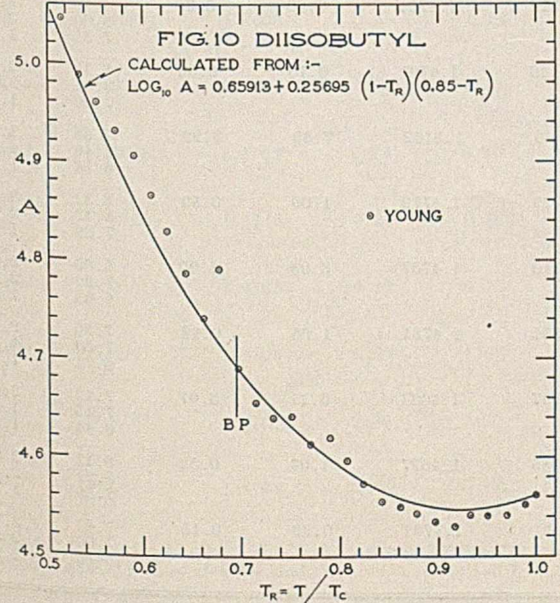

FIG. 10. DIISOBUTYL

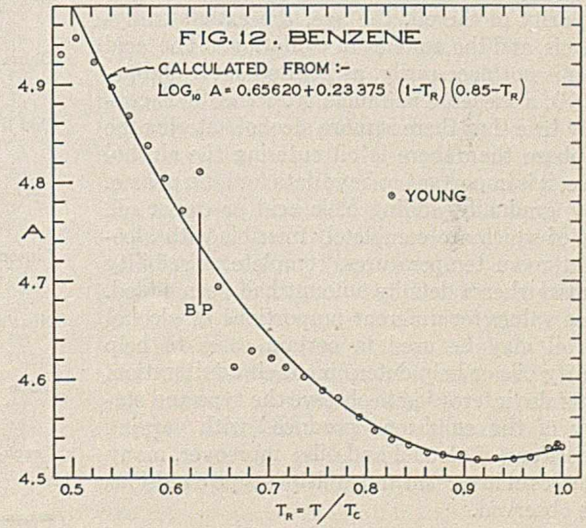

FIG. 12. BENZENE

octane; but the samples had mainly been purified with meticulous care by prolonged fractional distillation, fractional crystallization and chlorosulfonic acid treatment. If equal care were used in purifying samples, hydrocarbon vapor pressures would show better correlation. It was also brought out in the previous article (*2*) that methane and ethane were not correlative with the rest of the series as regards boiling points; therefore it is not surprising that they are not correlative as regards other thermodynamic properties.

The chief use of the equations given would be to determine accurately certain key points for the plotting of curves. They could be plotted on charts with the pressure axis logarithmic and the temperature axis laid off arbitrarily to make the steam curve a straight line, as suggested several years ago (*3*). It would be better still, probably, to lay off the temperature axis proportional to $1/T$ since this value is easily calculated. In either case most of the lines, though nearly straight, would have a slight curvature. With four points determined, they could be plotted with as good precision as desired.

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Miscibility of Alcohol and Oils

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A PHASE-RULE study of various systems consisting of oils, alcohol, and a third liquid has been in progress at this laboratory. At the beginning of the investigation concordant data giving quantitative statements of the miscibility of alcohol with oils were difficult to find except for a few of the most common ones. Miscibility determinations for most of the oils being used were made, therefore, at the outset to determine the oils most suitable for the study. The results of these measurements are being reported at this time, since the work will be interrupted. The complete data on some of the ternary systems will be reported later.

Davidson and Wrage (*1*) found that the miscibility of oils and alcohol was affected by free fatty acid. A knowledge of the free fatty acid content of the oils is, then, of importance in comparing solubility data of oils. According to Lewkowitch (*5*) the acid value is variable and depends upon the quality of the oil, which in turn varies with the purity of the oil, the age, the extent of hydrolysis, and the amount of oxidation. The acid value is not necessarily, as pointed out by Jamieson (*3*), a measure of rancidity. Since it is generally true that there is more alcohol entering the oil phase than there is oil entering the alcohol phase, it is important to have data for both phases.

By gradually adding oleic acid or castor oil, both of which are completely miscible with alcohol at room temperatures, complete miscibility resulted when a definite amount had been added. These values for different proportions of alcohol and oil may be used in certain cases to help identify oils or help determine their adulteration. It was also interesting to observe the type and stability of the emulsions produced with varying proportions of alcohol and oils; moreover, many examples of inversion and multiple-type emulsions were observed.

Materials

The oils were all of as good grade as could be obtained on the market. The small acid values (Table I) for most of the oils show that they had not undergone more than normal hydrolysis and were of good quality. Absolute alcohol with a density of 0.78515 at 25° C. was prepared by digesting three times with calcium oxide. A solution containing nearly 90 per cent alcohol by weight and having a density of 0.81282 at

Table I. Properties of Oils

Oil	Specific Gravity, 25°/4° C.	Refractive Index, 25° C.	Acid Value Mg. KOH/G. Oil	Per Cent Acidity as Oleic Acid	Oleic Acid for Complete Miscibility 90% alcohol Cc.	Abs. alcohol Cc.
Almond sweet	0.9112	1.4701	0.60	0.30	8.18[a] 8.30 7.81	2.72[a] 2.60 1.88
Apricot-kernel	0.9126	1.4701	0.10	0.05	8.10 8.34 7.80	2.70 2.66 1.87
China wood	0.9346	1.5162	7.80	3.92	7.68 7.46 6.14	1.78 1.80 1.30
Cod liver	0.9199	1.4772	1.00	0.50	8.31 8.42 7.89	2.92 2.72 1.92
Corn	0.9110	1.4707	3.98	2.00	6.86 7.00 6.68	2.00 2.00 1.40
Linseed	0.9251	1.4781	1.95	0.98	7.30 7.50 6.71	2.18 1.80 1.18
Neat's-foot	0.8937	1.4684	6.11	3.07	7.12 7.15 6.44	2.05 1.58 1.02
Olive	0.9085	1.4677	1.03	0.52	8.12 8.21 7.50	2.81 2.43 1.71
Peach-kernel	0.9100	1.4701	0.29	0.15	7.41 7.60 6.85	2.58 2.56 1.70

25° C. was prepared by adding distilled water to 95 per cent alcohol.

Experimental Results

The acid number of each oil was determined by the method outlined by Jamieson (*4*) and was calculated to percentage acidity as oleic acid. These values, together with the refractive index of the oils at 25° C. and the volume of oleic acid just necessary to cause complete miscibility of the alcohol and oils at 25.0° ± 0.3° C., are given in Table I. The volumes chosen for the miscibility tests were such that the ratio of oil to alcohol was 1 to 2, 1 to 1, and 2 to 1. As an increasing volume of oleic acid was added to the mixture, the volume of the alcohol phase decreased until it finally disappeared and complete miscibility resulted.

Miscibility data were obtained after shaking the samples vigorously with a motor shaker for 4 hours in the air thermostat regulated to 25.0° ± 0.3° C. This temperature is below the Crismer value (*2*) for all the oils except castor oil and oil of bitter almond, and represents an average room temperature. The samples were allowed to stand overnight, or longer in some cases, for settling and observation of type and stability of emulsion formed. Volume measurements were taken from the 100-cc. graduates in which the samples were shaken. Density determinations at 25.0° C. were carefully made for each layer before and after mixing by use of a small glass-bulb pycnometer. The usual precautions for such density measurements were taken. Refractive indices of all phases were measured to determine whether or not any correlation existed between them and the concentration changes in each phase. In most cases there were small regular changes, but the values were considered to be of little practical value.

Calculations were made from the above measurements and are reported on a weight basis in Table II in accordance with the suggestions of Seidell (*6*). Volume solubilities may be easily calculated from these results if desired. The following equations, which are useful in calculating the percentage composition by weight of other liquid mixtures from density measurements where little or no change in volume occurs in mixing, were used to calculate the results:

$$\text{Per cent oil in alcohol phase} = \frac{(\text{density oil})(\text{density alcohol phase} - \text{density alcohol})}{(\text{density alcohol phase})(\text{density oil} - \text{density alcohol})} \qquad (1)$$

$$\text{Per cent alcohol in oil phase} = \frac{(\text{density alcohol})(\text{density oil} - \text{density oil phase})}{(\text{density oil phase})(\text{density oil} - \text{density alcohol})} \qquad (2)$$

These equations may be written in the general form,

$$\text{Per cent } A \text{ in mixture } C \text{ of } A \text{ and } B = \frac{(a)(c - b)}{(c)(a - b)}$$

where a, b, and c represent the density of A, B, and C, respectively.

The calculations were made on the assumption that the oil going into solution had the same density as the oil sample. That this assumption is nearly true is supported by the experiments of Davidson and Wrage (*1*), in which they studied the solubility of different glyceryl esters and the distribution of free fatty acid in the alcohol and oil phase. It should be recognized, however, that the variation and uncertainty in the composition of the oils are factors to be considered in evaluating and comparing the results.

Discussion

The extent of the miscibility of alcohol and oils seems to be characteristic for each oil. The acid value is important, but a comparison of the values given in Table I with the miscibilities show that it is not the determining factor. High acid values increase the miscibility and also markedly increase the stability of the emulsions produced during shaking. A comparison of the normal iodine value of the oils with the solubility shows that there is no correlation between unsaturation and the miscibility of the oils.

In general there is two to three times as much alcohol going into the oil phase as there is oil going into the alcohol phase. Also more oil generally goes into the alcohol phase when the ratio of alcohol to oil is least. This may seem to indicate that some certain component of the oil is most readily dissolved by the alcohol, but it is not necessarily true. There is no regular variation in the amount of alcohol going into the oil phase with change in the ratio of alcohol to oil. The amount of alcohol dissolved and the variation with change in ratio seems to be characteristic of the oil. The solubility of the alcohol in the oil is more constant with change in ratio than is the solubility of oil in alcohol.

Many examples show the importance of phase-volume ratio in determining the type of emulsion formed. In many cases, particularly when equal amounts of alcohol and oil were used, multiple-type emulsions were observed. Often, when adding increasing volumes of oleic acid, we obtain first a multiple type and then an inversion. Increasing volumes of oleic acid when added to a mixture of alcohol and oil gradually decrease the volume of the alcohol phase and the stability and fineness of the emulsion formed until finally the solution is just cloudy and then clear. Apparently there is first an inversion of emulsion type from oil in alcohol to alcohol in oil and then a gradual decrease in size of droplets to molecular dimensions when a complete solution results. In this approach to or just beyond the range of colloidality may lie the explanation for part of the change in miscibility with change in ratio, though the solution of a particular component of the oil is probably responsible for most of the change.

TABLE I (*Continued*)

Oil	Specific Gravity, 25°/4° C.	Refractive Index, 25° C.	Acid Value Mg. KOH/G. Oil	Per Cent Acidity as Oleic Acid	Oleic Acid for Complete Miscibility 90% alcohol *Cc.*	Oleic Acid for Complete Miscibility Abs. alcohol *Cc.*
Peanut	0.9099	1.4695	0.48	0.24	7.40 7.48 6.80	2.65 2.70 1.88
Poppy-seed	0.9177	1.4735	1.01	0.51	7.55 7.65 6.94	2.25 2.01 1.39
Rapeseed	0.9085	1.4705	0.78	0.39	9.28 9.15 8.22	3.90 3.60 2.56
Sesame	0.9178	1.4719	0.24	0.12	8.10 7.90 7.50	2.88 2.60 1.68
Soy-bean	0.9163	1.4735	0.29	0.15	8.02 8.35 7.62	2.54 2.35 1.70
Sunflower	0.9241	1.4809	2.09	1.05	6.40 6.92 6.40	1.78 1.80 1.30
Walnut	0.9186	1.4757	7.39	3.72	6.54 6.63 6.10	1.66 1.50 0.98
Whale	0.9145	1.4748	2.10	1.06	7.35 7.58 6.95	2.60 2.49 1.60

[a] In each case, first figure represents results with 7 cc. of oil and 14 cc. of alcohol; second, 10.5 cc. of oil and 10.5 cc. of alcohol; and third, 14 cc. of oil and 7 cc. of alcohol.

Table II. Miscibility of Alcohol and Oil

Oil	90% Alcohol by Weight, Sp. Gr. 25°/4° = 0.81282								Absolute Alcohol, Sp. Gr. 25°/4° = 0.78515							
	Sp. gr., 25°/4° C.		Miscibility		Vol. of phases		Type of emulsion	Stability, time of settling	Sp. gr., 25°/4° C.		Miscibility		Vol. of phases		Type of emulsion	Stability, time of settling
	Alcohol phase	Oil phase	Oil in 100 g. alcohol phase	Alcohol in 100 g. oil phase	Alcohol phase	Oil phase			Alcohol phase	Oil phase	Oil in 100 g. alcohol phase	Alcohol in 100 g. oil phase	Alcohol phase	Oil phase		
			Grams	*Grams*				*Min.*			*Grams*	*Grams*				*Min.*
Almond sweet	0.8138[a]	0.9024	1.14	8.06	44.8	15.2	OA	300	0.7907[a]	0.8898	5.03	14.99	44.5	15.5	OA	30
	0.8147	0.9021	2.16	8.33	28.0	32.0	AO	30	0.7914	0.8912	5.67	13.98	24.1	34.9	AO	60
	0.8182	0.9023	6.11	8.15	11.7	48.3	AO	300	0.7928	0.8902	6.93	14.70	7.3	52.7	AO	300
Apricot-kernel	0.8143	0.9034	1.69	8.30	44.4	15.6	OA	45	0.7900	0.8906	4.35	15.23	44.8	15.2	OA	5
	0.8151	0.9033	2.69	8.39	28.0	32.0	OA	35	0.7911	0.8908	5.34	15.09	25.2	34.8	OA	7
	0.8180	0.9040	5.81	7.75	12.2	47.8	OA	20	0.7922	0.8914	6.33	14.62	6.0	54.0	AO	120
China wood	0.8143	0.9238	1.41	7.80	44.6	15.4	OA	12	0.7963	0.9114	8.72	13.38	44.5	15.5	OA	3
	[b]	....	...	...	29.0	31.0	OA	15	0.7989	0.9099	10.72	14.27	24.0	36.0	OA	5
	[b]	....	...	...	..	..	...	Not in 1 wk.	....	....	...	...	..	..	...	Not in 1 wk.
Cod liver	0.8140	0.9111	1.27	7.33	44.1	15.9	OA	...	0.7906	0.9006	4.66	12.49	45.0	15.0	OA	...
	0.8148	0.9114	2.11	7.08	26.5	33.5	OA	...	0.7910	0.9006	5.01	12.49	26.2	33.8	AO	...
	0.8178	0.9114	5.25	7.08	11.0	49.0	AO	...	0.7928	0.9015	6.55	11.90	8.1	51.9	AO	...
Corn	0.8130	0.9028	0.23	7.52	45.1	14.9	OA	8	0.7935	0.8905	7.57	14.36	46.1	15.9	OA	6
	0.8145	0.9026	1.94	7.70	27.5	32.5	OA	12	0.7973	0.8890	10.90	15.45	26.1	33.9	OA	7
	0.8192	0.9019	7.25	8.35	10.2	49.8	OA	30	[d]	....	...	...	5.0	55.0	OA	25
Linseed	0.8150	0.9127	2.22	9.84	44.4	15.6	OA	7	0.7970	0.8959	9.78	18.29	46.0	14.0	OA	7
	0.8170	0.9128	4.24	9.76	27.3	32.7	OA	7	0.7997	0.8940	11.99	19.52	24.2	35.8	OA	7
	0.8231	0.9129	10.30	9.68	11.0	49.0	AO	Not in 12 hr.	0.8045	0.8975	15.86	17.26	4.4	55.6	AO	Not in 12 hr.
Neat's-foot	0.8150	0.8843	2.98	10.64	[c]	..	OA	4	0.7943	0.8753	9.43	15.22	[c]	..	OA	1
	0.8174	0.8849	6.22	10.98	..	..	AO	6	0.7991	0.8722	14.32	17.83	..	..	AO	4
	0.8215	0.8846	11.70	10.33	..	..	AO	...	....	0.8703	...	19.45	..	..	AO	20
Olive	0.8141	0.8997	1.53	8.31	44.5	15.5	OA	15	0.7908	0.8874	5.22	15.15	44.5	15.5	OA	4
	0.8156	0.8994	3.26	8.59	28.8	31.2	OA	15	0.7922	0.8868	6.51	15.59	25.2	34.8	OA	4
	0.8183	0.9002	6.38	7.83	11.7	48.3	AO	10	0.7934	0.8860	7.62	16.17	6.4	53.6	AO	5
Peach-kernel	....	....	...	...	..	..	...	...	0.7897	0.8902	4.16	14.00	43.1	16.9	OA	2
	....	....	...	...	..	..	...	...	0.7904	0.8903	4.79	13.98	24.8	35.2	OA	3
	....	....	...	...	..	..	...	...	0.7896	0.8906	4.06	13.71	7.8	52.2	AO	60
Peanut	[b]	0.9005	...	8.74	48.0	12.0	OA	85	0.7901	0.8875	4.53	15.91	45.4	14.6	OA	60
	....	0.9001	...	9.11	[c]	..	OA	Not in 1 wk.	0.7905	0.8892	4.92	14.46	[c]	..	OA	Not in 1 wk.
	....	0.8975	...	11.57	28.0	32.0	AO	120	[b]	0.8892	...	14.46	17.0	43.0	AO	90
Poppy-seed	0.8145	0.9071	1.83	9.05	44.2	15.8	OA	10	0.7934	0.8926	7.16	16.67	45.0	15.0	OA	10
	0.8157	0.9069	3.11	9.23	27.3	32.7	AO	3	0.7952	0.8917	8.70	17.28	24.8	35.2	AO	20
	0.8194	0.9075	7.05	8.71	11.2	48.8	AO	Not in 5 hr.	0.7967	0.8928	10.00	15.53	4.9	55.1	AO	300
Rapeseed	0.8140	0.8994	1.40	8.57	44.3	15.7	OA	15	0.7889	0.8893	3.46	13.75	44.0	16.0	OA	5
	0.8150	0.8993	2.56	8.67	27.8	32.2	OA	15	0.7897	0.8895	4.20	13.61	25.9	34.1	OA	12
	0.8182	0.9003	6.27	7.74	12.0	48.0	AO	60	0.7914	0.8897	5.77	13.46	8.0	52.0	AO	30
Sesame	0.8146	0.8986	1.93	16.54	44.1	15.9	OA	...	0.7911	0.8959	5.16	14.47	45.0	15.0	OA	...
	0.8160	0.9069	3.43	9.31	28.0	32.0	OA	...	0.7919	0.8964	5.86	14.07	25.9	34.1	AO	...
	0.8195	0.9081	7.15	8.27	12.0	48.0	AO	...	0.7941	0.8975	7.85	13.40	8.2	15.8	AO	...
Soy-bean	0.8138	0.9068	1.09	8.23	44.8	15.2	OA	2	0.7921	0.8934	6.09	15.35	44.7	15.3	OA	2
	0.8152	0.9072	2.60	7.88	28.0	32.0	OA	2	0.7929	0.8938	6.79	15.08	25.5	34.5	OA	2
	0.8181	0.9078	4.56	7.35	11.4	48.6	AO	10	0.7933	0.8943	6.14	14.72	6.0	54.0	AO	7
Sunflower	0.8133	0.9153	0.51	7.02	44.5	15.5	OA	6	0.7955	0.8998	8.61	15.24	46.0	14.0	OA	3
	0.8146	0.9147	1.83	7.51	27.8	32.2	OA	15	0.7988	0.8984	11.86	16.16	24.8	35.2	OA	12
	0.8197	0.9158	6.99	6.64	10.0	50.0	AO	8	0.8016	0.8979	13.61	16.49	4.1	55.9	AO	5
Walnut	....	0.9073	...	9.57	44.1	15.9	OA	20	0.7941	0.8920	8.29	18.98	45.9	14.1	OA	6
	0.8139	0.9062	1.17	10.52	27.4	32.6	OA	17	0.7976	0.8888	11.50	21.33	25.0	35.0	OA	12
	0.8182	0.9061	5.69	10.60	9.1	51.9	OA	28	[d]	0.8900	...	20.43	2.5	57.5	OA	20
Whale	....	0.9058	...	7.68	42.4	17.6	OA	17	0.7905	0.8952	4.74	13.09	44.5	15.5	OA	46
	0.8152	0.9061	2.65	7.41	28.0	32.0	OA	20	0.7907	0.8947	4.92	13.45	26.2	33.8	OA	12
	0.8157	0.9060	3.20	7.50	11.8	48.2	AO	31	0.7937	0.8952	7.57	13.09	7.0	53.0	AO	120

[a] In each case first figure represents result with 45 cc. of alcohol and 15 cc. of oil; second, 30 cc. of alcohol and 30 cc. of oil; and third, 15 cc. of alcohol and 45 cc. of oil.
[b] Stable emulsion formed, with alcohol phase remaining cloudy.
[c] A white milky layer remained indefinitely between phases.
[d] Alcohol phase not large enough for sample.

Table I indicates that more oleic acid is generally required to make equal volumes of 90 per cent alcohol and oil completely miscible than for either greater or less ratios. The complete phase-rule diagrams for these systems will be interesting. The influence of small amounts of water on the miscibility of alcohol and oils can readily be seen from these results. It always takes less oleic acid to bring about complete miscibility the less the ratio of absolute alcohol to oil, indicating that the process of bringing the alcohol into the oil phase is the controlling factor for complete miscibility.

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Received January 10, 1936.

NICHOLS MEDAL AWARD

Presented to William Mansfield Clark, DeLamar Professor of Physiological Chemistry, Johns Hopkins School of Medicine, Baltimore, Md.

In 1902 the late W. H. Nichols established a fund whereby a gold medal was to be presented annually by the New York Section of the American Chemical Society to the author of a paper or papers published within the past three years in any of the Society's journals, which, in the judgment of the jury, would have an important influence in stimulating original research in chemistry. (For the previous recipients, see page 582 of the May, 1934, issue, and page 847 of the July, 1935, issue.)

The award for 1936 to Professor Clark, for researches "of incalculable value to human welfare," was made at a dinner meeting of the New York Section of the American Chemical Society at the Hotel Pennsylvania, New York, March 6, 1936. In presenting the medal, A. W. Hixson, chairman of the Jury of Award, said in part:

> Tonight we honor a foundation-builder. By working diligently and carefully in the field of oxidation and reduction equilibria, and by developing new and practical methods for the determination of hydrogen-ion concentration, Dr. Clark has given to American chemistry a set of fundamental principles that are basic in many fields of scientific endeavor. Wherever in pure and applied science water solutions enter into chemical reactions, the principles which Dr. Clark has discovered in his work on oxidation and reduction equilibria serve as a starting point for the explanation of the mechanism of these reactions. These studies, together with his methods for the determination of hydrogen-ion concentration, have made it possible for the workers in the fields of physiology, internal medicine, surgery, nutrition, water supply purification, sewage disposal, fermentation, and in hundreds of special fields of applied chemistry, to extend their researches and control their processes. Foundation stones of chemical science, truly, that will stand the tests of time.

William Mansfield Clark

D. D. Van Slyke of the Rockefeller Institute, spoke on the personal aspects of the medalist's career, and A. Baird Hastings, of the Harvard Medical School, discussed his scientific achievements in part as follows:

> Clark received the B.A. degree from Williams College in 1907, and the M.A. degree for studies in chemistry and physics from the same institution in 1908. During that year he was assistant in chemistry. He then entered the Johns Hopkins University where he held a University Fellowship; he received his Ph.D. degree in 1910. From 1910 to 1920 he was a chemist in the Bureau of Animal Industry, U. S. Department of Agriculture, working on the problem of eyes in Swiss cheese. This work marks his transition toward biological chemistry, for his interest was aroused in the activity of the microörganisms which produced the good and the bad eyes in the cheese. About 1914, partly stimulated by difficulties in preparing reproducible bacterial media, and partly by the papers of Sørensen and Michaelis, Dr. Clark became interested in the relation of hydrogen-ion concentration to his problems. Then came the series of classic papers in collaboration with Dr. Lubs, in which were clearly developed the meaning of pH, its place in biological problems, and a description of accurate methods for its determination. Here were reported in detail the preparation and characteristics of that beautiful series of acid-base indicators to be found today in every laboratory; and it was all written so clearly that anyone who could read could follow the directions and obtain good results. In 1920 he wrote a book which is now in its third edition, entitled "The Determination of Hydrogen Ions." Probably no scientific textbook since the war has found its way into the hands of workers in such a wide variety of fields.
>
> In 1920 Professor Clark left the Bureau of Animal Industry to become professor of chemistry of the Hygienic Laboratory of the U. S. Public Health Service. There he began publication of the now classic series, "Studies on Oxidation-Reduction," in 1923 with four articles. This series is now in its twenties and the end is not in sight.
>
> High scientific honors have come to Dr. Clark. He was elected to the National Academy of Sciences and has been a conscientious member of the editorial board of the *Journal of Biological Chemistry*. Both the Society of American Bacteriologists and the American Society of Biological Chemists made him their president in 1932.
>
> In his 1933 Harvey Lecture, Professor Clark stressed the conception of the oxidation-reduction continuum. This is the best word with which to describe his own scientific career. His contributions to chemistry—and I advisedly do not specify biological or bacteriological or organic chemistry—have been a continuum. Neither change of laboratory nor change of duty has seriously interrupted his scientific productiveness.

Then the medal address was given by Dr. Clark and is presented herewith.

A Little of the Perspective of Acid-Base and Oxidation-Reduction Equilibria

W. MANSFIELD CLARK

FOR the materials of this address I shall draw upon two subjects, acid-base equilibria and oxidation-reduction equilibria. I shall not deceive myself by assuming that I am qualified to discuss the refinements of theory. It is impracticable to attempt a brief summary of applications or of technics. There remains the general perspective. Since perspective necessarily has its reference center in an individual, I think you will wish me to draw my own conclusions. With these not all will agree. Nevertheless, I hope to reach a difficult problem in which all are vitally interested. For a brief discussion of this, I shall lay the ground by drawing material from the fields of research with which I am familiar.

Let us first consider the theory of the state of a weak acid in aqueous solution, setting aside detail and theoretical refinements to look only upon the larger features. Today we appreciate that many of the relations which gave initial guidance to practice are implicit in the simple, equilibrium equation of Arrhenius:

$$\frac{[H^+][A^-]}{[HA]} = K$$

As cases became more complicated, the descriptive equations became thicker; but their profitable use called merely for ingenuity in the practice of the algebra, which Swann aptly called the processes that save us the trouble of thinking. The physical principle remained simple.

Delay in Application

Many of the implications of the classical equation were recognized rather early. Then why the initial delay in general appreciation and of wide use? To answer this question would require more than the customary type of historical review and critical research. Nevertheless, I venture to suggest a few reasons. In the early days, collection of basic data kept attention upon simple, aqueous solutions. There was little general *emphasis* of a fact that several advanced students of the subject saw; namely, if the classical equation for the equilibrium state of a weak acid system be true, it should be true even if there were several original sources of the components. In short, the principle ought to work for the complex mixtures met in practice as well as for the simple solutions set up for theoretical purposes.

The wide circulation of Ostwald's dilution law helped to obscure this. For a good but restricted purpose, Ostwald eliminated from the fundamental equation the quantities that should have been held there for contemplation. If we go back to the classical equation, contemplate its four unknowns, and consider the sorts of information needed for numerical evaluations, we are led to the following conclusion. One of the neatest, sometimes the only, and usually the most general numerical solution will follow the combination of analytical data and the physical determination of hydrogen-ion concentration. We now add (and sometimes we should be cautious in doing so) the greatly simplifying assumption of the complete dissociation of salts. For present purposes we may assume, as we used to do, that the determination of hydrogen-ion concentration can be made with the hydrogen cell.

Hydrogen Cell

But the hydrogen cell was not in wide use and was not even mentioned in some texts as late as 1910. Measurements of conductivity and of the effects of electrolytes upon the properties of the solvent were the leading experimental interests. Both of these experimental modes of approach are invaluable. Neither is capable of resolving the complexities of the solutions met in practice to anything like the extent exhibited by certain uses of the hydrogen cell, and the principles of isohydric solutions.

I doubt that I could describe briefly the confluence of contributions that made the hydrogen cell practicable. I shall not attempt it here. But it is only fair to say that the complexities of the systems with which biochemists have to deal forced upon the attention of some of these investigators the possible advantage of this device and led them to make valuable contributions toward its practical development. Indeed it is significant that there was a good deal of surprise when biochemists came forward with their results. Professor Michaelis will understand the historically important atmosphere to which I refer when I say that his resolution of many problems with the aid of the hydrogen cell and indicators was so swift and decisive that he had to endure some smiles of incredulity. We have come a long way from that day to this, when, thanks to the glass developed by MacInnes, investigators confidently report upon solutions that poison the hydrogen electrode, destroy indicators, upset the quinhydrone system, and in one way or another render useless all devices except that of the glass membrane. Perhaps some people are a bit too confident. There are some advertisements that I would not hesitate to describe as evidence of the gullibility of readers.

These references to the early work concern the tricks of circumstance in deciding the placement of emphasis. Good ideas were blowing about and were already described, but, as Robert Morris said, "a good idea will blow about for years until someone comes along with a hammer and nails it down."

Then in 1909 two papers appeared that were destined to have profound influences. One was L. J. Henderson's more extensive, initial outline of acid-base equilibria in the blood. At the hands of numerous investigators, especially of Van Slyke's school, this was destined to become a beautifully documented subject, the value of which went beyond its immediate importance. In later years measurements of pH, uncorrelated with much of anything, were to be "the rage." During that period we could look to the developing knowledge of the blood as a model of penetrating analysis in which special methods were both elevated and subordinated to their proper uses.

Sørensen-Michaelis Map

Also in 1909 Sørensen's classic paper appeared. In the first place his system of buffers and indicators put into the hands of everyone a simple means of wide exploration. For example, with only a pocket kit of Lubs' more brilliant indicators, Wherry later was to explore the soils from Maine to Florida and open a new chapter in plant ecology. Accompanying the means of simple experiment was the means of broad appreciation. By introducing the pH scale, Sørensen provided a way of viewing the simpler outline of the entire subject. The outline was on one map. Michaelis elaborated Sørensen's map. These two nailed to that map the ideas that had been too much afloat. My part was merely to present to American readers this vision of the whole in its relation to improved technical methods. It was not merely that we were given a graphic description; the graphic description happened to be one that gave us a vision of the whole, linked with a quantity the significance of which I shall discuss later.

Of late years, when I have rather laboriously developed some of the elementary background and then am able to place before my students the Sørensen-Michaelis map, I feel again the satisfactions of early years. There, on one chart, or one sort of chart, is outlined the stabilizing effect of the so-called buffer solutions with which innumerable processes are controlled. We have there the essence of *physical,* indicator theory outlining the two main methods by which indicators are used for proximate determinations of hydrion concentration and also the rationale of choosing indicators for end-point titrations. By any one of several devices the bases are made amenable to description by this map. The peculiarities of ampholytes are then displayed, and the first outline of a systematic treatment of protein solutions is begun. There is revealed the nonsense of making any more fuss about "neutrality" than is made aboard ship when crossing the Equator, and some of the concern over the hydrolysis of salts is eliminated as inconsequential. Here we have a beautiful case of what President Bowman calls "Anaximandering." Anaximandering is the opposite of meandering. Anaximander was the first to draw a map of the known world. To show the relations of the parts is essential to the perspective that an elementary student should be given.

Because the hydrogen ion has become a center of interest, an aspect of great importance has been partly revealed and partly obscured. This can be shown if we return to the original equation, written in the following form:

$$\frac{[A^-]}{[HA]} = \frac{K}{[H^+]}$$

In innumerable cases we have no direct interest in the hydrogen-ion concentration itself, but only in the quantity that our premises have led us to express as the ratio between the dissociation constant of the particular acid and the hydrion concentration of the solution. This quantity, or ratio, determines the ratio of concentrations of anion and undissociated acid, and it is in this that our real interest often centers. An undissociated acid has one set of properties. Its dissociated anion has another set of properties. We desire to throw into mass action the one set of properties, while suppressing the display of the other set. Or we desire to strike a nice balance between the sets of properties that are to be on display. The elemental principle of the control is indicated in the equation and is "as plain as a pikestaff."

Within the limitations of the simple theory upon which the present discussion is based, and for the immediate purpose mentioned above, we can take an error in $[H^+]$ or K provided there is a certain relation between the two. The Sørensen-Michaelis "dissociation curve" shows what this relation should be.

Operating in the field of nonaqueous solutions, La Mer and others have focused attention upon this ratio of two real species and have brought us back to some fundamental elements. In finding his way to one of these amid what he calls "sophisticated" measures of acidity, Hammett is almost apologetic in describing his brilliant idea as "naïve." I prefer to call it sensible.

In the field of aqueous solutions it is often convenient to retain orientation by the measure that we call pH. I shall continue for the moment with this and shall return later to the broader view. If we do not know the constants or even the specific acids whose properties are on direct or indirect display, we can feel our way to control in accordance with the principle outlined. Faith in this principle has lèd to success in the correlation of pH number with event in each of countless cases where the chemical description of the event has not been attained.

It is for such fundamental reasons that we find the technic of the subject carried to the ocean, the soil, and the blood, to the factory and the analytical laboratory, to the control of microörganisms, and to the control of organic syntheses. Why cite specific applications when the principle is plain? It seems to me a very good sort of science that can carry a penetrating principle so far and leave detail to the art that inevitably must remain in specific practices.

Oxidation-Reduction Systems

Now let us turn to the field of oxidation-reduction. Some of the inorganic oxidation-reduction systems are amenable to study by means of the electric cell, and much has been made of this. Also it has been known for a long time that the electrode potentials of certain inorganic systems are subject to change with change in the hydrogen-ion activity of the solution. But so slight had been the interest in the latter aspect that tables of characteristic potentials did not include the constants for the "pH effect." While the analyst could find much of value in such limited data, the biochemist, who needs the broader data, finds little in this early work that suits his requirements.

Then about 1920 a remarkable coincidence occurred. Practically simultaneously and quite independently, Granger and Nelson at Columbia University, Clark in the United States Department of Agriculture, and Biilmann at Copenhagen published their first papers on organic oxidation-reduction systems. Only slightly later and again independently, Conant inaugurated the work that was to appear in many publications from Harvard. I did not begin with simple quinones as did all the others. Gillespie had introduced me to the study of the electrode potentials of bacterial cultures, and in trying to discover their significance I turned to the study of two reagents for biochemical reduction, methylene blue and indigo carmine.

In the quinone systems and particularly in the dye systems we have beautiful cases in which various species of oxidant and reductant are thrown into action or out of action as the "hydrogen-ion activity" of the solution is changed. Also, under certain conditions, the hydrion or proton participates in the oxidation-reduction process. Therefore, if there be no control of this factor, the electrode potentials can go "haywire." But investigators were prepared. The principles of acid-base equilibrium had been developed. By holding the "pH" practically constant, there is obtained the typical sigmoid curve relating electrode potential to percentage oxidation. By holding the percentage oxidation constant and varying the "pH" of the buffer, there is obtained the relation between electrode potential and "pH" showing the effect called "hydrion dilution" and inflections of the curve that correspond with the dissociation exponents of the components. The map of these systems thus becomes three-dimensional, the dimensions being electrode potential, percentage oxidation, and "pH." Any one system is described by a surface in these three dimensions.

I might exhibit a series of cases or one typical case. But, if I did so, interest in specific detail might obscure what deserves emphasis—namely, the elemental simplicity of the principles applied. The often complicated equations that represent the three-dimensional surfaces are but the result of the simultaneous solution of equations for the several sets of acid-base equilibria on the one hand and an orienting equilibrium equation for the oxidation-reduction process on the other hand.

Examples of Oxidation-Reduction Processes

Within the time at my disposal I cannot review all and can mention only some of the work in this field.

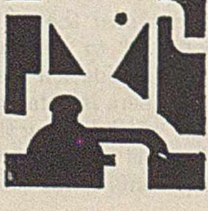
A by-product of considerable importance, and indeed, Biilmann's first concern, is the use of quinhydrone and similar systems for the determination of hydrogen-ion activities.

From various laboratories have come what are essentially measurements of the free energies of reduction of numerous organic compounds. These data are basic to many of the purposes of organic and biological chemistry. One use is illustrated in Fieser's elucidation of certain structures; another in the proof that the two equivalents required for reduction are in some cases energetically paired and (as Michaelis and Elema have shown) in other cases energetically separated. In biochemistry not the least service has been to bring to an end nonchalant proposals of mechanism that neglect matters of ten thousand or so calories.

Some of the more than sixty dye systems studied in my laboratory have provided cases favorable to a precision of measurement necessary to test certain fundamental matters—cases favorable to the study of the ionic strength effect and cases favorable to the study of aggregation in solution.

These dye systems, used as indicators in a manner somewhat analogous to that of acid-base indicators, have served in the exploration of the living cell. The results may not have solved many old problems but they have defined many new ones in a manner that will lead to some good things.

From various laboratories, including my own, have come characterizations of reversible systems found in the living cell. These systems include the hormone epinephrine, several hemochromogens, the flavines, numerous quinones, a few special pigments, and also two vitamins. It may now be predicted safely that the potentiometric characterization of some of these systems will enter all future treatments of biological oxidation-reduction. Perhaps most significant of all has been the use of dye systems as mediators. By combining their functions with those of specific enzymes, Lehmann measured the free energy of the reduction of fumarate to succinate. The results were checked by Schott and Borsook, both directly and with the aid of measurements that allow the application of the "third law." Wurmser and Mayer-Reich, on the one hand, and Barron and Hastings, on the other, are in substantial agreement in similar measurements of the free energy of reduction of pyruvate to lactate. Preliminary results with other systems were obtained in a similar way by Green and others. We now have meager data for free energy changes where before we could use only heat changes in discussing physiological engines that, whatever they may be, certainly are not heat engines. There is a long road to be traveled but we have come a long way from where we were when Gillespie and I conversed upon the subject in 1919.



Kinetics

One more thing—this regarding kinetics. Here are involved distinctive aspects of acid-base equilibria concerning which Brønsted has enlarged our views. These I shall not discuss. For the old proposition that the rate of a reaction is related to the free energy change there is no good evidence that I know. However, there is plenty of evidence that the rate of a reaction may depend upon the species that are in play. Some of these may be thrown into or out of action according to the principles discussed. We know, of old, correlations between the activity of a hydrolytic or oxidative enzyme, the pH of the solution, and the acid-base properties of enzyme and substrate. Are there analogous correlations involving oxidation-reduction potentials? La Mer, Barron, Green, and others are bringing to light cases where, in the sense specified, there is correlation between rates of oxidation and the potentiometric characteristics of catalysts and substrates. With regard to hydrolytic processes, my associates, Hellerman and Cohen, have succeeded in dispelling the too narrow view that glutathione is a special activator of certain hydrolytic enzymes. On a broader basis, which includes oxidative and reductive processes, they reversibly inactivated and activated urease, papain, and the hemolysin of the pneumococcus. Linderstrøm-Lang and Duspiva showed that the larva of the clothes moth can live on the wool of our clothes because both a hydrolytic process and a reductive process coöperate in its digestive tract; the reductive process was found by Goddard and Michaelis to be a prerequisite for the enzymatic hydrolysis of keratins.

Upon the broad basis that now lies in view I think we shall reach a better appreciation of life's marvelous coördinations.

Limiting Laws

The outlines of two large subjects have been recalled. These outlines were based originally upon the comparatively simple concepts of the Arrhenius theory. They are now embodied in limiting laws. These limiting laws remain invaluable ideals. Strictly they are applicable only in that mystic region called "infinite dilution." Nevertheless, when Debye showed the realistic nature of Lewis' activity coefficient and of what might be called the stabilizing effect of constant ionic strength, the experimenter found himself recalling his simple equations from the limbo and adding "constant μ" to his armaments of control. For example, the relation of degree of oxidation to potential takes the simple form that it does in most of our experiments not only because the buffer holds "pH" constant, but also because the buffer salts hold the ionic strength sufficiently constant for the purpose. As Debye has said, the modern theory of electrolytes is not incompatible with the Arrhenius theory. The old and the new stand in relation to one another in much the same way that the laws of ideal gases stand in relation to laws needed by the gas engineer who operates with wide variations of pressure and temperature. In the case of electrolytes the coulomb forces make a complication. Consequently, modification of the limiting laws to suit the needs of ordinary practice must be introduced early. Also, various technics are now known to give information of different kinds that, if not kept distinct, lead to entanglements.

To each of the more intensely cultivated fields of application has been brought the best of the advancing theory of solutions, but it is significant that the variety of current treatments makes impracticable even an outline of all the matters that have become important to our more refined practices. It must be said in no uncertain words that the principles with which we are now concerned frequently are but constituent parts of broader subjects. The student, who has many other things to learn about these broader subjects and who cannot afford to become a specialist, now has difficulty in finding his way about in the literature of the more specific subjects. What shall be done to recapture that unity of thought that swept a great generalization into practice?

Here I am tempted to poke some fun at the logodaedalists. According to the counts of lexicographers, there are being coined, on the average, more than one new technical term each day! One is reminded of the description of an ancient scene. The reporter wrote:

> And the Lord came down to see the city and the tower, which the children of men builded. And the Lord said, Behold the people is one, and they have all one language; and this they begin to do: and now nothing will be restrained from them which they have imagined to do. Go to, let us go down, and there confound their language, that they may not understand one another's speech. So the Lord scattered them.

Interpretation of pH Scale

Of many sorts of confusion there is one that I think could be remedied. It has to do with the interpretation of the pH scale, but it goes much deeper. At the expense of exposing myself to embarrassing questions as to how the following revival will help in certain practical difficulties, I propose to show that the success of the pH scale lies in its intrinsic nature and that we can remove some confusion by doing away with its form and preserving its substance.

Let us start with an inartistic use of pH. Recent studies of nonaqueous solutions have greatly enlarged our views. In presenting the invaluable new developments, several capable investigators have used the term "pH" and they know exactly what they mean. Make no mistake about that. But what about a pH value of -10? The student can no longer interpret this as an approximate representation of a hydrion concentration, for that would be ten billion normal. It has been called a representative of an "activity," but let the student beware lest he apply in the ordinary way the customary factors, activity coefficient and concentration, or he will have the tail wagging the dog. It were safer to tell the student the answer by the King in Alice in Wonderland. "If there's no meaning in it," said the King, "that saves a world of trouble, you know, as we needn't try to find any."

Neglecting the original, formal definition of pH and its inartistic uses, we find its experimental meaning as follows: Measured values of pH ultimately stand in linear relation to the electromotive force of a hydrogen cell in one half-cell of which is a standard system. If we could go beyond the proximate overcoming of a difficulty inherent in a cell with liquid junction, we would have in the electromotive force of such a cell at constant hydrogen pressure a direct measure of the difference between the chemical potentials of the protons, irrespective of the forms in which they exist, in the two compared solutions. In one case the form may be the solvated hydrogen ion, in another the dissociable proton of an acid molecule. Of course, as the form or state changes the chemical potential changes. Reference to the chemical potentials is fundamental to certain of our studies of proton exchanges, but having superimposed upon the thermodynamic function a set of mechanistic concepts which worked fairly, if not too well, for aqueous solutions, we now hold to form and divert attention from the substance.

Parenthetically it may be remarked that one difficulty inherent in cells with liquid junction is being removed by such beautiful work as that of Harned on cells without liquid junction. As to a more fundamental difficulty in determining the activity coefficient of a single species, it will probably be met by sensible adjustments to approximation theory.

The third edition of a book known as "The Determination of Hydrogen Ions" was queerly inconsistent because, as its author says, its function was to tell *about* a few of the more important matters in the terms then used. Tucked away in a late chapter is an indication of how certain elemental simplicities, regarding even aqueous solutions, have been obscured by use of pH. The thesis there presented has been borne out by studies on nonaqueous solutions. In other chapters the purely thermodynamic and the purely classical treatments are rather jumbled. When attention is focused upon pH, it is difficult to appreciate that the hydrogen ions of the blood are of no importance of themselves. What is important is the "calculation value" that determines the ratio of components present in considerable amounts. For a still distant date the author has contemplated a new edition of this book, written on a more consistent basis, and from it there *might* be eliminated the term "pH."

Lest this seem shocking let it be said at once that no serious alteration of the Sørensen-Michaelis map will follow the substitution of the electromotive forces for the pH numbers calculated therefrom. Indeed, tradition has established that we use the electrical potentials in the description of oxidation-reduction systems. Not only do we accept this without question; it has made it easier to perceive that we are dealing with a thermodynamic quantity and to perceive that we are at liberty to shift our postulates of mechanism in artistic adaptation to enlarging views. The really shocking part of the proposal to eliminate pH from an elementary treatise would be that there would have to be abandoned the grounds upon which almost all except graduate students are now prepared to assimilate the subject. There's the rub!

In my Harvey Lecture of 1933 I went a step farther than I had dared go before and considered the electromotive force of the cell as none other than the difference between the *electron chemical potentials* of the electrons in the two oxidation-reduction systems that are found in all ordinary cells, *including the hydrogen cell.* This provided a great simplification and a means of tying together by one scheme of development the bases upon which we organize oxidation-reduction equilibria and acid-base equilibria, in so far as use of the electric cell is concerned. Whether that scheme be found acceptable or not, there remains a great advantage in keeping attention focused upon the essential thermodynamics, and to that end many writers will return, as they have in the past, to one or another use of Gibbs' chemical potential.

Chemical Potential

In defining any such quantity, the mathematical definition is necessary, essential, indispensable; but most of us will not learn to appreciate the matter at the pen of those whose power of exposition is limited to use of the overworked expression, "We shall now define a new quantity by the following equation." These expositors may not have read what Clerk-Maxwell said: "For the sake of persons of different types, scientific truth should be presented in different forms and should be regarded as equally scientific, whether it appears in the robust form and vivid colouring of a physical illustration, or in the tenuity and paleness of a symbolic expression."

If I am not mistaken, Gibbs adapted to the uses of chemistry the generalized potential—that factor of potential energy which, in each of the unique gravitational, electrostatic, electromagnetic, and chemical fields, determines energy change in processes not subject to passive resistance.

Were the potential a quantity that is useful only in a narrow realm, it might deserve the fate that it has had. It has been relegated to the chapters on electricity in many an elementary physics text so that usually we are told only of electrical potential. In advanced treatises it has been developed in abstruse mathematical form unavailable to most of us. For a long period it was obscured in chemistry until it attained usefulness under the new name "partial molal free energy." Since the potential has wide uses throughout physics, chemistry, and physiology, I plead that we may be taught more of it as a possible means of keeping our basic thought of many subjects as simple and as rigid as may be. If the task of bringing it back to appreciation by elementary students seems large, let it not be forgotten that Newton's laws of motion, which at one time were considered hopelessly abstruse, have had much of their essential content brought even to the elementary school.

I think it suggestive that measurements of pH now appear to be second in frequency only to measurements of temperature. Both have the properties, although not the dimensions, of potential. Each describes a determinative factor in the flow of a unique kind of energy.

The Continuum

In the immediate future, if it be found impracticable to base the description of acid-base and oxidation-reduction equilibria on the concept of the chemical potential, we can put a little more generality into our views as follows: Carefully map the experimental data for any particular oxidation-reduction system, in solutions of widely varying buffer systems. Introduce on this map a little labeling to denote the chief species of oxidant and reductant and the chief species of the acid-base systems that are in play. In doing so be careful to use in a common-sense way only the more reasonable mechanistic ideas and focus attention only upon species that in any given situation are present in considerable and really significant amounts. Of course, in very acid, aqueous solutions the discrete, hydrated, hydrogen ion is important. In other cases it is not. The map shows clearly that those measured electrode potentials which refer to the acid-base systems and those measured electrode potentials which refer to the oxidation-reduction systems pass smoothly from situation to situation as if one set of species were picking up a function as another set of species fades in effectiveness. To describe this, I use the term "continuum," not in any narrow technical sense but to convey what has just been expressed concretely. The function that persists with changes of the species is a thermodynamic function. It persists in changes of a material continuum. It can be analyzed into free energies of reduction, of hydrogen-ion dilution, of acid ionizations, etc., but for many practical purposes this analysis may be neglected. Indeed, if we are not careful, such an analysis may trick us into employing a formality not suited to all cases.

In other words, there is a good deal to be said in favor of unloading special notations and of making maps with the raw data—standardized, of course. The elemental concept of a smooth passing on of functions, as species change, is essential to an appreciation of the living cell where we find the processes and energy changes of oxidation-reduction, of proton exchange, and of hydrolysis closely interlinked.

Conclusions

We had first a simple concept of acid-base equilibria. This now takes on the nature of a limiting law. When laid out before us in the large it still retains the inspirational value that in the first instance led to far-flung uses. Of a similar model is the outline of reversible oxidation-reduction systems. This has been integrated with the outline of acid-base equilibria, and here the map reveals more plainly the smooth passing on of function as one set of species fades in effectiveness and gives place to another set. In this shift of mechanism, unity of view is retained by organizing in terms of the energy changes, or the standardized cell potentials, measured directly or calculated from measurements of other types. Upon the outline of each subject have been superimposed the refinements brought in by the enlarging theory of solutions. These are invaluable and frequently they must be applied even in moderately precise practices. But also these refinements have taken special forms suited to particular cases. To retain perspective amid all this specialization, we may have to discard much that we thought useful and now find too particular, and we shall have to seek that which will preserve substance rather than form.

In seeking practical means, we encounter one of the most difficult of intellectual problems. There is demanded the broadest, the most nearly rigid, and yet the most available of theories. It cannot be too special for there must not be imposed upon the coming generation too many specializations. If a method is selected for its breadth and power and yet is found difficult, how shall it be made clear and how shall it become a part of preparative training?

The particular problem which I have placed before you is one that I would not press as necessarily important, although I think it is. My thesis would remain valid without the solution of this particular problem; for what is illustrated is the *type* of problem that is central to the future development of scientific education.

An accident of history or a temporary convenience has determined the course of many a scientific subject. To adopt what is current and convenient is the easiest of intellectual activities. To reorder the established old and the advancing new on a basis that can be made an integral part of the whole intellectual acquisition is the hardest of tasks. That it was not being done was complained of bitterly by Maxwell in his generation. That it is not now being done results from the fact that our whole scientific atmosphere encourages only the search for the new. As a result, we who try to teach are left holding a bag of pedagogical trivialities and have to deal with students who are stuffed with miscellaneous information and know few general principles. The archives of research show it. From the page that one investigator deposits to his scientific credit is omitted the common basis of understanding that he finds absent from the page deposited by another.

In closing I should like to drive home the point that we now have a new responsibility for directness, rigidity, and simplicity. Beyond the theory of the nature of solutions lie problems that call for knowledge of the first as a component part. They may be industrial problems of a complexity that would give the theoretical chemist the "jitters." Or they may be problems of a more philosophical nature that stand upon their own merit with importance coördinate with that of the basic themes of chemistry and physics. For example, the confluence of many different streams of thought and experiment has brought a knowledge of processes in respiration that are amazing. Here and elsewhere we find beauties of adaptation between chemical property and physiological function that have the intellectual value for some of us of this generation that celestial mechanics had for our forebears. Those who pursue problems of this complex type must have the best that contingent sciences can supply; but where so many different streams of thought converge, it is essential to keep the tributary waters clear.

We are learning what Whitehead said well: "The paradox is now fully established that the utmost abstractions are the true weapons with which to control our thought of concrete fact." The histories of the subjects that I have discussed bear this out forcefully. What has been forgotten is the selection of the means by which all of us may move forward together.

Received March 9, 1936.

MARKET REPORT—APRIL, 1936

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, APRIL 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Acetaldehyde, drums, lc-l., wks.	lb.	.16
Acetaldol, 50-gal. drums	lb.	.27
Acetamide, drums	lb.	.38
Acetanilide, U. S. P., powd., bbls.	lb.	.26
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks., c/l.	lb.	.09½
Acetphenetidin, bbls.	lb.	1.30
Acid, abietic	lb.	.07
Acetic, 28%, c/l., bbls.	100 lbs.	2.45
56%, c/l., bbls.	100 lbs.	4.75
Glacial, c/l., drums	100 lbs.	8.43
Glacial, U. S. P., c/l., carboys	100 lbs.	11.00
Acetylsalicylic, bbls.	lb.	.70
Adipic	lb.	.72
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, tech., bbls.	ton	95.00
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.03½
Chromic, 99%, drums	lb.	.14¾
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.27
Cresylic, pale, drums	gal.	.68
Formic, 90%, cbys., N. Y.	lb.	.11
Furoic, tech., drums	lb.	.35
Gallic, U. S. P., bbls.	lb.	.77
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.07
60%, bbls., wks.	lb.	.15
Hydrofluosilic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11½
Linoleic, drums	lb.	.16
Maleic, kegs	lb.	.29
Mixed, tanks, wks.	N unit	.07
	S unit	.008
Molybdic, 85%, kegs	lb.	1.25
Naphthenic, drums	lb.	.14
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11⅞
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.60
Salicylic, tech., bbls.	lb.	.33
Sebacic, tech., drums	lb.	.58
Stearic, d. p., bbls., c/l.	lb.	.09
Sulfanilic, 250-lb. bbls.	lb.	.18
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Tannic, tech., bbls.	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.25
Tungstic, kegs	lb.	1.35
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	4.485
Amyl, from pentane, tanks	lb.	.143
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.10½
Capryl, pure, for perfume	lb.	24.00
Cinnamic	lb.	3.50
Denatured, No. 5, comp. denat., c/l., drums	gal.	.40
Furfuryl, tech., 500-lb. drums	lb.	.35
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	.11½
Isopropyl, ref., drums	gal.	.55
Propyl, ref., drums	gal.	.75
Wood, *see* Methanol		
Aldol, 95%, drums, c/l.	lb.	.21
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.33
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks.	100 lbs.	7.00
Potash, lump, bbls., wks.	100 lbs.	3.00
Soda, bbls., wks.	100 lbs.	4.00
Aluminum, metal, N. Y.	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.18
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.35
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks.	lb.	.04½
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.15¼
Bromide, bbls.	lb.	.39
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.50
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	3.40
Linoleate, drums	lb.	.12
Nitrate, tech., cryst., bbls.	lb.	.08½
Oleate, drums	lb.	.10
Oxalate, kegs	lb.	.24
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls.	lb.	.08½
Stearate, anhyd, drums	lb.	.21
Sulfate, bulk, wks.	ton	23.00
Amylene, tanks, wks.	lb.	.09
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Amyl chloride, normal, drums, wks.	lb.	.56
Amyl chlorides, mixed, tanks, wks.	lb.	.06
Amyl mercaptan, drums, wks.	lb.	1.10
Aniline oil, drums	lb.	.16½
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.50
Antimony, metal	lb.	.13¼
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.13½
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.22
Argols, red powder, bbls.	lb.	.07
Arsenic, metal, kegs	lb.	.44
Red, kegs, cases	lb.	.15¾
White, c/l., kegs	lb.	.04½
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	45.00
Chloride, bbls., wks.	ton	74.00
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05
Nitrate, casks	lb.	.08½
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzidine base, bbls.	lb.	.72
Benzol, tanks, wks.	gal.	.18
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.60
Alcohol, drums	lb.	.75
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.00
Bismuth, nitrate. 25-lb. jars	lb.	1.10
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.30
Blanc fixe, dry, bbls.	ton	65.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	ton	40.00
Bordeaux mixture, bbls.	lb.	.10½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.75
Butyl acetyl ricinoleate, drums	lb.	.24
Acetate, drums, c/l.	lb.	.10½
Aldehyde, drums	lb.	.18
Carbinol, norm., drums, wks.	lb.	.60
Carbinol, sec., wks.	lb.	.60
Lactate, drums	lb.	.22½
Oleate, drums	lb.	.25
Stearate, drums	lb.	.25
Cadmium, metal, cases	lb.	1.05
Cadmium bromide, 50-lb. jars	lb.	1.54
Cadmium sulfide, boxes	lb.	1.00
Caffeine, U. S. P., 5-lb. cans	lb.	1.85
Calcium acetate, bags	100 lbs.	2.10
Arsenate, bbls.	lb.	.06½
Carbide, drums	lb.	.05½
Carbonate, U. S. P., precip., 175-lb. bbls.	lb.	.06½
Chloride, bags, wks., flake	ton	19.50
Cyanide, 100-lb. drums	lb.	.30
Gluconate, U. S. P.	lb.	.57
Tech.	lb.	.28
Nitrate, bags, 15% N	ton	25.50
Phosphate, monobas., bbls.	lb.	.07½
Tribas., bbls.	lb.	.11
Camphor, Jap., slabs	lb.	.55
Carbazole, bbls.	lb.	.80
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.04†
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.05¼
Casein, stand. gr., bbls.	lb.	.15
Cellulose acetate, bbls.	lb.	.80
Cerium oxalate, kegs	lb.	.25
Charcoal, willow, powd., bbls.	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq. c/l., cyl.*	lb.	.055
Chlorine, tanks	100 lbs.	2.15
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks.	bbl.	8.50
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	1.39
Copperas, c/l., bulk	ton	14.00
Copper, metal, elec.	100 lbs.	9.50
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls.	lb.	.17
Cyanide, drums	lb.	.37
Oxide, red, bbls.	lb.	.15
Sulfate, c/l., bbls.	100 lbs.	4.00
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.16¾
Crotonaldehyde, 50-gal. drums, c/l.	lb.	.26
Cyanamide, bulk, N. Y.	Ammonia unit	1.07½
Diaminophenol, kegs	lb.	3.80
Diamylamine, drums, wks.	lb.	1.00
Diamylene, tanks, wks.	lb.	.08½
Diamyl ether, drums, wks.	lb.	.09
Diamyl sulfide, drums, wks.	lb.	1.10
Diamyl phthalate, tanks	lb.	.18

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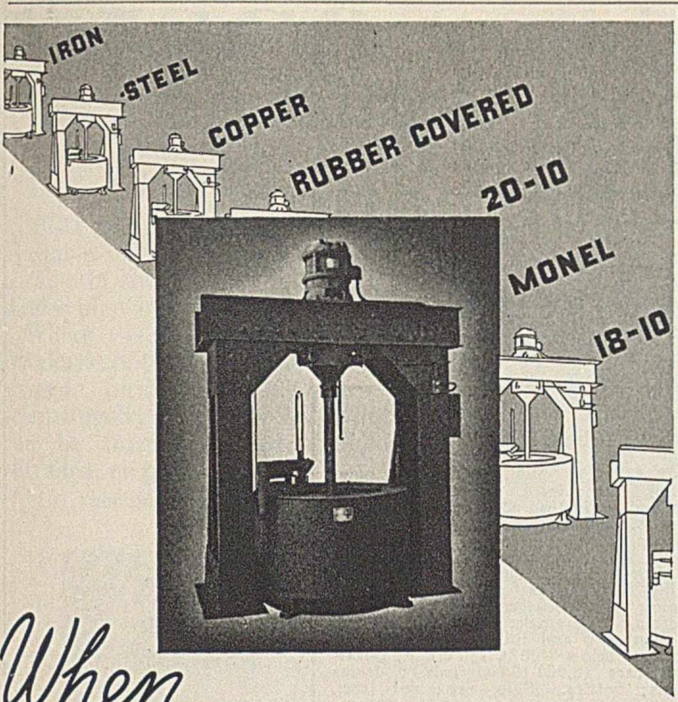
† This is the approximate F. O. B. shipping point price. Quotations are now all on a delivered basis and vary with the section.

* F. O. B. destination.

Dianisidine, bbls.	lb.	2.35
Dibutoxyethyl phthalate, wks., drums	lb.	.42
Dibutyl ether, drums	lb.	.30
Dibutylphthalate, drums, wks.	lb.	.20
Dibutyl tartrate, drums	lb.	.35
Dichlorethyl ether, 50-gal. drums, c/l.	lb.	.21
Dichloropentanes, tanks, wks.	lb.	.02½
Diethanolamine, drums	lb.	.31
Diethylaniline, drums	lb.	.52
Diethylene glycol, drums	lb.	.15½
Monobutyl ether, drums	lb.	.26
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.26
Diethyl carbinol, drums, wks.	lb.	.60
Diethyl phthalate, drums	lb.	.18½
Diethyl sulfate, tech., drums	lb.	.20
Diglycol oleate, drums	lb.	.24
Dimethylamine, pure 25.40% sol.—100% basis, drums	lb.	.95
Dimethylaniline, drums	lb.	.29
Dimethyl ethyl carbinol, drums, wks.	lb.	.60
Dimethylsulfate, drums	lb.	.45
Dimethyl phthalate, drums	lb.	.20
Dinitrobenzene, tech., drums	lb.	.17
Dinitrochlorobenzene, bbls.	lb.	.14½
Dinitronaphthalene, bbls.	lb.	.34
Dinitrophenol, bbls.	lb.	.23
Diphenyl	lb.	.15
Diphenylamine, bbls.	lb.	.31
Diphenylguanidine, bbls.	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.80
Ether, conc., drums	lb.	.09
Ether, nitrous, bot.	lb.	.75
Ethyl acetate, tanks, c/l.	lb.	.07½
Acetoacetate, 110-gal. drums	lb.	.37
Bromide, drums	lb.	.50
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorcarbonate, carboys	lb.	.30
Chloride, drums	lb.	.22
Ether, absolute, 50-gal. drums	lb.	.50
Furorate, 1-lb. tins	lb.	5.00
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride, 50-gal. drums	lb.	.05½
Ethylenechlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.17
Monobutyl ether, drums	lb.	.20
Monoethyl ether, drums	lb.	.15
Monoethyl ether acetate, drums	lb.	.16½
Monomethyl ether, drums	lb.	.21
Oxide, cylinders	lb.	.55
Feldspar, bulk	ton	10.00
Ferric chloride, tech., bbls.	lb.	.05
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls.	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	6.50
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls.	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.14½
Glyceryl phthalate, drums	lb.	.30
Glycol phthalate, drums	lb.	.29
Stearate, drums	lb.	.23
G salt, bbls.	lb.	.45
Hexamethylenetetramine, tech., drums	lb.	.37
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20% paste, bbls.	lb.	.12
Iodine, resubl., jars	lb.	1.65
Iron acetate, liq., 17°, bbls., c/l.	lb.	.03
Isobutyl carbinol (128–132° C.), tanks	lb.	.32
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	4.65
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls.	lb.	.08
Oxide, litharge, bbls., 20-ton lots	lb.	.0610
Peroxide, drums	lb.	.20
Red, bbls., 20-ton lots	lb.	.0735
Sulfate, bbls.	lb.	.06
White, basic carb., bbls.	lb.	.06½
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	280 lbs.	1.70
Limestone, ground, bags, wks.	ton	4.50
Lithopone, bbls.	lb.	.04½
Magnesite, calcined, 500-lb. bbls., wks.	ton	60.00
Magnesium, metal, wks.	lb.	.30
Magnesium carbonate, bags	lb.	.06½
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 100 lbs.	lb.	.81
Mercury flasks, 76 lbs.	flask	77.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.82
Meta-tolylenediamine, bbls.	lb.	.67
Methanol, pure, synthetic, drums, delivered, c/l.	gal.	.37½
Tanks, delivered	gal.	.35½
Methyl acetone, tanks	gal.	.44
Methyl chloride, cylinders	lb.	.40
Hexyl ketone, pure	lb.	1.20
Methyl propyl carbinol, drums, wks.	lb.	.60
Methyl salicylate, cases	lb.	.42
Michler's ketone, bbls.	lb.	2.50
Monoamylamine, drums, wks.	lb.	1.00
Monoethanolamine, drums	lb.	.31
Monomethylamine, drums	lb.	.75
Naphthalene, flake, bbls.	lb.	.06¼
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.13
Double, bbls.	lb.	.13
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.09
Octyl acetate, tanks	lb.	.15
Oil, castor, No. 1	lb.	.10¾
China wood, bbls.	lb.	.19
Coconut, tanks	lb.	.04⅜
Cod, N. F., bbls.	gal.	.40
Corn, crude, tanks, mills	lb.	.08¼
Cottonseed, oil refined, tanks	lb.	.09½
Linseed, boiled, bbls.	lb.	.10
Menhaden, crude, tanks	gal.	.34
Neat's-foot, pure, bbls.	lb.	.12¾
Oleo, No. 1, bbls.	lb.	.11
Olive oil, denat., bbls.	gal.	.72
Foots, bbls.	lb.	.08
Peanut, crude, tanks	lb.	.08¾
Perilla, bbls.	lb.	.07¼
Rapeseed, bbls.	gal.	.54
Red, bbls.	lb.	.09⅛
Soy bean, crude, tanks	lb.	.07½
Sperm, 38°, bbls.	lb.	.099
Whale, bbls., natural, refined	lb.	.075
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.06½
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.07
Ortho-toluidine, bbls.	lb.	.14
Paraldehyde, 110–50-gal. drums	lb.	.16
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.16
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.47
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.35
Para-phenylenediamine, bbls.	lb.	1.15
Para-tertiary amyl phenol, drums, wks.	lb.	.50
Para-toluidine, bbls.	lb.	.56
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.60
Phenylethyl alcohol, 1-lb. bot.	lb.	3.75
Phloroglucinol, tech., drums	lb.	15.00
c. p., drums	lb.	20.00
Phosphorus, red, cases	lb.	.45
Oxychloride, 175-lb. cylinders	lb.	.20
Trichloride, cyl.	lb.	.18
Phthalic anhydride, bbls.	lb.	.14½
Platinum, metal, solid	oz.	36.00
Potash, caustic, drums	lb.	.06¼
Potassium abietate	lb.	.06
Acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.07½
Bichromate, casks	lb.	.08½
Binoxalate, bbls.	lb.	.14
Bromide	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.06
Chlorate, kegs	lb.	.09
Chloride, crystals, bbls.	lb.	.04¾
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.13½
Muriate, fert., bulk, per K_2O unit		.40
Permanganate, drums	lb.	.18½
Prussiate, red, casks	lb.	.35
Yellow, casks	lb.	.18
Titanium oxalate, bbls.	lb.	.32
Pyridine, drums	gal.	1.30
Pyrocatechin, c. p., drums	lb.	2.40
Resorcinol, tech., kegs	lb.	.75
Rochelle salt, bbls., U. S. P.	lb.	.14
R salt, bbls.	lb.	.52
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	13.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.32⅝
Soda, ash, 58%, light, bags, contract, wks.	100 lbs.	1.23
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.60
Sodium abietate, drums	lb.	.06
Acetate, bbls.	lb.	.05
Alginate, drums	lb.	.64
Benzoate, bbls.	lb.	.46
Bicarbonate, bbls.	100 lbs.	1.85
Bichromate, casks	lb.	.06½
Bisulfite, bbls.	lb.	.03
Bromide, bbls., U. S. P.	lb.	.35
Chlorate, kegs	lb.	.05
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls.	lb.	.07½
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst.	100 lbs.	3.25
Metasilicate, gran., bbls.	100 lbs.	2.65
Naphthenate, drums	lb.	.13
Naphthionate, bbls.	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	ton	25.80
Nitrite, bbls.	lb.	.07¼
Perborate, bbls.	lb.	.17
Peroxide, cases	lb.	.20
Phosphate, disodium, bags	100 lbs.	2.10
Phosphate, trisodium, bbls.	100 lbs.	2.30
Picramate, kegs	lb.	.67
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls.	lb.	.05¾
Stannate, drums	lb.	.31½
Sulfate, anhyd., bbls.	100 lbs.	1.30
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.30
Thiosulfate, reg., cryst., bbls.	lb.	.02½
Tungstate, kegs	lb.	.85
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.08¾
Peroxide, 100-lb. drums	lb.	1.25
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Tetrachlorethane, 50-gal. drums	lb.	.08½
Thiocarbanilid, bbls.	lb.	.25
Tin	lb.	.4685
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.24¼
Oxide, bbls.	lb.	.51
Titanium dioxide, bbls., wks.	lb.	.17¼
Toluene, tanks	gal.	.30
Triamylamine, drums, wks.	lb.	1.25
Tribromophenol, cases	lb.	1.10
Trichloroethylene, 50-gal. drums	lb.	.09½
Triethanolamine, 50-gal. drums	lb.	.26
Trihydroxyethylamine oleate, drums	lb.	.40
Stearate	lb.	.35
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.37
Tungsten, powder	lb.	1.65
Urea, crystals	lb.	.0475
Vinyl chloride, 16-lb. cylinders	lb.	1.00
Whiting, bags	ton	7.00
Xylene, 10°, tanks, wks.	gal.	.30
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	4.90
Zinc ammonium chloride, bbls.	lb.	.0465
Chloride, granulated, drums	lb.	.05
Oxide, Amer., bbls.	lb.	.05
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25
Stearate, bbls.	lb.	.20
Zinc dust, bbls., c/l.	lb.	.065


IRON
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MONEL
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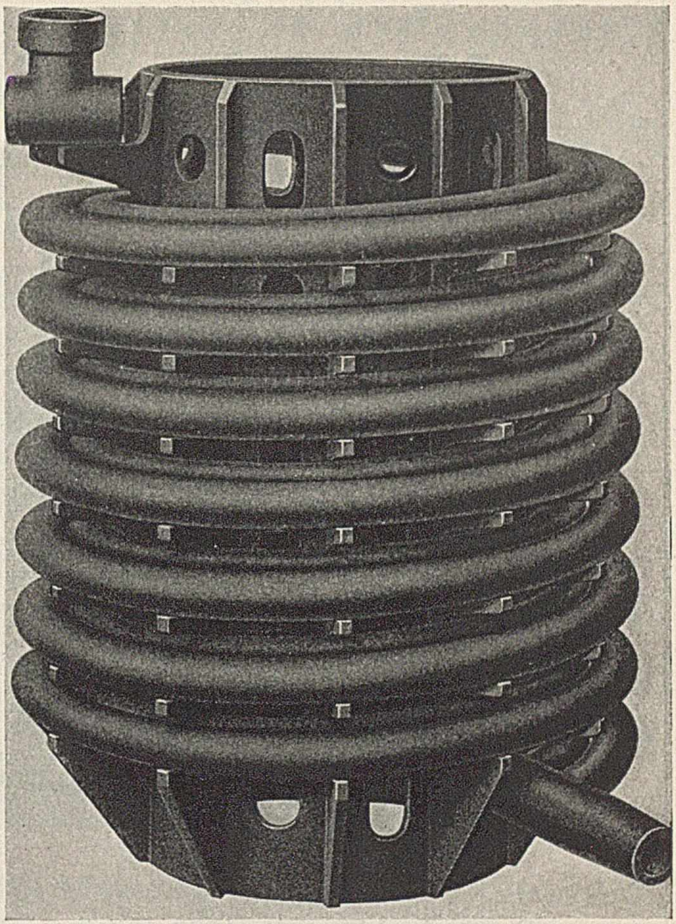

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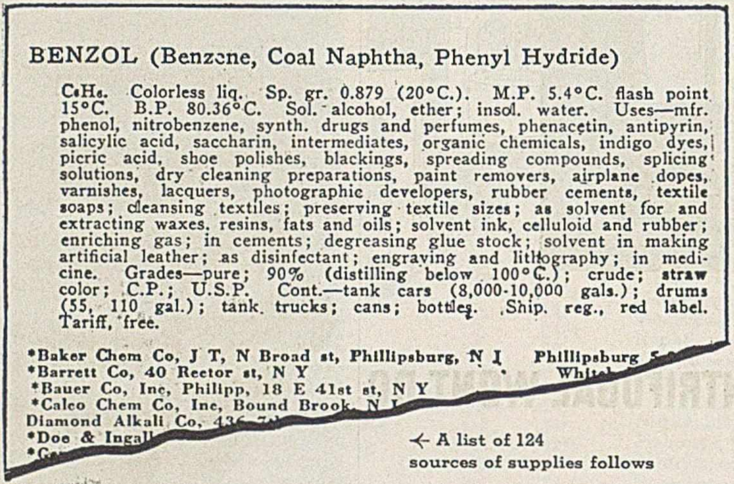

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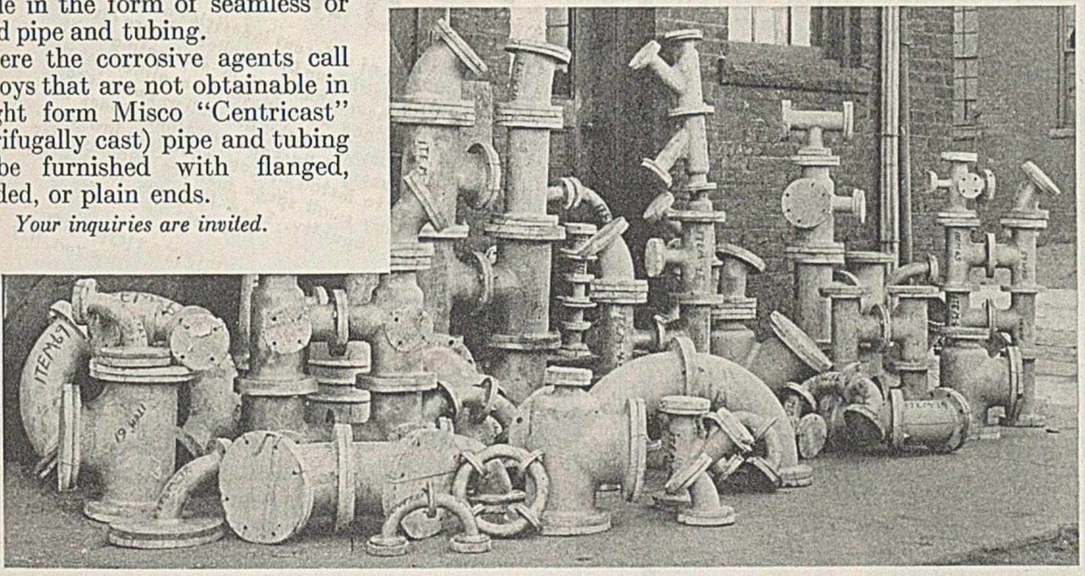

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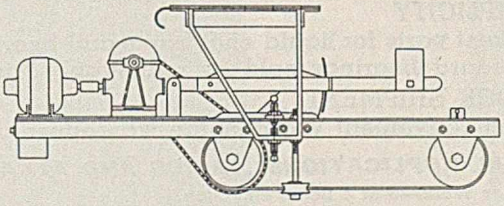

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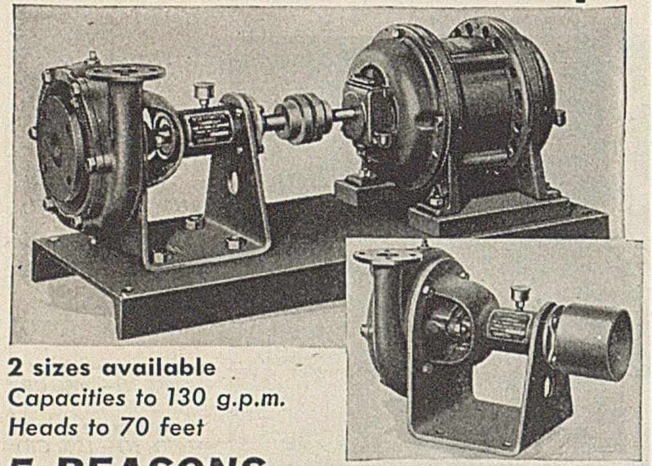

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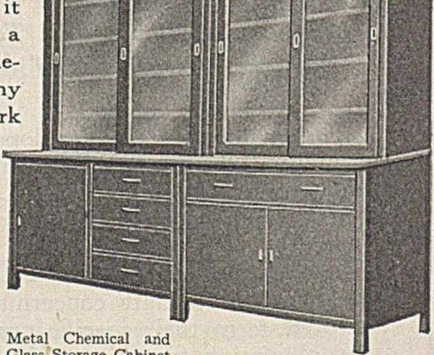

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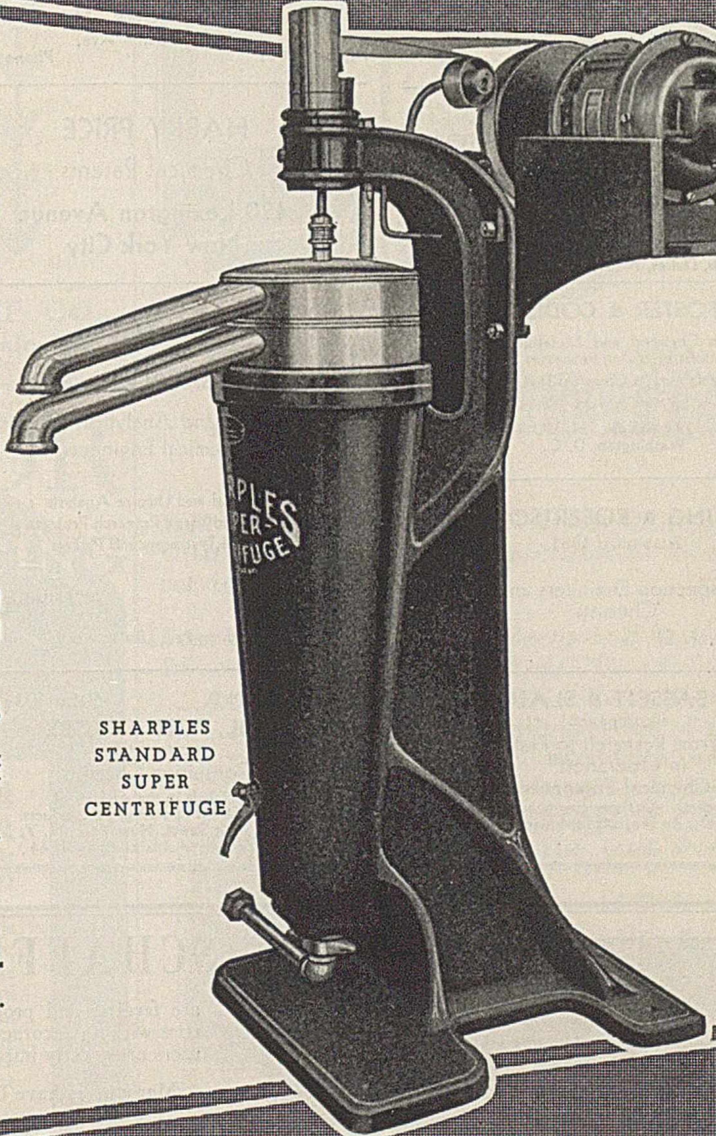

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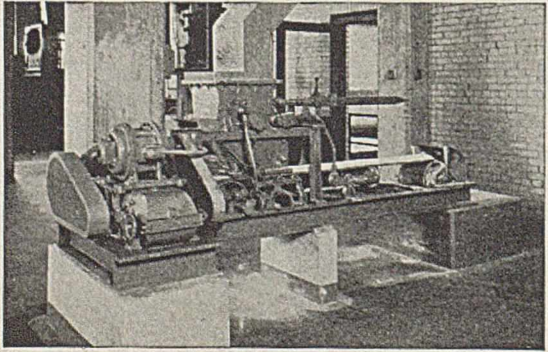

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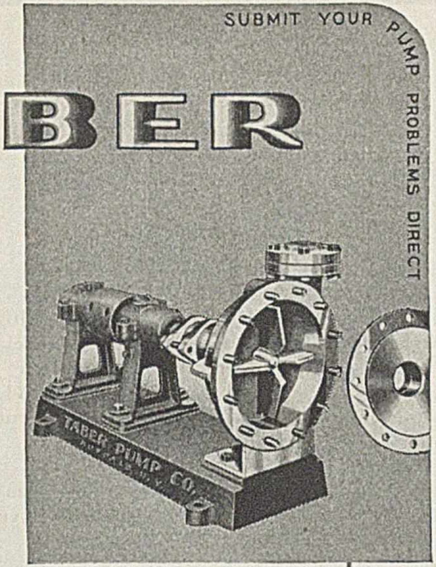

Taber has built a huge variety of pumps for special purposes. But in addition, every Taber Pump performs satisfactorily with the individual working conditions of each job. That is why it will pay you to put your pump problem up to Taber. ● Fig. 215 herewith is a Taber Liquid Foodstuffs Pump built to meet specific sanitary requirements. Easy accessibility provides a means for keeping it scrupulously clean with a minimum of labor. Handles soup, milk and similar fluids. Furnished in all castable alloys. Write for Bulletin L-630.

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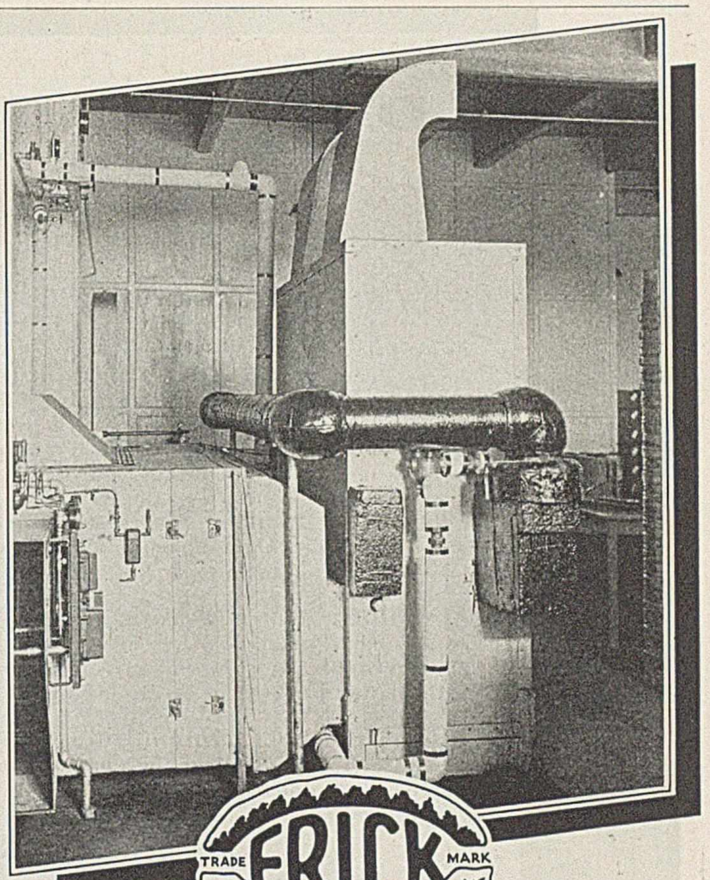

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