Industrial and Engineering Chemistry

Volume 37 • Number 7

JULY, 1945

REPRINT EDITION
ADVERTISING OMITTED

INDUSTRIAL AND ENGINEERING CHEMISTRY · INDUSTRIAL EDITION

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32,200 copies of this issue printed

Above is a bentonite stock pile and loading plant of the American Colloid Company at Upton, Wyo., plant of Federal Foundry Supply Company in background. (See article by Hendricks, page 625.)

ISSUED JULY 12, 1945 • VOL. 37, NO. 7 • CONSECUTIVE NO. 13

DEPARTMENTS

TECHNICAL ARTICLES

*** Indicates page number in the advertising section.**

Published by the American Chemical Society at Easton, Pa. Editorial Headquarters: 1155 16th Street, N. W., Washington 6, D. C., telephone, Republic 5301, cable, Jiechem (Washington). New York Editorial Branch, 60 East 42nd Street, New York 17, N. Y., telephone, Murray Hill 2-4662. Chicago Editorial Branch, 310 South Michigan Avenue, Chicago 4, Ill., telephone, Wabash 7376. Business Office: American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Advertising Office: 332 West 42nd Street, New York 18, N. Y., telephone, Bryant 9-4430.

Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 24 times a year—Industrial Edition monthly on the 1st, Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

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Annual subscriptions—Industrial Edition and Analytical Edition sold only as a unit, members $3.00, nonmembers $4.00. Postage to countries not in the Pan-American Union $2.25; Canadian postage $0.75. Single copies—current issues, Industrial Edition $0.75, Analytical Edition $0.50; back numbers, Industrial Edition $0.80. Analytical Edition prices on request; special rates to members.

The American Chemical Society also publishes *Chemical and Engineering News*, *Chemical Abstracts*, and *Journal of the American Chemical Society*. Rates on request.

INDUSTRIAL AND ENGINEERING CHEMISTRY

REPORTS ON THE CHEMICAL WORLD TODAY

Technology

Gasoline from Natural Gas. Ever since the fear of petroleum depletion and war shortages arose during World War I, gasoline from natural gas has been of great interest. It has been reported recently that under proper circumstances, gasoline can be made at about 5 cents per gallon, using the Fischer-Tropsch process and natural gas as starting material.

Enthusiasts claim all manner of favorable economics and conditions for the future operation of these plants. Lowest estimate I. & E. C. Editors have heard from those commercially interested is a guaranteed gasoline supply from natural gas to last ten years at our present rate of use.

In I. & E. C. Reports for January (advertising section, page 14) we questioned the supplies of natural gas, stating correctly, we believe, that for the long term our main reliance must be on coal and shale. The best survey of natural gas resources places them at 111 trillion cubic feet. Before the war the estimate was 60–70 trillion. The reason for the upward estimate is that in the Gulf Coast area increased reserves in natural gas have been recorded since the war in the deep-reservoir fields. The rate of discovery of reserves is said to be more than offsetting our present use. Two thirds of our national supply is located in Louisiana, Texas, and New Mexico.

The price of natural gas varies considerably, depending on the area. Carbon black manufacturers are paying about 5 cents per thousand cubic feet of gas, some contracts call for 4 cents, and distress gas is selling at 1.5 to 2 cents per thousand cubic feet.

The claim is made that, with natural gas at 5 cents, it is possible to make a 5-cent-per-gallon gasoline having an octane rating of 75, a Diesel oil with a 90–100 Diesel index, and various chemicals in the form of oxygenated compounds. These last are expected to be of considerable value and may be useful in underwriting much of the cost of producing the gasoline.

Using natural gas, 440 pounds or 10,450 cubic feet are necessary to make one barrel of gasoline. This is the best design and includes requirements for power, steam, and other processing facilities. The Fischer-Tropsch European design would require, on the same basis, some 505 pounds or 11,950 cubic feet. The American design, therefore, would be about 8% more efficient.

If it became necessary for the United States to convert all available natural gas to gasoline, the amount realized would be 11 billion barrels. At the 1940 rate of gasoline consumption, this quantity would last about eighteen years. However, obviously, all this gasoline would not be made from 5-cent gas, and the cost of production certainly would be more than 5 cents per gallon. As reserves became lower, costs would become higher.

As for investment, a plant capable of making 300,000 barrels of gasoline per day, American design, would require 660 million dollars, as compared to a plant of European design which would cost 1.4 billion. For comparison, present-day petroleum practice would necessitate only 210 million dollars for the same capacity.

As to costs, without depreciation, before taxes, and without profit, gasoline can be made at 3.6 cents per gallon with 5-cent natural gas. With depreciation sans taxes and profit, cost would be 4.8 cents per gallon. At present, refinery costs, with $1.20 crude, are 5.1 and 5.3 cents for the same conditions.

Operation Pluto. The announcement by British Information Services on Operation Pluto, the pipeline under the English Channel, came too late for the June issue. It did confirm vague rumors and sent us scurrying off to search out the experts. After some delays, involving the secret whereabouts of the British Petroleum Warfare Department, we interviewed Colonel H. R. Lynn, of the Canadian Engineers, and Squadron Leader Reid, of the Royal Air Force, both in this country as advisers.

Pluto delivered some 120 million gallons to the troops on the Continent, from the time it was put into operation August 12, 1944, to V-E Day. However, the August beginning was not full-scale, and it was September 21 before the twenty pipes were in full flow. We saw a portion of the HAIS cable (Hartley-Anglo-Iranian-Siemens) which was one of the two types used and which was manufactured in the United States. Hartley is chief engineer of the Anglo-Iranian Oil Company and is the designer of the pipe. Siemens is the British company. The other pipe is called "Hamel" and is steel instead of lead. The designers were H. A. Hammick, of Iraq Oil Company, and

(Continued on page 8)

An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries

B. J. Ellis, of Burma Oil Company. Pluto means "pipelines under the ocean", and the drums on which the pipes were wound were called "Conundrums".

The HAIS pipe is heavy, well-protected construction. The 3.08-inch tube is made of lead alloyed with antimony and tin. Wall thickness is 0.175 inch, and all joints are lead-burned. The part that surprised us was the protection on the outside of the cable and its weight. Over the lead and from the lead to the outside, in this order, are a bitumen or pitch coating, two layers of paper, one layer of cotton tape, a layer of steel tape, more pitch, a layer of jute, more pitch, a galvanized mild steel wire armoring also dipped in pitch, a layer of jute, another coating of pitch, one more of jute, and a finish coat of bitumen. The pipe is heavy, 20 pounds per foot; but the diameter, with all the layers, was not allowed to exceed 3.75 inches because of standard couples that were to be used. The cable was made up in 35-mile lengths, and its bursting pressure was between 3500 and 4200 pounds per square inch.

Technique of laying was worked out in preliminary trials over the Bristol Channel, and gasoline was delivered from Swansea to Ilfracombe eight months after the idea was conceived. For the sea operations 4000-foot lengths of pipe were welded together and wound on the huge floating drums, which were 90 feet long, 50 feet in diameter, and capable of carrying 70 miles of pipe line.

Of the twenty pipe lines, sixteen ran from Dungeness, on the southeastern coast of England, to Boulogne, a distance of about 20 miles; and four went from the Isle of Wight to Cherbourg, about 75 miles. The pipe was actually laid at night, and one Wight-Cherbourg line required 10 hours; the Dungeness-Boulogne pipes took about 5 hours each. One problem was the contour of the earth under the Channel, as allowance had to be made for variations. Fortunately results were available to the British of a topographical survey of every foot of the English Channel made a few years before the war by the Dutch in connection with reclaiming land under the Zuider Zee.

Pumping stations were hidden in blitzed houses, an ice cream factory, hot dog stands, and in the original "pillboxes" (Martello towers). These particular towers were erected by the British as defense against the threatened invasion of Napoleon III. Pumping pressures were increased to 700 pounds per square inch at the beginning of the run to determine cautiously whether the lines were kinked in any way. Full pumping operation called for pressures of 1500 pounds, and pressure drop amounted to about 300 pounds for the whole distance.

With all the protection given the pipe, life was assumed to be only one year. However, no data on corrosion have been obtained because of the press of important business. Of a total pipe mileage of 470, only 140 were made in this country, which ends our report except to state the reason for the pipe line in the first place: It was not mainly the danger to tankers in a war zone, but the tremendous 22-foot tides in the English Channel which made handling and unloading too hazardous.

(*Continued on page 10*)

New Products from Corn. The general expansion that is under way in the starch industry is due for acceleration in the postwar period. This confirms the industry's belief in the bright future of agricultural products as chemical raw materials. This belief is based on the assumption that the efficiency in growing crops has not even approached its limit, whereas the costs of some raw materials are going up.

In contrast to the oil and mining industries, where production methods have already reached a high level of efficiency, agriculture is continuing to advance. Outputs in the mineral extractive and the refining industries are leveling off, and costs are rising. Improvements in agriculture, on the other hand, are constantly being reported. For instance, the yield of corn owing to the development of hybrid varieties has gone up several bushels per acre in the past ten years.

Corn is the largest volume agricultural raw material going into industry. Last year the amount ground for industrial purposes was about four times the 800,000 tons of synthetic rubber produced in this country. The starch industry, however, has not confined itself to corn as the single raw material. When the supply of corn ran out wheat took its place. Looking toward possible new sources, work is being done in the industry on the grain sorghums as raw material for starch products.

Among the products from corn, zein (the protein) has been on the market for some time. Allyl starch, a new derivative with interesting properties, was recently developed at the Eastern Regional Research Laboratory at Philadelphia. Present indications of outlets for this product are toward resins and surface coatings.

Cornstarch consists of two fractions—amylose and amylopectin. Although it is not now separated into these fractions in industry, a variety of corn has been developed in which the starch is all amylopectin. This is waxy maize, and among other things, it has been useful as a substitute for tapioca.

Amylose acetate is a new derivative of the amylose fraction of starch. It was developed recently at the Northern Regional Research Laboratory at Peoria, Ill., and its usefulness in films and fibers has been demonstrated. But the utilization of amylose hinges on the development of a process for separating the two fractions in cornstarch or breeding a variety of corn in which the starch is all amylose.

An important by-product of industrial starch manufacture is corn-steep liquor. This was found to be an efficient medium for growing the mold used in the production of penicillin. Despite the requirements for penicillin, considerable corn-steep liquor is available for other purposes.

But the future of corn-steep liquor, which contains proteins and lactic acid to the extent of 20% on a dry basis, lies in its potential value as a source of new products. First of what promises to be a long line of products from this material are calcium phytate and inositol. Plants for these new products are beginning operation. Uses have not yet been developed for them, but these compounds will be available in pilot-plant quantities for exploratory work. A possible outlet for the interesting inositol molecule, hexahydroxycyclohexane, is in quick-drying esters.

(*Continued on page 14*)

I. & E. C. Reports on the Chemical World Today

Postwar

Hemp, Perennial War Baby. Strictly a wartime substitute as far as rope and cordage are concerned, hemp has served to supplement stocks of the hard fibers, jute, sisal, and Manila, in both World Wars. Although it is the strongest vegetable fiber known, its qualities as a soft spinning thread make it more suitable for textile, rug, and specialty uses than for rope and cordage where the cheaper hard materials are predominant. In this country the small prewar domestic production had gone principally into specialty items such as shoe threads and twine.

With the beginning of the war in the Pacific and the consequent denial of far-eastern sources of cordage, a program of domestic production was set up under War Hemp Industries, Inc., an agency of Commodity Credit Corporation, to conserve existing stock piles. This was essentially an emergency measure, quite apart from the usual domestic production and specialty uses of hemp. Hemp produced under this program was used for rope and cordage for the Navy and Army as a hard fiber extender, with hemp content of such materials held at 15%.

Economically hemp cannot compete with the hard fibers, which are cultivated in the tropics, are perennial, have a continuous growing season, need only cheap labor, and can be grown on cheap land. Requirements of hemp for soil, climate, fertilizer, and crop rotation are the same as those for corn. But whereas the cost of producing corn harvested with a mechanical picker may be 21 dollars per acre, the comparable cost would be 43 for hemp. Much of this difference is accounted for in the price of seed which is about 14 dollars per acre for hemp compared to $1.25 for corn. The net income on hemp, however, will equal or usually exceed that on corn. Current ceiling prices are 50 to 30 dollars per ton of retted hemp. Normal yields are 2 to 4 tons per acre. There is no prewar price with which this can be compared because all operations were conducted through cooperatives, but the net return to the farmer has been higher and has served as an inducement to farmers to grow this product.

Acreage devoted to hemp, which had averaged 14,000 annually, was increased by contract under this program to 165,000 acres; forty-two processing mills at a cost of about 300,000 dollars each were erected by Defense Plant Corporation in Iowa, Illinois, Indiana, Wisconsin, and Minnesota.

In 1944 only 63,000 acres of hemp were grown, with seventeen mills kept in operation to process the crop. Since the Philippines have been freed, no domestic hemp will be grown under the government program in 1945, and DPC plants will be available for sale or lease as surplus property. The last mill will probably close in about a year.

The ultimate disposition or use of these plants is a matter of speculation. Following World War I, eighteen hemp plants were abandoned, and at the beginning of the program in 1942 this neglect was regretted. It is presumed that regular sources of fiber will be sufficient to fill any normal postwar demands. Government retention of the plants and expansion of the domestic hemp industry are being urged by some, however, in the interest of national preparedness. But to utilize these plants in anything like the

(Continued on page 18)

scale at which they are capable of producing, the development of new industries for hemp other than cordage will be required.

Essential to its ultimate acceptance as a farm crop in this country are improvements in practices of production, including improved machinery. The low prewar acreage did not justify development or manufacture of this type of equipment. Hemp harvesting machinery is expensive and generally owned by the processing plant. Improvements in other phases of hemp culture and processing, however, are being pursued actively with several research programs in progress. Acreage costs and general farm problems are being studied at the University of Illinois, work on breeding hemp is being conducted at Wisconsin and Illinois, and at Iowa State College bacterial retting which promises to shorten and standardize postharvest treatment is being investigated.

Commercial development of hemp for clothing and textile in this country has attractive possibilities since hemp is both the longest and the most highly absorbent natural fiber known. Among other uses for hemp that have been suggested for domestic development are rug warp, fire hose, canvas, toweling, tropical clothing, by-product paper, and home insulation.

Calcium from Magnesium Plants. Electrolytic processes for the manufacture of magnesium have had two advantages over the ferrosilicon or Pidgeon process—by-products and low operating costs. In some electrolytic plants it is possible to recover chlorine; in others, various other products, such as calcium hypochlorite. There is a considerable disparity in magnesium manufacturing costs between plants using identical processes as well as between the electrolytic and ferrosilicon units.

Average costs of operating ferrosilicon magnesium plants compare unfavorably with the electrolytic side of the industry, and many have come to regard the former as necessary but uneconomical war projects. However, some recent technological developments tend to modify this appraisal, and there is a possibility that some of the ferrosilicon units after the war may be able to make other useful products instead of high-cost magnesium.

One of the products which can be manufactured efficiently in the ferrosilicon plants is a calcium of high purity. In the Pidgeon magnesium process dolomite is converted in a rotary kiln into dead-burnt dolomite. The latter is then mixed with magnesium oxide and ferrosilicon, and pressed into briquettes which are fed into a retort for thermal reduction. Some of the present ferrosilicon magnesium plants have several hundred such retorts. They are constructed of alloy steels for withstanding operating temperatures of around 2100° F., and a vacuum of 20 to 40 microns Hg.

For the manufacture of calcium in these plants, it is necessary to change the raw materials but not the equipment. A lime high in calcium content is substituted for the dolomite, and the carbon dioxide is removed through burning. This resulting high-calcium product is then mixed with aluminum metal and fed into the retort. The products are a calcium metal which distills off and aluminum oxide which remains in the retort.

(Continued on page 22)

I. & E. C. Reports on the Chemical World Today

Postwar

One immediate outlet for the high-purity calcium so obtained is for making calcium hydride, a means of producing hydrogen, and there are probably a large number of other important commercial uses for it. It is not inconceivable that research will show the way to the production of other essential materials in ferrosilicon magnesium plants now owned by the Government.

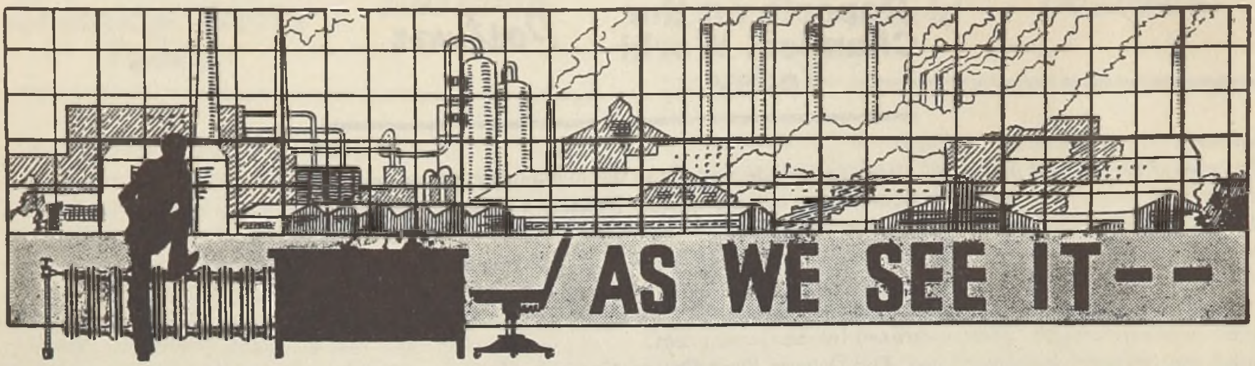
The Defense Plant Corporation is conducting engineering studies preliminary to disposal of the magnesium plants, and in a very able exposition of the problem in this issue of INDUSTRIAL AND ENGINEERING CHEMISTRY, Hans A. Klagsbrunn reveals that the Government's investment in aluminum and magnesium facilities represents more than 6% of its total federal expenditures for manufacturing facilities. Surely the convertibility of such projects to meet peacetime needs should be an important factor in their disposal after the war.

Fuel from Wastes. Work is proceeding at the Northern Regional Research Laboratory toward finding a liquid motor fuel that can be made from farm wastes. Originally $410,000 was appropriated for a three-year investigation of this procedure. Progress is already reported. The government chemists have been able to obtain 90 to 95 gallons of liquid fuel from one ton of waste, and the work is being enlarged to semicommercial scale. A new building will be constructed in the next six months. Contracts have been let to the manufacturers, and equipment, for the most part, has been delivered to the plant site.

The product is mostly ethyl alcohol, obtained through saccharification and fermentation of wastes such as corncobs and cottonseed hulls. The product is now about 50% ethyl alcohol and the rest butanols, acetone, and other flammables. No consideration is given to the utilization of possible process by-products such as plastics, sugars, etc. The problem is to see what kind of motor fuel can be made without consideration of cost. This is far-reaching research and has its being, not in economics, but in the welfare of the Nation during times of emergency.

It has been estimated that 100 million tons of farm wastes might be available for the production of liquid motor fuels. Corncobs will be the first of the waste materials to be tried on a large scale in the new pilot plant.

Inflation Report. Recently there came across our desk an article on a chemical process in China. One of the interesting items which will probably be eliminated in the final draft published in I. & E. C. is the cost of chemicals in that war-torn land, which shows adequately the viciousness of inflation. Prices at Chungking in August, 1944, for the following chemical items will give our technologists an idea of what it means to try to run a business in a country where inflation is out of hand. Lime is selling at 6000 dollars per ton, caustic soda at 200 per pound, coal at 300 per ton, and firewood at 3 dollars per pound. As for wages, one plant manager will be paid 20,000 dollars a month. But before being off to the Far East, remember these figures are in Chinese dollars.



Lead for this month is an excellent article of the wartime record of magnesium and aluminum production in the United States. Klagsbrunn, of the Defense Plant Corporation, takes apart the complex financial structure of every government plant making these materials and the result is a very interesting summary. Some of the costs and production records shown in the article are given for the first time outside congressional hearings and this article will be a very important addition to the permanent literature on the subject. The amount of money the DPC has invested in the plants throughout the country is shown and maps locate the production facilities.

A feature of this month is ion exchange, and we have combined the symposium, given by the Division of Industrial and Engineering Chemistry last year at Columbia University, with several papers on the subject that have come to us via the regular channels. First article from the division is by Sussman, Nachod, and Wood, of the Permutit Company, on the recovery of metals by ion exchange. This is the paper that had the editors puzzled last year, when the A.C.S. News Service began to get inquiries on a process which the correspondents said we had publicized, about an "electrical method of recovering metals". Clue came to what was meant when some inquirer used the words "electrical mist", and gave the editors the inkling that there are ions and ions.

The authors investigated the use of anion exchangers for metal recovery, though cation exchangers had been used often for that purpose. The metals to be recovered were complexes, and satisfactory results were obtained with chromium, gold, iron, molybdenum, and a host of other metals. The most extensive results were obtained with chromium, and this may have important meanings for the metal platers who, industrywise, suffer from acute loss of chromium. Now, perhaps, this disease may be cured.

Sterling Hendricks, of the U. S. Department of Agriculture, looks on plants as ion exchange agents, giving up hydrogen ions for nutritive cations from the soil. This is only one of the interesting concepts that are expounded in his paper on the crystalline silicates as base exchange agents. This also comes from the symposium, and there you can read all about the smallest statistically neutral system known to man.

Herr, of the Resinous Products and Chemical Company, discusses the use of ion exchange resins as a means of separating and recovering thiamine from solutions containing riboflavin. The method holds promise as an analytical tool, according to the author, and in conclusion he points out several commercial advantages of the resin exchange agents.

Buck and Mottern, of the Eastern Regional Research Laboratories, report on processes to make apple juice, now used as a tobacco humectant, palatable for food uses. They use an ion exchanger to eliminate the malic acid, which forms the bitter taste in apple juice. One of the benefits that accrues from the treatment is the removal of the metals used in insecticides and possibly present in the juice as a contaminant from the apple pressing.

Back to the symposium, though away from ion exchange, we have three papers on gas adsorption. One by Emmett, of the Mellon Institute, on methods of measuring surface area by gas adsorption, another by Hassler and McMinn, of the West Virginia Pulp and Paper Company, on active carbon, and the final paper of the symposium group in this issue, by Roger K. Taylor, of the Davison Chemical Company, on water adsorption measurements on silica gel.

Noncorrosive materials of construction are always of considerable interest to those in the field who are anxious to make one tank do where two served before, and Young and Harney, of Standard Oil Company of New Jersey, extensively report on their efforts in developing ways to make polyisobutylene linings stick to metal tanks. The method they describe yields linings capable of withstanding a pull of about 700 pounds per square inch, and the chemical resistance extends over a variety of chemicals.

Grant and Tiffany, of the Bureau of Mines, are working on the efficiency of detonators, a troublesome problem that keeps designers of these playthings awake nights. Results indicate that hexogen base detonators are the big noises as far as this branch of science is concerned.

Silica-alumina catalysts convert xylenes to toluene, diethylbenzene to xylene and toluenes, and are responsible for a host of other reactions and an interesting paper by Hansford, Myers, and Sachanen, of the Socony-Vacuum Oil Company. The results of the study are of prime importance to the petroleum industry which today is in a dither about such catalytic methods.

Artificial bristles from casein is a technique that has been subjected to the pryings of a research team from the Eastern Regional Research Laboratories, and their methods are in this issue. Coarse fibers may be produced by extruding a mixture of casein and water through a suitable die, and the fiber is stretched and hardened under tension, with quinone.

Sage, Lacey, Reamer, and Olds continue a now-famous series on "Phase Equilibria in Hydrocarbon Systems". The present article on volumetric behavior of ethane-carbon dioxide systems is No. 45 in the group, which is still going strong since it began way back in 1934. As long as the work continues, we hope to bring the results to I. & E. C. readers.

With the Departments. Brown in Equipment and Design, page 65, continues his story from last month on means of accurate measurement. Munch, page 71, has information about methods of continuous chemical analysis with reference to the infrared gas analyzer and visible recording polarograph. Von Pechmann, page 77, in a column about interdepartmental communication gives our readers another in his series on how to make a chemical business more efficient. I. & E. C. Reports on the Chemical World of Today, pages 5 to 22, begin with gasoline from natural gas, tell of an interview with British engineers who worked on Operation Pluto, and then continue for several pages more in reporting on its usual interesting résumé of chemical happenings.

F. S. Van Antwerpen

INDUSTRIAL AND ENGINEERING CHEMISTRY
PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

Editorials

WALTER J. MURPHY, EDITOR

Cessation of Controls

FROM here on, the fight against inflation becomes grim and hard. As a nation, never before have we been faced with problems of more importance to our economic future. The chemical industry must take a vital and active part in their solution. Within the country at present are the makings of a vicious inflation which, if not checked and prevented, will give us economic jitters for generations to come, if it does not actually ruin us. Every businessman, every chemist and chemical engineer, who has felt the desire to take a more active part in the social and political life of the Nation, should carefully contemplate every aspect of the coming of peace and the cessation of economic controls. Part of the problem came with V-E Day, and the announcement by J. A. Krug, chairman of War Production Board, on the need and methods of conversion. His statement on the partial reconversion is masterly, and some of the facts bring home to us the strength and immensity of the industry of the United States.

He reveals that our production of munitions has risen from $500,000,000 a month in 1941 to $5,000,000,000 a month today. Our munitions program this year will equal the 1943 rate—the year when most economists were saying that the United States had succeeded in building a war economy on top of a peace economy. Krug also claimed that, of a total employment of 51,000,000, only 6,600,000 will be affected by the cutbacks of partial conversion. He pointed out that in most cases workers could reconvert without shifting jobs. This can be interpreted in another way. Part of our labor force will be working at rates that leave much to spend when the necessities are satisfied. Another, probably inadequate labor force, will be available to supply normal peacetime goods. There will not be enough such goods to go around, and the competitive bidding will be high. That is, it will be high unless our war controls are continued.

Such a situation can have an even more serious effect. It can cause the prices on war materials to rise and our war effort to become much more expensive if reconverted industries vie with war industries for available labor and materials. This must not happen. These are the factors that must be guarded against. It is doubted that WPB means to allow any such thing to happen. In fact, although the major portion of Krug's statement is fairly bubbling over with promises and intimations of control relaxation, the concluding paragraphs are indicative of the action that will probably be followed. There he states that WPB's main objective will continue unchanged, "to see that munitions schedules are met". "Desirable though it may be", he continues, "to attempt to prevent temporary economic dislocations, the experience of those who have lived with controls during the war clearly dictates that controls are not suited to that job. Moreover, reason and history indicate that in any readjustment from a war to a peacetime economy, temporary dislocations are inevitable. We must not be stampeded by such dislocations into elaborate controls or special dispensations. Our economy is a jigsaw pattern. * * * Finally let me repeat, war production is still our first job. We must not remove controls until it is clear that war production will not be adversely affected."

Many of the other war controls will remain in effect even though WPB relaxes some of them. The Office of Price Administration, the War Manpower Commission, and others will still be with us. Krug's plan makes available to the Nation the unneeded raw materials and facilities of war, within a framework of the other economic controls. This is as it should be. At the end of World War I, inflation did not begin at once but took some time to make itself felt. We must be on our guard against these factors.

The Committee for Economic Development has issued a cautious analysis of this problem and with great courage it recommends that "the timing and the manner in which controls are to be ended must be coordinated not only with the progress of war production cutbacks, but with probable economic consequences. And, since the future will not always be certain or the consequences clear, the administrative suspension of controls might wisely precede the legislative authority. It is universally conceded that if the authority to control is ended and later needed, its timely restoration would be difficult, if not impossible."

At the end of World War I, von Hindenburg is reported to have said about American industry: "Her brilliant, if pitiless, war industry had entered the service of patriotism and had not failed it. Under the compulsion of military necessity a ruthless autocracy was at work and rightly, even in this land at the portals of which the Statue of Liberty flashes its blinding light across the seas. *They understood war.*"

Once again we have shown that we understand war. Once again we have an opportunity to show that we understand peace and peacetime economy. When, in the future days of partial conversion, and probably in the days of total peace, some wartime control irks, let us remember that it is the means of fighting another enemy that would destroy us. We do not advocate controls for American industry. We believe that the chemical industry should show an interest in the controls that are retained and in controls as they are released. We believe it ought to protest those kept unnecessarily and to protest those that are dropped at the insistence of any selfish lobby or group that would work to the degradation of free enterprise.

After World War I, according to reports, it was Herbert Hoover who wanted the controls maintained temporarily. The inflation that followed showed the wisdom of his suggestion. Business should approach such relaxation with even more care than it used in advocating the application of controls at the beginning of the war.

Research Atmosphere

FOR years the Chinese Government has been pursuing a systematic plan of obtaining technical training for its young men by sending them abroad for advanced study. Even during the war this plan has been continued. One such student, recently flown here from China, has completed his first semester of graduate study in a large university which normally maintains an extensive research program. But owing to depletion of the staff, the university cannot offer this student further course work in his major field, chemistry, for the present semester. Since he is permitted by his government to remain in this country for only six semesters, he is confronted with the prospect of starting his research before he is prepared for it, and of stopping it when course work is resumed in the fall.

The victim of this circumstance is the only able-bodied man in that particular graduate school; and although it is deplorable that nationals of our allies who have greater foresight than we are compelled to suffer the same injustices, the fact that he is Chinese is irrelevant. The situation serves primarily to illustrate the dangerous depths to which science, education, and research have fallen in this country because of the shortsighted policy of the High Command. The fact that it happened in a large university indicates a general situation. There are others in which conditions are worse.

Most fundamental scientific research and study at the college level have come to a halt in this country. The loss in scientific manpower, which is both cause and effect, has been deplored many times from this page, and the dearth of results from fundamental research will soon make itself felt in diminishing returns from applied science. But these are not the most important losses. The depletion of research staffs has affected the ability of even our greatest university laboratories to do, and teach, research. It has robbed them of that intangible thing called "research atmosphere". There are not enough scientists left to keep it alive.

Research atmosphere is a mysterious quality that transforms a scientific workshop into a research laboratory, a group of scientists into a research team. Through it the knack and spirit of research are passed from teacher to student, from one class to the next, and from the college to industry. It requires the coordination and teamwork of a staff to survive, but size alone will not guarantee it. How it is acquired no one knows. Those that had it do not know how they obtained it, and how to recapture it is a serious problem. Once lost it may never be regained.

Without research atmosphere, a laboratory devoted to research is a hollow shell—fruitless and sterile. By its loss the threads of fundamental research in this country have been broken. This is the loss, this is the damage wrought by the shortsighted policy of those in command. It is nothing less than tragic.

The extent of the tragedy cannot be measured at this time, nor can the damage be repaired. At best, there is a long, dry period ahead until departments can be restaffed and new students brought up the long path to graduate study. How long this will take cannot be predicted; this much is known, it cannot be done without teachers and students. Both are necessary. We must stop this foolish policy and begin restaffing at once.

A way has been made available. The McDonough Bill, H.R. 2827, pending in Congress, would provide for the release of scientists now in military service and for the deferment of a minimum number of students annually to pursue science studies in the universities. The passage of this bill would begin the restitution that must be made to rebuild our scientific resources. The responsibility for active support of this bill lies with every scientist in America. Write your Congressman now and enlist the support of others in your community to back this bill. It must be passed!

Health Needs

NORMALLY we think of the United States as a healthy, well-equipped nation, able to take care of all the illnesses, epidemics, and upsurges of disease that occur. Our thinking about our own standards is too often colored by looking down the scale, instead of looking up. We see the distance traveled instead of the distance yet to be journeyed. An inkling of the immensity of this task yet to be done can be seen in a study released by Senate Subcommittee on Wartime Health and Education.

In rapid-fire order let us present facts about the Nation's health and disease-preventive facilities as gleaned from the report: 40 per cent of the 22,000,000 men of military age are unfit for military duty; the average male worker loses 11 days of labor per year on account of illness; only 60 per cent of our counties have a full-time health service; sanitary facilities are especially bad with 5000 communities needing new water systems, 7700 needing sewerage systems, and 2800 communities possessing no sewerage system at all; the national average of hospital beds is only 3.4 per 1000 of population and some states have less than half this ratio.

No single fact in the above summary is startling or critical when viewed alone, but the facts put together indicate that there is yet a great deal for the sanitary experts, the biochemists, and the medical scientists to do before we attain the health goals we are seeking.

Courtesy Yet in Order

ON OCCASION the American Chemical Society has received complaints to the effect that prospective employers and employees using the Society's want ad pages failed to answer letters of application and inquiry. At first it was assumed that such complaints were isolated instances, and that our membership was, on the whole, meticulous concerning the courtesies normally expected in the business situation that job seeking and filling represents. Now for the first time we have at hand quantitative data and the results cause concern.

The director of research of a large corporation stated that recently, in replying to all letters received from 47 want ad applicants, the company received acknowledgments from only 22. This is a reply rate of 47 per cent, and represents, nonmathematically, bad manners on the part of 53 per cent of this particular segment of our profession. Naturally we hate to believe that such a percentage would hold throughout A.C.S. membership, but the figures in this isolated case give us no hope to the contrary.

Not only do courtesy and manners require that applicants and employers answer all letters, even anonymously if necessary, but the high ethics and standards of the profession demand that this be done. Frankly, we are ashamed that the subject must be mentioned. Let's hope it is the last time it will be necessary.

Forthright Defense

SELDOM do proponents of free enterprise and the capitalistic system get up on their hind legs and hand out a verbal sock in the nose to those in our country who look on business as something low and requiring frequent apologies. The businessman of today too frequently walks down another street rather than go past the home of the taunter, and when the issue is forced upon him, he retires behind the skirts of "Mama lawyer", public relations designed to appease, and mumbo jumbo about capitalism in general. Therefore it was with a general feeling of applause and gratitude that we read a recent speech by Beardsley Ruml, chairman of the Federal Reserve Bank of New York and treasurer of R. H. Macy and Company, on the protection of individual enterprise. Ruml minced no words:

> The protection of individual enterprise is not an end in itself, and our interest in its protection comes from a profound conviction that private enterprise is a bulwark of human freedom * * Individual enterprise is inextricably bound up with profits * * The underlying and unifying force, releasing all others and giving a meaning to all else, is profit. It is not merely the spark plug, it is the spark within the plug * * It is not what business is for, it is not the justification of business activity; but it is so important in getting business properly done that it is sometimes mistakenly taken to be the end and the purpose of business. We can properly deny to profits the exalted position of being the end and purpose of business and at the same time recognize the crucial importance of profits in releasing and guiding the powers residing in private enterprise * * Of the goods are sold squarely and priced competitively, if the costs of producing them are governed by the intelligence and by the use of fair and legal methods, and there is no direct or indirect public subsidy that makes prices higher or costs lower than the managers of the business themselves could make, then the higher the profits, the better the interests of all are served * * Public opinion today is skeptical of accepting the highest obtainable profit as a desirable social standard. This skepticism is the result of practices which have undermined the prestige of business. These practices are: improper representation and misbranding in selling; controlled and noncompetitive prices; exploitation of labor; adulteration of quality; the receipt of subsidies in the form of franchises, tariffs, tax exemption, and grants of the public domain; and, finally, undue monopoly privileges in the use of patents, trade-marks, and copyrights * * When profits are made (1) within the law, (2) under competitive enterprise, (3) without public subsidy, or (4) without public protection of exclusivity, the higher the profits the greater the honor to the profit maker. Under these circumstances, there should be no limitation on the amount of profits which a business can make, because the greater the profits the greater the service * * The dangers to individual enterprise arise in large measure from neglect and abuse of the profit system. The protection of individual enterprise will be substantially accomplished if the profit system is rehabilitated.

These are strong words, from a man who knows business and who knows government, having served both. He recognizes danger to our system and he tackles the problem by defending with vigor a principle which seems fundamental, but which recently has come in for more apologies than defense. There will be a scrap, whether business goes by the back road or not. To us it seems wise to get out the old principles upon which true free enterprise is founded and to polish and sharpen them as the best weapons.

Science has made of the world one community. We must expect to learn from every culture and regard every human being as a person entitled to some measure of our respect and consideration.

—James G. Vail

WARTIME ALUMINUM AND MAGNESIUM PRODUCTION

WIDE WORLD PHOTO

Hans A. Klagsbrunn

DEFENSE PLANT CORPORATION, WASHINGTON, D. C.

IN 1939 the United States reached a peacetime high of 327,095,000 pounds of aluminum produced by Aluminum Company of America and 6,700,000 pounds of magnesium by Dow Chemical Company. During the next two years, before our entry into the war, each company added to its capacity through private investment. With the aid of government loans, facilities for aluminum were built by Reynolds Metals Company and for magnesium by Permanente Metals Corporation.

When it became apparent that tremendous increases were necessary, Defense Plant Corporation, at the request of War Production Board, constructed two alumina plants, nine aluminum reduction plants, and thirteen magnesium metal plants. These additions gave a total designed capacity of 2286 million pounds of aluminum (about seven times the 1939 Alcoa peak) and 586 million of magnesium (about eighty-seven times the Dow high of 1939). Actual production, however, showed a larger capacity for all of the aluminum plants and for nine of the magnesium. Even without full use, supplies came so rapidly that cutbacks were ordered for aluminum by December, 1943, and for magnesium in May, 1944. During December, 1944, aluminum had been cut back to only 48.5% of capacity, magnesium to 16%. The problem of adequate supply of these metals had, within a space of four years, been completely overcome.

Government investments in the aluminum and magnesium facilities have been sizable, representing over 6% of the government's total expenditure for manufacturing facilities. They were distributed as follows (in thousands of dollars):

Alumina and aluminum	$263,648	Magnesium metal	$365,773
Aluminum fabricating	365,575	Magnesium fabricating	21,292
Miscellaneous (including sintering plants, power, etc.)	41,435	Miscellaneous (including power, gas transmission, etc.)	2,234
Total	670,658	Total	389,299

DPC grand total aluminum and magnesium, $1,059,957

In addition to the DPC investment, Reconstruction Finance Corporation granted loans of about $58,000,000 for aluminum and magnesium plants. Of this, approximately $35,000,000 went to Reynolds Metals for alumina and aluminum capacity at Listerhill and Sheffield, Ala., and for aluminum at Longview, Wash. Permanente Metals received about $22,000,000 for magnesium, with an additional $1,000,000 for miscellaneous facilities. Meanwhile the Navy invested around $1,800,000 in two aluminum powder plants.

Table I. Alumina Production Data

			Max. Production Attained			Official Cutback from Designed Capacity to Per Cent Allowed				Production					
Operator	Location	Designed Capacity, 1000 lb. Per Year	Month	1000 lb.	% of rated capacity	Month, 1944	%	Month, 1944	%	1942, 1000 lb.	% designed capacity	1943, 1000 lb.	% designed capacity	1944, 1000 lb.	% designed capacity
GOVERNMENT-OWNED PLANTS															
Alcoa	Hurricane Creek	1555	Oct., '43[a]	120,520	92.7	Jan.	59	Sept.	35	93,593	...	1,050,548	67.6	858,075	55
Alcoa	Baton Rouge	1000	Oct., '43[b]	80,510	96.6	April	18	[c]	..	...	...	531,660	18.9	231,010	23
	Total	2555								93,593		1,582,208	60.3	1,089,085	42.6
PRIVATELY OWNED PLANTS															
Alcoa	East St. Louis	840	Aug., '43	73,935	110	July	72	Sept.	54	765,707	91.2	834,592	99.4	594,703	74
Alcoa	Mobile	1300	Oct., '43	116,723	107.5	April	90	June	70	1,020,870	78.5	1,324,776	101.9	1,027,040	79
Reynolds	Listerhill	200	July, '44	19,444	117	...	..	...	..	147,606	74	194,946	97.4	193,276	96.5
	Total	2340								1,934,183	82.7	2,354,314	101.8	1,815,019	79
								Total all plants		2,027,776		3,936,522	80.4	2,904,104	59

[a] Initial production, July, 1942. [b] Initial production, March, 1943. [c] Closed August, 1944.

With such a stake in light metal plants, bearing in mind the proportion of new capacity to the total and the levels of past and prospective demands for metals, postwar utilization becomes a problem of major importance.

ALUMINUM INDUSTRY

Aluminum and magnesium are referred to collectively as the light metals. This grouping tends to create an impression of similarity in the metals and their uses, and points to common treatment of the problems of each. However, the raw materials, processes, and many of the uses vary greatly, and the factual materials of each industry require separate discussion. For aluminum there are four main divisions: (1) mining of bauxite (see photo, page 608), (2) production of alumina, (3) reduction of alumina, and (4) fabrication of sheets, shapes, forgings, castings, etc., for further manufacture or incorporation into finished products.

To obtain 1 pound of aluminum, 2 of alumina are required, the latter produced from about 4 pounds of grade A bauxite (55% alumina or more, 7% silica or less). Lower grades of bauxite require as much as 5 pounds or more.

Bauxite production in the United States in 1939 was only 350,000 tons. About half was used for metal purposes, giving an estimated 85–90 million pounds. This was less than the capacity of a three-pot-line aluminum plant, and with the government program calling for thirty-eight pot lines, not to mention expanding requirements of Alcoa and Reynolds, domestic prewar bauxite production was inadequate.

Consequently, the Metals Reserve Company entered into contracts with existing and new operators—some on the basis of firm purchase, a few on agreements involving advances against future production. Deliveries began in May, 1942, supplying alumina plants with 1,772,000 tons and building a stock pile of nearly 3,000,000 tons by the end of 1944.

Table II. Alumina Production Costs at Government-Owned Plants (May, 1943, through November, 1944)

				Production Costs, Cents per Pound[a]									
Alumina Plant	Month & Year	Production, 1000 Lb.	% Designed Capacity	Bauxite delivered	Labor	Lime & soda ash	Fuel & power	Repairs & maintenance	Other items	Total per lb.	Depreciation	Per lb., less depreciation
Baton Rouge, La. (designed annual capacity 1 billion pounds)	May, '43	34,425	41.3	1.77	0.19	0.42	0.11	0.08	0.28	2.85	0.14	2.71
	June	53,640	64.4	1.71	0.14	0.37	0.10	0.12	0.25	2.69	0.14	2.75
	July	60,405	72.5	1.77	0.14	0.40	0.09	0.05	0.22	2.67	0.02	2.65
	Aug.	66,811	80.2	1.44	0.12	0.40	0.09	0.10	0.26	2.41	0.10	2.31
	Sept.	68,746	82.5	1.50	0.12	0.42	0.08	0.13	0.29	2.54	0.10	2.44
	Oct.	80,510	96.6	1.48	0.11	0.41	0.08	0.13	0.21	2.42	0.10	2.32
	Nov.	76,903	92.3	1.65	0.12	0.43	0.09	0.12	0.21	2.62	0.10	2.52
	Dec.	60,811	73.0	1.53	0.14	0.32	0.09	0.24	0.22	2.54	0.06	2.48
	Jan., '44	51,285	61.5	1.39	0.15	0.29	0.10	0.15	0.34	2.42	0.14	2.28
	Feb.	45,803	55.0	1.22	0.15	0.27	0.10	0.17	0.32	2.23	0.15	2.08
	Mar.	44,289	53.2	1.35	0.17	0.16	0.10	0.21	0.33	2.32	0.16	2.16
	Apr.	33,862	40.6	1.42	0.30	0.14	0.11	0.26	0.50	2.73	0.21	2.52
	May	23,038	27.6	1.24	0.26	0.32	0.15	0.24	0.64	2.85	0.31	2.54
	June	22,342	26.8	1.08	0.26	0.25	0.15	0.23	0.72	2.69	0.32	2.37
	July	10,388	12.5	1.29	0.37	0.27	0.32	0.37	1.46	4.08	0.70	3.38
	Aug.	Shutdown	...	...	...	...	...	...	...	...	...	...
9-mo. av., 8/43–4/44		58,780	70.6	1.46	0.14	0.34	0.09	0.16	0.29	2.48	0.11	2.37
Bauxite, Ark. (designed annual capacity 1.555 billion pounds)	May, '43	82,998	64.1	0.60	0.09	0.45	0.09	0.08	0.19	1.50	0.07	1.43
	June	86,232	66.5	0.61	0.09	0.46	0.09	0.09	0.15	1.49	0.07	1.42
	July	100,545	77.6	0.61	0.08	0.47	0.08	0.05	0.16	1.45	0.06	1.39
	Aug.	100,283	77.4	0.67	0.10	0.49	0.08	0.09	0.15	1.58	0.06	1.52
	Sept.	108,751	83.6	0.63	0.08	0.56	0.08	0.10	0.14	1.59	0.06	1.53
	Oct.	120,520	92.7	0.61	0.07	0.54	0.07	0.08	0.14	1.51	0.05	1.46
	Nov.	102,954	79.2	0.65	0.08	0.60	0.08	0.07	0.15	1.63	0.06	1.57
	Dec.	100,196	76.3	0.67	0.09	0.84	0.08	0.11	0.16	1.95	0.10	1.85
	Jan., '44	72,425	55.7	0.62	0.12	0.79	0.10	0.10	0.23	1.96	0.10	1.86
	Feb.	73,821	56.8	0.59	0.11	0.67	0.10	0.10	0.22	1.76	0.10	1.69
	Mar.	80,868	62.2	0.57	0.11	0.58	0.09	0.08	0.21	1.64	0.09	1.55
	Apr.	89,782	69.0	0.55	0.11	0.49	0.09	0.08	0.23	1.56	0.10	1.44
	May	94,537	73.0	0.56	0.09	0.47	0.08	0.07	0.27	1.54	0.09	1.45
	June	89,840	69.4	0.53	0.09	0.47	0.07	0.08	0.26	1.50	0.09	1.41
	July	92,449	71.4	0.55	0.08	0.45	0.08	0.07	0.29	1.52	0.14	1.38
	Aug.	87,264	67.4	0.51	0.08	0.47	0.07	0.08	0.27	1.48	0.10	1.38
	Sept.	41,594	32.1	0.51	0.11	0.47	0.09	0.11	0.42	1.71	0.22	1.49
	Oct.	48,084	37.1	0.50	0.11	0.47	0.09	0.14	0.50	1.81	0.20	1.61
	Nov.	43,468	33.5	0.44	0.11	0.32	0.08	0.12	0.55	1.62	0.21	1.41
9-mo. av., 8/43–4/44		94,440	72.9	0.62	0.09	0.61	0.09	0.09	0.18	1.68	0.08	1.60

[a] Not including interest on working capital, state, local, and federal taxes, or general overhead expense. Costs are given as reported by operators; final figures are to be determined on basis of Certified Public Accountant audits.

Alumina. Large DPC investments were also required for the oxide. Prior to 1941 Alcoa produced alumina at East St. Louis, Ill. (from domestic bauxite supplied by its subsidiary, Republic Mining & Manufacturing Company), and at Mobile, Ala. (from ores imported from South America). Capacities of each plant had been expanded before DPC entered the field. Also, Reynolds Metals Company, Inc., with RFC financing, built an alumina plant at Listerhill, Ala., as part of its integrated operation for aluminum production. Initial expansion through the Government called for one alumina and three aluminum plants, and contract for their construction and operation was executed with Alcoa in August, 1941. The alumina plant, at Hurricane Creek, Ark., was within a six-mile trucking distance from Saline County mines. In later agreements the capacity of this plant was increased. Another was erected at Baton Rouge, La., to use Arkansas ores and, if conditions permitted, those imported from South America.

These programs, including capacities, locations, and operators, were determined by WPB and its predecessors after consideration

Table III. Aluminum Ingot Facilities and

Operator	Location	Cost of Facilities to 12/31/44, Millions	No. of Pot Lines	Capacities, Thousand Pounds: Contract or designed: Annual	Month	Attained maximum	Annual equivalent[a]
Alcoa	Burlington, N. J.	$ 17.636	3	96,000	8,000	9,495(Oct./43)	113,940
Alcoa	Jones Mills, Ark.	29.554	4	128,000	10,667	13,039(Oct./43)	156,468
Alcoa	Maspeth, N. Y.	33.714	8	256,000	21,333	25,222(Oct./43)	302,664
Alcoa	Massena, N. Y.	20.314	3	96,000	8,000	9,154(May/43)	109,848
Alcoa	Riverbank, Calif.	11.767	3	96,000	8,000	6,268(Jan./44)	d
Alcoa	Spokane, Wash.	23.090	6	192,000	16,000	18,570(Jan./44)	222,840
Olin	Tacoma, Wash.	6.297	2	41,500	3,458	3,616(May/44)	43,392
Alcoa	Torrance, Calif.	24.545	5	160,000	13,333	9,605(March/44)	f
Alcoa	Troutdale, Oreg.	18.665	4	128,000	10,667	11,802(Jan./44)	141,624
Total		$185.582	38	1,193,500	99,458		

[a] Maximum month's production, multiplied by 12.

[b] Omitting taxes (federal, state, local), general overhead, interest on investment, and depreciation. Costs as reported by operator; final figures to be determined on basis of C.P.A. audits.

Table IV. Average of Aluminum Production Costs for Nine Months (August, 1943, to April, 1944, Inclusive)[a]

Location of Plant	Cents per Pound: Total, before depreciation	Alumina	Power	Labor	Carbons	Other items, less depreciation	Depreciation
Spokane	10.605	5.584	1.844	1.044	1.103	0.664	0.426
Troutdale	11.036	5.752	1.940	1.269	1.142	0.515	0.595
Jones Mills	11.694	4.739	3.983	0.975	0.887	0.858	0.898
Los Angeles	13.652	5.658	4.279	1.623	1.153	0.610	0.746
Tacoma	15.379	5.745	1.947	2.568	0.873	3.034	...
Riverbank	14.336	5.624	4.546	1.497	1.506	0.776	0.540
Queens	15.194	5.508	5.548	1.231	1.528	1.195	0.327
Burlington	15.334	5.293	5.607	1.503	1.425	1.087	0.994
Massena	15.328[b]	5.607[b]	7.090[b]	1.115[b]	1.203[b]	Stand-by	0.888[b]

[a] Not including interest on working capital, federal, state, or local taxes, or general overhead expense. Costs are given as reported by operators; final figures are to be determined on basis of C.P.A. audits.

[b] Average for six months.

Table V. Aluminum Ingot Facilities and Production Data for Privately Owned Plants

Operator	Location	Max. Capacity Attained: 1000 lb.	Month & year	Annual Equivalent Capacity[a], 1000 Lb.	Annual Production, Thousand Pounds: 1939	1940	1941	1942	1943	1944
Alcoa	Alcoa, Tenn.	30,348	Dec./42	364,176	136,602	164,513	209,324	310,778	347,932	272,919
	Badin, N. C.	9,459	Oct./43	113,508	41,664	58,882	79,027	98,247	108,806	65,049
	Massena, N. Y.	14,277	Oct./43	171,324	113,657	142,003	144,799	152,069	160,453	143,492
	Niagara Falls, N. Y.	3,607	May/43	43,284	36,167	37,174	37,982	38,670	40,889	40,584
	Vancouver, Wash.	15,500	Jan./42	186,000	...	9,988	131,575	181,369	172,609	164,654
Reynolds	Listerhill, Ala.	8,751	Dec./43	105,012	...	...	12,260	62,975	96,456	100,408
	Longview, Wash.	5,396	May/44	64,752	...	...	3,242	52,040	62,331	63,876
Total, privately owned plants					328,090	412,560	618,209	896,148	989,746	850,982
Total all plants (government and private)					328,090	412,560	618,209	1,042,193	1,840,075	1,552,696

[a] Maximum month's production, multiplied by 12.

Table VI. Alumina Facilities and Production Data

Government-Owned Plants

Operator	Location	Cost of Facilities to 12/31/44, Millions	Capacities, Million Lb.: Contract or designed: Annual	Month	Attained Maximum	Construction Period: Started	Complete	Operation Readiness: Initial	Full	9-Mo. Av. Production, 8/43–4/44: Cost[a], cents/lb.	% designed capacity	Annual Production, 1000 Lb.: 1942	1943	1944
Alcoa	Bauxite or Hurricane Creek, Ark.	$38.938	1555	129.6	120.5 (Oct./43)	10/4/41	4/1/44	7/23/42	Feb./44	1.60	73	93,593	1,050,548	858,075
Alcoa	Baton Rouge, La.	26.679	1000	83.3	80.5 (Oct./43)	4/6/42	4/1/44	3/16/43	12/1/43	2.37	71	...	531,660	231,010
Kalunite	Salt Lake City, Utah	4.820	72	6.0	0.24 (Oct./44)	3/23/42	11/1/43	10/15/43	1/15/44	...	..	...	...	1,069
		$70.537											1,582,208	1,090,154

Privately Owned Plants

Operator	Location	Max. Capacity Attained, Million Lb.	Annual Production, 1000 Lb.: 1942	1943	1944
Alcoa	East St. Louis, Ill.	73.9(Aug./43)	765,707	834,592	594,703
Alcoa	Mobile, Ala.	116.7(Oct./43)	1,020,870	1,324,776	1,027,040
Reynolds	Listerhill, Ala.	19.4(July/44)	147,606	194,946	193,276
	Other plants	....	....	....	14,427
Total			1,934,183	2,354,314	1,829,446
Total, government and private				3,936,522	2,919,600

[a] Not including taxes (federal, state, local), general overhead, interest on investment, and depreciation. Costs as reported by operator; final figures to be determined on basis of C.P.A. audits.

Production Data for Government-Owned Plants

%, Max. Capacity to Designed	Construction Period		Operation Readiness		9-Mo. Av. Production, 8/43-4/44		Annual Production, Thousand Pounds		
	Started	Complete	Initial	Full	Cost[b], cents/lb.	% designed capacity	1942	1943	1944
119	July/42	May/43	5/20/43	Sept./43	15.33	73	...	48,549	22,454
122	Jan./42	March/43	7/31/42	Feb./43	11.69	117	20,704	133,885	134,096
118	May/42	May/43	2/27/43	Aug./43	15.29	86	...	177,245	86,465
114	Oct./41	May/43	5/31/42	Aug./42	15.33[c]	111[c]	44,133	105,137	9,059
...	June/42	Oct./43	5/15/43	[e]	14.34	69	...	29,848	43,976
116	Nov./41	May/43	5/14/42	Sept./43	10.61	107	34,933	143,109	191,698
104	Feb./42	Feb./43	9/7/42	March/43	15.38	93	4,667	37,174	36,719
...	Dec./41	Sept./43	7/3/42	[e]	13.65	65	16,299	80,530	72,651
111	Nov./41	May/43	5/17/42	Sept./43	11.04	102	25,309	94,852	104,776
							146,045	850,329	701,714

[c] Six-month average.
[d] Only two pot lines operated; maximum never attained.
[e] Never attained.
[f] Only three pot lines operated; maximum never attained.

by the armed services and other war agencies. After completion, the distribution of alumina production was as follows:

Plant	Ownership Operation	Rated Ann. Capacity, 1000 Lb.	Source of Bauxite
Hurricane Creek	DPC–Alcoa	1555	Ark.
Baton Rouge	DPC–Alcoa	1000	Ark., Surinam
Mobile	Alcoa	1300	Surinam, Ark.
East St. Louis	Alcoa	840	Ark., a little from Surinam
Listerhill	Reynolds	200	Surinam, Ark., Ala.
	Total	4895	

In terms of capacity, ownership was in the following proportions:

DPC	2,555,000,000 lb.	52.2%
Alcoa	2,140,000,000	43.7
Reynolds	200,000,000	4.1

Alumina recovery depended upon the efficiency of the Bayer process used by all plants. Certain quantities of alumina and process materials were lost in the waste materials (red muds). To decrease losses, conserve limited resources, and utilize lower-grade bauxite ores, lime-soda-sinter processing facilities were installed by DPC in its own and in two Alcoa plants. Expenditures for these items, segregated on an estimated basis out of over-all expenditures for total facilities were:

Hurricane Creek	$ 7,250,114
Baton Rouge	6,400,955
East St. Louis	8,917,618
Mobile	8,123,101
Total	$30,691,788

ALUMINA FROM NONBAUXITE SOURCES. To augment alumina facilities, DPC built four small plants to develop processes using materials other than bauxite. They were constructed through private operators and are described in the following table:

Location	Operator	Cost, in Thousands: Authorized	Cost, in Thousands: Disbursed to Jan., 1945	Ann. Capacity, Million Lb.	Initial Operation
Salt Lake City, Utah	Kalunite, Inc.	$5254	$4820	72	July, '44
Salem, Oreg.[a]	Columbia Metals Co.	4945	2369[b]	36	Sept., '45[d]
Laramie, Wyo.	Monolith Portland Midwest Co.	4629	2185[c]	36	Sept., '45[d]
Harleyville, S. C.	Ancor Corp.	3162	3018	36	April, '45

[a] Built by Chemical Construction Company.
[b] 52% complete.
[c] 55% complete.
[d] Estimate.

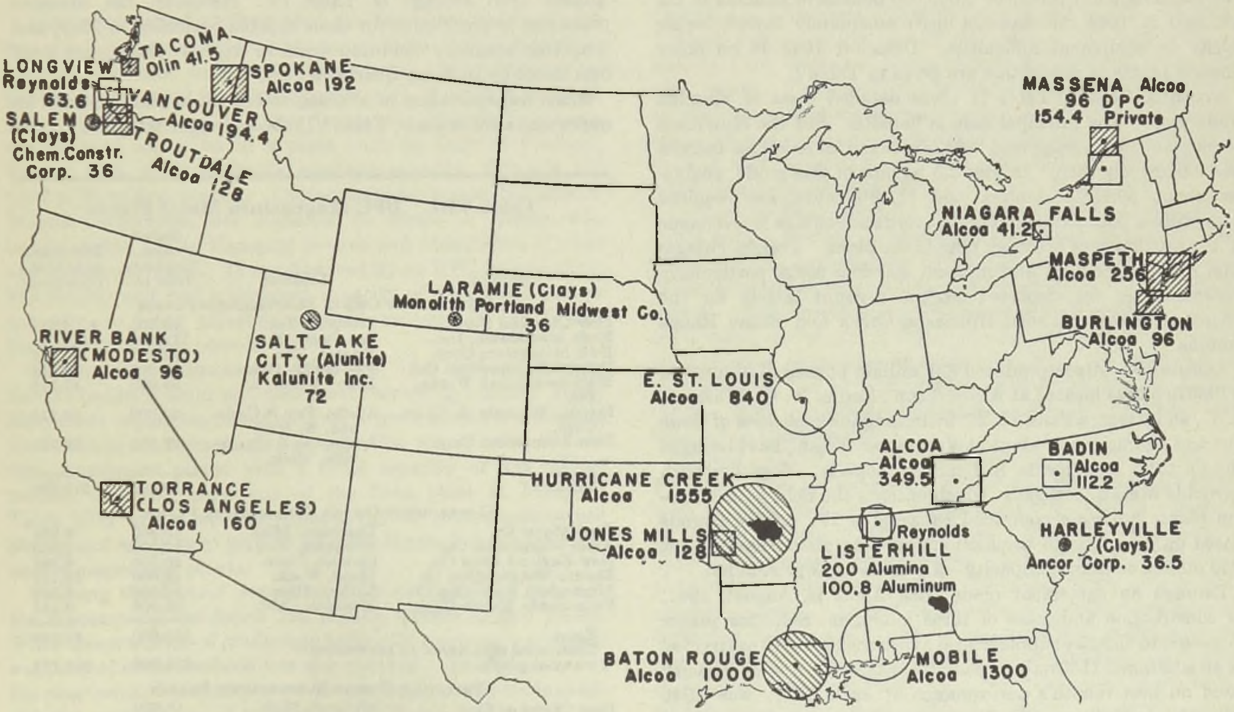


Figure 1. Distribution of Alumina and Alumium Ingot Industry in the United States

Black areas indicate bauxite mines; shaded areas, ownership by DPC; white areas, private ownership. Circles indicate alumina; squares, aluminum ingot. Names of cities given in capital letters; operators in small letters. Numbers indicate designed capacities in millions of pounds per year; area of symbols are proportional to volume of alumina produced or required for ingot.

Table VII. Freight Rates on Alumina from Plants to Reduction Centers

Origin	Destination	Miles	Rate		Aluminum Equivalent, Cents/Lb.
			Net ton	Cent/lb.	
Baton Rouge, La.	Alcoa, Tenn.	745	$ 5.00	00.25	0.50
	Badin, N. C.	900	11.80	00.59	1.18
	Longview, Wash.	2649	8.00	00.4	0.8
	Los Angeles, Calif.	1871	8.00	00.4	0.8
	Spokane, Wash.	2331	8.00	00.4	0.8
	Troutdale, Oreg.	2590	8.00	00.4	0.8
	Vancouver, Wash.[a]	2610	8.00	00.4	0.8
	San Francisco, Calif.	2340	8.00	00.4	0.8
E. St. Louis, Ill.	Alcoa, Tenn.	553	4.60	00.23	0.46
	Badin, N. C.	842	6.40	00.32	0.64
	Burlington, N. J.	994	6.20	00.31	0.62
	Longview, Wash.	2211	8.00	00.4	0.8
	Los Angeles, Calif.	1946	12.00	00.6	1.2
	Maspeth, N. Y.	1073	6.60	00.33	0.66
	Massena, N. Y.	992	6.40	00.32	0.64
	Niagara Falls, N. Y.	725	4.60	00.23	0.46
	Riverbank, Calif.	2144	12.00	00.6	1.2
	Spokane, Wash.	1902	8.00	00.4	0.8
	Tacoma, Wash.	2200	8.00	00.4	0.8
	Troutdale, Oreg.	2153	8.00	00.4	0.8
	Vancouver, Wash.	2173	8.00	00.4	0.8
Hurricane Creek, Ark.	Alcoa, Tenn.	593	5.00	00.25	0.50
	Badin, N. C.	882	6.40	00.32	0.64
	Jones Mills, Ark.	26	0.81	00.0405	0.081
	Longview, Wash.	2347	8.00	00.4	0.8
	Tacoma, Wash.	2336	8.00	00.4	0.8
	Troutdale, Oreg.	2289	8.00	00.4	0.8
	Vancouver, Wash.	2308	8.00	00.4	0.8
	Los Angeles, Calif.	1775	8.00	00.4	0.8
	San Francisco, Calif.	2244	8.00	00.4	0.8
Mobile, Ala.	Longview, Wash.	2768	8.00	00.4	0.8
	Los Angeles, Calif.	2077	8.00	00.4	0.8
	Maspeth, N. Y.	1232	7.80	00.39	0.78
	Massena, N. Y.	1484	8.20	00.41	0.82
	Riverbank, Calif.	2380	8.00	00.4	0.8
	Niagara Falls, N. Y.	1222	7.80	00.39	0.78
	Spokane, Wash.	2458	8.00	00.4	0.8
	Tacoma, Wash.	2757	8.00	00.4	0.8
	Troutdale, Oreg.	2710	8.00	00.4	0.8
	Vancouver, Wash.	2729	8.00	00.4	0.8

[a] The same rates are applicable to Tacoma, Wash.

The Kalunite plant produced 1,069,000 pounds of alumina in the last half of 1944 but has not been adequately tested, owing chiefly to equipment difficulties. Data for 1942–44 on other alumina plants in production are given in Table I.

ALUMINA COSTS. Table II gives detailed costs of alumina production. The principal item is bauxite. For the Hurricane Creek plant the average cost is $4.50 per ton for Arkansas bauxite used exclusively there. About 2.5 pounds of this grade, analyzing about 50.15% alumina and 11.43% silica, are required to produce a pound of alumina, but its disadvantage is overcome by the proximity of ore stock piles to the plant. Freight charges from Arkansas sources and unusual wartime costs, particularly transportation, for imported bauxite account largely for the difference in cost between Hurricane Creek and Baton Rouge alumina.

ALUMINUM. Alcoa produced 327 million pounds of aluminum in 1939 in plants located at Alcoa, Tenn., Badin, N. C., Massena, N. Y., and Niagara Falls, N. Y.; increasing the capacities of these four and adding a new plant at Vancouver, Wash., have brought Alcoa's total capacity to 878 million pounds. Together with Reynolds Metals Company, which entered the field with reduction plants having a combined capacity of 171 million pounds (based on peak month production), private plants have about 1050 million combined capacity—3.2 times 1939 production.

Through an agreement made with Alcoa in August, 1941, for construction and lease of three aluminum reduction plants (increased to eight by supplemental agreements), DPC contracted for an additional 1152 million pounds capacity. (Actual capacity based on best month's performance at each plant was 1346 million.) In addition, Olin Corporation built a 43 million pound plant for DPC.

Initial production from DPC facilities was achieved in May, 1942, at Spokane, Wash., Troutdale, Oreg., and Massena, N. Y. Peak production for all DPC plants was reached in December, 1943, with 104,500,000 pounds. At the end of that month cutbacks occurred at two DPC plants and in Alcoa operations in three locations. In addition, three lines were completed but never put in operation.

Thus, within sixteen months from the time the DPC program was inaugurated, production was well ahead of current and anticipated requirements. Within three to four years the 1939 production capacity was increased nearly eight times. Figure 1 shows the location of aluminum operations, and Tables III, V, and VI present general data on alumina and aluminum operation and capacity.

PRODUCTION COSTS. Total costs for aluminum, before depreciation and overhead, vary from 10.6 cents per pound at the Spokane plant to 15.4 at Tacoma, using the nine-month average of August, 1943, to April, 1944. One important item is the basic raw material, alumina, while transportation and power are others. The Jones Mill plant in Arkansas had the lowest alumina cost because of nearness to bauxite mines and to the Hurricane Creek alumina plant. Spokane's average power cost was 1.84, and only two other plants enjoyed comparable rates—these obtaining power from the Bonneville Power Authority. Eastern DPC plants have had the highest power costs, about 5.6 cents per pound, with one as high as 7 cents. Whether these ranges and relative levels will hold for the postwar period is problematical and may determine postwar survival of particular plants. With decreasing war demands, power surpluses may develop to make the continuous load of a pot line or two most welcome.

Table IV gives unaudited costs for aluminum metal production. The Massena plant was in stand-by condition for the last three months of the August–April average. Figures available for the period May–August, 1944, have not been averaged but would not materially affect the August–April average of Table IV. However, the Massena plant was in production for three months beginning in May, and went into stand-by condition again in August; Burlington went into stand-by in June, Queens in July.

Since transportation of alumina to reduction plants is such an important item in costs, Table VII shows freight rate data.

Table VIII. DPC Magnesium Metal Plants

Operator	Location	Rated Ann. Capacity, 1000 Lb.	Disbursed to 1/1/45, Thousands
GOVERNMENT-OWNED ELECTROLYTIC PLANTS			
Dow Chemical Corp.	Freeport, Tex.	18,000	$ 8,333
Basic Magnesium, Inc.	Las Vegas, Nev.	112,000	131,014
Dow Magnesium Corp.	Velasco, Tex.	72,000	56,401
Diamond Magnesium Co.	Painesville, Ohio	36,000	14,749
Mathieson Alkali Works, Inc.	Lake Charles, La.	54,000	47,736
Intern. Minerals & Chem. Corp.	Austin, Tex. & Carlsbad, N. Mex.	24,000	18,715
Dow Magnesium Corp.	Ludington & Marysville, Mich.	72,000	39,785
Total		388,000	316,733
GOVERNMENT-OWNED FERROSILICON PLANTS			
Ford Motor Co.	Dearborn, Mich.	40,000	9,981
Amco Magnesium Co.	Wingdale, N. Y.	10,000	7,068
New England Lime Co.	Canaan, Conn.	10,000	4,889
Electro Metallurgical Co.	Mead, Wash.	48,000	16,121
Magnesium Reduction Co.	Luckey, Ohio	10,000	4,839
Permanente Metals Corp.	Manteca, Calif.	20,000	6,142
Total		138,000	49,040
Total rated capacity of all government-owned plants		526,000	365,773
PRIVATELY OWNED ELECTROLYTIC PLANTS			
Dow Chemical Co.	Midland, Mich.	18,000	....
Dow Chemical Co.	Freeport, Tex.	18,000	....
PRIVATELY OWNED CARBOTHERMIC PLANTS			
Permanente Metals Co.	Permanente, Calif.	24,000	....
Total		60,000	....

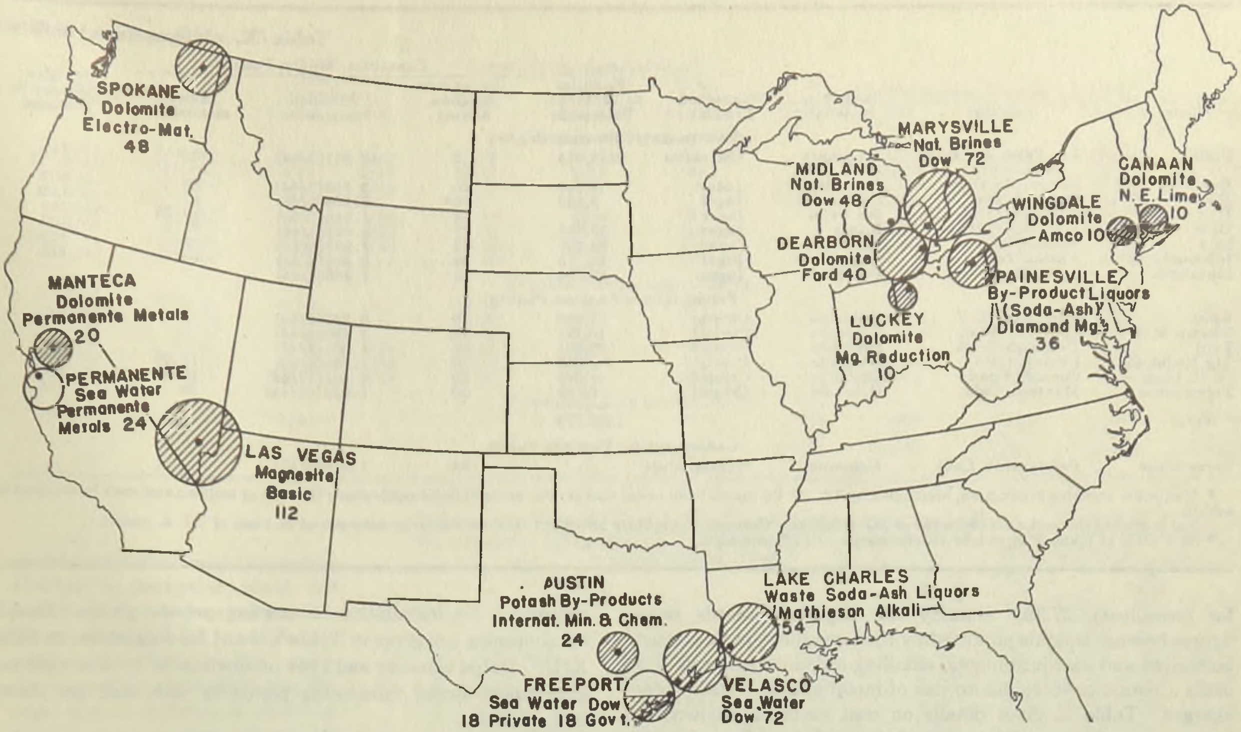


Figure 2. Distribution of Magnesium Reduction Plants in the United States

Shaded circles indicate ownership by DPC; white circles, private ownership. Names of cities given in capital letters; operators, in small letters. Numbers indicate designed capacities in millions of pounds per year; areas of circles are proportional to capacities.

MAGNESIUM INDUSTRY

During the period 1926–41 when the Dow Chemical Company was sole producer of magnesium metal in the United States, its capacity increased to 9 million pounds by 1938. Further expansion undertaken in 1939 brought it to 18 million in April, 1941. That year saw the first commercial production of magnesium from sea water in a plant built by Dow at Freeport, Texas. This doubled Dow's previous capacity, bringing the total to 36 million pounds. During the same period Permanente Metals Corporation was organized by Henry J. Kaiser, who bought rights to the Hansgirg process and constructed a plant at Permanente, Calif. It was financed by an RFC loan of about $22,000,000 and had a designed capacity of 24 million pounds annually, to bring privately planned capacity in the United States to 60 million pounds.

Government Expansion Program. As with aluminum, private facilities could not meet ever-increasing military needs. Immediate expansion of capacity as a government undertaking was necessary. Accordingly, construction was started of thirteen magnesium plants with a rated capacity of 526 million pounds, including expansion of the Dow plant at Freeport. Table VIII gives capacity, investment in government-owned plants, and capacity of private plants. Figure 2 shows the location of magnesium plants.

Utilizing the trained personnel of Dow Chemical Company, the Government developed 222 million pounds at five plants. While this extension of production by the Dow process was underway, use of other methods was also planned. Among them was the magnesium Elektron process used in England and made available for construction of a plant at Las Vegas, Nev. Built for 112-million-pound capacity, it was by far the largest. The program also provided for six ferrosilicon magnesium plants with a total capacity of 138 million pounds. Another plant, using an electrolytic process and a newly developed cell, was built for the Government by The Mathieson Alkali Works (Inc.), at Lake Charles, La. This had a planned capacity of 54 million pounds.

These various processes required several raw materials not used by Dow Chemical, whose experience had been exclusively with brines. Probably this diversity of tested and untested methods and materials accounts largely for the range of performance and unit costs among government plants. The contrast is marked with production and cost performance among government-owned aluminum plants.

Operating Performance. By 1943 production had mounted to 324 million pounds, an increase of 224 million over 1942 which reflected the contribution from government-owned plants. While production mounted rapidly, performance among plants varied. Nine exceeded planned capacity by 3 to 30%. On the other hand, the plants at Lake Charles and Dearborn failed by wide margins to achieve expected capacities. In peak months they attained but 27 and 30% of planned production, respectively. Both equipment difficulties and novel processes contributed to these results.

Earliest production from government capacity came from the Freeport plant in November, 1941. By May, 1943, all plants were in production, and monthly output climbed to a peak of 41 million pounds in January, 1944. This was equivalent to 84% of rated capacity of all plants. Surplus ingot to the extent of 60 million pounds accumulated, and production continued to outstrip demand. Accordingly a series of cutbacks was ordered, beginning February 1, 1944. These continued throughout the year and affected all government-owned plants except the facility at Freeport. By December, 1944, production was down to 8.5 million pounds or 17% of designed capacity. Table IX gives a record of operations.

Costs. Among government-owned plants, total costs ranged from 11.51 to 57.26 cents per pound for the lowest cost month. Weighted average costs for electrolytic plants was 18.24 cents,

Table IX. Magnesium Facilities

Operator	Location	Basic Raw Material	Magnesium Product	Cost of Facilities to 12/31/44, Thousands	Capacities, Million Pounds: Contract or designed, annual	Capacities, Million Pounds: Attained maximum	Capacities, Million Pounds: Annual equivalent[a]	%, Max. Capacity to Designed
			ELECTROLYTIC PROCESS PLANTS					
Basic	Las Vegas & Gabbs, Nev.	Magnesite	Cell metal	$131,014	112	10.311(3/44)	124	111
Diamond	Painesville, Ohio	Dolomite	Ingot[e]	14,749	36	3.250(1/44)	39	107
Dow	Freeport, Tex.	Sea water	Ingot	8,333	36[d]	3.905(1/43)	47	130
Dow	Midland, Mich.	Sea water	Ingot	....	18	1.645(1/43)	19.75	110
Dow	Marysville, Mich.	Brines	Ingot	39,785	72	5.985(1/44)	72	100
Dow	Velasco, Tex.	Sea water	Ingot	56,401	72	7.263(3/43)	87	121
International	Austin, Tex.	Dolomite	Ingot	18,715	24	2.335(8/43)	28	117
Mathieson	Lake Charles, La.	Dolomite	Ingot	47,736	54	1.208(2/44)	..	..
			FERROSILICON PROCESS PLANTS					
Amco	Wingdale, N. Y.	Dolomite	Crystal	7,068	10	0.649(4/44)	..	..
Electro Met.	Spokane, Wash.	Dolomite	Crystal	16,121	48	2.180(3/44)	..	..
Ford	Dearborn, Mich.	Dolomite	Crystal	9,981	40	1.001(2/44)	..	..
Mg Reduction	Luckey, Ohio	Dolomite	Crystal	4,839	10	1.050(4/44)	12.60	126
N. E. Lime	Canaan, Conn.	Dolomite	Crystal	4,889	10	0.861(12/43)	10.30	103
Permanente	Manteca, Calif.	Dolomite	Crystal	6,142	20	1.922(12/44)	23	115
Total				$365,773				
			CARBOTHERMIC PROCESS PLANT					
Permanente	Permanente, Calif.	Dolomite	Crystal-Dust	....	24	1.619(6/43)	....	..

[a] Maximum month's production, multiplied by 12. [b] To convert cell metal and crystal costs to ingot equivalent, the cost of melting and melt losses must be added.
[c] Not including interest on investment or depreciation. Costs as reported by operator; final figures to be determined on basis of C.P.A. audits.
[d] Only 50% of plant is owned by Government. [e] 97% complete.

for ferrosilicon, 27.39. Actually the disparity exceeds these figures because crystals produced by the ferrosilicon process must be melted and cast into ingots, entailing an additional cost of 3 cents a pound or more due to loss of metal and to certain other charges. Table X gives details on unit costs of production; lowest operating costs for electrolytic and ferrosilicon plants December, 1943, to October, 1944, are shown in Table XI.

FABRICATION AND POSTWAR PRODUCTION

Following through the program for aluminum and magnesium production DPC invested in fabricating plants proper and in equipment for installation in existing private plants. Details for aluminum are given in Table XII and for magnesium in Table XIII. Rated capacity and 1944 production for both private and government-owned fabricating plants in each field are shown in Table XIV.

In preparation for the day when its facilities will be available for disposition, DPC is making engineering studies of the plants. The plan is to follow these with studies of potential markets, sources of materials, convertibility of facilities, power and transportation costs, new and cheaper sources of raw materials, and

Table X. Lowest Cost[a] Attained in Government Magnesium

Electrolytic Process

Rank in lowest cost for process	1	2	3	4	5	6	
Operator	Dow	Diamond	Basic	Dow	International	Mathieson	Total, six plants
Plant	Velasco	Painesville	Las Vegas	Marysville	Austin	Lake Charles	
Subprocess	Dow, sea water	Dow, dolomite	English (Earben), magnesite	Dow, brines,	Dow, potash wastes, dolomite	Mathieson, dolomite	.....
Form of product	Ingot	Ingot	Cell metal	Ingot	Ingot	Ingot	.....
Capacity per mo.							
Designed, lb.	6,000,000	3,000,000	9,333,333	6,000,000	2,000,000	4,500,000	30,833,333
Max. attained, %	121.1	108.3	110.7	99.8	116.7	26.8	98.4
Production at lowest unit cost attained							
Period	May/44	Sept./44	July/44	April/44	Dec./43	Feb./44	.....
Volume, lb.	6,728,002	2,808,396	6,185,220	5,355,457	2,066,175	1,207,504	24,350,754
Operating rate, %	112.1	93.6	66.3	89.3	103.3	26.8	79.0
							WEIGHTED AV.
Lowest unit cost[b], cents per lb.							
Raw materials	1.14	5.19	4.36	2.62	6.88	17.88	4.07
Operating labor	2.31	1.74	2.76	2.31	2.02	14.83	2.95
Power (source)	1.58 (own plant, gas fuel)	4.77 (Cleveland electricity)	2.33 (Boulder Dam)	6.55 (Detroit Edison)	4.64 (Lower Colo. River)	1.11 (own plant, gas fuel)	3.47
Supplies							
Operating supplies	0.26	0.67	1.06	0.27	1.84	3.25	0.79
Fuel	0.20	0.38	0.12	0.99	....	2.91	0.49
Water, steam, air	0.27	0.48	0.10	1.40	....	0.64	0.50
	0.73	1.53	1.28	2.66	1.84	6.80	1.78
Repairs							
Labor	0.81	0.10	1.08	0.50	0.62	4.52	0.90
Supplies	0.42	0.04	0.76	0.07	0.37	3.84	0.55
Retort or cell	1.20	0.67	....	0.81	1.08	....	0.68
	2.43	0.81	1.84	1.38	2.07	8.36	2.13
Overhead and administration	1.88	0.95	3.34	1.45	1.46	5.03	2.17
Fees, taxes, miscellaneous							
Management & royalties	1.17	0.93	0.59	1.00	0.67	....	0.85
Taxes, Social Security	0.15	0.16	0.81	0.21	0.08	2.09	0.56
Insurance	0.02	0.04	0.52	0.03	....		
Laboratory	0.03	0.10	0.19	0.09	0.25	1.16	0.17
Other expenses	0.07	0.17	....	0.08	0.38	....	0.09
	1.44	1.32	2.11	1.41	1.38	3.25	1.67
Total unit cost	11.51	16.31	18.02	18.38	20.29	57.26	18.24

[a] The cost figures in this table are those reported by operators and are subject to final C.P.A. audits.

and Production Data

Construction Period		Operation Readiness		Lowest Production End Cost[b]			Production, Thousand Pounds				
Started	Complete	Initial	Full	Cents/ lb.[c]	Month	% of plant operating	1941	1942	1943	1944	Total
				ELECTROLYTIC PROCESS PLANTS							
10/1/41	6/30/44	9/42	7/43	18.02	7/44	66	...	2,837	90,976	68,730	162,543
12/15/41	4/15/43	9/42	1/43	16.31	9/44	94	...	4,652	33,894	32,156	70,702
3/10/41	4/15/42	11/41	1/42	...		..	14,413	42,731	43,191	41,161	141,496
Private	...	(Prior to 1941)		...		..	18,246	19,512	16,871	10,595	65,224
4/7/42	12/1/43	4/43	1/44	18.38	4/44	89		...	25,812	36,783	62,595
11/8/41	5/1/43	6/42	1/43	11.51	5/44	112	...	20,752	80,253	60,740	161,745
12/17/41	10/31/43	11/42	1/43	20.29	12/43	103	...	2,158	25,539	17,936	45,633
1/31/42	3/15/44[e]	1/43	...	57.26	2/44	27	...	...	2,384	2,985	5,369
				FERROSILICON PROCESS PLANTS							
6/24/42	8/15/43	3/43	...	29.13	3/44	77	...	...	1,509	2,943	4,452
5/4/42	10/1/43	5/43	...	19.40	5/44	52	...	...	5,500	18,358	23,858
2/42	1/43	5/42	...	55.05	3/44	30	...	715	6,791	2,272	9,778
7/15/42	4/1/43	1/43	4/43	18.32	4/44	125	...	...	8,474	11,249	19,723
3/9/42	7/29/43	9/42	1/44	22.17	5/44	79	...	970	8,049	7,037	16,056
3/15/42	6/30/44	5/42	9/43	27.82	2/44	106	...	2,991	16,113	6,540	25,644
				CARBOTHERMIC PROCESS PLANT							
Private	...	9/41	...	...	...	..	118	2,659	15,618	4,353	22,748
							32,777	99,977	380,974	323,838	837,566

other factors which might determine whether a particular plant can justify itself in the postwar market. Every effort will be made to expedite sale or lease of DPC facilities when they are available for disposal and to achieve, in so far as possible through these plants, the continuity of employment and production which is vital to postwar stability and prosperity.

Table XI. Lowest Operating Costs for Electrolytic and Ferrosilicon Magnesium Plants from December, 1943, to October, 1944

	Plant					Lowest Unit Cost: Single month		Lowest Unit Cost: 3-mo. moving av.	
Rank	Operator	Location	Process	Product[a]	Capacity, Million Lb./Mo.	Operating rate, %	Cents/ lb.	Operating rate, %	Cents/ lb.
1	Dow	Velasco	E	Ingot	6.00	112	11.51	109	12.10
2	Diamond	Painesville	E	Ingot	3.00	94	16.31	93	16.50
3	Dow	Marysville	E	Ingot	6.00	89	18.38	74	18.86
4	International	Austin	E	Ingot	2.00	103	20.29	102	21.27
5	Mathieson	Lake Charles	E	Ingot	4.50	27	57.26	23	73.28
1	Basic	Las Vegas	E	Cell metal	9.33	66	18.02	104	18.70
1	Mg Reduction	Luckey	FS	Crystal	0.83	125	18.32	120	18.92
2	Electro Met.	Spokane	FS	Crystal	4.00	52	19.40	49	20.21
3	N. E. Lime	Canaan	FS	Crystal	0.83	79	22.17	77	25.09
4	Permanente	Manteca	FS	Crystal	1.67	106	27.83	111	28.53
5	Amco	Wingdale	FS	Crystal	0.83	77	29.13	75	29.44
6	Ford	Dearborn	FS	Crystal	3.33	30	55.05	27	64.78

[a] To convert cell metal and crystal costs to ingot equivalent, the cost of melting and melt loss must be added.

Plants Operated for DPC (All Costs before Depreciation)

Ferrosilicon Process									
1 Mg Reduction Luckey	2 Electro Met. Spokane	3 N. E. Lime Canaan	4 Permanente Manteca	5 Amco Wingdale	6 Ford Dearborn	Total, six plants		Total, All Processes	
.....	.....	.....	....	....	.....	....		....	
Crystal	Crystal	Crystal	Crystal	Crystal	Crystal	....		....	
833,333	4,000,000	833,000	1,666,667	833,333	3,333,333	11,500,000		42,333,333	
126.1	54.5	103.4	115.3	77.9	30.0	66.6		89.8	
April/44	May/44	May/44	Feb./44	March/44	Feb./44	....		....	
1,043,408	2,081,288	660,419	1,763,007	639,230	1,000,870	7,188,222		31,538,976	
125.2	52.1	79.3	105.8	76.7	30.0	62.5		74.5	
						WEIGHTED AV.		WEIGHTED AV.	
						Cents per lb.	% of total	Cents per lb.	% of total
9.54	2.98	6.41	11.40	7.34	12.78	8.07	29.4	4.98	24.5
1.69	3.57	4.27	3.80	5.71	11.30	4.68	17.1	3.35	16.5
0.44 (Toledo Edison)	2.26 (Grand Coulee Dam)	0.86 (Conn. Power)	0.33 (Pacific Gas & Elec.)	1.12 (N. Y. Gas & Elec.)	1.89 (Ford, River Rouge)	1.24	4.5	2.96	14.6
0.61	0.50	0.57	1.33	0.82	0.59	0.77		0.79	
1.97	1.02	3.90	1.20	3.86	6.69	2.51		0.95	
0.01	0.71	....	....	0.15	....	0.22		0.43	
2.59	2.23	4.47	2.53	4.83	7.28	3.50	12.8	2.17	10.7
0.25	0.96	0.74	0.91	1.51	3.79	1.27		0.98	
0.19	3.39	0.18	1.66	0.48	0.69	1.57		0.78	
2.00	....	2.29	4.20	3.50	0.25	1.87		0.95	
2.44	4.35	3.21	6.77	5.49	4.73	4.71	17.2	2.71	13.3
0.96	2.19	1.83	1.84	3.74	15.47	3.88	14.2	2.56	12.6
0.14	1.04	0.38	0.43	....	1.10	0.62		0.80	
0.21	0.54	0.37	0.19	0.39	{0.50				
0.11	0.07	0.05	0.10	0.17		0.45		0.54	
0.05	0.15	0.32	0.42	0.34	....	0.21		0.18	
0.15	0.02	....	0.01	....	....	0.03		0.08	
0.66	1.82	1.12	1.15	0.90	1.60	1.31	4.8	1.60	7.8
18.32	19.40	22.17	27.82	29.13	55.05	27.39	100	20.33	100

[b] Lowest total unit cost, not necessarily reflecting lowest component costs.

Table XII. Government-Owned Aluminum Fabricating Plants

Forging Plants

Lessee	Location	Ann. Rated Capacity, 1000 Lb.: Large hammer	Ann. Rated Capacity, 1000 Lb.: Small hammer & pressings	Approx. Cost, Thousands	Start of Production
Aluminum Co. Am.	New Castle, Pa.	...	21,000	$9,200	1/15/43
Aluminum Co. Am.	Canonsburg, Pa.	66,480	8,400	26,600	5/26/43
Aluminum Co. Am.	Monroe, Mich.	...	42,000[a]	13,200	6/26/43
Aluminum Forgings[b]	Erie, Pa.	11,520	4,080	9,700	4/29/43
GM-Chevrolet	Anderson, Ind.	...	37,500	4,300	11/14/43
GM-Chevrolet	Saginaw, Mich.	69,120	43,920	9,900	12/1 /42
Reynolds Metals	Louisville, Ky.	...	2,400	2,500	1/1 /44

Extrusion Plants

Lessee	Location	Ann. Rated Capacity, 1000 Lb.: Shapes	Ann. Rated Capacity, 1000 Lb.: Tube blooms	Ann. Rated Capacity, 1000 Lb.: Rod & bar	Approx. Cost, Thousands	Start of Production
Aluminum Co. Am.	Phoenix, Ariz.	32,900	27,800	....	33,700	5/20/43
Aluminum Co. Am.[c]	Cressona, Pa.	29,500	26,200	....	25,100	4/28/43
Bohn Aluminum & Brass	Adrian, Mich.	36,000	....	....	16,400	5/1 /43
Bohn Aluminum & Brass	Los Angeles, Calif.	9,600	1,200	900	8,100	1/11/43
Extruded Metals	Grand Rapids, Mich.	10,800	....	....	6,700	12/12/42
Revere Copper & Brass[b,d]	Halethorpe, Md.	....	10,800	....	[e]	3/15/44
Reynolds Metals	Louisville, Ky.	7,200	4,300	34,000	4,700	April/41

Tube Drawing Plants

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
Aluminum Co. Am.	Phoenix, Ariz.	15,500	[f]	5/20/43
Aluminum Co. Am.[g]	Cressona, Pa.	14,700	[f]	4/28/43
Reynolds Metals	Louisville, Ky.	2,400	[f]	April/41

Rolling Mills: Sheet, Strip & Plate

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
Aluminum Co. Am.	Chicago, Ill.	288,000	45,665	6/2 /43
Aluminum Co. Am.	Spokane, Wash.	288,000	47,230	4/1 /43
Reynolds Alloys	Listerhill, Ala.	78,000	[e]	7/21/41

Rolling Mills: Rolled Rod & Bar

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
Aluminum Co. Am.	Newark, Ohio	300,000	24,500	5/4 /43
Reynolds Alloys	Listerhill, Ala.	60,000	[e]	7/21/41

Sand Castings (Excluding Cylinder Heads)

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
GM, Delco-Remy	Bedford, Ind.	10,200	3,000	7/15/42
Natl. Bronze & Aluminum	Cleveland, Ohio	13,200	2,200	6/10/43

Cast Cylinder Heads for Air-Cooled Engines

Lessee	Location	Ann. Rated Capacity: No. of heads	Ann. Rated Capacity: 1000 lb.	Approx. Cost, Thousands	Start of Production
Aluminum Co. Am.	Kansas City, Mo.	1,200,000	42,006	$ 5,700	2/25/43
Ford Motor[h]	Dearborn, Mich.	1,020,000	30,100	8,100	10/16/42
GM-Buick	Flint, Mich.	1,800,000	43,200	10,000	7/23/42
Natl. Aluminum Cylinderhead	Cleveland, Ohio	480,000	14,400	4,600	8/10/42
Chrysler-Dodge[i]	Chicago, Ill.	600,000	24,000	7,478	7/1 /43
Wright Aeronautical[i]	Lockland, Ohio	1,200,000	46,300	6,600	4/1 /41

Permanent Mold Castings

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
Reynolds Metals[j]	Springfield, Mass.	9,000	3,000	Jan./45

Rivets

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
Huck Manufacturing	Detroit, Mich.	800	500	11/11/41
Bell Aircraft	Buffalo, N. Y.	600	[i]	......
Consolidated-Vultee Aircraft	San Diego, Calif.	1,400		......
Ford Motor	Dearborn, Mich.	4,700		......
Goodyear Aircraft	Akron, Ohio	100		......
Lockheed Aircraft	Burbank, Calif.	400		......

Aluminum Powder

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
McAleer Manufacturing	Rochester, Mich.	18,000	200	3/20/44
National Smelting[k]	Cleveland, Ohio	36,000	400	......

Plants Owned by Navy Department

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
Aluminum Co. Am.	Glassmere, Pa.	24,000	1,300	8/5 /44
Metals Disintegrating	Webster Groves, Mo.	21,000	500	6/10/44

Multiple Product Plants

Lessee	Location	Products	Approx. Cost, Thousands	Start of Production
Revere Copper & Brass	Halethorpe, Md.	Al extrusions, Mg extrusions & forgings	7,500	3/15/44
Reynolds Alloy	Listerhill, Ala.	Al sheet, blooms, rods, & bars	20,000	7/21/41

[a] Figure is for forged cylinder heads; can produce 60,000,000 pounds of scalped ingots in excess of forging capacity.

[b] Management and operations plant.

[c] Shutdown October, 1944; some equipment has been removed.

[d] Has magnesium fabricating facilities. [e] See Multiple Product Plants. [f] Included in extrusion plant.

[g] Shutdown October, 1944. [h] Lease cancelled, plant closed. [i] Part of aircraft engine plants.

[j] Originally constructed for Springfield Bronze and Aluminum Company but never operated by them; has now been leased to Reynolds and went into production January, 1945.

[k] Also contains facilities for smelting magnesium scrap, costing $425,000.

Table XIII. Government-Owned Magnesium Fabricating Plants

Lessee	Location	Ann. Rated Capacity, 1000 Lb.	Approx. Cost, Thousands	Start of Production
	Sand Castings			
Bendix Aviation	Teterboro & North Bergen, N. J.	3,600	$1200	1/15/42
Chrysler-Dodge[a]	Chicago, Ill.	18,000	7000	7/ 1/43
Dow Chemical	Bay City, Mich.	1,600	1700	4/26/43
Howard Foundry	Chicago, Ill.	7,200	2600	8/15/42
Maryland Sanitary Mfg.	Baltimore, Md.	6,000	2000	6/ 1/43
Wellman Bronze & Aluminum	Cleveland, Ohio	3,000	700	
Wright Aeronautical[a]	Lockland, Ohio	9,000	5000	4/ 1/41
	Permanent Mold Castings			
Metal-Mold Magnesium[b]	Cedarbury, Wis.	2,200	200	2/25/44
	Die Castings (Cold Chamber)			
Precision Castings	Fayetteville, N. Y.	2,400	400	2/ 1/45
	Extrusions and Forgings			
Revere Copper & Brass	Halethorpe, Md.	5,500[c] 1,800[d]	7500	6/15/44

DPC Magnesium Equipment Installed in Lessee's Plants

Product	Lessee	Location	Approx. Cost, Thousands
Sand casting foundries	Am. Radiator	Louisville, Ky.	$630
	Am. Radiator	Elyria, Ohio	580
	Am. Radiator	Litchfield, Ill.	480
	Ebaloy Foundries	Rockford, Ill.	130
	GM-Chevrolet	Saginaw, Mich.	600
	Hills-McCanna	Chicago, Ill.	220
	Humphreys Mfg.	Mansfield, Ohio	520
	Marshall Stove	Lewisburg, Tenn.	340
	Mich. Light Alloys	Grand Rapids, Mich.	1180
	U. S. Radiator	Geneva, N. Y.	700
			5380
Die castings	Hoover Co.	N. Canton, Ohio	50
Extrusions	Dow Chemical	Midland, Mich.	1600
Sheet & plate	Revere Copper & Brass	Baltimore, Md.	2000
		Grand total	9030

[a] Part of engine plant.

[b] Molds are owned by lessee.

[c] Extrusions. [d] Forgings.

Table XIV. Rated Capacity and 1944 Production of Fabricating Plants

	Annual Rated Capacity					1944 Production				
	Government owned		Privately owned		Total, thousands of pounds	Government owned		Privately owned		Total, thousands of pounds
	Thousands of pounds	% of total	Thousands of pounds	% of total		Thousands of pounds	% of total	Thousands of pounds	% of total	
Aluminum										
Castings	232,400	26.6	639,900	73.4	872,300	109,700	20.3	430,500	79.7	540,200
Sand, general	23,400	8.2	260,900	91.8	284,300	17,800	8.0	206,500	92.0	224,300
Sand, cylinder heads	200,000	73.5	72,200	26.5	272,200	91,900	73.3	33,400	26.7	125,300
Permanent mold	9,000	5.3	161,300	94.7	170,300	...	..	106,300	100.0	106,300
Die	...	..	145,500	100.0	145,500	...	..	84,300	100.0	84,300
Rolled products	1,014,000	40.6	1,485,200	59.4	2,499,200	409,800	33.4	816,900	66.6	1,226,700
Sheet, strip & plate	654,000	40.8	949,800	59.2	1,603,800	291,500	33.0	592,800	67.0	884,300
Foil	...	..	55,800	100.0	55,800	...	..	33,300	100.0	33,300
Rod & bar	360,000	44.3	452,400	55.7	812,400	118,300	40.2	175,800	59.8	294,100
Structural shapes	...	..	27,200	100.0	27,200	...	..	15,000	100.0	15,000
Extruded products	231,200	45.7	274,300	54.3	505,500	71,400	30.1	166,100	69.9	237,500
Rod & bar	34,900	39.5	53,500	60.5	88,400	9,400	22.8	31,800	77.2	41,200
Shapes	126,000	51.0	121,200	49.0	247,200	43,800	34.2	84,300	65.8	128,100
Tube blooms	70,300	41.4	99,600	58.6	169,900	18,200	26.7	50,000	73.3	68,200
Tubing	32,600	30.8	73,200	69.2	140,100	7,100	15.1	39,800	84.9	46,900
Forgings	306,400	47.0	345,300	53.0	651,700	101,800	38.1	165,200	61.9	267,000
Heavy hammer	147,100	59.4	100,700	40.6	247,800	57,600	44.5	71,900	55.5	129,500
Light hammer & pressings	159,300	39.7	242,300	60.3	401,600	44,200	32.4	92,200	67.6	136,400
Impact extrusions	...	..	2,300	100.0	2,300	...	..	1,100	100.0	1,100
Wire & cable	...	..	72,300	100.0	72,300	...	..	49,100	100.0	49,100
Rivets	800	2.5	30,600	97.5	31,400	750	2.9	24,800	97.1	25,550
Powder & paste	99,000	55.5	79,500	44.5	178,500	25,300	26.7	69,500	73.3	94,800
Magnesium										
Sand cutting	48,400	36.6	84,000	63.4	132,400	14,600	19.4	60,600	80.6	75,200
Permanent mold casting	2,200	1.2	176,000	98.8	178,700	1,000	4.0	23,900	96.0	24,900
Die casting	2,400	20.0	5,600	80.0	12,000	...	00.0	2,400	100.0	2,400
Forging	1,800	50.0	1,800	50.0	3,600	...	00.0	400	100.0	400
Extrusion	5,500	41.7	7,700	58.3	13,200	650	6.3	9,740	93.7	10,400
Sheet & plate	...	00.0	8,300	100.0	8,300	...	00.0	2,300	100.0	2,300

A polystyrene-silica replica of the surface of pure magnesium is produced by fracturing with a sharp blow. The hexagonal symmetry of the metal is demonstrated, and orientation of the crystal of the fracture can be readily determined (reproduced through courtesy of Dow Chemical Company).

←

Workman inspecting aluminum castings manufactured in a plant of Aluminum Company of America. Casting facilities have been expanded to several times prewar capacity.

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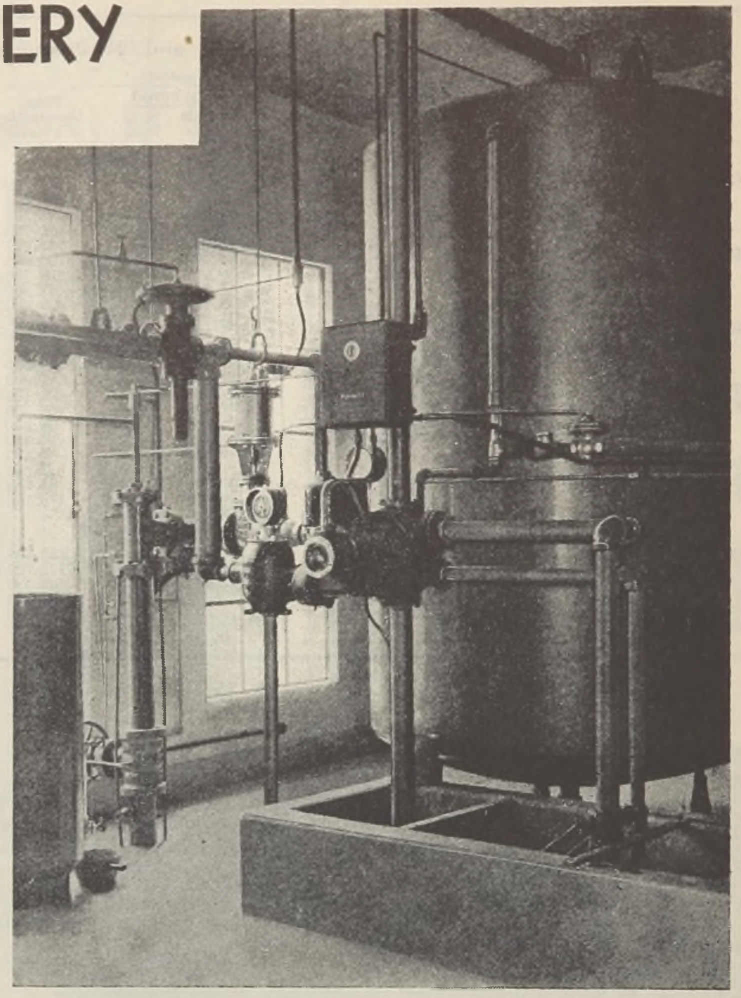
METAL RECOVERY by ANION EXCHANGE



Little has appeared in the literature on anion exchange reactions for metal recovery, although organic cation exchangers are being used for this purpose. The present investigation was undertaken to study anion exchange for recovery of metals which form complex anions. Satisfactory adsorption and recovery have been demonstrated with chromium, gold, iron, molybdenum, palladium, platinum, and vanadium, using different types of complex anions. A more extensive study was made of chromium recovery. The anion exchange mechanism of the adsorption was demonstrated. Adsorption on different anion exchanger salts and from several influents was carried out. Best results were obtained with adsorption from a neutral chromate solution on the anion exchanger chloride. Recovery experiments were run with several salts, bases, mixtures of the two, and with an acid. Alkaline regenerants were found best. Acid regenerants caused oxidation of the anion exchange resin and reduction of the chromate. Precious metals are recoverable by ashing the resin. Metal concentrations of more than twenty-five times the influent concentration were obtainable without recycling . . . A typical automatic ion exchange unit is reproduced at the right; this equipment may be used for processes ranging from the softening of water to the recovery of metal.

Sidney Sussman, Frederick C. Nachod[1], *and William Wood*

THE PERMUTIT COMPANY, BIRMINGHAM, N. J.

MORE than thirty years ago Duggan (*7*) suggested the recovery of gold from dilute solutions by the relatively new synthetic inorganic zeolites. With the recent introduction of the more versatile and rugged sulfonated coal (*3*) and synthetic resin (*1*) types of cation exchangers, interest in ion exchange methods for metal recovery increased rapidly (*1, 5, 7, 8, 11–14, 17–20, 22, 25, 27*); these methods provided obvious advantages in the removal of metals from very dilute solutions and their recovery as much more concentrated solutions without the use of precipitation or evaporation processes. Cation exchange reactions were used in the investigations cited, but little, if anything, has been published on the use of anion exchange reactions for metal recovery.

Treatment of an anion exchanger salt with a solution of a salt whose anion has a higher valence or weight than that of the anion already adsorbed on the anion exchanger results in the displacement of the adsorbed anion by that of the salt in the influent solution. In view of these facts and their well-known acid adsorption properties, it seemed likely that anion exchangers might be used for the recovery of those metals which form complex anions, and an experimental program was initiated. Satisfactory adsorption and recovery were demonstrated with chromium, gold, iron, molybdenum, palladium, platinum, and vanadium. The present investigation was in the nature of an exploratory study to evaluate the scope of anion exchange metal recovery. More detailed studies are now in progress, both in this laboratory and in the field.

The broad features of the use of anion exchangers for acid removal and anion exchange reactions have been described (*1, 16, 28*), as have details of the tube or column technique used in most of the experiments (*2, 16, 26*).

Some modification of the usual tube technique was required in those cases where an alkaline recovery agent proved most effective, but the metal adsorption reaction was a true anion exchange. In these cases, after recovery of the metal by treatment of the anion exchanger bed with the alkaline recovery solution, the bed was rinsed with water, treated with an acid solution to convert the anion exchanger to the desired salt, and again rinsed with water to remove the excess acid before the start of the next adsorption cycle.

In a typical example of this procedure, a 100-ml. bed of an alkali-regenerated, synthetic resin anion exchanger in a 23-mm.-diameter tube was treated with 200 ml. of 1.4 *N* hydrochloric acid at 5 ml. per minute in order to convert the anion exchanger to the chloride. The tube was backwashed and then rinsed at 50 ml.

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[1] Present address, Atlantic Refining Company, Philadelphia, Pa.

per minute with water until the chloride content of the effluent rinse was below 50 parts per million. The waste metal solution was passed through the tube at 25–50 ml. per minute until the metal appeared in the effluent and its concentration rose to a predetermined figure. The tube was then rinsed free of excess waste metal solution with water at 50 ml. per minute, and 200 ml. of 3 *N* ammonium hydroxide were introduced at 5 ml. per minute, followed by a water rinse at 5 ml. per minute, for a volume equal to the displacement volume of the bed, then at 50 ml. per minute until the recovered metal content of the rinse effluent dropped to a negligible concentration. The tube was then ready for a new cycle starting with the acid treatment.

The tube technique requires an appreciable investment in time and materials. For high spotting, an equivalent amount of information may often be obtained by equilibrium exchange experiments. This technique was used in a number of experiments; a weighed sample of the anion exchanger was placed in an Erlenmeyer flask, and a measured amount of reactant or regenerant solution was added from a pipet. The flask was sealed and attached to a frame rotating at about 15 r.p.m. After the desired time of reaction had elapsed, the flask was removed from the frame, the contents were decanted, and the liquid was analyzed.

Most of the experimental work reported in this paper was carried out with an aliphatic amine resin (*28*). A few experiments of early date were carried out with a granular insoluble emeraldine or aniline black (*15*).

Analyses for chromate were carried out by the standard iodide-thiosulfate titration. Analyses for the other complex anions were made by colorimetric methods adapted from standard analytical methods for these ions; a Klett-Summerson photoelectric colorimeter and calibration curves, prepared with the aid of carefully standardized solutions, were utilized.

CHROMIUM

Probably the most common waste metal recovery problem to which anion exchange can be applied is that of chromium-containing wastes from plating plants (*10*) in which the metal occurs as the chromate. Experiments were carried out with both the tube and equilibrium techniques, to explore the possibility of removing chromates from different influent solutions and for recovering them by various regenerants.

Equilibrium Experiments. Preliminary experiments were carried out to determine whether there was any substantial difference between the adsorption reaction using the hydrochloric acid salt of the ion exchanger or using the sulfuric acid salt. The results obtained with several ratios of standard solution to weight of anion exchanger salt were plotted as adsorption isotherms to obtain estimates of adsorption capacities at comparable final solution concentrations. Such values (Table I) indicated that no appreciable differences exist between the equilibrium values for adsorption of chromate on the anion exchanger sulfate as compared with the chloride.

Equilibrium studies were also made on the use of various recovery reagents. These experiments (Figure 1) indicated that alkaline regeneration of the exhausted anion exchanger chromate is far superior to salt regeneration.

The probable explanation for this behavior lies in the fact that the primary, secondary, and tertiary amines, of which the anion exchange resin may be considered a mixture, are not such strong bases as the inorganic hydroxides. The corresponding substituted ammonium hydroxides do not ionize completely, and this ionization may be considerably reduced by the presence of a strong base. The equilibrium involved may be represented by the equation,

$$(R_3NH)OH \rightleftharpoons (R_3NH^+)OH^- \qquad (1)$$

where R represents one or more alkyl or aryl groups, or hydrogen. It is rather difficult to conceive of an ionic system in which the anion is freely mobile in the usual sense while the cation comprises a substantially immobile charged locality on a macromolecular insoluble resin. It is possible that, under these conditions, ionization can consist of little more than a limited mobility of the anions among different cationic groups on the resin. Therefore, the authors have indicated the ionization of the anion exchanger base by the symbol given on the right hand side of Equation 1 rather than by the more conventional $(R_3NH^+) + OH^-$. A similar ionic designation is used for anion exchanger salts.

The regeneration of an anion exchanger chromate by a salt may be illustrated by the following equation:

$$(R_3NH^+)_2CrO_4^{--} + SO_4^{--} \rightleftharpoons (R_3NH^+)_2SO_4^{--} + CrO_4^{--} \qquad (2)$$

The regeneration of an anion exchanger chromate by a base may be illustrated by the following equation:

$$(R_3NH^+)_2CrO_4^{--} + 2OH^- \rightleftharpoons 2(R_3NH^+)OH^- + CrO_4^{--} \qquad (3)$$

It becomes clear that, whereas an excess of a salt as regenerant will shift Equation 2 to the right, the excess of a base will not only shift Equation 3 to the right but, in addition, will shift Equation 1 to the left by furthering formation of the nonionized base; the chromate is thereby liberated more completely.

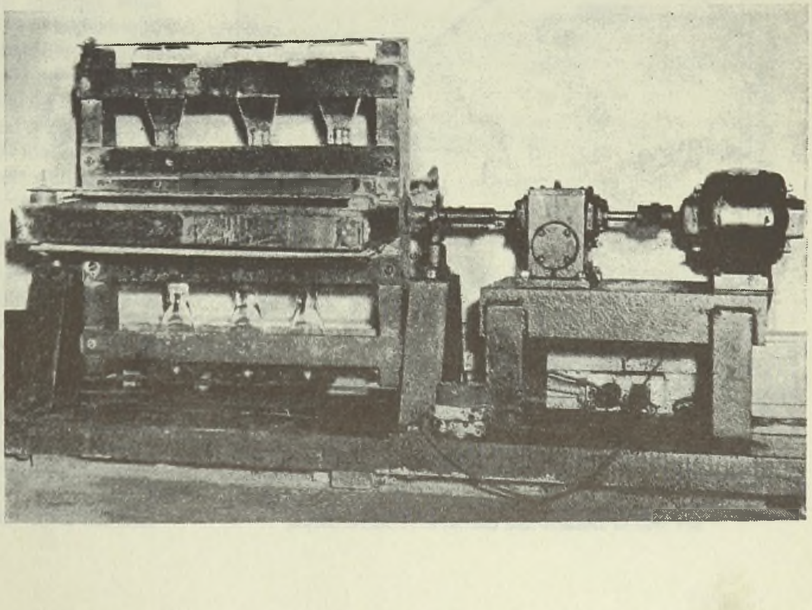
This situation is analogous to that encountered in the operation of cation exchangers for softening hard waters on the sodium (Equation 4) and hydrogen (Equation 5) cycles:

$$Ca^{++} + Na_2{}^+Z^{--} \rightleftharpoons Ca^{++}Z^{--} + 2Na^+ \qquad (4)$$

$$Ca^{++} + H_2{}^+Z^{--} \rightleftharpoons Ca^{++}Z^{--} + 2H^+ \qquad (5)$$

Table I. Chromate Adsorption-Equilibrium Capacity Values at Five Milliequivalents per Liter Final Chromate Concentration

Reaction Time, Hr.	Anion Exchange-Resin Salt, Meq./G.	
	Chloride	Sulfate
0.5	2.65	2.55
1	2.96	2.90
5	3.09	3.05



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At the Right Is a 15 R.P.M. Rotating Flask Rack for Equilibrium Experiments on Metal Recovery by Anion Exchange

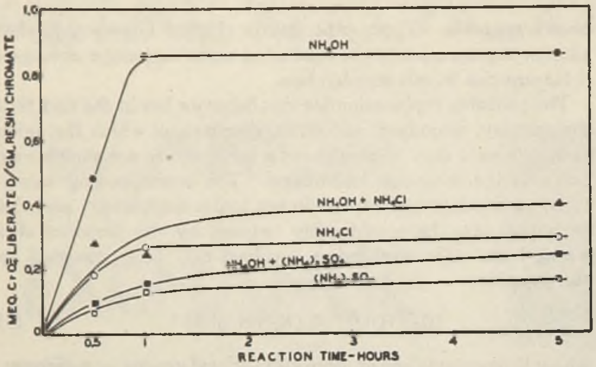


Figure 1. Liberation of Adsorbed Chromate (Equilibrium Experiments)

Results are interpolated at 25 milliequivalents per liter final chromate concentration from adsorption isotherms obtained with equivalent amounts of 1 *N* recovery agents. Mixed recovery agents were 0.5 *N* in each component. A single batch of saturated anion exchange resin chromate was used for all experiments.

With the sulfonated coals or resinous cation exchangers, containing weakly acidic groups as well as strongly acidic groups, a higher capacity is obtained on the sodium cycle than on the hydrogen cycle. Apparently this is caused by repression of the ionization of the solid acid by the hydrogen ion formed during the exchange reaction:

$$H_2^+Z^{--} \rightleftharpoons H_2Z \qquad (6)$$

Equation 6 is shifted to the right, which results in a limited shift to the left in Equation 5.

A similar case is that of acid-regenerated cation exchangers where higher capacities are obtained with salts of weak acids than with salts of strong acids. Tiger and Sussman (*28*, page 188) have explained this phenomenon.

Tube Experiments. In this preliminary study tube experiments were carried out to examine several factors, including applicability to various metals and to various types of anions, nature of the reaction, effect of type of feed and anion exchanger salt, effect of regenerant type, and concentration of recovered metal obtainable. (The reader is cautioned to keep in mind that throughout this paper references to milliequivalents of chromate or other ions invariably refer to acidimetric equivalents, not to the more usual oxidimetric equivalents. For those more familiar with the usual water treatment terminology, these units may be simply converted by means of the relation 1 milliequivalent per liter = 50 p.p.m. as $CaCO_3$.) Other factors still being studied include effect of feed concentration, flow rate, regenerant dosage, excess regenerant recovery, and anion exchanger life.

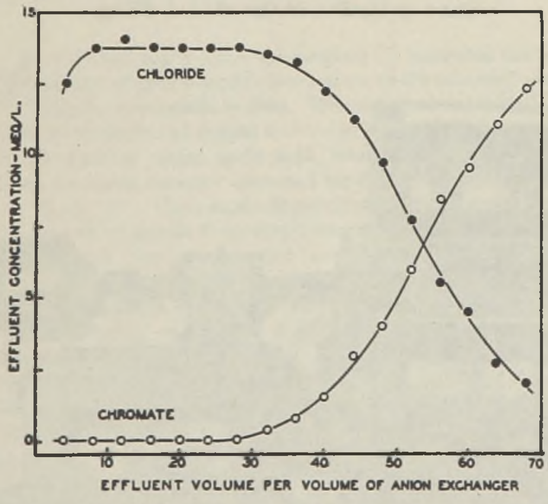


Figure 2. Chromate-Chloride Exchange during Adsorption of Chromate by an Anion Exchange Resin Chloride

13.6 milliequivalents Na_2CrO_4 per liter of solution passed through a 50-ml. bed of anion exchange resin chloride at 50 ml. per minute.

Reaction Mechanism. While it seemed obvious that the adsorption of chromium should take place by a true anion exchange mechanism, this point was verified experimentally. A feed containing sodium chromate was passed through a tube containing an anion exchange resin chloride, and consecutive portions of the effluent were analyzed for both chromate and chloride ions. Throughout the run the difference between the chromate content of the influent and that of the effluent was accounted for by the appearance of an equivalent amount of chloride in the effluent. Figure 2 illustrates a typical experiment.

Table II. Repeated Cyclic Chromate Adsorption and Recovery on an Anion Exchange Resin Chloride

(100-ml. bed of anion exchange resin chloride in 23-mm.-diameter tube; feed flow rate, 50 ml./min.; recovery and regenerant flow rates, 5 ml./min.; regenerant, 200 ml. of 1.4 *N* HCl; feed, 13.5 meq./liter CrO_4^{--}; end point, 2.0 meq./liter CrO_4^{--} in effluent)

Run No.	Adsorption Capacity, Meq./Liter	NH₄OH Recovery		Chromate Recovery, %
		Normality	Dosage, eq./liter	
1	781	1.0	2.6	76
2	705	2.8	10.5	84.8
3	648	13.4	53.6	81.2
4	662	13.4	46.9	85.5
5	665	13.4	46.9	84.0
6	630	13.4	46.9	85.2
7	624	13.4	46.9	89.5

NATURE OF ADSORBENT. In view of the well-known observation that multivalent anions displace monovalent anions from the anion exchanger salts of the latter, this investigation initially made use of the reaction between the chromate ion and the anion exchange resin chloride. However, when the equilibrium experiments indicated approximately the same capacity for adsorption of chromate by the anion exchange resin chloride and sulfate, it was thought best to study the adsorption of chromate by an anion exchange resin sulfate in a tube test. Parallel experiments demonstrated that a higher capacity was obtained with the anion exchange resin chloride than with the sulfate when operating to the break-through point—i.e., the first appearance of chromate in the effluent. Figure 3 indicates the comparative efficiency of chromate removal in these experiments.

The disagreement between equilibrium and tube experiments is more apparent than real. Because the sulfate ion more nearly approaches the chromate ion in ionic charge, ionic weight, and ionic volume than does the chloride ion, the sulfate is less readily displaced than the chloride from the anion exchanger. As a result, under parallel conditions the break-through point will occur sooner when a chromate solution is contacted with an anion exchanger sulfate than with an anion exchanger chloride. However, after reaching the break-through point, the anion exchanger tube will continue to adsorb a diminishing amount of chromate for an appreciable period. Comparison of the relative equilibrium capacities with the relative tube capacities calculated when the tubes are completely saturated—i.e., when the effluent composition equals the influent composition—would probably show better agreement between the two types of experiments.

In another experiment an anion exchange resin base (alkali-regenerated anion exchanger) was used for the adsorption of chromate from an acidic solution. A synthetic feed was prepared containing 4.72 milliequivalents sodium chromate and 5.95 milliequivalents sulfuric acid per liter. This solution closely approximated the composition of an actual plating waste whose treatment by another method was previously reported by Hoover and Masselli (*10*). In treating this solution, it was believed that the acid would be adsorbed by the anion exchanger in the usual manner and that the adsorbed anion subsequently would be displaced by the chromate ion.

The results of this experiment fulfilled expectations qualitatively but were disappointing quantitatively. Figure 4 shows that the acid was adsorbed throughout the run, that chromate was completely adsorbed during the early part of the run, and that the rate of increase of chromate concentration in the effluent was slow after the break-through point. The chromate removal capacity to the break-through point was only 47 milliequivalents per liter of exchanger; at the last point shown on Figure 4, it was 362 milliequivalents per liter.

In water treatment, anion exchangers are normally run only to the break-through point and are rated accordingly. There is, however, no reason why they should not be overrun to the maximum possible economic capacity when used in metal recovery or other special applications. Under such circumstances it is possible to utilize the maximum exchange capacity of the anion exchanger by using one or more well-known procedures, such as recycling or the use of multiple units with countercurrent regeneration.

The case under consideration is somewhat complicated by the fact that the chromate-containing effluent appearing after the break-through point is no longer acid and, therefore, will not be adsorbed by an additional fresh bed of alkali-regenerated anion exchanger. Several alternate methods of treatment have been proposed and are now being tested. In one of them the neutral chromate-containing effluent is passed through a bed of an anion exchanger salt for removal by anion exchange. A second method calls for the neutralization of the original acidic waste and its complete treatment by an anion exchanger salt, rather than a base. A modification of this second method requires neutralization of the acidity by lime in order to precipitate the bulk of the sulfate and thereby improve the capacity during the subsequent anion exchange reaction.

Table III. Comparison of the Anion Exchanger Chloride–Sodium Chloride Cycle with the Anion Exchanger Sulfate–Sodium Sulfate Cycle

Run No.	Anion Exchanger Salt	Capacity, Meq./L.		Recovery Agent (5%)	Dosage, Meq./Liter	Recovery, %	
		Break-through	End point				
C-1	Chloride	362	565	NaCl	1710	44.3	
C-2	Chloride	206	362	NaCl	1710	71.8	
C-3	Chloride	165	293	NaCl	1710	73	
S-1	Sulfate	226	467	Na_2SO_4	1410	48.2	71.7
S-2	Sulfate	0	226	Na_2SO_4	1410	120	
S-3	Sulfate	0	199	Na_2SO_4	1410	83.8	

RECOVERY. In various tube runs during the course of this investigation, chromate recovery was attempted with sodium chloride, sodium sulfate, sodium carbonate, sodium hydroxide, ammonium hydroxide, an ammonium hydroxide–ammonium chloride mixture, and hydrochloric acid. All of these reagents proved more or less effective with the exception of hydrochloric acid.

With the latter, recovery as chromate was less than 1%. The recovery effluent contained a substantial concentration of chromic ion, an indication that the chromic acid probably formed by the action of hydrochloric acid on the anion exchange resin chromate had promptly oxidized the anion exchanger and had been itself reduced to the chromic ion. While a substantial chromate removal capacity could be obtained following this acid regeneration, it was apparent that continued use of this recovery method would result in rapid destruction of the anion exchange resin.

In conformance with the data obtained by equilibrium experiments, alkaline recovery agents generally gave best results. Consistent recoveries of 80–90% over a series of runs have been obtained using excessive dosages of ammonium hydroxide (Table II). Such treatment can be made economical by recycling chromate-containing recovery liquors at the beginning of subsequent recovery cycles until substantially all of the alkali content has been utilized. In the particular case of ammonium hydroxide it is also possible to recover the bulk of the excess alkali by distillation, and this has been done.

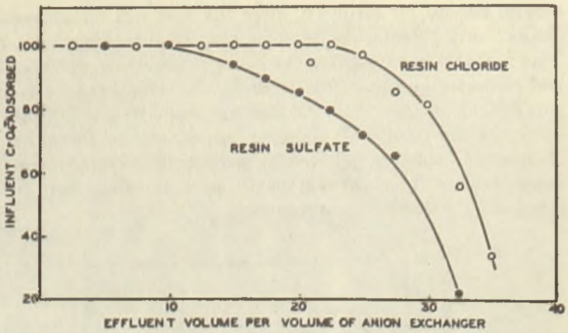


Figure 3. Comparative Chromate Adsorption Efficiencies of an Anion Exchange Resin Chloride and Sulfate

18.1 milliequivalents per liter Na_2CrO_4 adsorbed by 100-ml. beds of anion exchanger resin chloride and sulfate at a flow rate of 25 ml. per minute.

The adsorbed chromate unaccounted for in the recovery process has been located in the anion exchanger bed by drying and ashing after a thorough treatment with a large excess of ammonium hydroxide. Thus, in the seven cycle series cited, the net deficit of chromium was 77.8 milliequivalents. The anion exchange resin, after treatment with a large excess of ammonium hydroxide until only traces of chromate appeared in the effluent, was dried and ashed. The ash content, corrected for the ash content of the pure resin, was 14%. Calculated as Cr_2O_3, this corresponded to 57.9 milliequivalents of chromate, or 74.5% of the previously unaccounted for chromium.

It seems likely that, even under the alkaline conditions sustained during the adsorption and recovery process, some oxidation of the anion exchange resin took place. A portion of the chromate was probably reduced to chromic ion which, at the prevailing pH, precipitated as the hydroxide. This view accounts for the fact that this much chromium was retained by the anion exchanger without reducing the capacity of the latter by a proportionate amount.

It should be possible to recover this reduced chromium by periodic treatment of the anion exchanger with an acid solution, after thorough alkaline regeneration to avoid excessive oxidation of the resin.

Recovery by solutions of salts gave poorer results together with reduced capacities on the adsorption cycle. In the case of the cycle using the anion exchanger sulfate for adsorption and

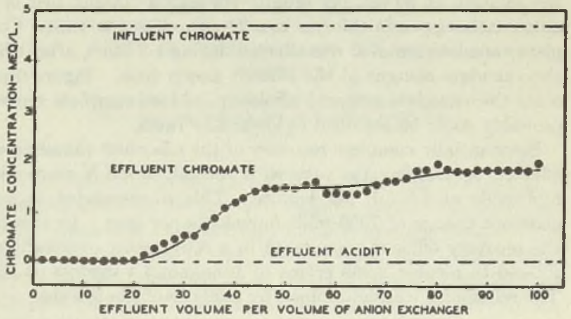


Figure 4. Adsorption of Chromate from an Acid Solution

Adsorption by a 100-ml. bed of alkali-regenerated anion exchange resin from a feed containing 4.72 milliequivalents Na_2CrO_4 and 5.95 milliequivalents H_2SO_4 per liter, introduced at 25 ml. per minute.

sodium sulfate for recovery, after the first run no appreciable amount of chromate-free effluent was obtainable during a run. This probably resulted from the closer resemblance of the sulfate and chromate ions than, for example, the chloride and chromate ions in ionic charge, ionic volume, and ionic weight. Table III compares the results obtained by adsorption on the anion exchange resin chloride followed by sodium chloride recovery with those obtained by adsorption on the anion exchange resin sulfate followed by sodium sulfate recovery.

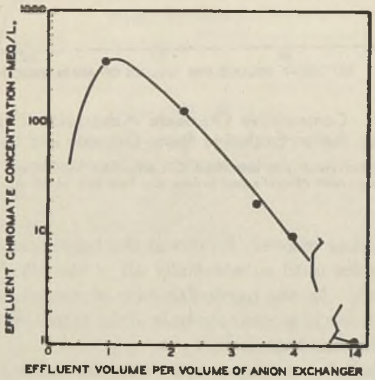


Figure 5. Chromate Concentration in a Typical Recovery Effluent

Recovery agent was 13.4 *N* NH_4OH applied in a dosage of 46.9 equivalents per liter of anion exchanger.

Recovered Chromate Concentration. With fresh recovery reagent solutions it has been found possible to recover more than 80% of the adsorbed chromium in concentrations ten to twenty-five times the influent concentration. These relative values depend, of course, upon the influent concentration. A better view of the possibilities of concentrating dilute solutions by this process is given by the fact that a recovery effluent was obtained which contained 356 milliequivalents of chromate per liter, corresponding to 2.77% as sodium chromate.

Figure 5 shows the composition of a typical recovery effluent during the regeneration and rinse periods. In this case the influent for the adsorption run was 13.5 milliequivalents of chromate per liter, and the recovery agent was 13.4 *N* ammonium hydroxide. Recycling the weaker recovery effluent fractions with added make-up alkali should result in even greater chromate concentrations.

VANADIUM

Vanadium was removed from a solution of ammonium metavanadate containing 25.6 milliequivalents per liter by passing the solution at 50 ml. per minute through a 100-ml. bed of an anion exchange resin chloride in a 23-mm.-diameter tube. Complete vanadate removal was effected during 1.2 liters, after which the vanadate content of the effluent slowly rose. Figure 6 presents the vanadate removal efficiency. More complete removal probably could be obtained at lower flow rates.

Substantially complete recovery of the adsorbed vanadate was effected by treating the tube with 250 ml. of 2.8 *N* ammonium hydroxide at 4.5 ml. per minute. This corresponded to a regenerant dosage of 7000 milliequivalents per liter. In this case the recovery effluent was placed in a refrigerator overnight and filtered to recover 2.968 grams of ammonium vanadate as such. The remainder was determined by analysis of the filtrate.

MOLYBDENUM

A solution containing 25 milliequivalents of ammonium molybdate per liter was passed through a 100-ml. bed of an anion exchange resin chloride in a 23-mm.-diameter tube at 25 ml. per minute. The molybdate removal is indicated by Figure 7.

Recovery was attempted by treating the tube with 200 ml. of 20% sodium chloride solution at 6 ml. per minute. A 77% recovery was obtained. From the data obtained on chromium recovery, it appears probable that an improved recovery would result from the use of an alkaline regenerant.

IRON

As an example of a multivalent anion and of a complex anion containing no oxygen, the removal of the ferrocyanide ion from a solution of potassium ferrocyanide was effected. A solution of 20 milliequivalents of potassium ferrocyanide per liter was passed through a 100-ml. bed of an anion exchange resin chloride in a 23-mm.-diameter tube at 25 ml. per minute. Figure 8 shows the ferrocyanide removal efficiency.

Following a rinse, the ferrocyanide was recovered by treating the bed with 200 ml. of 0.75 *N* sodium hydroxide at 5 ml. per minute, corresponding to a dosage of 1500 milliequivalents per liter; 97% of the adsorbed ferrocyanide was recovered.

PRECIOUS METALS

The platinum group metals and gold, generally classed as the precious metals, readily form complex anions in the presence of free acidity and, indeed, are commonly handled in that form. Recovery of these metals from waste solutions has heretofore been accomplished by one of four methods—namely, precipitation, reduction with organic compounds, cementation, and electrolytic deposition. Each of these processes has certain disadvantages (*9, 21*).

Adsorption on activated carbons has also been suggested as a means of recovering precious metals from dilute solutions (*4, 23, 24, 29*). While Burrell (*6*) proposed the recovery of gold from solutions by cation exchange, the use of anion exchange reactions would seem to be more effective than either of these methods in view of the more common occurrence of the precious metals as complex anions. Our experiments indicated that this is true (*16A*)

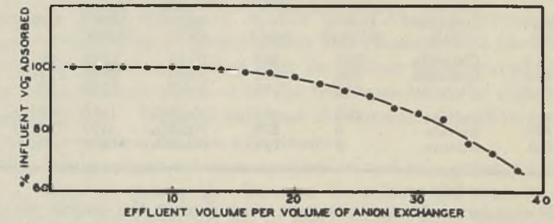


Figure 6. Vanadate Adsorption Efficiency

Adsorption from 12.8 milliequivalents per liter ammonium metavanadate by a 100-ml. bed of anion exchange resin chloride (flow rate, 50 ml. per minute).

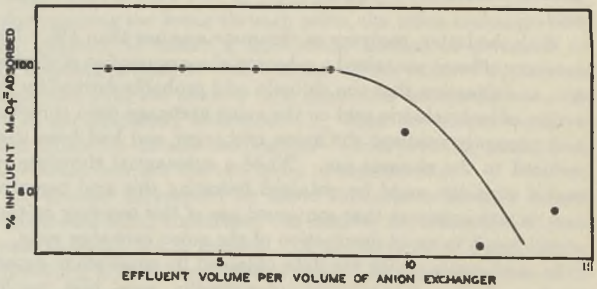
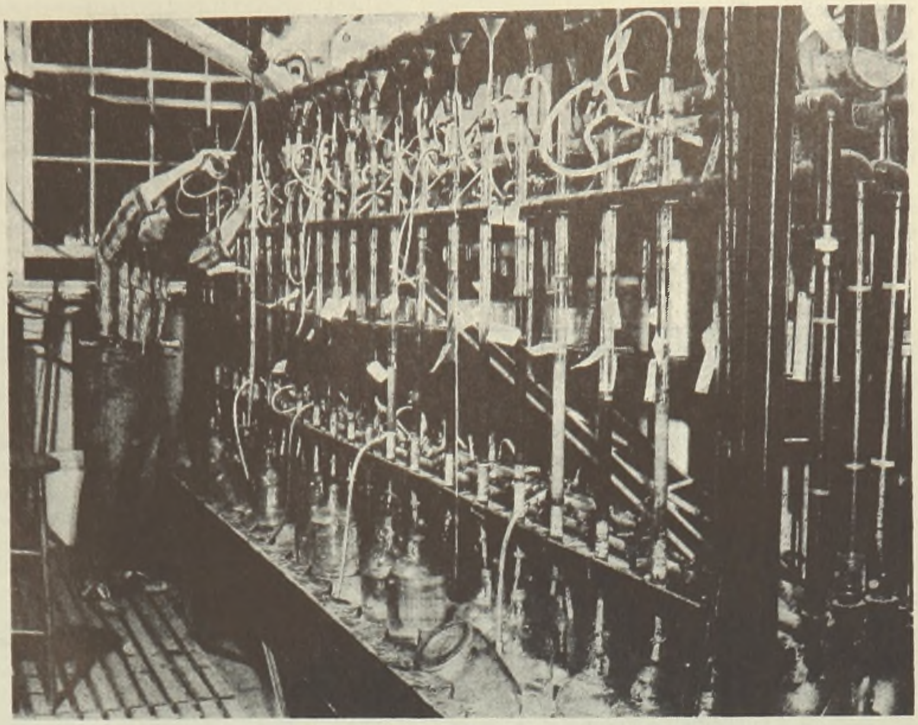


Figure 7. Molybdate Adsorption Efficiency

Adsorption from 25 milliequivalents ammonium molybdate per liter by a 100-ml. bed of anion exchange resin chloride (flow rate, 26 ml. per minute).



Photograph at the Right Shows a Multiple Tube Rack Used for Experimental Ion Exchange Studies

Both tube and equilibrium experiments were carried out to test the removal of the precious metals from solutions by anion exchange.

Platinum. Equilibrium experiments were carried out on the removal of chloroplatinic acid by two different types of anion exchangers and by two different activated carbons. The results of these experiments are plotted as adsorption isotherms in Figure 9. Extrapolated to 1 milliequivalent per liter, final H_2PtCl_6 concentration, the capacities were 2.20 milliequivalents per gram for a synthetic resin anion exchanger, 1.18 milliequivalents for an emeraldine anion exchanger, 0.38 milliequivalent for activated carbon D, and 0.16 milliequivalent for activated carbon N.

Tube type experiments were carried out with two different anion exchangers and with activated carbon D. In parallel experiments 53-ml. beds of activated carbon and of an emeraldine anion exchanger in 15-mm.-diameter tubes were used for treating 19.7 milliequivalent per liter solutions of chloroplatinic acid at 10 ml. per minute. The chloroplatinic acid removal efficiency during these two runs is plotted in Figure 10. The activated carbon is much less effective than the anion exchanger because, in addition to its lower ultimate capacity as indicated by the equilibrium tests described above, it did not completely remove the chloroplatinic acid from the solution at any point during the run.

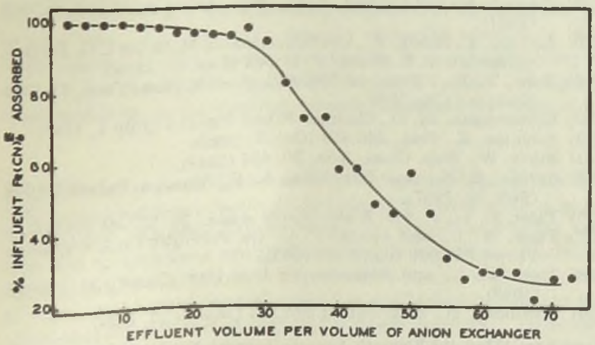


Figure 8. Ferrocyanide Adsorption Efficiency

Adsorption from 20 milliequivalents potassium ferrocyanide per liter by a 100-ml. bed of anion exchange resin chloride (flow rate, 25 ml. per minute).

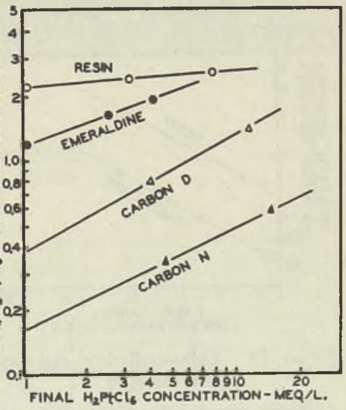


Figure 9. Chloroplatinate Adsorption Isotherms

Equilibrium adsorption from chloroplatinic acid solutions on two anion exchangers and two activated carbons.

The precious metals are an unusual case in that their value is sufficiently great to warrant recovery by ashing the anion exchanger containing the adsorbed metal-containing anion. The anion exchanger from the above tube test was ashed. Solution of the resulting ash in aqua regia and analysis of the solution thus formed indicated complete recovery of the adsorbed platinum within the limits of experimental error.

Recovery of platinum by regeneration with ammonium hydroxide is complicated by the insolubility of ammonium chloroplatinate. An attempt was made to avoid this difficulty by the use of a hot regenerant solution. A chloroplatinic acid solution containing 7.15 milliequivalents per liter was passed at 10 ml. per minute through a 50-ml. bed of a synthetic resin anion exchanger. Chloroplatinic acid appeared in the effluent only after 3200 ml. had passed. The bed was then treated with 1 liter of 1 *N* ammonium hydroxide at 80° C. The resulting effluent contained only 37% of the adsorbed platinum. An additional 60% was recovered by ashing the anion exchanger bed.

A similar experiment carried out with sodium carbonate as the regenerant resulted in the recovery of 17% of the adsorbed platinum in the regenerant effluent and 80% by ashing the anion exchanger bed.

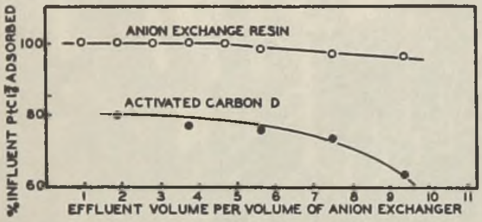


Figure 10. Comparative Chloroplatinate Adsorption Efficiencies of an Anion Exchanger and an Activated Carbon

Adsorption of 19.7 milliequivalents chloroplatinic acid per liter by 53-ml. beds of adsorbent at 10 ml. per minute.

Palladium. Equilibrium experiments indicated that chloropalladic acid was adsorbed to a smaller extent than chloroplatinic acid by both emeraldine and synthetic resin anion exchangers. At 1 milliequivalent per liter final chloropalladic acid concentration, equilibrium adsorption values were 0.63 milliequivalent per gram of emeraldine and 1.25 milliequivalents per gram of synthetic resin. Figure 11 presents the adsorption isotherms.

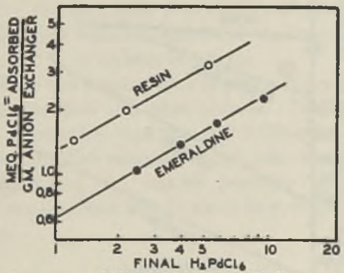


Figure 11. Chloropalladate Adsorption Isotherms

Equilibrium adsorption from chloropalladic acid solutions on two anion exchangers.

Gold. Equilibrium adsorption capacities of emeraldine and synthetic resin anion exchangers for chloroauric acid were between those obtained for chloroplatinic acid and those obtained for chloropalladic acid. Figure 12 gives the adsorption isotherms from which equilibrium capacities at 1 milliequivalent per liter final chloroauric acid concentration were found to be 1.1 milliequivalents per gram for the emeraldine and 1.4 milliequivalents per gram for the synthetic resin anion exchanger.

Additional equilibrium experiments indicated that increases in the hydrochloric acid–auric chloride ratio increased the capacity of the anion exchangers for gold removal, probably because of a shift to the right of the equilibrium represented in Equation 7 as a result of the increased chloride ion concentration:

$$4Cl^- + Au^{+++} \rightleftharpoons (AuCl_4)^- \tag{7}$$

SUMMARY

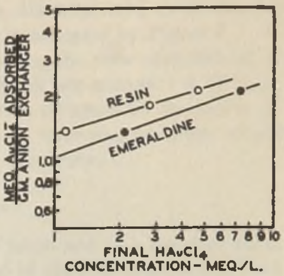


Figure 12. Chloroaurate Adsorption Isotherms

Equilibrium adsorption from chloroauric acid solutions on two anion exchangers.

Chromium, gold, iron, molybdenum, palladium, platinum, and vanadium, in the form of complex anions, have been recovered from dilute solutions by anion exchange. The process was independent of the valence of the complex anion and of the nature of the nonmetallic elements included in the complex anion.

Recovery of the adsorbed anions has been effected by a number of reagents, but alkaline solutions were most effective. The concentration of the complex anion in the recovery effluent was more than twenty times that in the influent.

The method offers interesting possibilities for relatively low-cost metal recovery from waste effluents. In contrast to certain other waste metal recovery methods, the metal may generally be recovered in the form of a salt directly re-usable in the process producing the waste.

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Presented before the Eleventh Annual Chemical Engineering Symposium (Adsorption and Ion Exchange) held under the auspices of the Division of Industrial and Engineering Chemistry, American Chemical Society, at Columbia University, New York, N. Y.

Base Exchange of CRYSTALLINE SILICATES

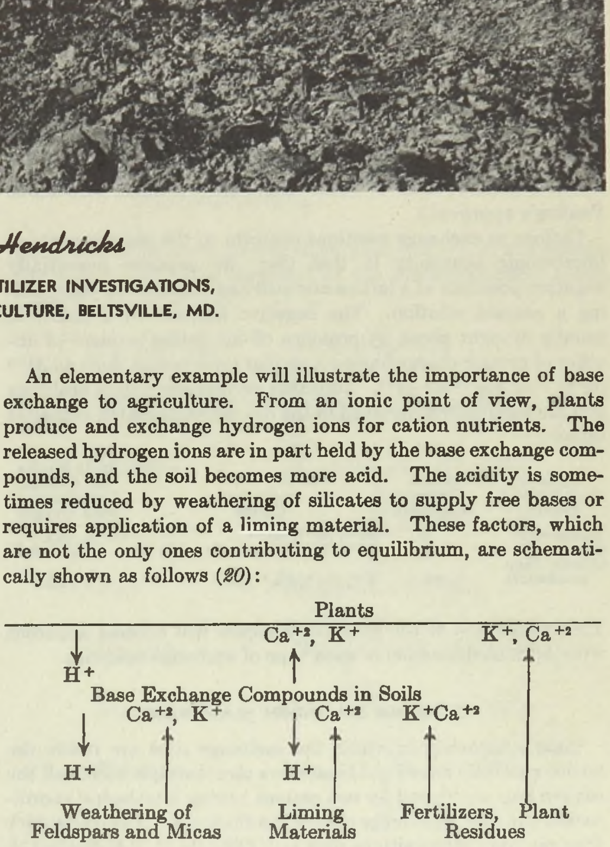
Sterling B. Hendricks

DIVISION OF SOIL AND FERTILIZER INVESTIGATIONS,
U. S. DEPARTMENT OF AGRICULTURE, BELTSVILLE, MD.

Concepts fundamental for an understanding of base exchange by silicates are presented. Necessary conditions for cation exchange in zeolite structures are the presence of negative portions in the lattice frameworks and of multiconnected channels large enough for ionic migration. The ways in which negative portions of lattices arise in zeolites and clay minerals are discussed in detail. Termination of an ionic lattice at a surface often involves incomplete balancing of charge with a corresponding requirement for presence of external ions. Base exchange capacity of kaolin minerals is due to this factor . . . Strip mining of bentonite in eastern Wyoming is shown in the above picture (courtesy, American Colloid Company); montmorillonite is the essential mineral constituent of bentonites.

BASE exchange of silicates and organic materials in soils is the most prominent factor in maintaining nutrient supply to plants. Its discovery by Way (*18*) almost a century ago was due to questions arising from the introduction of soluble salts as artificial manures. Way made a second essential step in showing that exchange of cations is particularly exhibited by aluminum silicates and he prepared the first permutit. In recent years some insight has been gained into the mechanism of base exchange, and the purpose of this paper is to describe the process for silicates.

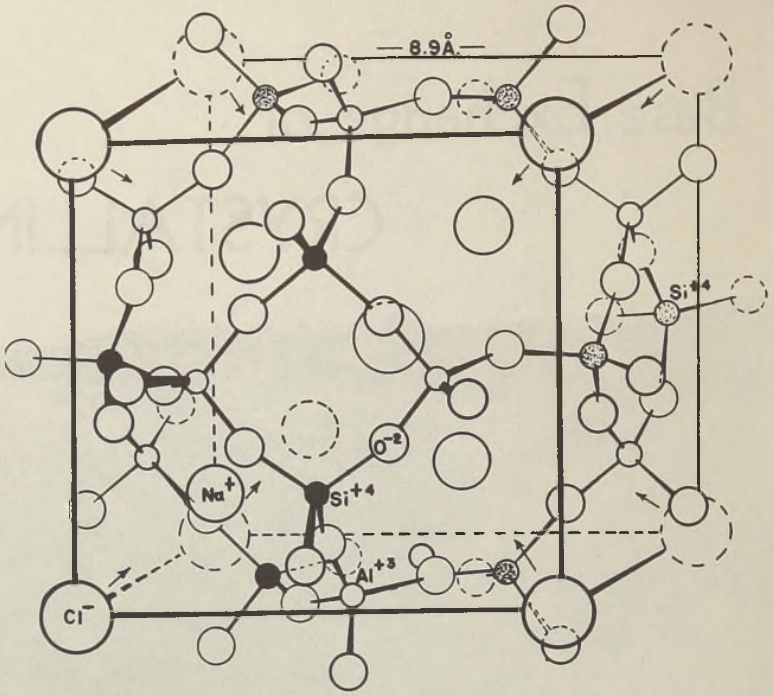
An elementary example will illustrate the importance of base exchange to agriculture. From an ionic point of view, plants produce and exchange hydrogen ions for cation nutrients. The released hydrogen ions are in part held by the base exchange compounds, and the soil becomes more acid. The acidity is sometimes reduced by weathering of silicates to supply free bases or requires application of a liming material. These factors, which are not the only ones contributing to equilibrium, are schematically shown as follows (*20*):



Base exchange compounds are heterogeneous electrolytes, and cation replacement is simply the process of exchanging an ion from the environment of a solution to that of a solid in contact with solution. The following work deals with the nature of the solids, which includes demonstrations of the causes for base exchange. Three distinct types of base exchange compounds are observed in crystalline materials in a classification, depending upon the nature of the exchange site:

1. Within the structural framework: zeolites, ultramarines, noselite
2. External to the structural framework
   a. Upon an inner surface accessible by swelling: montmorillonite-type clay minerals, graphitic acid
   b. At the limiting surfaces of the crystals: micas including glauconite (greensand), illite (present in many shales and soils)
   c. On the side faces of tabular crystals: kaolin minerals, gibbsite, etc.
3. Upon negative organic groups in close proximity to positive groups, proteins

Amorphous materials will not be considered; since the discussion is limited to silicates, the last group, although the best understood of all, will not be mentioned again.



SODALITE $Na_8Al_6Si_6O_{24}Cl_2$

Figure 1. Portion of Aluminum Silicate Framework in the Structural Unit of Sodalite That Is Present in a Distorted Form in Chabazite

Connections from one void to another are indicated by arrows.

Structural features of ionic solids are too well known to require detailed restatement here, but some factors of particular importance in silicates should be mentioned. In the simplest terms, silicate structures are determined by the ratios of the positive to the negative ions, which are usually oxygen, the ratios of the ionic radii which determine the coordination figures of the positive ions, and a general "principle of microscopic neutrality". This principle, one of the most fundamental in chemistry, was first recognized by Pauling (*12*) as the "electrostatic valence principle". It can simply be stated as follows: "Ionic systems are statistically neutral on the smallest possible scale". (This restatement is made with Linus Pauling's approval.)

Cations at exchange positions conform to the requirements of microscopic neutrality in that they are opposite potentially negative positions of a lattice and still have a pathway for reaching a contact solution. The negative position in a lattice is usually brought about by presence of one cation in place of another of greater charge having a similar ionic radius, such as Al^{+3} for Si^{+4} or Mg^{+2} for Al^{+3}. Ions that occupy equivalent positions and are particularly involved in the discussion of cation exchange follow:

Type of Coordination Position	No. of Oxygen Neighbors	Important Cation	Ionic Radius for Obsvd. Coordination with Oxygen
Tetrahedral	4	Si^{+4}, Al^{+3}, Be^{+2}	0.55Å.
Octahedral	6	Al^{+3}, Mg^{+2}, Fe^{+2}, Fe^{+3}, Li^{+1}	0.55 to 0.80Å.
Greater than octahedral	>6	K^+, Na^+, Ca^{+2}, Ba^{+2}	0.95Å.

The importance of the general principles will become apparent with detailed discussion of each type of exchange material.

EXCHANGE SITE WITHIN FRAMEWORK

Ionic compounds in which the exchange sites are inside the lattice generally have rigid framework structures, in which all the oxygen ions are shared by two cations having tetrahedral coordination but with an average charge less than +4. The framework thus can have compositions such as $[(AlSi_3)O_8]^{-1}$, $[(Al_2Si_3)O_{10}]^{-2}$, $[(Al_2Si_7)O_{18}]^{-2}$, etc., and it is like a house in including large volumes. Other cations required to balance the charge and water molecules with which they are associated are located in the open spaces in such a way as to make the structure microscopically neutral. A necessary condition for base exchange, entirely overlooked in the past, is for the volumes enclosed by the framework to be multiconnected by channels sufficiently large for cation migration. Compounds such as beryl, $Al_2(Be_3Si_6)O_{18}$, having biconnected voids (that is, unconnected channels which often contain appreciable numbers of alkali ions) do not show base exchange.

ZEOLITES. Base exchange compounds having framework structures (*4, 16*) are well illustrated by zeolites. There are at least four distinct structural types of crystalline zeolites, differing in framework, shape of enclosed volume, and multiplicity of volume connections, as follows:

Zeolite	Formula	Multiconnection of Voids
Analcite	$[(AlSi_2)O_6]^{-1}Na^{+1}.H_2O$	4
Chabazite	$[(Al_2Si_4)O_{12}]^{-2}Ca^{+2},Na_2^{+1}.6H_2O$	8
Natrolite	$[(Al_2Si_3)O_{10}]^{-2}Na_2^{+1}.2H_2O$	6
Heulandite	$[(Al_2Si_7)O_{18}]^{-2}Ca^{+2}.6H_2O$	Unknown

The first two approach cubic symmetry which permits approximately isotropic diffusion of an exchanging cation through the multiconnected voids. Natrolite is typical of the fibrous zeolites which are tetragonal or pseudotetragonal in symmetry, and in which diffusion is still possible in the principal directions that are not equivalent. Heulandite, the structure of which is unknown but which probably is a framework of limited thickness, is monoclinic and apparently the voids are connected only parallel to (010) and not along the *b* axis; thus ionic diffusion is restricted to nonequivalent directions in parallel planes (*17*).

Structural features of the zeolites are here illustrated by the framework unit of the ultramarines, sodalite and helvite, which is present in a distorted form in chabazite (*21*). Figure 1 shows the actual unit for sodalite, and directions of possible ionic migration are indicated. In this and other figures the usual convention

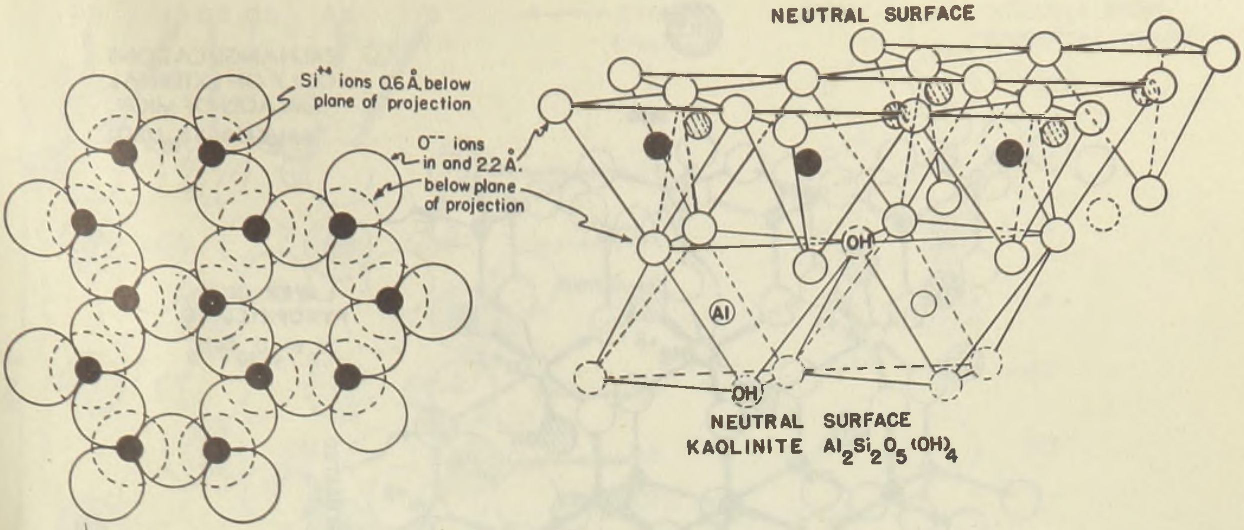


Figure 2. Plan and Elevation of Hexagonal Network of Silica Groups Present in Kaolins, Pyrophyllite, and Structurally Related Silicates

Its combination with ions, coordinated about A^{+3} to form the kaolinite structure, is shown on the right.

is followed of indicating ionic centers by small circles. Frameworks of analcite and the fibrous zeolites are illustrated in standard books on structures of solids (*1*).

Ions within the voids of zeolites can be completely exchanged with varying ease, depending upon the potential barrier between sites. A large external cation, such as tetramethyl ammonium $N(CH_3)_4^{+1}$, cannot enter the connecting channels, and exchange does not take place (*19*). This is also true for replacement of water by larger molecules such as benzene (*15*). The formulas as shown are only typical, and there can be some variation due to the presence of Al^{+3} in place of Si^{+4} in the framework. In this way the number of exchangeable cations in heulandite can vary from 1.8 to 3.0 per unit of 36 oxygen ions, the formulas (*21*) varying between about $[(Al_{3.6}Si_{14.4})O_{36}]Ca_{1.8}.12H_2O$ and $[(Al_5Si_{13})O_{36}]$-$Ca_{2.0}Na.12H_2O$. The extent to which Al^{+3} is present in the framework appears to be limited by the attainment of microscopic neutrality through the arrangement and numbers of positive ions and water molecules that can be situated in the voids. This limiting amount of Al^{+3} in chabazite is such as to give an Al^{+3}:Si^{+4} ratio of about 1:2, while it can be 1:1 in the structurally related noselite and sodalite where additional negative groups are present in the voids instead of water molecules.

EXCHANGE SITE EXTERNAL TO FRAMEWORK

Silicate base exchange compounds of the second type have sheetlike structures in which the determinative structural element is the hexagonal network shown in Figure 2 (*13*). This network is built up from tetrahedral groups of oxygen ions around Al^{+3} or Si^{+4} cations. Many silicates contain this network, joined through the unshared oxygen ion of each tetrahedral grouping to groups of oxygen and OH^- ions octahedrally coordinated about Al^{+3}, Mg^{+2}, Li^{+1}, etc. Composite structural sheets of kaolinite, $Al_2Si_2O_5(OH)_4$, and pyrophyllite, $Al_2Si_4O_{10}(OH)_2$ (Figures 2 and 3), show the two principal types of structures to be discussed.

Two striking features influencing cation exchange of the sheetlike silicate structures are to be emphasized. First, the sheets are too compactly filled to allow ionic migration through them. Second, one third of the octahedral coordination positions are vacant in the pyrophyllite sheet. This second feature and the presence of Al^{+3} in place of Si^{+4} in the network of Figure 2 play the most important part in determining the extent of base exchange in the important class of clay minerals related to montmorillonite, which are industrially known as bentonites.

MONTMORILLONITES. Silicates of the montmorillonite group have structural sheets similar to that shown in Figure 3 for pyrophyllite (*5*). The sheets, however, have an excess negative charge which is balanced by external and exchangeable cations. Formulas for members of the group derived from analyses of many pure minerals (*14*) can be expressed in the following manner:

Sheet	Ions in octahedral coordination	Ions in tetrahedral coordination	$O_{10}(OH)_2$
	↓ Exchange cations external to sheet held because of a deficit in the positive charge in octahedral or tetrahedral positions		

Particular formulas of pyrophyllite, talc, muscovite, and phlogopite micas, and some members of the montmorillonite group, indicated by italics, are:

Pyrophyllite	$(Al_2)(Si_4)O_{10}(OH)_2$
	↓ Ex_0^+
Montmorillonite	$(Al_{1.67}Mg_{0.33})(Si_4)O_{10}(OH)_2$
	↓ $Ex_{0.33}^+$
Beidellite	$(Al_{2.17})(Al_{0.83}Si_{3.17})O_{10}(OH)_2$
	↓ $Ex_{0.33}^+$
Muscovite	$(Al_2)(AlSi_{3.0})O_{10}(OH)_2$
	↓ K^+
Talc	$(Mg_{3.0})(Si_{4.0})O_{10}(OH)_2$
	↓ Ex_0^+
Hectorite	$(Mg_{2.67}Li_{0.33})(Si_{4.0})O_{10}(OH)_2$
	↓ $Ex_{0.33}^+$
Saponite	$(Mg_{3.0})(Al_{0.33}Si_{3.67})O_{10}(OH)_2$
	↓ $Ex_{0.33}^+$
Phlogopite	$(Mg_{3.0})(Al_{1.0}Si_{3.0})O_{10}(OH)_2$
	↓ K^+

Hectorite and saponite illustrate limiting cases where the presence of external cations is due to deficits of positive charge in octahedral and tetrahedral coordination, respectively, within the structural sheets. Analyses of minerals of the montmorillonite group show that these exchangeable ions are restricted to one

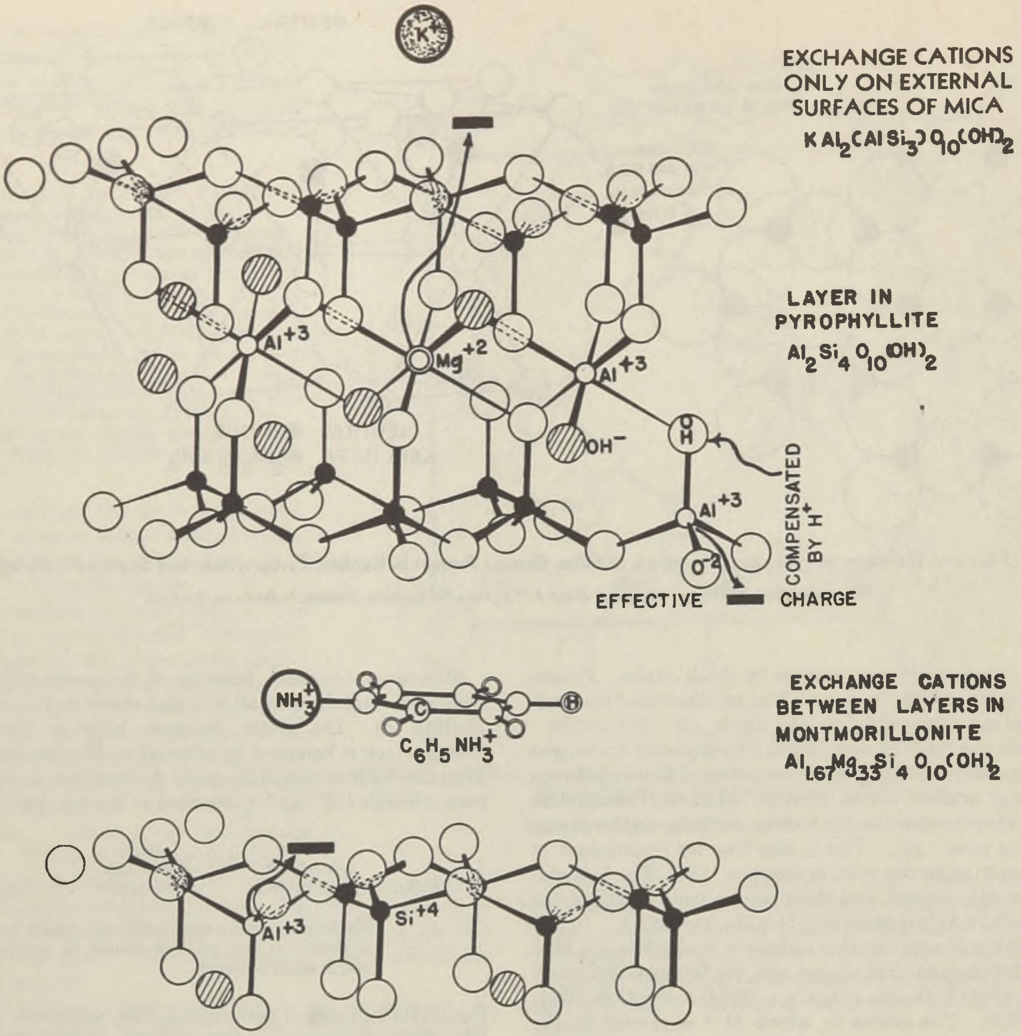


Figure 3. Structural Layer of Pyrophyllite and Its Modifications in the Micas and Montmorillonites

Various types of positions for exchange cations are indicated.

third of an equivalent per $O_{10}(OH)_2$ unit. They occupy positions, between the layers, that are completely filled in the micas. In the micas, however, the K^+ ions bring about microscopic neutrality for excess negative charge due to the presence of Al^{+3} in place of Si^{+4} in the immediate region in the layer above and below. They thus serve to bind the layers together and prevent ready exchange with other cations. In minerals of the montmorillonite group an exchangeable cation seems to be required for microscopic neutrality by only one of the neighboring sheets, even though all sheets carry the same average charge. The forces between the layers thus are sufficiently small to permit hydration of the surface and wandering of the ions.

An excellent illustration of the principle of microscopic neutrality is afforded by beidellite. In it the amount of Al^{+3} in tetrahedral coordination approaches that required for a mica. The number of ions external to the structural sheet, however, is reduced by increase of the Al^{+3} ions in octahedral coordination, microscopic neutrality thus being attained by internal compensation. Here conditions within the framework keep the equivalence of the external ions constant, which is in contrast to the behavior of the zeolites.

Micas. While cations between the structural sheets are difficult to exchange in the micas and micalike minerals, such as muscovite, phlogopite, glauconite, and illite, they are not restricted at the limiting surfaces of the crystals. Base exchange is, apparently, due chiefly to these ions at the surfaces, and the equivalence is determined by the extent of the surface. In a mica having a cleavage surface of 60 M^2 per gram, a value attained in many soils, there is 0.1 milliequivalent per gram of exchangeable cations on the cleavage surfaces. Additional places for cation exchange occur at the lateral surfaces, as will be discussed in detail for kaolin minerals, and the equivalence of this exchange may be as great as that at the cleavage surfaces. In the more finely divided micaceous minerals, such as glauconite of greensands and illite of soils and shales, there is probably some availability of exchange sites between structural sheets, near the edges. The total exchange capacity of these materials is in the order of 0.25 milliequivalent per gram, which is approximately one third to one fourth that of montmorillonite group minerals.

Kaolins. Structural sheets of kaolin minerals (Figures 2 and 4) are formed from the hexagonal network found in the micas and the corresponding layer of ions with octahedral coordination. The sheets, however, are terminated by $(OH)^-$ ions on one surface and are neutral. Slight departure from neutrality, due to the presence of Al^{+3} in place of Si^{+4} in tetrahedral coordination, is compensated by increase in the number of ions in octahedral

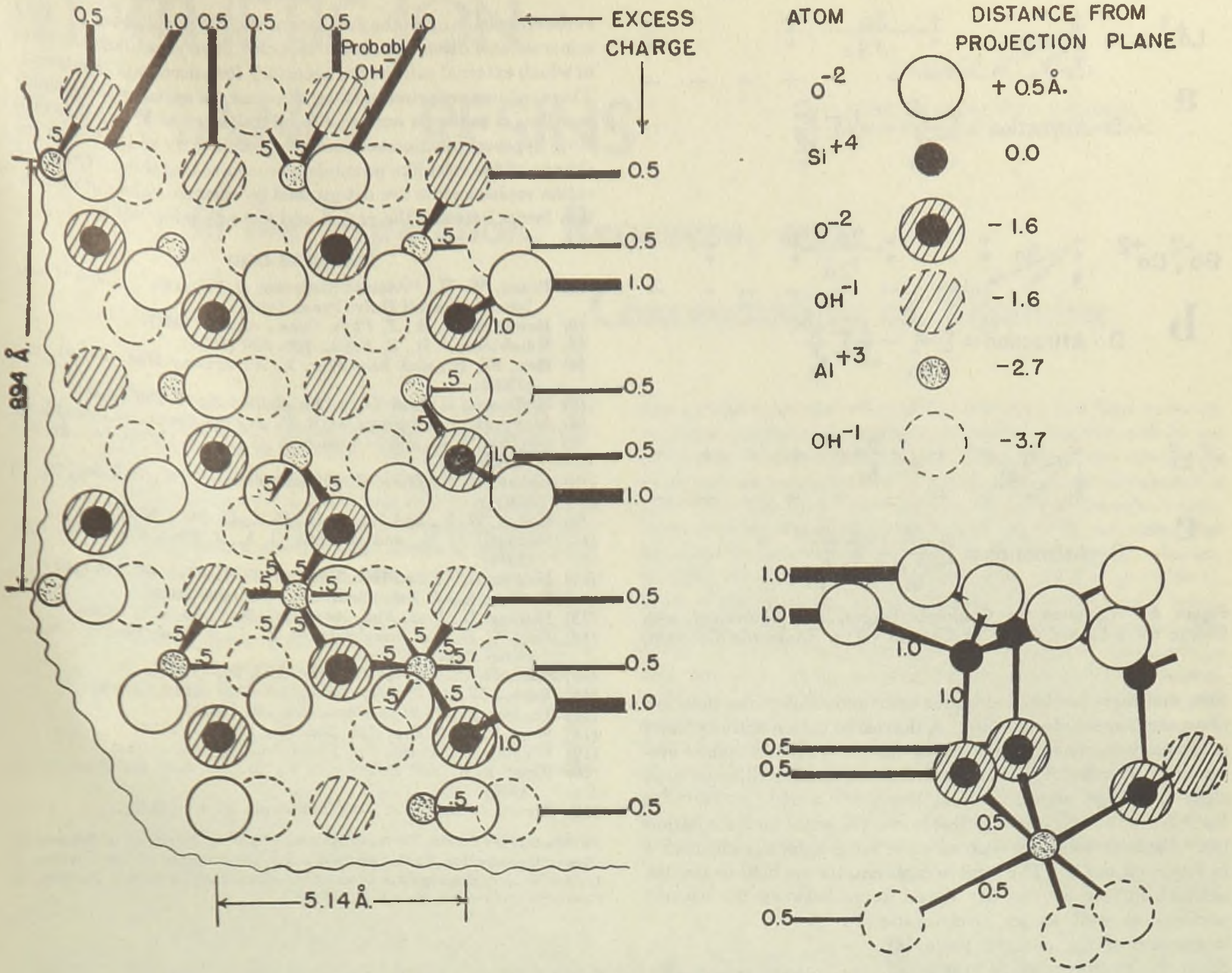


Figure 4. Cation Exchange Positions Due to Lateral Termination of Kaolinite Crystals (Plan and Elevation)

Attainment of microscopic neutrality about Al^{+3}, O^{-2}, and OH^{-1} is shown in detail.

coordination in the same way as for beidellite. While the structural sheets in kaolinite are neutral, there is considerable attraction between them due to hydrogen bonding of the $(OH)^-$ ions on the bottom of one layer to oxygen ions in the top of the neighboring layer (*3*). Relatively large crystals are built up in this way with neutral instead of charged cleavage surfaces.

Dependence of cation exchange in kaolinite on the exposed surface is shown in Figure 5 (*7*). Earlier evidence had been obtained from changes in base exchange capacities brought about by grinding (*8, 9*). Surface areas of kaolinite separated from soil are as great as 80 M^2 per gram, of which about 20% is due to lateral faces (*11*). With a base exchange capacity of 0.12 milliequivalent per gram, an area of about 20 sq. Å. would be available for each univalent cation. This would correspond to about two univalent cations for each laterally terminating structural sheet, which is about the expected value (Figure 4).

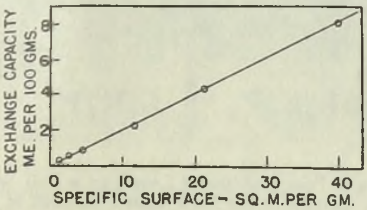


Figure 5. Variation of Cation Exchange of Kaolinite with Particle Size (7)

Sepiolites. All silicates and other ionic structures would be expected to show ion exchange due to lattice termination, but the amount might be very small on account of large particle size. Another group of silicate minerals, the sepiolites, having considerable cation exchange capacity should be mentioned. Attapulgite, the principal constituent of Florida fuller's earth, is of this type. The group as a whole cannot be discussed further since little information is available about their structures and cation exchange behavior.

EXCHANGE IN NETWORK TYPES

Cation exchange of the network type structures in the clays differ in several important dynamic ways from that of the zeolites, which possibly will be apparent without detailed explanation. Exchange reactions are extremely rapid in the clays at room temperature, while elevated temperatures and relatively long times are required in zeolites because of the limitation of diffusion. Instability of the framework has prevented formation of hydrogen zeolites whereas hydrogen clays are rather stable. Large cations, as previously mentioned, cannot enter the zeolites, while clays exhibit greater affinity for these ions than for Li^+, Na^+, etc.

Relative distributions of cations at equivalent concentrations between a solution and an exchange material have been determined as a measure of cation affinities at exchange sites. The orders too often have been discussed in vague terms of ionic hydra-

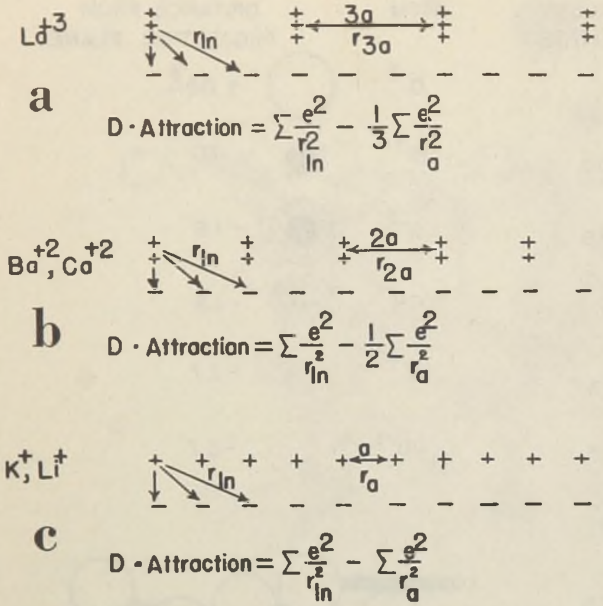


Figure 6. Variation of Coulomb Forces, per Equivalent, with Charge for a Linear Array of Charges (D = Dielectric Constant)

tion, and there are few values for ionic activities in the presence of an exchange material (*10*). A decreased cation activity must accompany increased attraction of the ion to the exchange material. An order of cation attraction to montmorillonite type clays is: large organic cation, brucine$^+$ > H^+ > La^{+3} > Ba^{+2} > Ca^{+2} > K^+ > Li^+; this is also the series for flocculation (*6*). Partial reasons for such an order are graphically illustrated in Figures 3 and 6. The large organic cations are held to the flat network surface by van der Waals forces between the neutral portions as well as by electrostatic interaction of the charged parts (*2*). Since the hydrogen ion is very small, it can penetrate the lattice more than is possible for other positive ions (*10*, page 1089). If coulomb forces alone are considered, the repulsion term decreases with increased charge on the cation, distributed in an array as shown for a linear array of points in Figure 6*c*. More detailed considerations are necessary to account for the relatively greater attraction of the larger ions of a given charge.

The purpose has been to present here the few concepts that are fundamental for an understanding of base exchange. While they are known to several workers, none has presented them as a whole. Experimental details and discussions of interesting topics, such as the relations of water molecules to exchange cations, were necessarily omitted.

SUMMARY

The principal types of crystalline silicates showing considerable cation exchange capacity have framework or sheetlike structures. Zeolites belong to the first class in which exchange of cations depends upon the presence of multiconnected voids. Clay minerals and other micaceous silicates have sheetlike structures in which external cations are necessary for microscopic neutrality. These cations are principally on the cleavage surfaces of the montmorillonite minerals and on the lateral faces of kaolin minerals. Both types of positions contribute prominently to the cation exchange of the micalike minerals, glauconite and illite. Orders of cation replacements are determined by relative values of interaction forces between the cation and the adjoining lattice.

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PRESENTED before the Eleventh Annual Chemical Engineering Symposium (Adsorption and Ion Exchange) held under the auspices of the Division of Industrial and Engineering Chemistry, AMERICAN CHEMICAL SOCIETY, at Columbia University, New York, N. Y.

Barley Growing at Four Nutritional Levels on a Soil Whose Lack of Fertility Is Due Chiefly to the Low Cation Content of the Soil Clay

Unit levels per acre: L_1, one ton limestone; K_1, 100 pounds of 50% KCl; P_1, 375 pounds of 20% superphosphate. All pots received NH_4NO_3 at a rate of 400 pounds per acre.

SYNTHETIC ION EXCHANGE RESINS

in the Separation, Recovery, and Concentration of Thiamine

Donald S. Herr

RESINOUS PRODUCTS & CHEMICAL COMPANY, INC., PHILADELPHIA, PA.

The principles of chromatographic adsorption and base exchange have been applied to the recovery of natural products through the use of synthetic ion exchange resins. In particular, the adsorption, separation, and concentration of thiamine by the acid-regenerated form of the resin have been studied. An adsorption column technique, utilizing resin with a particle size near 0.40 mm. rather than the usual finely powdered material, completely removes thiamine, for which the resin has a large capacity, in the presence of riboflavin. Since riboflavin is not adsorbed under the conditions in which thiamine is completely removed, the separation is satisfactory. The vitamin is eluted in excellent yields by passage of strong mineral acid through the column, although other reagents may be used to advantage in specific instances. These results are achieved with percolation rates equivalent to as much as 5 gallons per square foot per minute with beds no greater than 0.5 foot in depth. The practicability of the process has been demonstrated by the recovery of thiamine from rice bran extracts. The resin stability, particularly in strong acids, makes possible its application where such pH conditions are necessary to protect products from alkaline degradation.

When Adams and Holmes (*1*) announced in 1936 that phenol-formaldehyde resins exhibited ion exchange properties, a new era of exchange adsorbents was opened. These synthetic ion exchange resinous materials have been described by several authors (*3*, *4*, *7–11*) and may be grouped into two major types. The first, cation active, will exchange or adsorb substances which possess a positive ionic charge or which, owing to their electronic configuration, can form positive ions by the addition of a proton such as the substituted ammonium group. The second type will adsorb or exchange acidic substances. Neutral materials adjusted to the zwitter ion condition by pH or other controls are not adsorbed or exchanged; substances of greater basicity or acidity will be affected proportionately over and above those of lesser reactivity. The gel structure of the resins gives them many of the properties of a highly porous surface-active adsorbent. Resinous exchangers are insoluble in water and all common solvents. They operate with a high specific reaction rate which, however, varies with the subject ions. They exhibit different adsorptions for various ions. This principle may be the basis for many separations by the simple adjustment of contact times of solution with resin. The resins are effective in relatively large particle size so that the flow of the solution may be rapid and unobstructed by any packing of the adsorbent. Under these conditions commercial application is feasible.

Consideration of these properties of the resinous exchangers suggests their adaptation to the Tswett chromatographic adsorption technique which has found widespread application (*12*, *13*, *14*). Differential adsorptions have already been reported by Myers, Eastes, and Urquhart (*11*) who observed that sulfuric acid was bound in preference to hydrochloric, and copper was exchanged in preference to zinc. The chemical nature of these adsorbents offers advantages over such adsorbents as sugar, precipitated lime, carbon, alumina, fuller's earth, etc.

ADSORPTION OF THIAMINE

Two of the more familiar vitamins, thiamine and riboflavin, were selected for preliminary experiment; the resin was Amberlite IR-100. Thiamine and riboflavin were determined quantitatively by the methods of Hennessy and Cerecedo (*5*) and Conner and Straub (*2*), using a Klett fluorimeter (*6*). For comparison several parallel experiments were run with typical nonresinous adsorbents. The initial experiments were performed on solutions prepared from crystalline thiamine hydrochloride and riboflavin.

The adsorption of thiamine by the sodium form of IR-100 and by other materials, including Amberlite IR-4, an acid-active resinous exchanger, was investigated first (Table I). The diameters of the modified Tswett columns were approximately 1.5 cm. The synthetic zeolite and the resinous cation exchanger are excellent adsorbents of the vitamin; alumina is unsatisfactory. Adsorption by Amberlite IR-4 was not anticipated and, for practical purposes, none was noted.

The recovery of the vitamin was considered next. A hot 25% solution of sodium chloride gave a 76% recovery from the zeolite using a volume of solution ten times the volume of the zeolite, but the recovery from IR-100-Na was only about 31% in a corresponding volume. This indicated that the vitamin is bound more tenaciously by the active groups of the resinous exchanger than by those of the zeolite. However, since the resinous materials may be regenerated with acid, the possibility existed of elution with the acid.

Preliminary experiments revealed that thiamine is removed from solution just as satisfactorily by the acid as by the sodium form of the resin; however, the type of adsorption was such that good recovery is not possible with the conventional concentrations (2–7%) of acid. Since these resinous materials are not acid sensitive, still greater concentrations were investigated.

Sorption by Amberlite IR-100-H. A 25-cm. column of Amberlite IR-100-H (average particle size 0.40 mm.) was prepared (bed volume 41.6 ml.), and a solution of 5 p.p.m. thiamine hydrochloride was passed downflow at a rate 28 ml. per minute (equivalent to about 4 gallons per square foot per minute). A total of 5 liters containing 25 mg. of thiamine was passed through the bed. There was no detectable quantity of vitamin in the effluent. After a brief rinse, a solution of 18% hydrochloric acid at room temperature was passed downflow at a flow rate of 10 ml. (equivalent to 1.5 gallon per square foot) per minute until twenty 50-ml. samples of effluent were collected. The samples were analyzed for thiamine. Figure 1 gives the recovery data.

There appears to be no truly chemical exchange, for on an equivalent basis a considerable excess of hydrochloric acid is necessary to elute the vitamin. Using this concentration of acid,

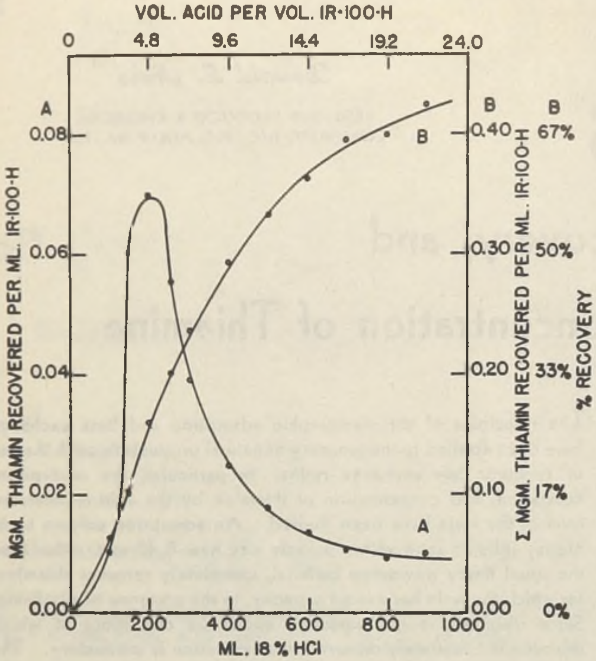

Figure 1. Recovery of Thiamine from Amberlite IR-100-H by 18% Hydrochloric Acid

about 50% of the vitamin is recovered in the first ten volumes of acid regenerant, each equal to the bed volume; more than 75% is recovered if twenty-five volumes are used.

A portion of synthetic zeolite was packed in a similar column and pretreated with 25% sodium chloride solution, and upon it were adsorbed 25 mg. of vitamin B_1. The vitamin was eluted with 25% sodium chloride; the same general type of recovery with about the same degree of efficiency was obtained as with 18% hydrochloric acid on IR-100-H (Figure 2).

Table I. Adsorption of Thiamine by Various Adsorbents

[2000 ml. of thiamine (1 p.p.m.) solution passed at a flow rate of 20–35 ml. per min.]

	Activated Alumina	Synthetic Zeolite	Amberlite IR-100-Na	Amberlite IR-4
Bed volume, ml.	45.6	40.6	41.2	41.1
Bed depth, cm.	25.4	25.4	25.4	25.4
Particle size, mesh	80–200	30–50	30–50	30–50
Thiamine removal	None	Complete	Complete	Trace

The use of even stronger acid to improve the characteristics of the recovery process was contemplated, since no deleterious effect was noted upon the resin by contact with 18% hydrochloric acid for a considerable time during repeated runs. To that end the usual type column was packed with 41.0 ml. of Amberlite IR-100-H over which were passed 8 liters of a 250 p.p.m. thiamine solution at a rate of 35 ml. (equivalent to 5 gallons per square foot) per minute. Since no detectable amount of the vitamin could be discerned in the effluent even at this high concentration and flow rate, it was evident that 2 grams of vitamin had been adsorbed. The recovery was carried out with 37% hydrochloric acid at a rate of 7 ml. per minute (equivalent to 1 gallon per square foot per minute); twenty 50-ml. samples were collected.

The characteristics of the recovery curve are indicated in Figure 3 which shows that the elution is most rapid in this system, for the peak is reached after only two volumes of eluent, each equal to the volume of the adsorbent, are passed. It will be seen that 60% of the vitamin is recovered in the first five volumes; if twenty volumes or more are passed, the recovery efficiency approaches 100%.

While concentrated hydrochloric acid is preferable to sulfuric acid because of the density and the thermal and oxidative characteristics of the latter, the recovery may be carried out just as readily with 32% sulfuric acid (Figure 4).

Of interest in regard to possible commercial application is the total capacity of the resin for the vitamin. Through a 10-cm. bed of Amberlite IR-100-H (bed volume 18.7 ml.) was passed a 250 p.p.m. solution of thiamine hydrochloride at a rate of 35–50 ml. (equivalent to 5–7 gallons per square foot) per minute. This corresponds to a retention time of 22–30 seconds, but even higher

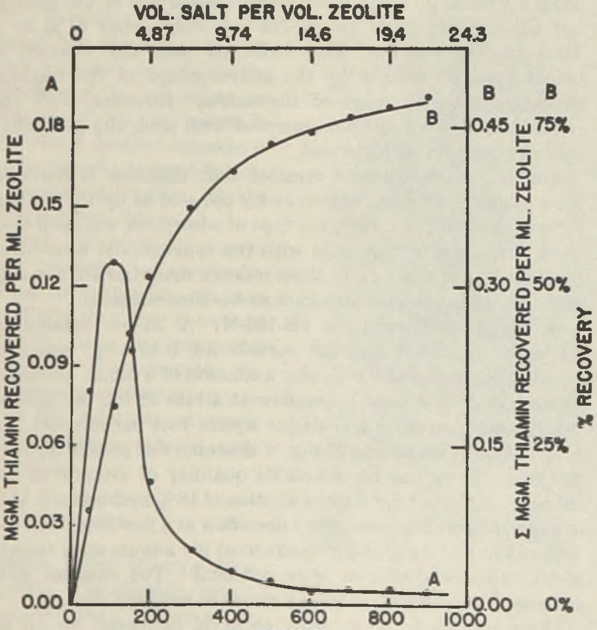

Figure 2. Recovery of Thiamine from Synthetic Zeolite by 25% Sodium Chloride

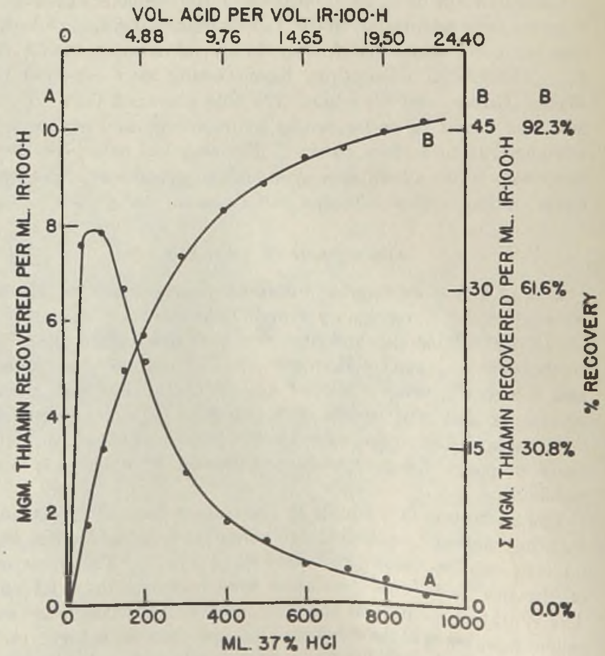

Figure 3. Recovery of Thiamine from Amberlite IR-100-H by 37% Hydrochloric Acid

Table II. Adsorption of Thiamine by Amberlite IR-100-H and Synthetic Zeolite (Freundlich Adsorption Isotherms)

	Amberlite IR-100-H				Synthetic Zeolite				Amberlite IR-100-H			
Sample No.	1	2	3	4	1	2	3	4	1	2	3	4
Original concn., p.p.m.	96.2	72.2	48.2	24.1	92.6	72.2	48.2	24.1	1420	1064	710	355
Equilibrium concn., p.p.m.	0	0	0	0	43.5	20.2	17.5	4.4	990	822	470	181
Capacity, mg./g. dry adsorbent	Greater than 65 at 100 p.p.m.				28.7	28.2	16.7	10.7	291	164	162	118

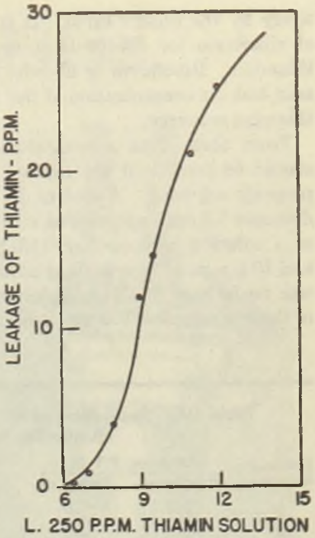

Figure 5. Adsorption of Thiamine by Amberlite IR-100-H

rates of flow would be feasible if a deeper bed of resin were used (Figure 5).

A small concentration of the vitamin was noted in the effluent just as the fifth liter had passed, at which point the capacity is 68 mg. thiamine per ml. of resin (4.2 pounds thiamine per cubic foot) or 168 mg. per gram dry weight. Although the rate at which the concentration of thiamine in the effluent increases as a function of the volume of solution passed is fairly rapid, even after 12 liters have been treated the column is still 90% efficient. This means that a type of countercurrent operation employing a second column of exchanger to adsorb that vitamin which has passed the first would considerably increase the practical capacity of the resin.

The amenability of the resin to static experiments is indicated in Table II and Figure 6. These data were obtained by stirring 0.200 gram of resin (or zeolite) in 100 ml. of solution for 3 hours and then determining the residual concentration of thiamine in the solution.

The binding tendency of Amberlite IR-100-H is so strong at low concentrations that essentially all the thiamine is removed; only after a much more concentrated solution was substituted was a measurable equilibrium concentration found. The capacity of around 160 mg. per gram is in good agreement with that from the column technique.

ADSORPTION OF RIBOFLAVIN BY AMBERLITE IR-100-H

SEPARATION OF THIAMINE FROM RIBOFLAVIN. Since the relative degree of basicity of these two compounds would be the determining factor in any successful separation, it was necessary to establish conditions under which riboflavin is adsorbed by Amberlite IR-100-H. Eight liters of a solution of 4.7 p.p.m. riboflavin were passed downflow over a bed (volume 40 ml., diameter 1.5 cm.) of Amberlite IR-100-H at a rate of 7 ml. per minute. Leakage occurred throughout the run and had risen to a 50% value at the end of the eighth liter. The average leakage over the entire run was 26%. Further exploratory experiments showed that under the same conditions the leakage from fuller's earth was never greater than 0.1 p.p.m., whereas Amberlite IR-4, the acid-active material, failed to adsorb riboflavin.

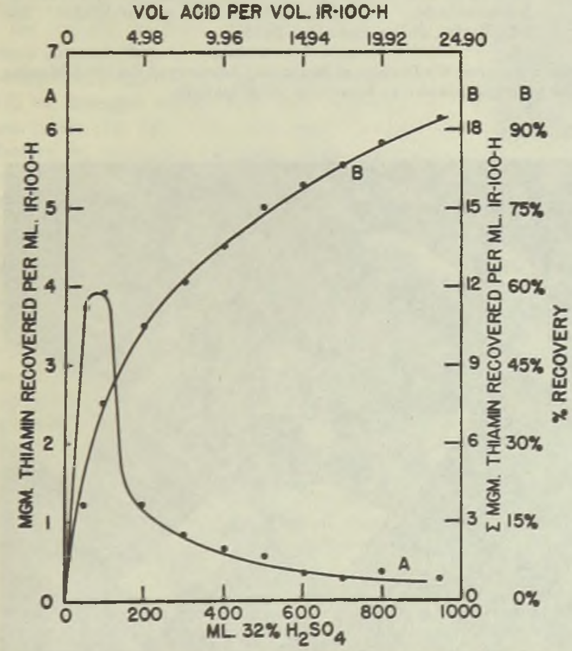

Figure 4. Recovery of Thiamine from Amberlite IR-100-H by 32% Sulfuric Acid

The adsorption was then checked in a static system where excessive contact time could be allowed. Freundlich adsorption isotherms were run using 0.200 gram of resin (or fuller's earth) stirred with 100 ml. of riboflavin solutions of various initial concentrations for 3 hours. The results are shown in Table III.

Therefore, the equilibrium total capacity of IR-100-H is equal to that of fuller's earth, although in a dynamic system with limited contact time the riboflavin is bound much more effec-

Table III. Adsorption of Riboflavin by Amberlite IR-100-H and Fuller's Earth (Freundlich Adsorption Isotherms)

	Amberlite IR-100-H				Fuller's Earth			
Sample No.	1	2	3	4	1	2	3	4
Original concn., p.p.m.	50.0	37.5	25.0	12.5	50.0	37.5	25.0	12.5
Equilibrium concn., p.p.m.	28.3	21.9	15.6	7.3	27.6	17.2	13.0	5.7
Capacity, mg./g. dry adsorbent	12.9	9.3	5.6	3.1	12.3	11.2	6.6	3.7

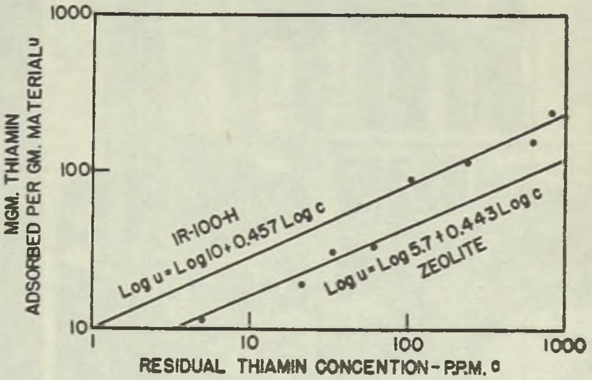

Figure 6. Adsorption Isotherm of Thiamine by Amberlite IR-100-H and Synthetic Zeolite

tively by the fuller's earth. It is also evident that the affinity of riboflavin for IR-100-H is much less pronounced than for thiamine. Riboflavin is likewise liberated reversibly to strong acid, but the concentration of this acid need not be so great as for thiamine recovery.

From these data a separation of riboflavin from thiamine should be possible if the contact time of solution with resin is properly adjusted. A bed of IR-100-H (bed volume 41.2 ml., diameter 1.5 cm.) was packed, and through it were drained 5 liters of a solution composed of 150 p.p.m. thiamine hydrochloride and 10 p.p.m. of riboflavin at a rate of 35 ml. per minute. There was no leakage of thiamine, although throughout the last 60% of the run complete leakage of riboflavin was noted (Table IV).

Table IV. Separation of Riboflavin from Thiamine by Amberlite IR-100-H

Liters of Solution	Leakage, P.P.M. Riboflavin	Leakage, P.P.M. Thiamine	Liters of Solution	Leakage, P.P.M. Riboflavin	Leakage, P.P.M. Thiamine
1	6.0	0.0	6	9.9	0.0
2	8.2	0.0	7	10.2	0.0
3	9.0	0.0	8	10.6	0.0
4	9.5	0.0	9	10.3	0.0
5	9.7	0.0			

The apparent initial adsorption of riboflavin is probably due to dilution of the influent by the water on the resin at the beginning of the run and to a small degree of adsorption of the van der Waals type. This means of separation is both controllable and practical. Since it is possible to replace one nitrogeneous substance adsorbed upon IR-100-H by another more alkaline substance, an additional means of elution is available and has been used in a few instances.

ISOLATION OF THIAMINE FROM RICE BRAN EXTRACT

The practicability of the procedure was tested by the extraction of thiamine from a rice bran extract. Using a flow rate of about 50 ml. (equivalent to 7 gallons per square foot) per minute with a shallow bed (12 cm.), complete leakage of riboflavin was noted while about 60% of the total thiamine in the solution was adsorbed. It seems probable that only the free vitamin was adsorbed, but acid or enzymatic hydrolysis of the cocarboxylase (pyrophosphate ester) or other complexes converts the vitamin to a form amenable to adsorption by Amberlite IR-100-H. Recovery characteristics of an acid regeneration of the resin are similar to those described previously. The vitamins can be subsequently released for use by chemical means already well known.

APPLICATIONS

The application of this method may proceed in two directions—as an analytical tool or in the recovery of thiamine and riboflavin from waste solutions. As an analytical tool the purity of the eluate is satisfactory for thiochrome analysis. No interfering substances have been encountered. If desired, thiamine may be readily crystallized from the eluate without extensive further purification. As a process tool to recover thiamine from natural sources, the resin offers a distinct potential advantage over zeolite as an adsorbent; namely, elution can be accomplished with a volatile acid instead of a salt which cannot be removed readily from the eluate. The volatile acid can be recovered and used repeatedly.

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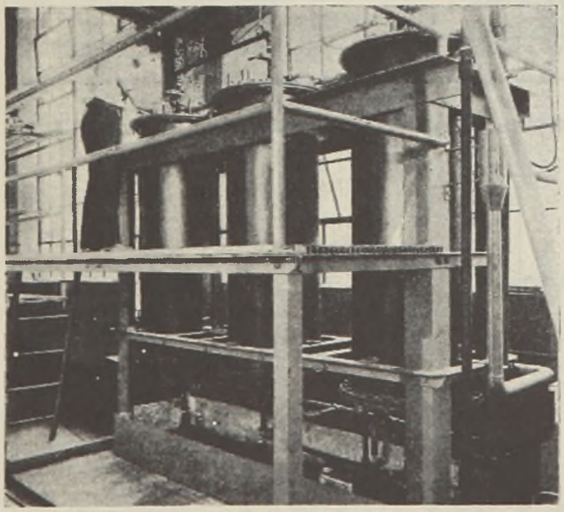

Amberlite Plant Unit to Produce Process Water

Vitamin Assay after Amberlite Separation

APPLE SIRUP by ION EXCHANGE PROCESS

R. E. Buck and H. H. Mottern

EASTERN REGIONAL RESEARCH LABORATORY
U. S. DEPARTMENT OF AGRICULTURE
PHILADELPHIA 18, PA.

MANY attempts have been made to produce an apple sirup of satisfactory flavor for food uses. An apple sirup developed in this laboratory has found industrial application as a moisture-retaining agent because of its high levulose content (*1*, *7*). It is objectionable for food uses, however, because of a slightly bitter aftertaste due to the calcium malate formed in the liming process.

The ability of ion exchangers to remove acid and basic constituents from solution suggested their possible use in preparing an edible sirup. Removal of malic acid prior to liming would prevent the formation of calcium malate. It was thought that ion exchanger treatment might also reduce the lead and arsenic contents.

A number of applications of ion exchangers to process industries have been reported. Englis and Fiess (*3*) state that elimination of the acid and mineral constituents from artichoke extract by ion exchangers produced a sirup of improved quality and flavor. They found that the ash content was reduced to about two thirds of its original value by one cation exchanger treatment and to one fourth by two treatments. Aside from the effect on the pH value of the extract, no data were reported on the actual amount of acid constituents removed by the anion exchanger. Ion exchangers removed 87% of nonsugar solids from beet and sugar cane juices (*11*, *14*); they were slightly more effective in removing inorganic than organic impurities. The treatment also resulted in an increased purity and higher yields of sugar.

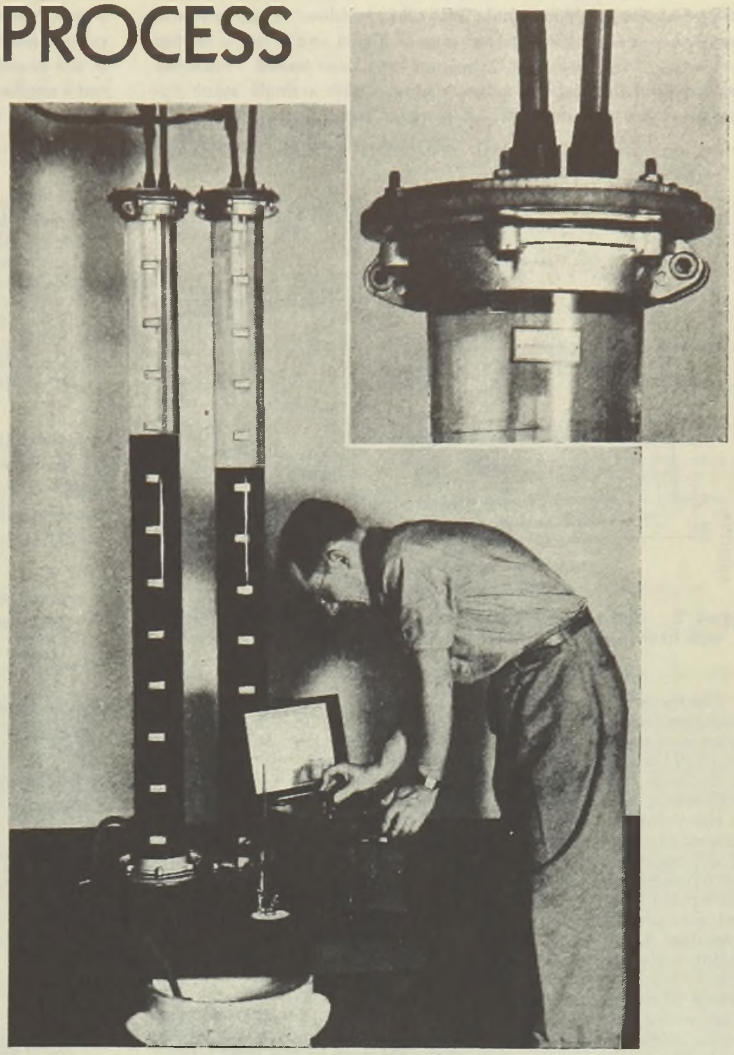

Figure 1. 4-Inch Exchanger Columns of Standard Pyrex Pipe and Flanges, with Saran Fittings; (*Above*) Means of Attaching Saran Fittings to Pyrex Pipe

The usual procedures for making apple sirup include neutralization of the acid with lime, calcium carbonate, or alkali carbonate (*1*, *2*, *4*, *5*, *7*, *10*). This treatment, however, imparts undesirable flavors. Haines (*6*) added sugar to dilute the acid, which is common practice in preparing many fruit sirups. The apple sirup developed in this laboratory and used as a tobacco humectant (*1*, *7*) is prepared by liming apple juice to a pH value of 8.0–8.5 to hydrolyze and precipitate the pectin, heating to 80° C., filtering, reacidifying to a pH value of 5.0–5.5 to improve color and flavor and prevent alkaline oxidation of sugars, and concentrating under vacuum to a total solids content of approximately 75%. The procedure described in this paper is similar, with the addition of ion-exchanger treatment before the liming step.

EXPERIMENTAL PROCEDURE

Before being passed through the exchanger beds, the juice was treated with activated carbon[1] and filtered with the aid of diatomaceous earth of medium porosity to remove colloidal material that might be absorbed by the exchanger with consequent reduction of its effective capacity. The clear filtrate was then treated with the ion-exchanger materials as described. After being treated, it was heated to 57° C. (135° F.) and limed until a flocculent precipitate appeared, usually at a pH value of 8.0 to 8.5. It was then filtered, reacidified with citric acid to a pH of 5.0 to 5.5, and evaporated under vacuum to 75% total solids.

Glass columns of 1-inch (25-mm.) and 4-inch (100-mm.) inside diameters were used for exchanger beds. The volumes of the beds were approximately 200 ml. and 7.5 liters, respectively. The 1-inch columns were set up in the conventional manner (*9*). The 4-inch columns (Figure 1) were constructed of standard 5-foot lengths of 4-inch Pyrex piping. The ends were closed by Saran flanges cut from a $^{3}/_{8}$-inch sheet, backed by a $^{1}/_{4}$-inch steel plate, and bolted to the piping with Corning companion flanges. The data reported here were obtained with the 1-inch laboratory columns, although similar results were obtained with the 4-inch columns.

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[1] Later work has shown that carbon treatment is unnecessary and that passage of screened (150-mesh) but unfiltered juice through the exchangers reduces the capacity by only 10 to 15%. Before this procedure can be recommended, however, further work must be done to determine whether this reduction is cumulative or constant.

The removal of most of the malic acid from apple juice by anion adsorption avoids the bitter aftertaste of calcium malate formed by liming the original juice in the preparation of apple sirup. Anion adsorption also removes arsenic from spray residue. Lead is almost completely removed in the final step of liming and is not a serious problem. Three methods of treatment have been tested. From the standpoint of flavor the simplest treatment with a single anion exchanger is the most practical. It removes about 80 to 90% of the acid and produces a palatable sirup with little flavor other than that of sweetness. A variable amount of arsenic is removed by the single treatment. To ensure more complete removal when it becomes necessary, a two-step (cation-anion) or a three-step (anion-cation-anion) exchanger treatment must be used. As much as 96% of the arsenic content has been removed by the three-step method, and a smaller amount has been eliminated by the two-step method. In addition, the cation exchanger removes about 90% of the ash.

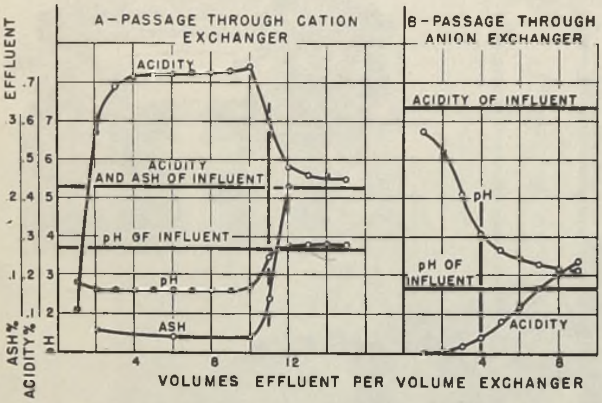

Figure 2. Changes in Composition of Apple Juice on Treatment with Exchangers (of Manufacturer *A*) According to Method II

The mode of action and general procedure for the use of ion exchangers has been discussed in detail elsewhere (*8, 9, 12, 13*). Juice was run downflow through the columns at a rate of 5 gallons (19 liters) per minute per square foot of cross-sectional area of the bed. After exhaustion, the beds were backwashed upflow with water at such a rate that there was a 50 to 75% expansion in the volume of the bed. After backwashing, the beds were regenerated. To regenerate the anion exchangers, four volumes of 4% sodium carbonate solution for each volume of exchanger were passed downflow at the rate of 2 gallons (7.6 liters) per minute per square foot of cross-sectional area. This quantity of regenerant was probably in excess of the amount actually needed but was used to ensure complete regeneration. To regenerate the cation beds, two volumes of 2%, or one volume of 4%, hydrochloric acid per volume of exchanger were found sufficient. The excess of regenerant was rinsed out downflow with water. The rinse water for the anion beds was softened by passage through a cation exchanger to avoid precipitation of insoluble carbonates by hard water. The progress of the reaction as the juice passed through the beds was followed by either the pH value or the titratable acidity of the effluent juice. With the cation exchangers, operating on a hydrogen cycle, there was a sharp change in pH and acidity at the break-through point; with the anion exchangers there was a gradual change, and the end point of the run had to be arbitrarily selected. The plotted data were obtained from successive samples taken during progress of the run.

In passage of juice through the cation-exchanger bed (Figure 2*A*) there was an increase in acidity and reduction in ash content as the bases were exchanged for hydrogen. The pH value decreased and remained at a constant level until the break-through point was reached, whereupon it increased rapidly to that of the influent juice. Thus, measurement of the pH value of the effluent served as an excellent means of determining the break-through point.

With the anion exchangers (Figure 3*A*) the pH value of the first effluent was between 7.0 and 8.0; in succeeding fractions it gradually dropped until it approached that of the influent juice. Likewise, the acidity was at first zero but gradually increased and approached that of the influent, which indicated a gradual decrease in the efficiency of anion removal as the run progressed. Exhaustion of the exchanger was arbitrarily taken as the point at which the pH of the combined effluent was about 5.0. At this point there was about an 80% removal of acid from juice of average acidity. This end point is indicated by the vertical lines on the graphs.

CAPACITIES

Different Exchangers. "Capacity" is used to indicate the volume of effluent juice per volume of exchanger when the latter is considered exhausted. A more precise definition of capacity, in terms of equivalents of ions removed, is not practical in the case of apple juice because of its complex and varying nature:

Constituent	Per Cent	Constituent	Per Cent
Total sugar	9.6-12.0	Malic acid	0.11-1.68
Levulose	5.8- 6.3	Other solids	0.48-2.35
Dextrose	0.5- 3.5	Ash	0.22-0.41
Sucrose	0.6- 3.9		

Figure 4 shows curves for pH *vs.* volume of effluent for cation exchangers of four manufacturers. The capacities of exchangers *A* and *B* were 13 volumes; those of *C* and *D* were 11 and 10 volumes, respectively. *A*, *B*, and *C* removed about 90% of the ash; *D* removed a slightly smaller amount, as Table I shows.

Table I. Ash Removed from Apple Juice by Cation Exchangers and Capacity of Exchangers

Exchanger	Ash[a] in Combined Effluent, %	Ash Removed, %	Capacity, Vol. Effluent per Vol. Exchanger
A	0.02	90.7	13
B	0.02	90.7	13
C	0.02	90.7	11
D	0.03	86.1	10

[a] Ash of influent juice = 0.215%.

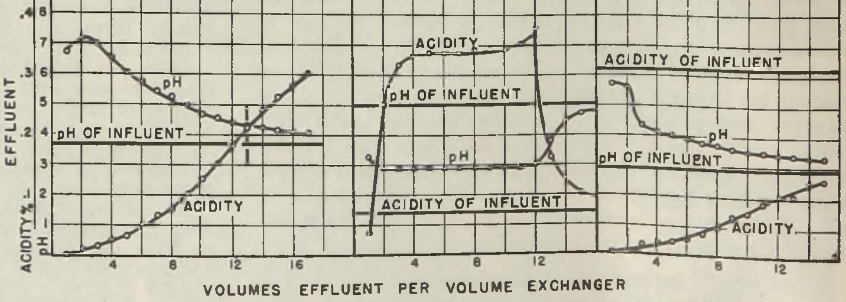

Figure 3. Changes in Composition of Apple Juice on Treatment with Exchangers (of Manufacturer *A*) According to Method III

Single treatment according to method I is illustrated by section on left.

The capacity of a cation exchanger naturally varied with the ash content of the juice. The tests just described were conducted on the same lot of juice; for different juices the capacities ranged from 10 to 40, the average being between 15 and 20.

The capacities of the different anion exchangers for the same juice varied over a wide range (Figure 4). The rapid drop in pH value shown by curves *C* and *D* indicates that the capacities of these two exchangers were low. Capacities of *A* and *B* were nearly equal and considerably higher than those of *C* and *D*.

Juices of Different Acidity. Juices having a malic acid content ranging from 0.12 to 0.49% were used with anion exchanger *A* (Figure 5). The capacities ranged from 12 to 40 volumes and, in general, varied inversely with the acidity of the influent. However, the relation was not exact enough to use acidity as a means of predicting capacity. The reversal of order between juices V and VI might have been due to qualitative differences in the anions of the juices and their differential adsorption by the exchanger. The following generality may be permissible and useful: For apple juices of average acidity, 0.3 to 0.4%, the capacities of good anion exchangers range from 15 to 20.

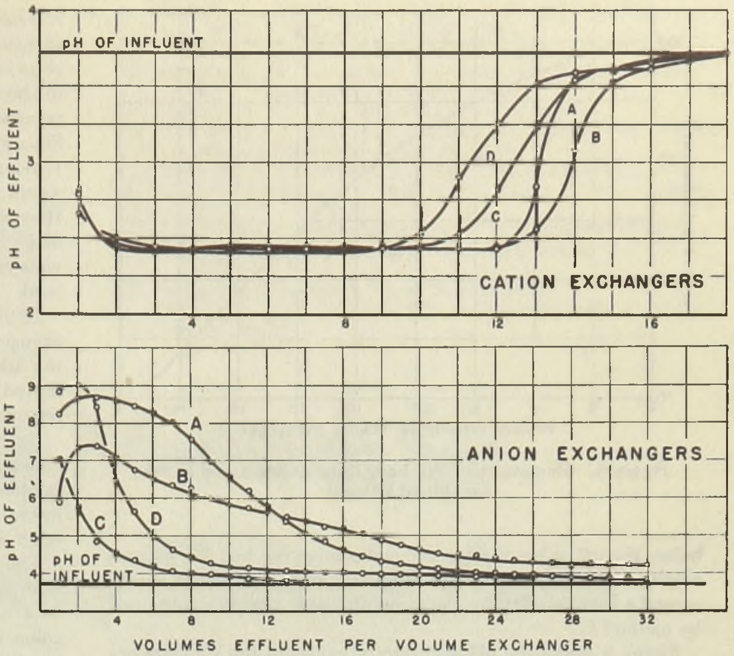

Figure 4. Effective Capacities of Cation and Anion Exchangers

METHODS FOR USING ION EXCHANGERS

Three methods of treating apple juice have been tested: (I) single treatment with an anion exchanger; (II) treatment with a cation exchanger followed by treatment with an anion exchanger; and (III) treatment first with an anion exchanger, then with a cation exchanger, and lastly with a second anion exchanger (suggested by F. I. L. Lawrence). Consideration was given to two other possible methods. One consisted in treating a limed juice by method II. This imposed a heavy load on the cation exchanger, owing to the added calcium, and was therefore abandoned. The other involved the use of a pectin-hydrolyzing enzyme before the anion exchanger treatment in method I, but this proved more expensive than the liming process and also produced darker sirup.

The simplest treatment is a single passage of the juice through an anion exchanger (method I). Figure 3*A* shows typical curves for pH and acidity of successive portions of the effluent juice; Figure 6 shows the percentage of acid removed from the combined effluent. From the thirteenth volume of the effluent, only about 50% of the acidity of the influent had been adsorbed, whereas from the combined 13 volumes about 82% of the acid had been removed. This represents an adsorption of about 47.5 grams of malic acid per liter, or 3 pounds per cubic foot of exchanger.

Since most of the free acid is removed by this treatment, only 0.020 to 0.025% lime is necessary to bring the pH value to 8.5 to hydrolyze the pectin, as compared with 0.25 to 0.30% required without anion-exchanger treatment. This liming process causes no increase in ash content; in fact a slight reduction may occur, probably because the added lime is precipitated as calcium pectate. Considerable color is occluded in the pectin precipitate. After the juice is filtered, only a small amount of citric acid is necessary to adjust the pH value to between 5.0 and 5.5 before concentration. Removal of the malic acid prevents the formation of calcium malate and thus prevents the bitter aftertaste characteristic of sirups prepared without this treatment. The sirup contains the natural ash but has little flavor other than sweetness. Addition of the recovered volatile constituents of the juice produces a sirup with a pleasing apple flavor.

Although methods II and III effect a more complete removal of arsenic as compared with method I, flavor improvement is not sufficient to justify their use unless arsenic removal is necessary. Removal of arsenic is discussed in a later section.

In method II passage of the juice through the cation exchanger before passage through the anion exchanger converts combined acid to free acid and permits more complete adsorption of the anions. Figure 2 shows the ash, acidity, and pH values of the effluents from the cation and anion exchangers. The cation-exchanger treatment reduced the ash content by about 90% and increased the acidity from 0.43 to 0.64%. The increase in acidity reduced the volume of juice which could be treated by the anion exchanger in the next step, only four volumes passing through

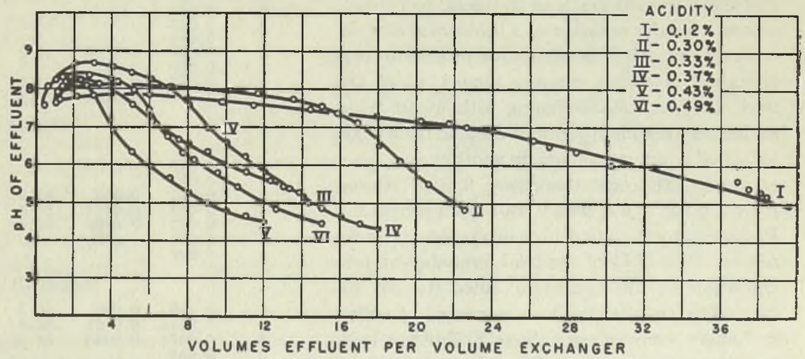

Figure 5. Effective Capacities of Anion Exchanger *A* with Juices of Different Acidity

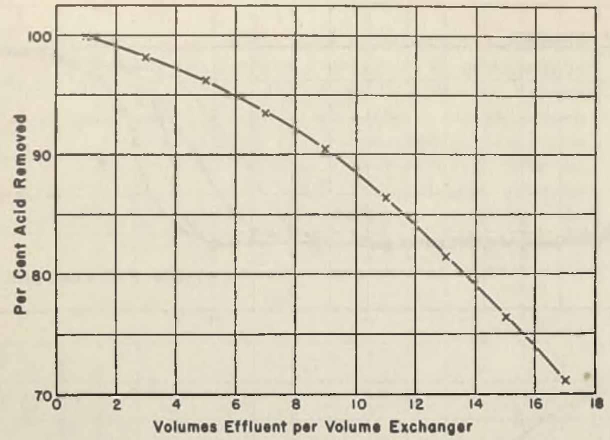

Figure 6. Removal of Acid from Juice as Measured in the Combined Effluent

before the pH value of the combined effluent reached 5.0, with an acidity of 0.02%. The more complete removal of buffer anions caused a lower acidity for the same pH value than that obtained by method I.

Figure 3 shows the pH and acidity values of the effluents obtained in method III, in which the juice was passed through anion, cation, and anion exchangers in succession. Comparison with Figure 2 shows that the capacity of the cation exchanger was increased by about two volumes by a previous anion-exchanger treatment. An increase in the juice capacity of the anion exchanger was also attained in this method, as compared with method II, by operating the first anion exchanger to a greater degree of saturation and using the second one as a scavenger to adsorb the acid that passed through the first. The acidity and pH value of the effluent from the second anion exchanger were so low that a pH value of 5.0 for the combined effluent was not practical for determining the exhaustion of the exchanger. The end point may be declared when the acidity of the combined effluent is 25% of that of the influent.

SPRAY RESIDUE REMOVAL

Since apple juice prepared from unwashed sprayed fruit may contain quantities of lead and arsenic which, in the prepared sirup, would be in excess of the tolerance, assuming a sixfold concentration of juice to sirup, it was considered advisable to determine the extent of lead and arsenic removal by ion exchanger treatment. Willits and Tressler (*15*) found that the base exchange material Zeo-Karb reduced the lead content of maple sap from as much as 36 p.p.m. to 1 p.p.m. or less. Lead is not so great a problem as arsenic, however, inasmuch as the liming process for precipitation of pectin removes almost all of the lead. In one instance liming without an anion exchanger treatment reduced the lead from 0.004 to 0.0002 grain per pound; in another case, after an anion exchanger treatment, liming reduced it from 0.005 to less than 0.0001 grain per pound. Passage through anion exchangers generally removed 20 to 50% of the lead, probably by precipitation as the hydroxide, since the pH increased as the fruit acids were removed. A cation exchanger removed only about 50% of the lead, possibly because of its presence in an un-ionized form.

Arsenic analyses were made on the juices (Table II) but were calculated to the basis of a sixfold concentration of juice to finished sirup, since the tolerance applies to the latter. Although most of the samples were low in arsenic, they exceeded the tolerance, especially sample 1, which was pressed from peels and cores. Since single passage of juice through an anion exchanger (method I) removed a small and variable amount of arsenic, this method would not be satisfactory for juice containing excessive amounts. However, adequate washing of the fruit before pressing might make this simple treatment satisfactory. To ensure a more complete removal of arsenic, other ion exchanger treatments could be used.

In method II passage of the juice through the cation exchanger prior to passage through the anion exchanger increased the adsorption of arsenic. Exchangers of manufacturer *A* removed 50 to 80% of the arsenic; exchangers of manufacturer *B* removed a smaller and more variable amount.

By the three-step treatment (method III), exchangers of manufacturer *A* were 96% effective, even in the high-arsenic sample (No. 1), and the final concentration was considerably below the tolerance. Smaller amounts were removed by the other exchangers.

The results show that arsenic can be successfully removed from apple juices by a suitable ion exchanger treatment. No data have been collected on the continued effectiveness of the anion exchangers in this respect. It is not known whether regeneration as ordinarily practiced completely removes the arsenic from the exchanger. Removal, however, might be effected by occasional regeneration with a concentrated solution of a strong acid, causing displacement of the more strongly adsorbed anion.

LIFE OF EXCHANGERS

An essential point in the use of ion exchangers is their effective life or capacity after many cycles. It is difficult to compare their capacities accurately when they are used with a natural product like apple juice because of its varied and varying composition. However, some of the laboratory columns have been used for seventy-five cycles with no noticeable loss in capacity.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Infilco, The Permutit Company, Research Products Corporation, and The

Table II. Arsenic Removed from Juice by Anion Exchangers in Terms of As_2O_3 per Pound of Sirup of 75% Solids

Sample No.	Original, Grains per Lb.	Exchanger *A* Grains per lb.	Exchanger *A* % removed	Exchanger *B* Grains per lb.	Exchanger *B* % removed	Exchanger *C* Grains per lb.	Exchanger *C* % removed	Exchanger *D* Grains per lb.	Exchanger *D* % removed
Method I. Anion Exchanger									
1	0.156	0.114	26.9	...	...	...	...	...	...
2	0.0462	0.0456	1.3	...	...	...	...	...	...
3	0.033	...	...	0.0306	7.3	...	...	...	...
3	0.033	...	...	0.0234	29.2	...	...	...	...
3	0.033	...	...	0.0192	41.8	...	...	...	...
3	0.033	...	...	0.0186	43.6	...	...	...	...
4	0.027	0.0198	26.7	...	...	...	...	...	...
4	0.027	0.0252	6.7	...	...	...	...	...	...
4	0.027	0.0204	24.5	...	...	...	...	...	...
5	0.0228	0.0192	15.8	...	...	...	...	...	...
Method II. Cation-Anion Exchanger									
1	0.156	...	...	0.096	38.5	...	...	...	...
1	0.156	...	...	0.054	65.4	...	...	...	...
6	0.072	...	...	0.0636	11.7	...	...	...	...
6	0.072	0.012	83.4	...	...	...	...	...	...
3	0.033	0.0144	56.4	...	...	...	...	...	...
3	0.033	0.0108	67.3	...	...	...	...	...	...
4	0.027	...	...	0.0054	80.0	...	...	...	...
4	0.027	...	...	0.006	77.8	...	...	...	...
Method III. Anion-Cation-Anion Exchanger									
1	0.156	0.006	96.2	...	...	...	...	...	...
7	0.0618	0.0084	86.4	0.0162	73.8	0.0414	33.0	0.0156	74.6
8	0.0576	0.0048	91.7	0.0156	72.9	0.0276	52.1	...	...
3	0.033	...	...	0.0156	52.8	...	...	...	...
4	0.027	0.0006	97.8	...	...	...	...	...	...

Resinous Products & Chemical Company, which furnished the exchangers and gave helpful advice in carrying out the experiments. The contributions of Clara Day Rehrig and Nancy O'Connell Buck (formerly of this laboratory), who assisted in the analytical determinations and routine tests, are also acknowledged.

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Gas Adsorption Methods for Measuring Surface Area of Adsorbents

Paul H. Emmett

MELLON INSTITUTE OF INDUSTRIAL RESEARCH, PITTSBURGH, PA.

Methods for measuring surface areas by gas adsorption may, for convenience, be subdivided into two groups. The first group is based on the postulate of the existence of multilayers of physically adsorbed gas and makes use of adsorption isotherms of gases near their boiling points. The second group assumes that the adsorption of a vapor is a combination of monomolecular physical adsorption and of capillary condensation. Published proposals for measuring surface areas by gas adsorption are critically discussed. It is concluded that the use of low-temperature adsorption of some gas, such as nitrogen, near its boiling point is the best substantiated procedure thus far described, and that this procedure is capable of yielding reliable values for the surface areas of porous and finely divided materials or even of materials which have relatively small surface areas.

UNTIL 1935 no satisfactory method existed for measuring the surface areas of both porous and nonporous adsorbents. For nonporous solids a number of fairly satisfactory methods existed, including calculations based on the rate of sedimentation of particles in a suitable liquid, on the rate of fluid flow through packed beds of the adsorbent (*6*), on direct microscopic or ultramicroscopic particle counts, or on the adsorption (*13, 14*) of a suitable solute from solution. For porous adsorbents, adsorption from solution and deductions based on the adsorption isotherms of vapors, as interpreted by capillary condensation, could be used. However, the only method common to both porous and nonporous solids, the adsorption of solutes from solution, had many limitations when applied to a porous adsorbent. Equilibration was frequently slow because of the difficulty of diffusion of solute molecules through tiny capillaries filled with solvent. It was also difficult to know the point on the liquid adsorption curves corresponding to the formation of a complete layer of adsorbed solute.

Within the last ten years, a number of new approaches to the problem have been made for measuring the absolute surface areas of both porous and nonporous solids. These new methods involve the measurement of the adsorption of gases by the solid adsorbents at temperatures close to the boiling points of the gases. The purpose of the present paper is briefly and critically to summarize these published methods with a view to assessing their relative usefulness and general applicability.

For convenience, the adsorption methods for measuring surface areas may be divided into those that postulate the existence of polymolecular adsorption at pressures close to the liquefaction pressures of the adsorbates and those that assume S-shaped adsorption isotherms to be a combination of monomolecular physical adsorption and capillary condensation. To the first classification belong the methods proposed by the author and coworkers (*4, 5, 10*) as well as those by Harkins and Jura (*16, 17*), by Askey and Feachem (*1*), and by Smith and Greene (*23*). In this category, too, falls the work of Wooten and Brown (*24*) who showed how the adsorption method can be applied to materials having surface areas so small as to be unmeasurable by other procedures. In the second category fall the recent works of Harvey (*18*) and of Kistler, Fischer, and Freeman (*19*), as well as earlier papers by McBain (*22*), by Lowry (*20*), and by Draper (*7*).

MULTIMOLECULAR LAYER FORMATION

About ten years ago a search was begun at the Fixed Nitrogen Research Laboratory for a method by which the surface area of iron synthetic ammonia catalysts could be determined. It was desirable to find a method for measuring the surface area of reduced catalysts without, at the same time, effecting any change in the extent or even the activity of the catalyst surface. To this end the adsorption of a number of gases was determined at temperatures close to the boiling points of the respective gases. The results of this first series of determinations are shown in Figure 1 (*10*). It was suspected that the long linear part of the isotherms consisted of the building up of multilayers of gas on the catalyst surface. If this were true, it was possible that the point corresponding to a monolayer might be selected on the isotherm

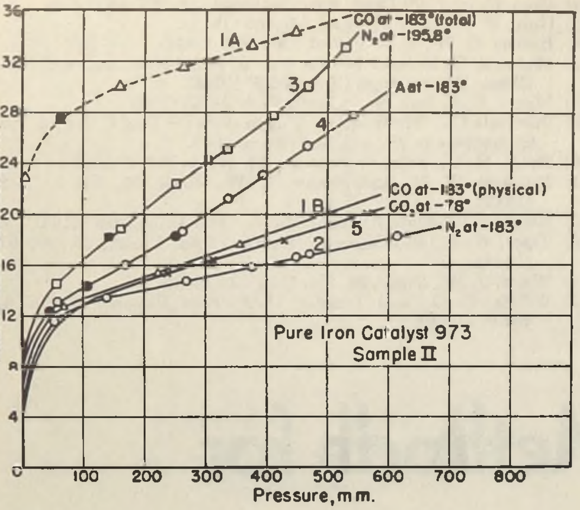

Figure 1. Low-Temperature Adsorption Isotherms on a Pure Iron Synthetic Ammonia Catalyst (*10*)

of one of the inert gases—nitrogen, for example. In succession, three different methods were used to select the point on the isotherm corresponding to a monolayer. In each case the multiplication of the number of molecules in a monolayer by the average cross-sectional area of each molecule would yield an absolute value for the surface area. The first suggestion (*4*) was that the extrapolation of the linear part of the curve to the zero pressure axis (point *A*, Figure 2) would yield a value for the volume of nitrogen and hence the number of nitrogen molecules required to form a monolayer. This apparently was the interpretation being placed on low-temperature argon isotherms independently by Askey and co-workers (*1*) in England about the same time. A more detailed comparison of the adsorption of a number of different gases on several catalysts led to the conclusion that point *B*, where the long linear part of the isotherms begins, was the best empirical choice of a point for calculating the surface area of the catalyst from the low-temperature adsorption isotherm. Later a mathematical treatment of the theory of adsorption in collaboration with Teller (*5*) led to a third and more useful way of interpreting the isotherms. It resulted in an equation from which the value of V_m, the volume of gas corresponding to a monomolecular layer, could be determined by plotting a portion of the isotherm in such a manner as to obtain a linear plot. The fact that V_m and the volume of nitrogen adsorbed at point *B* have always agreed within about 10% has given added weight to the conclusions based on interpreting V_m as the volume of gas required to form a monolayer over the adsorbent. The simplicity of the method using the linear equation for obtaining V_m has led to the general adoption of this method of interpreting the low-temperature adsorption isotherms in our recent work. It is believed that the method gives values for relative surface areas of different adsorbents that are accurate to a few per cent, and values for the absolute surface areas that appear to be correct within about 20%. The details of this work will be briefly presented.

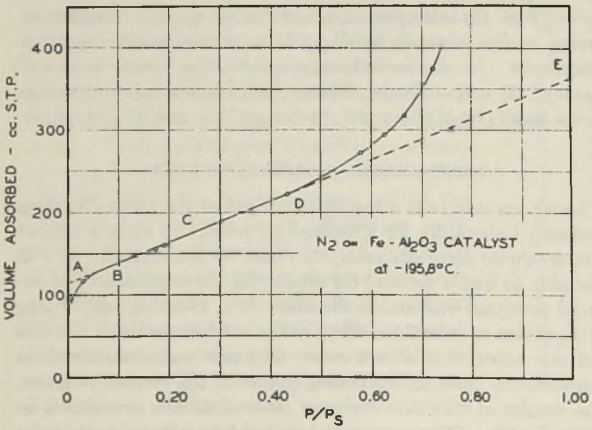

Figure 2. Adsorption of Nitrogen on Iron-Alumina Catalyst at −195.8° C.

***A, B, C, D, E* represent definable points tested in comparing surface areas by various gases (*10*).**

The apparatus for low-temperature adsorptions has been described on a number of occasions (*9, 15*) and need not be discussed here in detail. It will suffice to point out that a standard adsorption technique is employed, the dead space around the adsorbent being determined by helium at the temperature at which the measurements are to be made (about −195° C., for example, if the adsorbate is nitrogen).

Brunauer, Emmett, and Teller (*5*) showed that if the S-shaped isotherms, of the type illustrated by Figures 1 and 2, are interpreted as representing the building up of multilayers at the higher relative pressures, they can be plotted according to the equation,

$$\frac{p}{V(p_o - p)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\frac{p}{p_o} \tag{1}$$

where V = volume of gas adsorbed at pressure p
V_m = volume of gas required to form a monolayer
C = a constant
p_o = liquefaction pressure of adsorbate used at temperature of experiments

A plot of the left-hand side of the equation against p/p_o yields a straight line, from the slope and intercept of which V_m and C can be calculated directly. Figure 3 shows a typical set of these linear plots (*5*).

Application of the method to several thousand finely divided or porous substances (*8, 11*) has shown that a linear plot of Equation 1 for nitrogen adsorption at −195° C. is always obtained between relative pressures of 0.05 and about 0.35 except for a few porous solids such as charcoal and chabasite in which most of the sorption capacity is centered in pores less than 20 Å. in diameter. This relative pressure range correspond to a coverage varying from a little less than a monolayer up to about 1.5 monolayers. It does not extend to such relative pressures as would involve capillary condensation.

Many examples of surface area measurements employing this method have been published and might be cited. For brevity, however, only a few will be given. They were selected because some independent estimate of surface area is available in each instance.

Table I list surface area measurements made on a selected group of zinc oxide samples (*11*); for comparison area determinations are shown by several other methods. The agreement between the particle sizes calculated from adsorption surface areas and those obtained by Carman's permeability method is excellent and well within the combined experimental error of the two methods. The particle sizes obtained by microscopic examination and liquid phase adsorption are a little larger than those obtained by the gas adsorption method. This is to be expected in view of the fact that the gas adsorption measurements include some surface of pores or small particles that would probably be missed by the other procedures. Table II gives area measurements on glass spheres (*8, 9*) prepared by Bloomquist and Clark (*3*). The adsorption measurements indicated an area about 40% greater than one would have expected from the size of the spheres as observed under a microscope. To demonstrate that this dis-

Table I. Surface Area Measurements on Zinc Oxide Pigments (*11*)

Pigment No.	F-1601	K-1602	G-1603
Area by adsorption, sq. m./g.	9.48	8.80	3.88
Av. particle size, microns			
By direct microscopic count[a]	0.21	0.25	0.49
By adsorption of methyl stearate	0.19	0.24	0.55
By ultramicroscopic count	0.135	0.16	0.26
By permeability	0.12	0.15	0.25
By adsorption of N_2 (liquid)	0.115	0.124	0.28
By adsorption of N_2 (solid)	0.135	0.145	0.33

[a] This calculated value is from measurements of the number of particles per gram.

crepancy might well be due to some roughening of the bead surface by the washing with cleaning solution to which they had been subjected, a second washing by cleaning solution was employed. The area increased an additional 40% (Table II). This is at least consistent with the idea that even the 40% discrepancy between the area estimated by microscopic and adsorptive methods is due to a slight roughening of the glass spheres by exposure to cleaning solution. A third illustration is shown in Table III which summarizes data obtained in recent months for the surface area of carbon black particles as judged by the particle size measurements made by an electron microscope in comparison with area measurements made by adsorption. The two carbon blacks that show greater areas from the adsorption than the electron microscope measurements have been so treated as to produce porosity. The standard blacks that are supposedly nonporous show excellent agreement between the areas determined by the two methods. In passing it should be emphasized that the electron microscope yields particle size directly and not surface area; the adsorption measurements, on the other hand, yield directly the number of molecules required to form a monolayer and hence, with certain assumptions, the surface area. These three examples in themselves are strong evidence that the areas obtained by the low-temperature nitrogen adsorption method are approximately correct.

Table II. Surface Area Measurements on Sized Glass Beads (*8, 9*)

Area by adsorption of N_2 (liquid), sq. m./g.	0.532
Av. diam. calcd. from adsorption of N_2, microns	
Liquid	4.50
Solid	5.30
Diam. by microscopic observation, microns	7.00
Area after cleaning beads with soln., sq. m./g.	0.748

Table III. Surface Areas of Carbon Blacks (Square Meters per Gram)

Carbon Black	By N_2 Adsorption	Calcd. from Electron Microscope Measurements[a]
P-33 (thermal decomposition black)	20.7	20.9
Lampblack (type T)	25.5	23.5
Lampblack (type T activated)[b]	208	27.4
Acetylene black (Shawinigan)	64.5	55.9
Grade 6 (channel black)	110	74.8
Mogul (long ink black)	450	85.4

[a] Density of 2.00 assumed in converting microscope diameters to surface areas.
[b] Treated with air for 3 hours at 800° F.

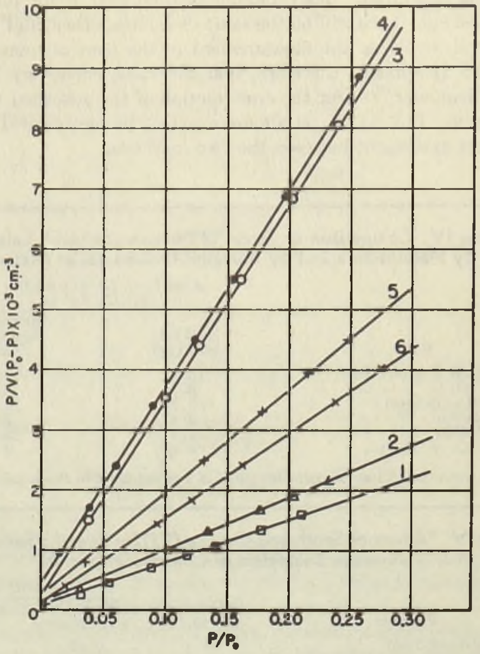

Figure 3. Plot of Low-Temperature Nitrogen Adsorption Isotherms According to Equation 1 (*5*)

Recently Harkins and Jura (*17*) announced a method for measuring the absolute surface area of a finely divided nonporous solid that does not even require one to assume a cross-sectional area for the adsorbate molecule. Their method entails measuring the heat evolved when a sample of finely divided titanium oxide is immersed in water after having been presaturated by exposure to a relative pressure of water vapor sufficiently high to form an average of about five adsorbed layers. The curve obtained by plotting the heat evolved on immersion per gram of titanium oxide against the amount of adsorbed water levels off rather quickly to a constant value. By assuming that this constant value for the heat of immersion is the same as that of the surface energy of pure water (118 ergs per sq. cm.), they were able to calculate the number of square centimeters of surface possessed by the titanium dioxide sample. The result obtained by them was 13.8 square meters per gram. Their determination of the area of this same titanium dioxide by the nitrogen adsorption method making use of Equation 1 yielded a value of 13.9 square meters per gram. The agreement speaks for itself in adding weight to the contention that the low-temperature nitrogen isotherm method yields approximately the correct absolute value of the surface area. The heat of immersion method is more useful as a separate procedure for checking the areas of nonporous solids; it is probably too difficult experimentally to employ as a routine method.

Harkins and Jura (*17*) also developed an independent method for plotting the low-temperature nitrogen adsorption data and calculating surface areas. They discovered that plotting $1/V^2$ against $\log p/p_0$ according to the equation

$$\log p/p_0 = B - (A/V^2) \qquad (2)$$

where V is the volume of nitrogen adsorbed at low temperature at the relative pressure p/p_0, yields a straight line over a long relative pressure range extending usually from 0.05 to about 0.7. From the absolute surface area measurements employing the heat of immersion of partially saturated titanium dioxide described above, they showed that the area of the titanium dioxide is given by the equation

$$\text{area} = k(S)^{1/2} \qquad (3)$$

where S = slope of plot of Equation 2

For nitrogen, k has a value of 4.06. Thus by plotting the data for adsorption of nitrogen at −195° C. according to Equation 2 and employing a value of 4.06 for k in Equation 3, it becomes possible to obtain values for the surface areas of finely divided materials. Their comparison of the results obtained by this method with those obtained by using the plots for Equation 1 is shown in Table IV. The agreement between the two methods is unbelievably close. It should be borne in mind that the values obtained by Harkins and Jura (*17*) by Equations 2 and 3 do not involve any assumption as to the cross-sectional area of the adsorbed molecules. They merely assume that k for one finely divided substance will be the same as k for another, and that the method involving the measurement of the heat of immersion is valid. It appears, therefore, that the value chosen by Emmett and Brunauer (*10*) for the cross section of the adsorbed nitrogen molecule, 16.2 sq. Å., is almost exactly the one needed to give perfect agreement between the two methods.

Table IV. Comparison of Areas of Nonporous Solids Calculated by Harkins-Jura and by Brunauer-Emmett-Teller Methods

Solid	Area from N_2 Adsorption at −195° C., Sq. M./G.	
	Harkins-Jura (*17*)	Brunauer-Emmett-Teller[a]
TiO_2 I (standard)	13.8	13.8
TiO_2 II	8.7	8.6
SiO_2 (quartz)	3.2	3.2
$BaSO_4$	2.4	2.4
$ZrSiO_4$	2.9	2.8
$TiO_2 + Al_2O_3$	9.6	9.5

[a] A value of 16.1 sq. A. per N_2 molecule was assumed in these calculations.

Table V. Values of Smith and Greene (*23*) for Specific Surfaces and Average Diameters of Common Pigments

Pigment	Sp. Surface, Sq. M./G.	d^3 in Microns[a]	
		By H_2O adsorption	By microscopy
ZnO (Green Seal)	2.4	0.45	0.44
ZnO heated 0.5 hr. at 800° F.	2.3	0.47	0.47
ZnO heated 0.5 hr. at 1100° F.	2.3	0.47	0.50
ZnO heated 0.5 hr. at 1400° F.	1.8	0.59	0.59
ZnO heated 0.5 hr. at 1700° F.	1.7	0.63	0.66
Pigment Black 8	12.	0.29	0.26
Lithopone	2.3	0.61	0.43
Titanium dioxide	8.2	0.19	0.43
Antimony oxide	0.61	1.7	0.61
Basic-carbonate white lead	1.1	0.80	0.66
Hansa Yellow Toner	2.6	1.5	0.21
Orange Mineral	0.76	1.3	0.43
Chrome Yellow Medium	3.9	0.26	0.32
Ultramarine blue	13.	0.20	0.59

[a] Calculated according to the equation:

$$d_3 = 6/\rho S$$

where ρ is density, S is surface area in sq. m./g., and d_3 is diameter in microns.

Harkins and Jura (*17*) have gone farther and applied their method to about eighty-six porous solids. In all cases the agreement between the areas obtained by Equation 1 and those using a value of 4.06 for k in Equations 2 and 3 is within 20%. If they use their measurements to calculate the cross-sectional area that would have to be assigned to the nitrogen molecule to bring perfect agreement between their method (using Equations 2 and 3) and the method (*5*) of Brunauer, Emmett, and Teller (using Equation 1), they find that the areas per molecule range from 13.7 to 16.9 sq. Å. Furthermore, when the number of samples is plotted against the area value per molecule that has to be used, three peaks seem to occur corresponding to 14.05, 15.25, and 16.05 sq. Å. They conclude that, if one uses a value of 15.25 sq. Å. for the cross-sectional area of the nitrogen molecule, the agreement between the Brunauer-Emmett-Teller and the Harkins-Jura methods of using the low-temperature nitrogen adsorption isotherms is within ±10%.

Harkins and Jura may be correct in concluding that on porous materials a different cross section of the nitrogen molecule should be used for each solid in order to obtain accurate results. On the other hand, there is no assurance that constant k will be the same for porous and for nonporous materials. In any case, the agreement between the two methods is sufficiently good to warrant the conclusion that the adsorption of nitrogen at −195° C. can be relied upon for measuring the surface areas of finely divided and porous materials.

The amount of water vapor adsorbed from an air–water vapor mixture was used by Smith and Greene (*23*) for measuring the surface areas of a number of solids. Table V gives a summary of their results. Only those values are included for which there is an independent check by direct microscopic observation. It is evident that fair agreement exists between the water adsorption method and the microscopic method, though in some cases the results by the water sorption method are several fold greater or smaller than those obtained by direct microscopic examination. The authors are fully cognizant, apparently, of several sources of error in the measurements and take precautions to avoid them. They realize, for example, that strongly hygroscopic solids cannot be used with water vapor as the adsorbate because of chemical reaction between the water vapor and the solid. The same would hold true for solids on which water vapor is strongly chemisorbed. It is also necessary to avoid using the water vapor method on solids such as charcoal that adsorb little or no water vapor up to 0.5% relative humidity. Furthermore, they point out that careful drying of the solid initially is necessary to get rid of any surface water that might be present. Temperatures as high as 185° C. are employed for this purpose. They also realize the possible complications that might arise from the occurrence of capillary condensation, since the initial relative humidity is in the neighborhood of 50% and is accordingly high enough to cause condensation in very fine capillaries. The authors believe they avoid all such complications by taking their equilibrium readings after an equilibration time so short as to preclude the occurrence of the much slower capillary condensation. In only one respect does it appear that their method may be faulty. No precautions are mentioned for ensuring that the final relative pressure of water vapor is approximately the same for all samples of adsorbent. Unless the relative pressure of water is the same from sample to sample, as much as 100% error could easily be made in the relative surface areas. For example, if, as is probable, the water adsorption isotherms are S-shaped and conform roughly to Equation 1, the adsorption at 50% relative humidity would be twice as great as at about 10% relative humidity. Since the apparatus described by them contains only about 20 cc. of water vapor (at standard temperature and pressure) initially, and since the samples in Table VI would require, for a monolayer, amounts of water vapor ranging from 2 to 48 cc. per gram, this source of error would have to be guarded against. The simplicity of the apparatus and technique required for this method makes it attractive. If due precautions are taken to avoid the sources of error and if sufficient independent evidence is at hand to ensure that the water isotherms on a given adsorbent are normal, the method should yield useful results.

The evidence, then, for the existence of multilayer physical adsorption now appears to be overwhelming, because S-shaped nitrogen adsorption isotherms have been found on a variety of solids so prepared as to minimize any effect due to capillary condensation. For example, nitrogen adsorption isotherms at −195° C. on glass spheres that had been prepared by blowing sized ground glass through a hot flame show S-shaped curves even though the spheres were not in contact with liquids of any kind

Table VI. Comparison of Surface Areas of Solid Adsorbents Calculated by Harvey (*18*) and Estimated by Brunauer-Emmett-Teller Method

System	Surface Area. Sq. M./G.		
	Harvey adsorption	Harvey desorption	Estimate[a]
Silica aerogel–C_4H_{10} (0° C.)	607	722	393 (248)
Water-aged silica aerogel–C_4H_{10} (0° C.)	300	342	186 (123)
Silica aerogel II–C_6H_6 (15° C.)	438	525	(490)
TiO_2–CCl_4 (0° C.)	221	315	(310)
TiO_2 gel–C_6H_6 (20° C.)	214	...	(412)
TiO_2 gel–C_6H_6 (0° C.)	24	44	(29)
Fe_2O_3 gel–C_2H_5 OH	179	245	(211)
Water-aged Fe_2O_3 gel–C_2H_5OH	36	46	(52)
Cu–MnO_2–H_2O	158	...	(200)

[a] Values in parentheses were estimated by Harvey by the point B method.

after preparation and, therefore, presumably had no chance to form rough surfaces. Furthermore, adsorption on carbon black particles of a variety of sizes (as described in Table III), zinc oxide particles (*11*), and finely divided potassium chloride (*4*) and other nonporous crystals all yield uniformly S-shaped curves. Since the same type curve is obtained, regardless of the particle size, the shape cannot be explained on the basis of capillary condensation between the particles. It must be recognized that capillaries too small to be seen microscopically might be present on all these solids. However, it would be fortuitous if the tiny cracks and capillaries happened to be present on all of these various solids with sufficient uniformity to produce substantially the same type of S-shaped adsorption isotherm. Finally, the agreement between the measurements by Harkins and Jura (*16*) on titanium dioxide by the heat of wetting method and by the nitrogen adsorption method argues against the possibility that S-shaped nitrogen isotherms on this substance are due to cracks or capillaries, since the latter would cause erroneous surface area results by the water immersion method.

MONOMOLECULAR PHYSICAL ADSORPTION COMBINED WITH CAPILLARY CONDENSATION

During the last two years, two different groups of workers have made interesting approaches to the old suggestion (*21*) of calculating surface areas of porous materials by assuming that S-shaped adsorption isotherms are made up of monomolecular physical adsorption combined with capillary condensation. Even though it appears to be fundamentally incorrect thus to neglect multilayer adsorption, it is interesting to recapitulate briefly the results obtained by their respective procedures.

Table VII. Volume of Adsorbed Nitrogen in a Monolayer on Various Adsorbents (8)

(Values obtained from nitrogen adsorption isotherms at about 77° K.)

Adsorbent	V_m, Cc./G.	Point *B*, Cc./G.
Unpromoted Fe catalyst 973 I	0.13	0.12
Unpromoted Fe catalyst 973 II	0.29	0.27
Fe–Al_2O_3 catalyst 954	2.86	2.78
Fe–Al_2O_3 catalyst 424	2.23	2.09
Fe–Al_2O_3–K_2O catalyst 931	0.81	0.76
Fe–Al_2O_3 catalyst 958	0.56	0.55
Fe–K_2O catalyst 930	0.14	0.12
Fused Cu catalyst	0.05	0.05
Commercial Cu catalyst	0.09	0.10
Cr_2O_3 gel	53.03	50.5
Cr_2O_3 glowed	6.09	6.14
Silica gel	116.2	127.0

Harvey (*18*) suggested that, by assuming the S-shaped adsorption isotherms to be due to capillary condensation, it is possible to calculate the surface area of porous solids. He used the Kelvin equation to transform adsorption data into a curve relating the total volume of gas absorbed to the radii of the capillaries of the solid adsorbent. By subdividing this curve into a series of connected straight lines and assuming that the capillaries are cylindrical, he showed that the total area wetted by the capillary condensation would be the sum of the areas corresponding to each segment of the volume-radius curve. The area, ΔS, of each segment is given by the equation,

$$\Delta S = \frac{r^{*2}\, 4.607(V_2 - V_1) \log (r_2/r_1)}{(r^* - d)^2\, (r_2 - r_1)} \qquad (4)$$

where V_2, V_1 = volume of adsorption at and below radii r_2 and r_1, respectively

$r^{*2}/(r^* - d)^2$ = correction factor to take into account finite thickness d of monolayer of adsorbed gas

Table VI reproduces all of the results given in Harvey's original paper, for which a cross comparison of areas with those found by the multilayer interpretation of the adsorption is possible and for which Equation 4 was used.

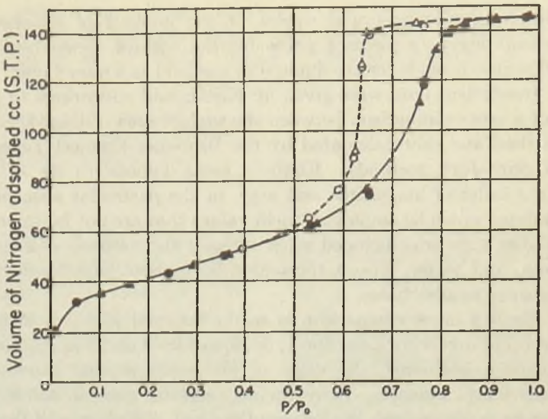

Figure 4. Adsorption of Nitrogen at −194° C. on Porous Glass (*8, 12*)

Solid triangles and circles indicate adsorption
Open triangles and circles, desorption

In connection with Table VI, Harvey realized that some uncertainty must arise from the fact that his calculations might be applied either to adsorption or to desorption curves. Usually when capillary condensation exists, the desorption curve lies well above the adsorption curve down to some definite low relative pressure. Such a curve is shown in Figure 4 for porous glass (*8, 12*). Columns 2 and 3 list the surface areas calculated by Harvey (*18*) with the help of Equation 4 for adsorption and desorption isotherms of various gas-solid systems. Column 4 compares surface area values calculated by him by means of Equation 1; in parentheses are the surface area values estimated by the point *B* method. As pointed out in an earlier paper (*5*), the point *B* method may give erroneously low values for certain gas-solid combinations, although, as Table VII shows, it appears to agree with the method using Equation 1 if nitrogen is employed as adsorbate.

The areas obtained with Equation 4 have the same approximate magnitude as those deduced by the multilayer interpretation of the isotherms. In general they are within ±50% of each other. As a matter of fact, with about three exceptions the Brunauer-Emmett-Teller or point *B* values are intermediate between the Harvey values for adsorption and desorption. Further experimental work is needed to compare with more certainty the results obtained by the two methods.

Kistler, Fischer, and Freeman (*19*) suggested a method for measuring surface areas similar to that of Harvey. It, too, is based on the assumption that capillary condensation accounts for all sorption in excess of a monolayer; it leads to an evaluation of the surface area of the capillaries that are filled during this process. Their method differs from that of Harvey, however, in that they make no assumptions as to the shapes of the capillaries involved.

From the fundamental equation,

$$p/p_o = e^{-ME/RT} \qquad (5)$$

where p/p_o = relative pressure
M = molecular weight
E = energy required to remove 1 gram of adsorbate from capillaries in which it has condensed

they derive the relation,

$$dA = \left(\frac{2.3RT}{M\sigma}\right) \log (p_o/p)\, dW \qquad (6)$$

where dA = an increment of area covered by capillary condensation of dW grams of adsorbate at relative pressure p/p_o
σ = surface tension
M = molecular weight of adsorbate

Graphical integration of a plot of the amount of adsorption against log p_o/p yields a value for the surface area when due allowance is made for the amount of gas held as a monolayer.

Insufficient data were given by Kistler and co-workers to permit a cross comparison between the surface area obtained by his method and that calculated by the Brunauer-Emmett-Teller or Harkins-Jura methods. Kistler's areas appear to be of the right order of magnitude and may, in the particular adsorption systems which he employed, yield values that are not far in error. Kistler's systems included silica aerogels and xerogels as adsorbents, and water, silicon tetrachloride, carbon tetrachloride, or benzene as adsorbates.

Until a cross comparison is made between Kistler's method and that involving Equation 1, or Equations 2 and 3 as applied to nitrogen isotherms, the value of his measurements cannot be accurately assessed. Nevertheless, certain general comments can be made on both the proposed method of Harvey and that of Kistler and co-workers. Both appear to require considerably more calculation and many more points on the adsorption isotherm than do the method of Brunauer, Emmett, and Teller (*5*) or of Harkins and Jura (*17*) using nitrogen adsorption isotherms. Both methods assume that complications due to multilayer adsorption can be neglected. Kistler and co-workers point out the certainty of the existence of capillary condensation in any system in which vapor is in contact with a proper capillary system under the right conditions of temperature and pressure. It is equally certain, however, that multilayer adsorption occurs on porous and nonporous solids at sufficiently high relative pressures. It is, therefore, probably not justifiable to ignore multilayer adsorption in calculations based on the occurrence of capillary condensation. Finally, surface area calculations from any adsorption isotherms involving hysteresis must involve a small degree of uncertainty, since values obtained for adsorption isotherms are somewhat different from those obtained for desorption isotherms.

Both the Brunauer-Emmett-Teller (*5*) and the Harkins-Jura (*17*) methods can be used to determine areas without resorting to relative pressures sufficiently high to form capillary condensation. Accordingly the contention of Kistler and co-workers (*19*) that the surface area determinations by the use of Equation 1 is in "error" because it neglects capillary condensation appears to be without foundation.

CONCLUSIONS

1. Low-temperature adsorption isotherms of nitrogen still seem to afford the simplest and most direct basis for measuring the surface area of finely divided porous adsorbents. The value of the surface area may be calculated either by plotting the data according to Equation 1 and evaluating V_m, the volume of gas required to form a monolayer, or by plotting them according to Equation 2 and calculating the area with the help of Equation 3. Ambiguity will arise only if the adsorbent has a large number of pores with diameters in the range 10 to 20 Å. For all other adsorbents the nitrogen adsorption method yields an apparently well substantiated value for the surface area of the solids.

2. Isotherms of gases other than nitrogen can also be interpreted on the basis of either Equation 1 or Equations 2 and 3. If Equation 1 is used, it is necessary to use some value for the molecular cross-sectional area of the adsorbate in order to calculate surface areas in absolute units. Such molecular areas can conveniently be calculated from the density of the liquefied adsorbate by a method already described (*10*). On the other hand, if the method of plotting proposed by Harkins and Jura is adopted (Equations 2 and 3), it is necessary to have a k value for the particular adsorbate involved. Only four numerical values of k have so far been provided by Harkins and Jura (*17*): for nitrogen at −195.8° C., 4.06; for water at 25° C., 3.83; for butane at 0° C., 13.6; and for *n*-heptane at 0° C., 16.9. Values for other gases may be obtained by direct determination of the isotherm of the desired adsorbate on the same sample of titanium oxide on which Harkins and Jura made the heat of immersion measurements, or on some other nonporous solid for which an area is available, based on low-temperature nitrogen adsorption.

3. The proposal of Wooten and Brown (*24*) affords an excellent means for extending the gas adsorption method to small surface areas by using an adsorbate whose vapor pressure at the temperature of the runs is small. They used ethylene at −195° and −183° C. and butane at −116° C. Beebe (*2*) suggested the use of krypton at −195° C. The extension of the gas adsorption method to adsorbates of low liquefaction pressures should greatly augment its general usefulness.

4. For many isotherms that yield S-shaped curves, the approximate position of the point corresponding to the completion of a monolayer is *B* on Figure 2. If, however, the heat of adsorption is sufficiently small, point *B* will have an erroneously low value for the volume of gas contained in a monolayer. To the author's knowledge, point *B* never yields values for a monolayer higher than V_m by more than experimental error. Hence, in general, as pointed out in an early publication, point *B* should not be depended upon in obtaining surface areas unless the gas used is nitrogen.

5. Methods of measuring surface areas based on the assumption that the S-shaped curves are a combination of monomolecular adsorption and capillary condensation are of doubtful validity because of their neglecting multilayer adsorption. Such methods require a larger number of adsorption points on the isotherms than do methods using either Equations 1 or Equations 2 and 3 and also somewhat more involved and extensive calculations. They are particularly questionable for adsorbents that are sufficiently finely divided to cause the outer or geometric surface to be an appreciable fraction of the total. In spite of these objections, the methods proposed by Harvey (*18*) and by Kistler and co-workers (*19*) seem to yield surface area values of the right order of magnitude. An exact and detailed cross comparison of the various methods on a number of sets of standard low-temperature nitrogen adsorption isotherms has not yet been made.

6. A method for measuring surface area proposed by Smith and Greene (*23*) and involving the adsorption of water vapor, can be used provided care is taken to avoid complications due to capillary condensation, chemisorption effects, and variations in the final equilibrated relative pressures of water vapor.

7. The numerous types of experimental evidence that seem to support the proposed methods for measuring surface areas by low-temperature adsorption isotherms lend a feeling of security to its employment. Nevertheless, the author prefers to consider the methods as still being in a test period and suggests that they be used critically and carefully.

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Presented before the Eleventh Annual Chemical Engineering Symposium (Adsorption and Ion Exchange) held under the auspices of the Division of Industrial and Engineering Chemistry, American Chemical Society, at Columbia University, New York, N. Y.

THE NATURE OF ACTIVE CARBON

John W. Hassler and William E. McMinn

WEST VIRGINIA PULP & PAPER COMPANY, TYRONE, PA.

Carbon is activated by mild oxidation with steam or carbon dioxide at 800–950° C. or by air at lower temperatures. Individual modifications of the basic process leave characteristic imprints on adsorptive properties. Specific compounds are adsorbed on appropriate active centers. Various species of active centers coexist on the carbon surface, and the over-all adsorptive power of the parent carbon is a function of the quantity and ratio of the different species. Evidence is found in several experimental approaches as follows: (1) the relation of activation time and methods to the development of specific adsorptive powers, and (2) the influence of prolonged grinding, chemical agents, and the solvent on existing adsorptive powers.

MANY types of active carbon are manufactured to provide for the divergent needs of different industries. Table I illustrates variations that exist in the specific adsorptive powers of different commercial carbons. It is apparent that a carbon which is best for one purpose can be quite inferior for another use; e.g., carbon J gave the greatest adsorption of phenol and yet was the poorest for adsorbing caramel or molasses color.

How should we interpret the variations in specific adsorptive power shown in Table I? Should we assume that on carbon A there is a single homogeneous surface having all the adsorptive powers of the parent carbon and, similarly, that a different type of homogeneous surface exists on each of the other carbons?

In an attempt to clarify some of these points, stock solutions were prepared as follows:

Solvent	Solute	Concn., G./L.	Other Conditions
Water	Methylene Blue	0.80	....
Water	Malachite Green	0.91	....
Water	Alizarin Red	0.73	Buffered to pH 6.2
Water	Ponceau Red	1.09	Buffered to pH 7.0
Water	Blackstrap Molasses	26.00	Buffered to pH 6.5
Water	Caramel	4.00	Buffered to pH 6.5
Water	Phenol	1.00	....
Water	Iodine	2.70	4.0 g. KI per l.
Alcohol	Methylene Blue	0.50	....
Alcohol	Malachite Green	0.43	....
Alcohol	Alizarin Red	0.23	....

Into 250-ml. Erlenmeyer flasks were introduced 100-ml. portions of the solutions with weights of carbon suitable to give an adsorption range between 60 and 99% removal of the solute originally present. The flasks were agitated on a Fisher Gyrosolver for 1 hour at 25° C. and then filtered. The residual concentrations of dye, molasses, and caramel were determined in a Klett-Summerson colorimeter. This instrument was calibrated by suitable dilutions of the original solution, a correction being made for the solute adsorbed by the filter paper. Iodine concentrations were determined by titrating an aliquot portion of filtrate with 0.01 *N* sodium thiosulfate and phenol by the bromate-bromide method (*4*). The data were then expressed in terms of the Freundlich equation (*1*) and plotted on log-log paper.

The adsorptive powers of the different carbons were compared at an equilibrium solution concentration of 0.1 millimole per liter for dyes and at 1.0 millimole per liter for phenol and iodine. Molasses and caramel adsorptions were compared at 90% color removal corresponding to a residual color of 35 yellow and 14 red (Lovibond scale) in a $2\frac{5}{8}$-inch column.

The adsorption of dye, phenol, and iodine were calculated as millimoles adsorbed per gram carbon. There is no definite knowledge of the color constituents of caramel and molasses; therefore, arbitrary color values were employed. The original solution was considered to contain 1 unit of color per 100 ml., and the adsorption was then calculated as color units per gram of carbon. Such values have no independent significance but establish the relative value of different carbons.

Where carbons have different isotherm slopes, obviously their relative value will be influenced by the equilibrium concentration selected for comparisons. In industry the equilibrium point is based on economic and individual technological factors, whereas in this work the selection is based on analytical considerations. The selection of another equilibrium point would not change the nature of the trends described in this paper, but would alter the relative value of carbons having different isotherm slopes. Therefore, to avoid unwarranted prejudices on any commercial carbons, they are reported under a code.

The selection of proper time of contact presented some difficulty since the rate of adsorption is not the same for all solutes or for all carbons. In all cases the rate of adsorption was very rapid during the first 5 or 10 minutes, and then fell off sharply. After an hour further changes were slight in most cases.

The bulk densities were determined by placing 100 grams of carbon in a graduated cylinder and tamping until no further shrinkage in volume occurred.

When the powdered active carbons of Table I were ground for an additional time, the adsorptive power at first increased slightly but then decreased as grinding continued (Table II). This was true of adsorption from aqueous solutions and also from the vapor phase. The extent of the change varied. Some carbons were greatly altered whereas a few were not measurably affected; this is not surprising since the mechanical strength of a carbon varies according to the raw material and the type of processing.

The changes that occurred within an individual carbon shed light on the nature of the active surface. If the surface of an individual carbon were homogeneous, a partial destruction of such a surface should produce the same relative change in all specific adsorptive powers. Frequently this relation did not hold; e.g., for carbon A the reduction ranged between 15% for phenol to 50% for molasses color (Tables I and II). Such variation in the effect of grinding on different specific adsorptive powers is evidence of a heterogeneous surface.

Table I. Specific Adsorptive Power[a] of Different Active Carbons (Aqueous Solution)

Carbon Code	Methylene Blue[a]	Malachite Green[a]	Alizarin Red[a]	Phenol[b]	Iodine[b]	Molasses Color[c]	Caramel[c]
A	0.84	1.07	1.25	1.35	5.1	0.8	1.3
B	0.74	0.74	1.10	1.24	4.6	0.6	0.9
C	0.70	0.74	1.00	1.30	4.5	1.1	1.6
D	0.37	0.45	0.62	0.60	2.8	0.7	1.2
E	0.30	0.34	0.45	0.60	2.5	0.6	1.3
F	0.44	0.19	0.39	1.20	4.3	0.2	0.4
G	0.83	1.15	1.10	0.83	3.1	1.0	1.0
H	0.73	1.10	0.95	0.57	2.9	1.1	1.0
J	0.50	0.27	0.60	1.60	4.6	Nil	Nil

[a] Millimoles adsorbed per gram carbon at an equilibrium solution concentration of 0.1 millimole per liter.

[b] Millimoles adsorbed per gram carbon at an equilibrium solution concentration of 1 millimole per liter.

[c] Color units adsorbed per gram carbon at 90% decolorization.

Table II. Adsorptive Power[a] of Carbons after 200 Hours of Additional Grinding (Aqueous Solution)

Carbon Code	Methylene Blue	Malachite Green	Alizarin Red	Phenol	Molasses
A_2	0.64	0.68	0.90	1.15	0.4
C_2	0.66	0.52	0.84	1.05	0.7
D_2	0.36	0.42	0.59	0.57	0.7
G_2	0.66	0.64	0.64	0.70	0.6

[a] Same basis as Table I. Subscripts of code letters indicate carbon was ground for 200 additional hours.

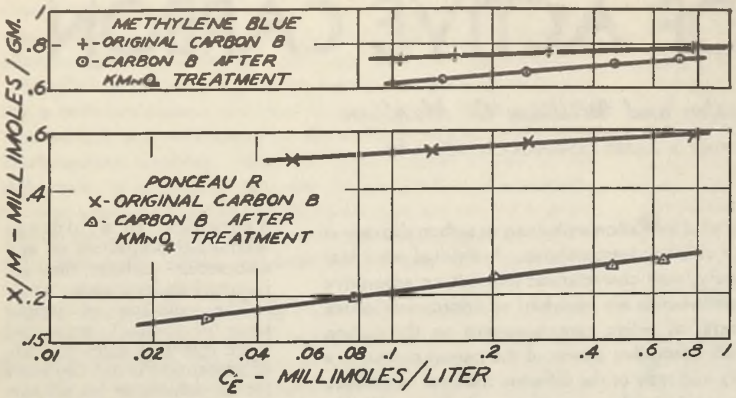


Figure 1. Change in Adsorptive Power Due to Treating Carbon with Potassium Permanganate

The concept of a heterogeneous active surface on carbon is supported by the changes resulting from the action of certain oxidizing chemicals; carbon B was allowed to react for several hours with 50% by weight of potassium permanganate in an acidified solution, bisulfite was added to reduce any unchanged permanganate, and then the inorganic constituents were removed by suitable washing. This treatment reduced the adsorptive power of the carbon, a reduction which ranged between 15% for Methylene Blue to 60% for Ponceau R (Figure 1). These facts indicate preferential oxidation of certain specific adsorptive powers. To date, this phase of our study has been limited to the action of potassium permanganate on two different carbons, but will be extended to cover other carbons and a greater variety of oxidizing reagents.

ACTIVATION

Another approach is found in activation data. Lengthening the time of activation generally increased the over-all adsorptive power, but in some processes all specific adsorptive powers do not develop simultaneously or at the same rate. Thus, in a study to produce active carbon from cellulose waste, the adsorptive power for phenol developed rapidly and reached a maximum value within a 30-minute activation period; the adsorptive power for molasses developed more slowly but continued to increase up to 60-minute activation:

Activation Time, Min.	Adsorption[a]	
	Phenol	Molasses
10	0.7	Nil
20	1.0	0.3
30	1.2	0.6
40	1.2	0.8
60	1.2	1.1

[a] Same basis as Table I.

Apparently the adsorptive powers for phenol and molasses were developed independently of each other.

It is convenient to define adsorption as occurring on active centers, but until more is known of the mechanism whereby an adsorbed molecule is attached to the carbon surface, there are advantages in broadly defining an active center as the sum of the forces which hold an adsorbed molecule. In line with this definition, let us further consider that several species of active centers are present on a heterogeneous surface.

There is evidence that an individual substance can be absorbed by different types or species of active center. This is revealed through several experimental approaches, one being the influence of the solvent. The carbons adsorbed less dye from solutions in alcohol than from water. This behavior could be due to many factors, including the effect of the solvent on the solubility, association, orientation, and ionization of solute, and the extent of such influence would vary from one dye to another. But these factors would not alter the relative adsorptive power of different carbons for a specific substance. Comparison of Tables III and I shows that changing the solvent altered the relative adsorptive power of certain carbons; e.g., carbons A and H were equivalent for adsorbing Malachite Green from an aqueous solution, but with alcohol as the solvent, carbon H had less than half the efficiency of A. Thus, the active centers which adsorb Malachite Green on carbon A have different properties from the corresponding centers on carbon H. Other examples can be developed from the data.

Support for the concept that an individual substance can be adsorbed on different species of centers is found in a study of adsorption isotherms. In the Freundlich isotherms (Figures 1 to 7) the vertical distance represents concentration on the carbon surface, and the horizontal distance represents the concentration remaining in solution. The slope of the line gives the rate of change of the equilibrium relation between adsorption and solution concentration. When different carbons are found to have different adsorptive capacity for a typical substance (e.g., iodine) and the isotherms are parallel, the difference between such carbons could arise from a greater number of active centers on the more powerful carbons (*2*). But such an interpretation is inadequate where the isotherms do not have the same slope, for the change in slope is evidence of different surface properties, and hence the active centers differ not only in number but also in kind.

Table III. Adsorption[a] of Dyes from Ethyl Alcohol Solution

Carbon	Methylene Blue	Malachite Green	Alizarin Red
A	0.26	0.113	0.35
C	0.15	0.029	0.43
D	0.07	0.017	0.14
E	0.08	0.008	0.17
F	0.12	0.018	0.12
H	0.07	0.050	0.24

[a] Millimoles per gram carbon at an equilibrium solution concentration of 0.1 millimole per liter.

The carbons in Figure 2 were produced from cellulose waste, activated by carbon dioxide at 850° C. for different periods. The parallel slope of the isotherms indicates that lengthening the time of activation created additional centers of a type characteristic of that process. Different methods were used to prepare each of the carbons shown in Figure 3; in one case the raw material was impregnated with calcium chloride, in the other, with zinc chloride. The difference in isotherm slope reveals that each

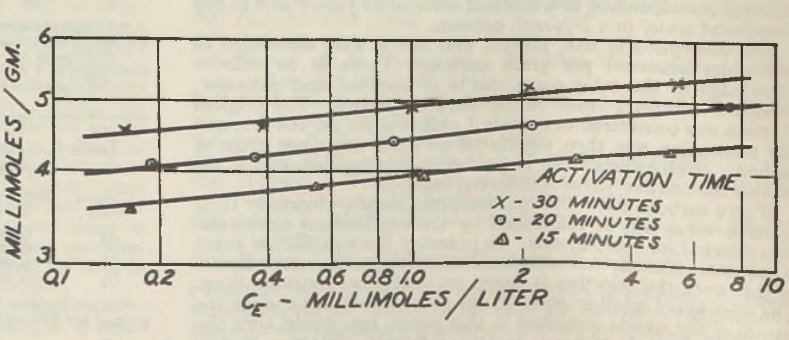


Figure 2. Influence of Time of Activation on Iodine Adsorption

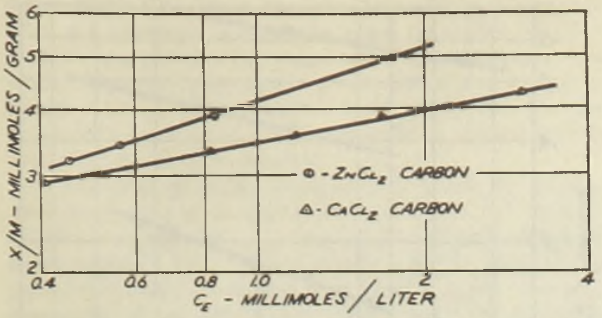


Figure 3. Iodine Adsorption by Different Types of Active Carbon

of these processes produced a distinct type of active center capable of adsorbing iodine. However, it does not always follow that a different activation process will result in a different isotherm slope; e.g., in Figure 4 several of the commercial carbons have the same slope and others have different slopes. No hard and fast rule can be drawn.

COMPETITION FOR ACTIVE CENTERS

Thus far the specific individuality of active centers has been emphasized, but this does not imply that an individual species has adsorptive power for only one kind of substance. The ability of many adsorbable compounds to displace one another's adsorption indicates competition to occupy the same active centers, although in this we must not exclude other factors—e.g., a steric hindrance by the more strongly adsorbed molecules. The different species of active centers may be so close together that there is not sufficient room for the simultaneous adsorption of all the different kinds of molecules that could be held independently.

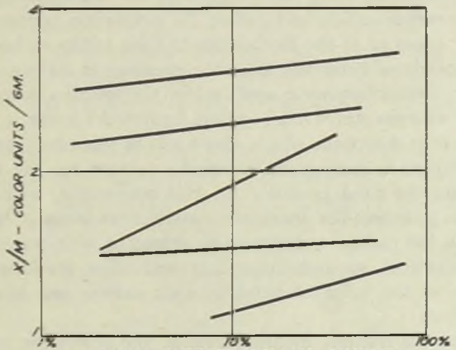


Figure 4. Adsorption of Blackstrap Molasses Color by Commercial Carbons

If displacement of adsorption were accepted as evidence that an individual species of center can attract different substances, then many of the differences between carbons could arise from various assortments of a relatively few species. This can be illustrated by three hypothetical species with indicated adsorptive powers:

Species	Relative Adsorptive Power		
	Methylene Blue	Iodine	Molasses
X	1	3	2
Y	2	1	3
Z	3	2	1

Various proportions of a few such species could provide many variations in adsorptive power. There is no present knowledge of how many species exist, and the number 3 is used here only as a convenient number for illustration.

If a substance is adsorbed simultaneously on several species of centers, then an isotherm derived from experimental data would be a composite of these individual primary centers. Experimental evidence of such composite nature would be indicated if a partial loss of adsorptive power were accompanied by a change in isotherm slope. An indirect study consisted of adsorbing one substance and then using the carbon to adsorb a second substance, under such conditions that the first material would not be displaced. In one case a dye was adsorbed from an aqueous solution, and the carbon was separated, washed, dried, and then used to adsorb vapors of the solvent in which the dye is not soluble. The procedure was also reversed; the solvent vapor was adsorbed first, and the carbon then used to decolorize an aqueous solution of the dye. The upper isotherm in Figure 5 shows the adsorption of Methylene Blue by the original carbon; the lower isotherm is for the same carbon containing adsorbed carbon tetrachloride. The presence of carbon tetrachloride decreased the adsorption and resulted in a steeper slope. Here we can assume that adsorbed carbon tetrachloride preferentially blankets certain species of centers and leaves the dye to be adsorbed on only those types of centers which do not strongly adsorb carbon tetrachloride.

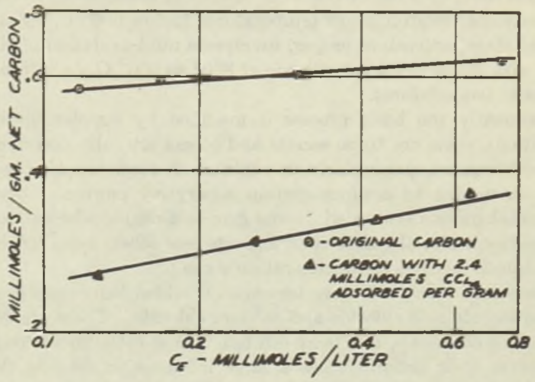


Figure 5. Influence of Prior Adsorption of Carbon Tetrachloride on Dye Adsorption

The effect of other treatments was also studied. Frequently the evidence provided by a change in isotherm slope is not clear-cut. In many cases the treatment appreciably reduced the adsorptive capacity of the carbon and yet made little if any change in the slope. Before deciding that this disproves the theory of a composite nature of experimentally derived isotherms, we should examine the possible mechanism of the change. First, there is no reason to conclude that a treatment (e.g., grinding or the use of a chemical agent) operates exclusively on only one species of primary center. Probably there is partial though unequal destruction of many species. The reduction in the amount of adsorption is the sum of the individual effects, whereas a change in isotherm slope is a function of a difference. To illustrate (Figure 6), an observed isotherm *O* is assumed to be a composite of two primary isotherms *X* and *Y*. If *X* and *Y* are reduced to the same proportionate extent, then the composite isotherm *O* will move to a lower level but the slope will not change. The slope will change only if *X* or *Y* is destroyed to a greater extent than the other. Moreover, the difference between experimentally determined isotherms is seldom large; if this carries through to primary isotherms, there would have to be considerable excess destruction of one surface before a change in the observed slope would be clearly defined in experimental work.

In using isotherm slopes to differentiate between the species of active centers, it is important to make comparisons under identical experimental conditions. In an experiment to adsorb Malachite Green from various mixtures of alcohol and water

(Figure 7), any increase in the proportion of alcohol resulted in a decreased adsorption of dye and a change in isotherm slope. Here the change in slope is not necessarily evidence of different types of centers; other factors could produce this effect since the solubility, degree of ionization, and association change as the composition of the solvent is altered.

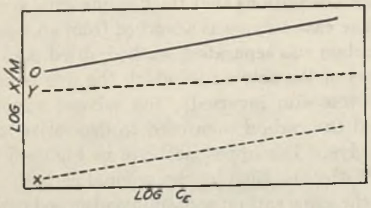


Figure 6. Isotherm Slopes

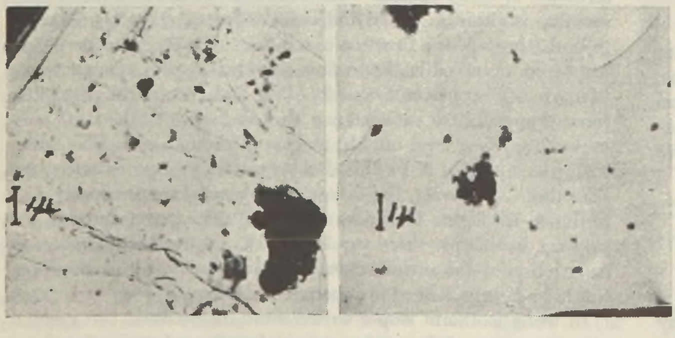
The factors responsible for variations in specific adsorptive power reside in the process of activation. Generally speaking, the process of activation embraces two broad divisions or stages. First is the carbonization of the raw material in which the wood, coconut shell, or other carbonaceous material is subjected to carbonization at relatively low temperatures (below 600° C.). The second stage, activation proper, involves a mild oxidation of the char with steam or carbon dioxide at 800° to 900° C. or with air at lower temperatures.

Frequently the basic process is modified by supplementary conditions, some are trade secrets and others are fully described in the literature, particularly in patents. A sequence of stages may be needed to produce certain adsorptive powers. Often various chemicals are added; some give best results when added to the raw material before charring, whereas others need not be added until just before the activation stage.

Chemicals which are more beneficial if added before carbonization include zinc chloride and calcium chloride. These are dehydrating chemicals, but their full function is little understood. Whatever their action, it has a large influence in shaping the specific adsorptive powers finally developed.

Table IV. Effect of Grinding on Adsorptive Power of Carbons

Carbon	Condition	Bulk Density, G./100 Ml.	Adsorption of Dyes from Ethanol Soln., Millimole/Gram Carbon: Methylene Blue	Malachite Green	Alizarin Red
A	Original	25	0.26	0.11	0.35
A_2	Ground 200 hr.	45	0.23	0.09	0.34
G	Original	31	0.12	0.07	0.25
G_2	Ground 200 hr.	40	0.12	0.12	0.22
H	Original	33	0.07	0.05	0.24
H_2	Ground 200 hr.	60*	0.11	0.08	0.23



Original powdered form After additional grinding for 200 hours

Figure 8. Electron Photomicrographs of Carbon G (× 5000), Inked Lines Represent One Micron

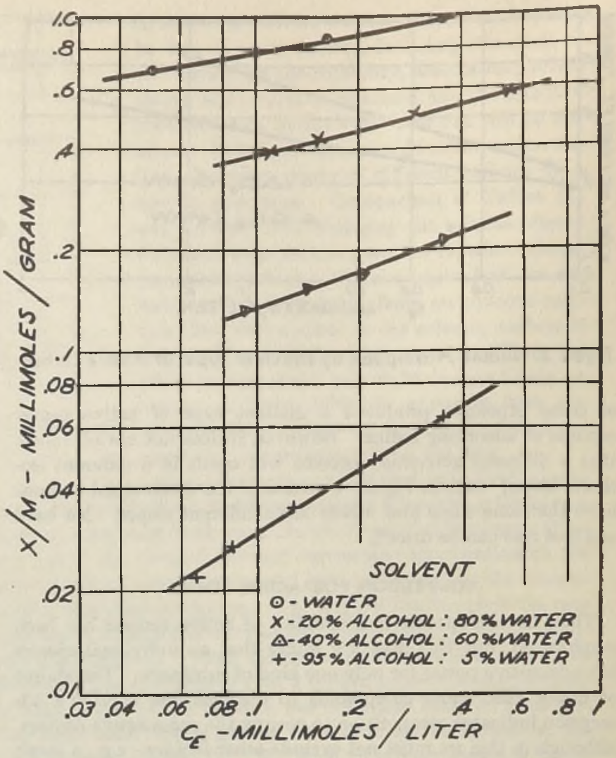


Figure 7. Adsorption of Malachite Green from Mixtures of Ethyl Alcohol and Water

Many chemicals have been suggested for impregnating char after the carbonization and before the activation proper. We can only guess as to the mechanism of their influence based on certain associated behavior; thus, the presence of certain chemicals (e.g., orthophosphoric acid) raises the ignition point of a charcoal, whereas others (e.g., sodium hydroxide) lower it. This influence may determine which atoms will be selectively oxidized during activation and, in turn, set the pattern for the atomic spacing on the final product. In this connection, with some activation processes the inorganic constituents initially become bonded to the carbon and cannot be extracted with water until after activation, an indication that activation involves some oxidation at the point of bond between carbon and inorganic constituents.

Each of the various modifications of the activation process leaves a characteristic imprint which is revealed by the relation between the specific adsorptive properties. This imprint can be of value when investigating a possible infringement of a patented manufacturing process.

EFFECT OF GRINDING

It is not apparent why long grinding causes a loss in absorptive power (Figure 8); probably many factors contribute to the change. The carbons after grinding showed an increase in apparent wettability and also in bulk density (Table IV). The latter suggests that long grinding destroys capillaries in which much adsorptive power may reside. A little longer time was required for the finely ground carbons to reach adsorption equilibrium.

The detrimental effect of grinding was much less apparent when comparisons were made using alcohol as a solvent, and in some cases a carbon had greater adsorptive capacity after grinding than before (Table IV). There appears to be a relation between this effect and a decrease in adsorptive power for alcohol (as measured in vapor phase). This suggests that some carbons in their original form (i.e., before grinding) adsorb alcohol so strongly as to form a blanket through which it is difficult for dye molecules to penetrate and find the room to occupy active centers on which they otherwise would be adsorbed.

In conclusion we quote a comment of Robinson (*3*), made in connection with work on the vitamin B_2 complex: "At the present time, our knowledge . . . . . is rather like a partially completed jigsaw puzzle, in which the final picture is still invisible, though parts are beginning to assume recognizable shapes. One day, presumably, all the pieces will fit together and it will be possible to see the complete picture, though one can only guess at it at the moment."

ACKNOWLEDGMENT

The authors express appreciation to George B. Hughey and Daniel O. Adams, West Virginia Pulp & Paper Company, for the preparation of the electron photomicrographs.

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PRESENTED before the Eleventh Annual Chemical Engineering Symposium (Adsorption and Ion Exchange), held under the auspices of the Division of Industrial and Engineering Chemistry, AMERICAN CHEMICAL SOCIETY, at Columbia University, New York, N. Y.

WATER ADSORPTION MEASUREMENTS ON SILICA GEL

Roger K. Taylor

THE DAVISON CHEMICAL CORPORATION, BALTIMORE 3, MD.

ADSORPTION measurements for water on silica gel have been made, by both static and dynamic methods, over a range of relative humidities in the neighborhood of room temperature (*5*, *8*). Over the limited range of temperature the adsorption at a given P/P_o value appeared to be virtually independent of temperature. The present work was undertaken to obtain data over a wider range of temperatures; and it was hoped that some simple relation might be found to hold, at least approximately, between temperature and pressure for a given ratio of water to gel.

As it has been considered that the presence of permanent gases is the cause of adsorption-desorption hysteresis (*7*, *8*, *11*), it was decided to make measurements by the static method in the absence of air, using all-glass apparatus with no stopcocks exposed to the evacuated system (Figure 1). The sample was contained in bulb *A*, provided with a thermocouple well. The dead space above the sample was small, the volume between the top of the sample and the mercury surface in the connecting tube being 5–10% of the (apparent) volume occupied by the gel. Two tungsten contacts were sealed into the tube connecting *A* with the rest of the apparatus, so that when mercury completed an electric circuit between them, its surface was in a reproducible position. The sample tube was surrounded by a glass jacket, with asbestos packed over the top and into the bottom; the jacket, in turn, was surrounded by a tube furnace, which could be regulated to give the desired temperature. During a run a slow stream of air was led downward through the jacket to equalize the temperature.

Pressures were measured on a closed-end manometer, *B*, provided with a scale divided into millimeters. Upper limit of the scale was about 900 mm. The manometer was so arranged that the space above the mercury could be freed of gas by raising the mercury and sweeping the gas through capillary trap at the top.

A modified McLeod gage, *C*, was used both for measurement of low pressures of air or water vapor and for low concentrations of air in water vapor (*9*). The comparison tube was closed, and the relative volumes were such that if water vapor was present in excess of about 20% of its vapor pressure, condensation occurred both in the gage and in the comparison tube when the mercury was raised to the reference marks; accordingly, the pressure of water vapor canceled out. The reading of pressure of permanent gas was taken just as if water vapor were absent.

Unit *D* provided measurement of the quantities of water transferred to and from the sample. By cooling, water could be condensed in either of two calibrated tubes for measurement; and in case a portion of water was being removed, it might then be distilled into one of the small bulbs and sealed off, for a gravimetric check.

The unit providing air-free water is shown in Figure 2 (*1*, *10*). It was essentially a fractionating column; permanent gases accumulated at the top and were removed by opening the unit periodically to vacuum. The water in the reservoir was circulated by a small flame beneath the double-wall side tube. As the water in the side tube warmed up, increasing vapor pressure forced it up the outlet tube; it could not return to the reservoir through the lower connection because of the floating spherical check valve. It finally blew over, spreading in a thin film on the wall of the reservoir; thereupon a fresh portion entered through the check valve, and the cycle was repeated. Passage of cool tap water through the condenser at the top ensured the continuous flow of water vapor up the column.

In the absence of air, pressure-temperature measurements for silica gel–water have been made, up to about 900 mm. pressure, with 1 to 30% added water. The data give a straight-line relation on a Cox chart. In the absence of air, no hysteresis is detected for changes of temperature or of composition. In the presence of 10 mm. partial pressure of air, no hysteresis is detected for changes of temperature.

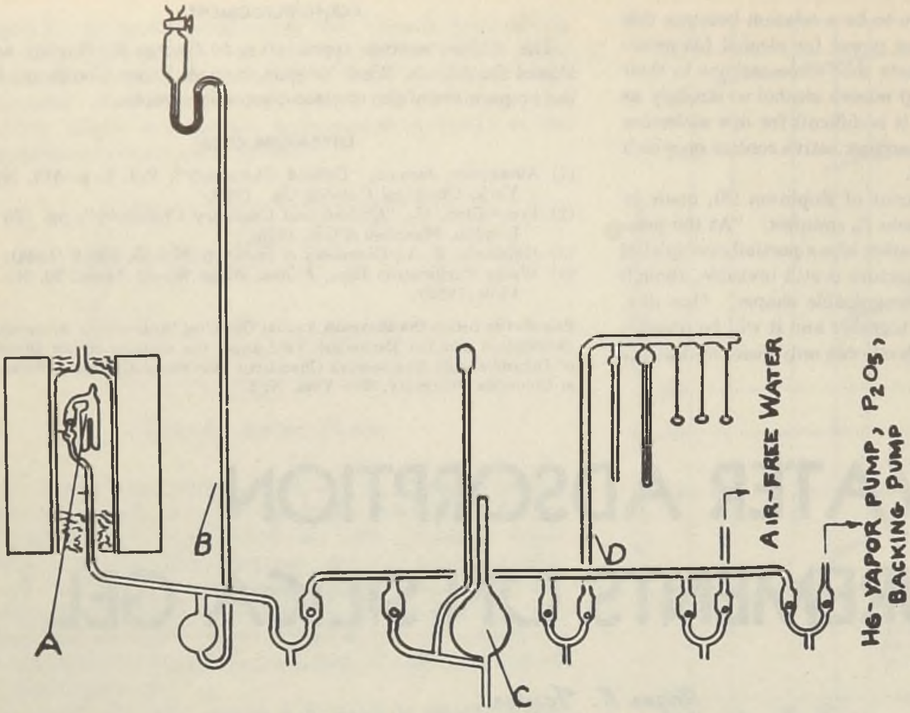

Figure 1. All-Glass Apparatus for Measuring Adsorption

The various units were connected to the manifold through Y-traps with floating spherical check valves (Figure 3). By suitable manipulation of the stopcocks, the mercury was brought to and held at the desired position.

METHOD OF OPERATION

A weighed sample of silica gel, of known water content, was introduced into the sample tube and the latter was sealed. Pumping was then commenced and continued until the partial pressure of air was low. As a general rule, in pumping either the sample or the water unit, direct communication was not made between the unit and the pump; rather, the manifold and gage were opened alternately to the pump and to the unit. Air was removed from the sample by alternate adsorption, and desorption at elevated temperature, of water, and required considerable time. In the earlier stages the desorbed water was condensed in one of the measuring tubes, the vapor phase being pumped off whenever the partial pressure of air built up enough to interfere with distillation. Later, when air removal was more nearly complete, the water was distilled directly into the water unit; most of the air remained above the top plate and was transferred to the evacuated gage for measurement almost completely by a single expansion.

During the course of air removal, it was observed that when water was removed from the sample by progressive increase of temperature, the last portions at the highest temperatures carried the highest concentrations of air; the first fraction might show virtually none. This is not in accord with the view that adsorbed gases should be displaced from the silica gel by the preferential adsorption of water.

When the air had been removed to the extent that at no stage did its partial pressure amount to more than a few thousandths of a millimeter, the sample was brought to the chosen activation temperature and held there for several hours while in communication with the water unit, the pressure being noted. This defined the initial state of the sample. An appropriate quantity of water was then condensed in a measuring tube, and the sample was cooled while open to this measured portion of water. After it had been adsorbed, mercury was brought to and kept at the reference contact, and pressure readings were taken at various temperatures. As the dead space between the sample and the mercury surface was small, the graph obtained may be regarded as an isostere. Successive measured portions of water were added in the same way, to obtain isosteres for various water contents. Water could also be removed from the sample; it was collected in a measuring tube and then distilled into one of the small bulbs and sealed off for gravimetric determination.

At the completion of tests on a given sample, dry air was admitted and the sample tube was cut from the apparatus to permit determination of the final water content of the sample; from this and from the measurements of quantities of water added and subtracted, the ratio of water to sample corresponding to the various isosteres was computed. Values thus obtained could be compared with those calculated from the temperature and pressure of activation at the beginning of the series.

Temperatures were taken by thermocouple, which was calibrated against a National Bureau of Standards certified thermometer. Additional check was obtained by taking pressure and temperature readings with liquid water in the sample bulb; temperatures from vapor pressure of water checked thermocouple indication within 1° C.

At the time these experiments were made, equipment for the precise automatic control of temperature was not available, and manual control was used. Temperature variation probably represents the major source of error in the data; low thermal conductivity of the sample was a complication as the thermocouple was at the center and did not immediately reflect temperature changes of the environment. Technique finally adopted was to bring pressure to a chosen value by manipulation of heating and to hold it there until drift of thermocouple reading apparently ceased.

In some of the accompanying data, pressures with ascending and descending temperatures do not agree. At first sight this might be taken as evidence of hysteresis; but as the higher pressures are observed with rising temperatures and hysteresis would produce the opposite effect, the explanation must be sought elsewhere. Incomplete attainment of thermal equilibrium, in these cases, appears a plausible cause for the disagreement; with rising temperature and temperature gradient from surroundings to thermocouple, the thermocouple at the center of the gel would show a reading lower than the average temperature of the sample.

Pressure measurements are subject to correction for vapor pressure and for lower density of mercury in the manometer leg connected to the sample when it is at elevated temperature. These corrections were not applied; they are opposite in sign and, in most instances, probably of no greater magnitude than variations caused by temperature fluctuations. Data obtained are presented in Table I.

Table I. Water Adsorption Measurements

T, ° C.	P, Mm. Hg	P/P_o	T	P	P/P_o	T	P	P/P_o	T	P	P/P_o	T	P	P/P_o
1% H_2O			3% H_2O			2% H_2O			5% H_2O			10% H_2O		
94.5	4.0	0.0064	69	10.5	0.0469	114	60	0.0489	50	7.8	0.0865	53	18	0.168
121	19.3	0.0126	97	48	0.0704	149	218.5	0.0630	59	14.3	0.0990	60	28	0.187
149	67	0.0193	111	92.5	0.0831	168	387	0.0684	67.5	24	0.1148	67	41.6	0.203
167	134.3	0.0243	126	165	0.0832	191	713	0.0741	75.5	36.8	0.1248	68.5	45.4	0.207
181	213	0.0277	138	243.5	0.0950				84	54	0.1310	75	64.2	0.222
197	353	0.0322	149	346.5	0.0998	4% H_2O			94	86	0.1387	86	108.4	0.240
207	467	0.0347	157	465	0.1082	71	19	0.0779	105.5	140	0.1518	94.5	148	0.238
221	650	0.0366	162	560	0.1149	100	75.5	0.0994	117	216	0.1595	104	230	0.263
232	862	0.0396	170	687	0.1158	126	213.5	0.1189	128	334	0.1752	115	346	0.273
						146	431	0.1346	138	447	0.1744	132	602	0.280
15% H_2O			20% H_2O			157.5	643	0.1525	146	587	0.1832	137	699	0.281
40.5	15.4	0.272	41	20.3	0.348	168	825	0.1457	154.5	756	0.1906	143	869	0.294
57	37.8	0.291	47	29.5	0.371							139	751	0.285
62	50.3	0.307	56	48.4	0.391	25% H_2O						138	725	0.283
71	84	0.344	64	74.8	0.416	29	13.1	0.436	45	32.5	0.452	131	570	0.273
81	128	0.346	73	120	0.451	29	13.3	0.444	59	70.7	0.496	124	455	0.270
89	184	0.364	83	180	0.449	39	23.3	0.445	71	132	0.541			
100.5	302	0.391	94.5	284	0.456	47	37.9	0.476	81	207	0.560			
121.5	612	0.392	103	407	0.482	54	56.5	0.501	86	263	0.582			
125	697	0.400	110	528	0.491	60	77.6	0.520	100	427	0.562			
132.5	837	0.383	111	575	0.517	67	111	0.542	110	630	0.586			
127	731	0.395	113	613	0.516	73	151	0.568						
119	538	0.372	122	809	0.510	84	236	0.566	30% H_2O					
117	509	0.376	125	905	0.519	91	316	0.579	24	12.9	0.575	28	14.9	0.526
116	491	0.375	126	895	0.499	94.5	353	0.568	37	28.7	0.609	64	119	0.665
114	468	0.382	122	772	0.487	95	367	0.580	42	39.3	0.639	79	238	0.699
111	396	0.356	100	335	0.441	103	514	0.608	49	58	0.660	94	435	0.711
105.5	306	0.332				108	637	0.634	51	68	0.700	26	13.7	0.545
101	271	0.344	26	6.6	0.262	110	647	0.601	62	111	0.677	105	606	0.670
96	220	0.334	49	31.7	0.360	118	869	0.622	70	170	0.726	108	711	0.708
86	139	0.308	73	115	0.432	116.5	834	0.625	82	276	0.717			
			93	269	0.457	103	468	0.554	94	434	0.710			
			109	530	0.510	100	416	0.548	106	662	0.706			
			119	735	0.509									

ISOSTERES

Plotted on a Cox chart (Figure 4), a graph of log P *vs.* modified 1/T (*2*, *3*, *4*), the points lie reasonably close to straight lines; greatest deviations are at the lower pressures, where pressure readings are proportionately less accurate. A similar graph is shown elsewhere (*6*), but with no information as to source of data or experimental details.

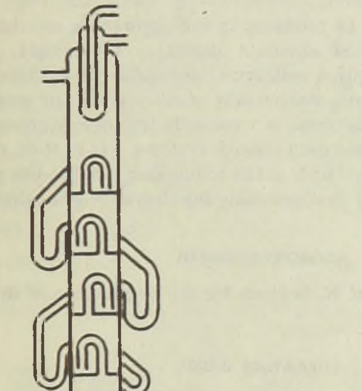

Figure 2. Unit for Providing Air-Free Water

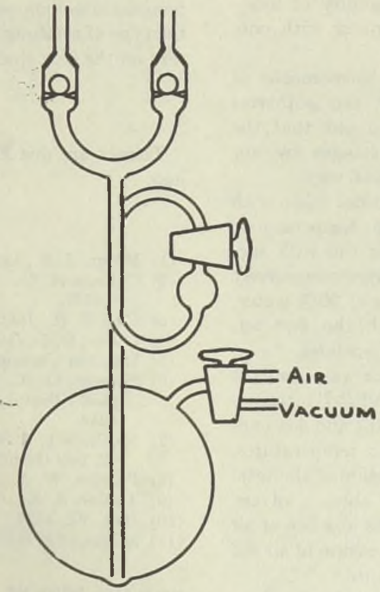

Figure 3. Y-Trap with Spherical Floating Check Valve

The same data are presented in another form (Figure 5), as isosteres on a graph of relative humidity *vs.* temperature. This plot gives somewhat greater separation of the isosteres. It is very sensitive to errors in temperature readings. Over the range of measurements, the relation appears to be linear; but linearity must obviously fail at sufficiently high or sufficiently low temperatures and pressures. It may be speculated that the approach to the 0 and 1 values of P/P_o would be asymptotic.

The data are typical of those obtained with this apparatus. The concentrations of water given are subject to some uncertainty; accidental admission of air to the sample on one or two occasions necessitated reactivation, and it was found late in the investigation that apparently the activation procedure was not sufficiently prolonged to bring the water content to the same value in all cases. Most of the data presented here are self-consistent in that they are from the same series of measurements without reactivation, and the differences in water content are known from direct measurement. In some of the runs after reactivation, the water content may have been different by as much as 2% from the supposed value. In all cases the data for given isosteres gave straight lines on the Cox chart, but the straight lines were not always coincident with others for supposedly the same water content. For this reason some of the later data are omitted, although the P-T values are probably better from improved technique and give smoother graphs. This unfortunate lack of precise definition of water content, however, does not in any way alter the general pattern of converging straight lines on the Cox chart. The point of convergence is approximately 3.5×10^6 mm., 1000° C. Silica gel of another type was tested in the same way and gave similar results; spacing between the isosteres and the point of convergence were slightly different from those shown here.

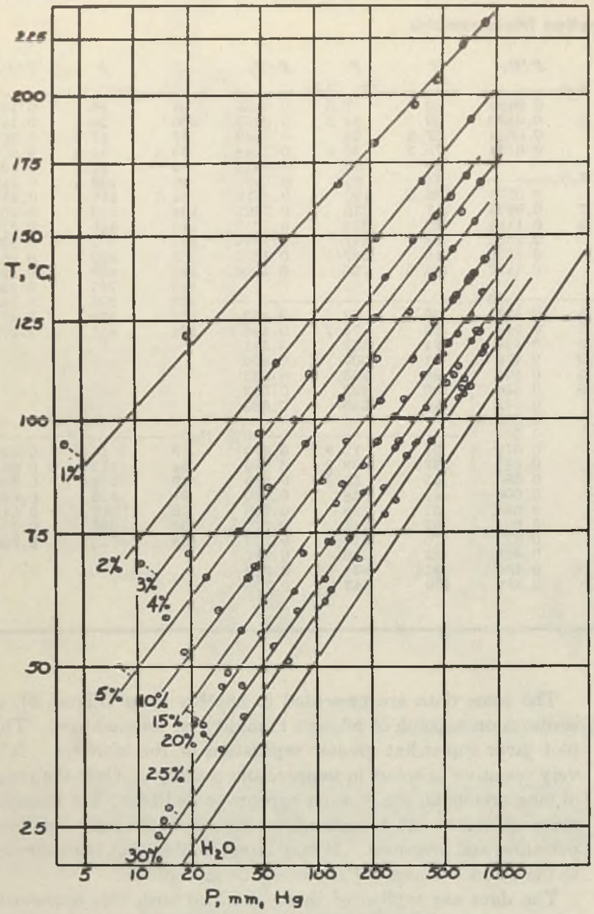

Figure 4. Cox Chart

Per cent water is amount added to activated (525° F.) gel, based on weight of activated gel.

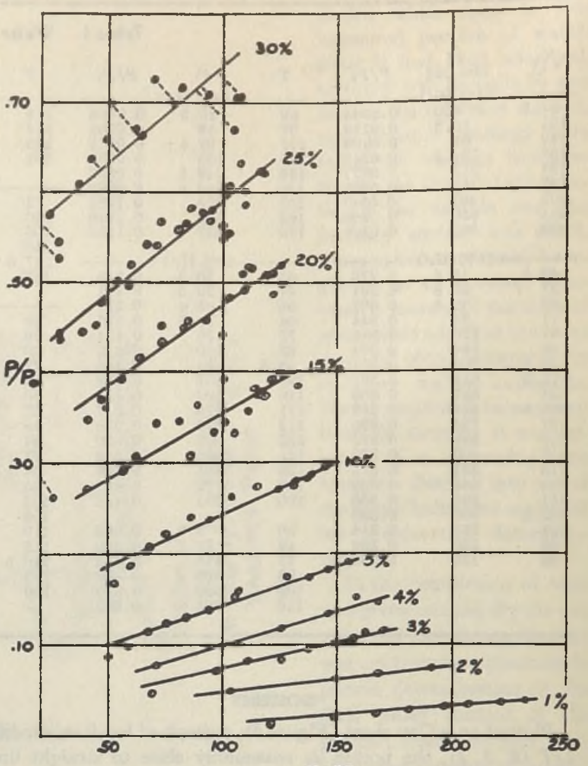

Figure 5. Isosteres of Relative Humidity vs. Temperature

The utility of the Cox chart lies in the possibility of locating an isostere with only two experimental points or with only one if the point of convergence is known.

Considerable attention has been given to the phenomenon of hysteresis in adsorption. Commonly, however, the isotherms have been involved; and it should be pointed out that the following observations involving temperature changes are not directly applicable to isotherms followed in the usual way.

No consistent trend was detected between readings taken with ascending and those taken with descending temperatures. Furthermore, after a series of isosteres had been run with successive additions of water, the same quantities were successively removed and check runs were made at 30, 25, and 20% water; the second set of isosteres was coincident with the first set. Points from both sets are plotted together on the isosteres.

With 5% and again with 30% added water, air was admitted to the extent of about 10 mm. partial pressure, and *P-T* measurements were taken. In both cases data for ascending and descending temperatures were coincident; at the higher temperatures, where the 10 mm. of air pressure was a small fraction of the total pressure, the data checked those taken in the absence of air. Thus in this work no evidence of hysteresis in the absence of air was found; and the presence of 10 mm. partial pressure of air did not cause it, in changes of pressure with temperature.

Aside from questions of precision and accuracy of the data here submitted, an explicit statement should be made as to the range of applicability. Silica gel is not a substance of absolutely fixed composition and properties; rather, by suitable changes in methods of preparation, corresponding variations over an appreciable range can be produced in such properties as adsorption characteristics and apparent density. Accordingly, the above data, or adsorption isotherms obtainable from them by cross plotting, are representative only of silica gel of the specific type employed; and the same is necessarily true of any pressure-temperature-composition data on such systems. It is, then, only the type of relationship (such as the converging straight-line pattern on the Cox chart) that possesses any degree of generality.

ACKNOWLEDGMENT

Thanks are due Earl K. Seybert for the preparation of drawings.

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Presented before the Eleventh Annual Chemical Engineering Symposium (Adsorption and Ion Exchange) held under the auspices of the Division of Industrial and Engineering Chemistry, American Chemical Society, at Columbia University, New York, N. Y.

Thermodynamics of Producer Gas Combustion

Application to Internal Combustion Engines

A. P. OLESON AND RICHARD WIEBE

Northern Regional Research Laboratory,
U. S. Department of Agriculture, Peoria, Ill.

The composition and heats of combustion of producer gas derived from various raw materials are given. A nomograph is presented for calculating the heats of combustion of producer gas mixtures containing hydrogen, carbon monoxide, and methane. The theoretical air-fuel ratios of producer gas are compared with those of other fuels used in internal combustion engines, and attention is called to their importance in connection with carburetor design. The heat of combustion of a mixture of producer gas with theoretical air is considerably lower than that of gasoline or alcohol; and lower power output must be expected from such a mixture run under identical conditions with the liquid fuels mentioned above. The thermodynamic properties of two typical producer gas mixtures are calculated, and the results shown on charts. A sample calculation gives temperatures and pressures at various points of the Otto cycle, as well as work, mean effective pressure, and efficiency. The effects of compression ratio and intake-manifold pressure on mean effective pressure and thermal efficiency are shown by charts. It is pointed out that extreme compression ratios are not so practicable for an Otto cycle engine as an increase in manifold pressure, since a relatively low supercharge pressure gives a power output equivalent to that of gasoline. It would be possible to use such a fuel in a Diesel gas engine.

THIS laboratory has been interested in the possible utilization of agricultural residues as sources of producer gas in this country. A comprehensive laboratory investigation was made with two gas generators, from which certain results are drawn for use in this paper. A detailed account of these investigations will be published later. As a supplement to the experimental work, thermodynamic calculations on two representative gaseous mixtures are presented here in order fully to evaluate all the possibilities in the use of such a fuel. These calculations enable one to predict temperature, maximum pressure, mean effective pressure, work, and thermal efficiency of these mixtures when used as fuels in internal combustion engines, as well as to make comparisons with similar data obtained for octane (*13*, *14*, *26*) and for alcohol (*27*).

A large amount of work has been done on various fuels that may be used in portable gas generators, as evidenced by a voluminous literature. An extensive bibliography on "Theory, Design, Fuels, Performance, Utilization, and Economics of Gas Producers" is available on application to this laboratory. Woods (*29*) made two series of calculations of the maximum temperature of combustion of a producer gas mixture having the following composition: carbon dioxide, 2%; carbon monoxide, 31%; methane, 0.5%; hydrogen, 9.5%; nitrogen, 57%. This gas was mixed with various proportions of air at a fixed compression ratio of 6 to 1 and at an initial temperature of 212° F. In his first series Woods took into account only the dissociation of water into hydrogen and oxygen, and of carbon dioxide into carbon monoxide and oxygen; in the second set of calculations the formation of nitric oxide was also included. For a theoretical mixture the maximum temperature of combustion was 4627° Rankine by the first method, and 4597° R. by the second, a lowering of 30° R. due to the nitric oxide reaction. Making the same assumptions, a temperature of 4595° R., almost identical with the second of the two figures, was obtained when the data for producer gas mixture 2 (Table II) were used, although in this work the formation of atomic hydrogen and oxygen, as well of OH, was also considered. This should tend to reduce the temperature still further; however, the slight difference in composition may, at least in part, account for the discrepancy. The importance of dissociation at high temperatures and pressures is illustrated in Table I. Even though the concentrations of some components may seem insignificant, these values, when multiplied by their heats of dissociation, make an appreciable contribution to the internal energy of the system.

TABLE I. EQUILIBRIUM CONCENTRATION OF DISSOCIATION PRODUCTS, IN MOLE PER CENT, AS A FUNCTION OF PRESSURE AND ABSOLUTE TEMPERATURE

Component	3960° R.			4680° R.		
	312.16 lb./sq. in.	954.7 lb.	1947.7 lb.	316.76 lb.	964.4 lb.	1963.4 lb.
NO	0.128	0.101	0.094	0.560	0.445	0.391
N_2	75.335	75.416	75.462	74.310	74.646	74.822
OH	0.129	0.086	0.070	0.624	0.426	0.336
H_2	0.038	0.028	0.021	0.139	6.104	0.084
H	0.003	0.001	0.001	0.032	0.016	0.010
H_2O	6.370	6.408	6.427	5.937	6.104	6.184
CO	0.539	0.397	0.300	2.243	1.688	1.377
CO_2	17.264	17.422	17.528	15.989	15.368	16.336
O	0.003	0.001	0.001	0.048	0.022	0.013
O_2	0.191	0.140	0.096	0.739	0.560	0.447

Component	5400° R.		
	326.6 lb.	988.4 lb.	2003.9 lb.
NO	1.434	1.246	1.115
N_2	71.977	72.859	73.309
OH	1.707	1.250	1.015
H_2	0.373	0.270	0.222
H	0.210	0.102	0.066
H_2O	4.909	5.362	5.579
CO	5.918	4.502	3.769
CO_2	11.246	12.848	13.672
O	0.342	0.169	0.106
O_2	1.884	1.392	1.147

(Composition at 520° R.: CO_2, 2%; CO, 30%; H_2, 10%; CH_4, 1%; N_2, 57%)

Table II gives the average composition on a dry basis and the heat of combustion at constant volume (water as vapor) of producer gas made from various fuels in portable gas generators as well as in a unit designed in this laboratory.

It should be understood that there are considerable variations of gas composition, depending on type of generator, moisture content of the fuel or charge when water is added separately, and changing conditions within the gas generator during combustion, as well as variations due to starting, acceleration, and speed of the engine used in combination with the unit. Spiers and Giffen (*23*) made extensive tests on the performance of a converted gaso-

TABLE II. AVERAGE COMPOSITIONS AND HEATS OF COMBUSTION OF PRODUCER GAS MADE FROM VARIOUS FUELS

Source of Producer Gas	Gas Composition					H, B.t.u./ Cu. Ft.*	E, B.t.u./ Cu. Ft.*
	CO_2	CO	H_2	CH_4	N_2		
Charcoal (*28*)	2.0	31.0	9.5	0.5	57.0	130.1	129.5
Low-temp. coke (*10*)							
Water added	0.5	30.6	5.3		63.6	...	...
No water added	6.25	23.15	17.95	0.70	61.95	129.9	129.3
Anthracite (*28*)	4.5	26.0	15.0	1.4	53.1	137.3	136.7
Wood (*25*)	13.8	17.2	18.0	1.9	49.1	121.8	121.4
Corncobs[a]							
Chopped in small pieces	10.7	14.7	21.9	3.2	49.5	136.3	135.8
Whole	15.5	15.4	11.8	4.1	53.2	119.1	118.7
Producer gas mixt.[b]							
No. 1	14.0	16.0	18.0	2.0	50.0	118.9	118.4
No. 2	2.0	30.0	10.0	1.0	57.0	132.8	132.2

* Values used for low heats of combustion (water as vapor) at 60° F. and 14.7 pounds per square inch are as follows:

H = heat of combustion at constant pressure; E = heat of combustion at constant volume

For $CO + {}^1/_2O_2 = CO_2$:
$H = 121{,}693$ B.t.u./mole (320.9 B.t.u./cu. ft.)
$E = 121{,}172$ B.t.u./mole (319.5 B.t.u./cu. ft.)
For $H_2 + {}^1/_2O_2 = H_2O\ (g)$
$H = 104{,}038$ B.t.u./mole (274.3 B.t.u./cu. ft.)
$E = 103{,}518$ B.t.u./mole (273.0 B.t.u./cu. ft.)
For $CH_4 + 2O_2 = CO_2 + 2H_2O\ (g)$
$H = E = 345{,}276$ B.t.u./mole (910.4 B.t.u./cu. ft.)

[a] Unpublished results obtained at the Northern Regional Research Laboratory.

[b] Representative values based on experimental data used for calculations in this paper. These fuels form the basis for calculations throughout this discussion.

line engine with different producer gas fuels; they showed that fuels containing larger quantities of volatile matter will give greater variation in composition of gas during operation than, for instance, a good grade of charcoal.

HEAT OF COMBUSTION

The nomograph (Figure 1) may be used to calculate the heat of combustion at constant volume (water as vapor) as a function of carbon, hydrogen, and methane; it is thus possible to take into account a variable methane content. However, the heat of combustion of a mixture of fuel and air is of still greater interest, and in order to facilitate rapid calculation of the heat of combustion of any producer gas containing carbon monoxide, hydrogen, and methane as combustible constituents, the following data are presented:

The amount of air required to burn 1% by volume of carbon monoxide or hydrogen in 1 cubic foot of fuel gas is 0.0238 cubic foot; the corresponding value for methane is 0.0952. Producer gas mixture 1 (Table II) is taken for illustration:

$$\begin{aligned} CO&:\ 16 \times 0.0238 = 0.3808 \text{ cu. ft.} \\ H_2&:\ 18 \times 0.0238 = 0.4284 \text{ cu. ft.} \\ CH_4&:\ 2 \times 0.0952 = \underline{0.1904} \text{ cu. ft.} \\ & \qquad\qquad\qquad\quad 0.9996 \end{aligned}$$

Every cubic foot of fuel gas requires, therefore, 0.9996 cubic foot of air. The low heat of combustion (at constant volume) of 1 cubic foot of mixture of producer gas mixture 1 with 0.9996 cubic foot of theoretical air at 60° F. is, therefore, (118.4/1.9996) = 59.2 B.t.u. per cubic foot. A similar calculation for producer gas mixture 2 indicates a value of 64.6 B.t.u. per cubic foot; the corresponding value for gasoline is 102 (*24*). In actual practice, the above computed values for the heats of combustion will be somewhat lower since the gas is generally saturated with water vapor at the exit temperature of the purifier.

The large difference in the theoretical air-fuel ratios by volume between producer gas and octane (gasoline) shown in Table III necessitates changes in carburetor design. Lichty (*17*) discussed the fact that, for gasoline, maximum power is obtained from a mixture slightly richer than the one having the correct air-fuel ratio. For producer gas, however, maximum power is obtained from a mixture containing from 92 to 98% of theoretical fuel (*23*). Woods (*28*) found that the "power mixture strength curve for producer gas is of a sharply peaked nature", and further stated that "differences of the order of ±10%, in the mixture strength which are tolerated in the petrol engine, where the effect on power is small, would lead to serious power loss in the gas engine". Schnürle (*21*), too, found that maximum power output was obtained with a definite mixture containing 90% of theoretical fuel. The engines used in the two experiments were very different.

The thermodynamic calculations were made similarly to those previously mentioned (*13, 27*). The perfect gas law has been assumed to hold throughout the calculations. The equation for the combustion of mixture 1 with air reads as follows (proportions by volume):

$$0.14CO_2 + 0.16CO + 0.18H_2 + 0.02CH_4 + 0.50N_2 + 0.21O_2 + 0.79N_2 = 0.32CO_2 + 0.22H_2O\text{ (vapor)} + 1.29N$$

On the basis of this equation, the material unit chosen was the theoretical weight of fuel necessary to effect complete combustion with one pound of air. The requisite amounts for mixtures 1 and 2 are, respectively, 0.878 and 0.847 pound of fuel per pound of air. The above equation represents only the stoichiometric basis for our calculations; actually the composition of the mixture after combustion will vary with temperature and pressure, as shown in part in Table I. The fact that, in actual practice, the composition of the cold exhaust does not correspond to the equilibrium concentration present at the exhaust valve, but depends on the range of temperatures at which the various equilibria are "frozen" while the gas is passing through the exhaust system, does not invalidate our calculations. Two diagrams are shown for each mixture, Figures 2 and 4 for mixture 1 and Figures 3 and 5 for mixture 2; one set represents the physical properties before combustion and the other, the state of equilibrium after combustion. The reference state, symbols, and units follow:

ABSOLUTE TEMPERATURE. T = ° Rankine or ° F. + 460° (base temperature = 520° R. or 60° F.)

VOLUME. V = cubic feet (dashed lines)

PRESSURE. P = pounds per square inch (solid lines)

INTERNAL ENERGY, SENSIBLE. E_s = B.t.u., defined by the equation:

$$E_s = \int_{520}^{T} C_v dT$$

E_s is zero at the base temperature.

INTERNAL ENERGY, HEAT OF COMBUSTION. E_c = B.t.u. = heat of combustion at constant volume. E_c represents the change in internal energy at the base temperature (520° R.) when using a stoichiometric weight of air to burn the fuel mixture to carbon dioxide and water (vapor). E_c is added at the base temperature to the value of E_s obtained from the compression charts. The method is purely a convenience since:

$\frac{dE_c}{dT} = C_v$ (reactants) $- C_v$ (products), where heat evolved is assumed positive (*16*)

$$E_{c(T)} + \int_{520}^{T} C_v \text{ (products) } dT = E_c\,(520) + \int_{520}^{T} C_v \text{ (reactants) } dT$$

TABLE III. THEORETICAL AIR-FUEL RATIOS

Fuel	Air-Fuel Ratios By volume	Air-Fuel Ratios By weight
Hydrogen	2.38	34.2
Methane	9.52	17.2
Octane (vaporized)	59.50	15.09
Benzene (vaporized)	35.60	13.2
Ethyl alcohol (vaporized)	14.28	8.98
Methyl alcohol (vaporized)	7.14	6.45
Carbon monoxide	2.38	2.46
Producer gas mixt. 1[a]	1.00	1.14
Producer gas mixt. 2[a]	1.048	1.18

[a] Composition given in Table I. In the computation of the air-fuel ratios, CO_2 and N_2 were added to the weight and volume of the fuel content of the mixture.

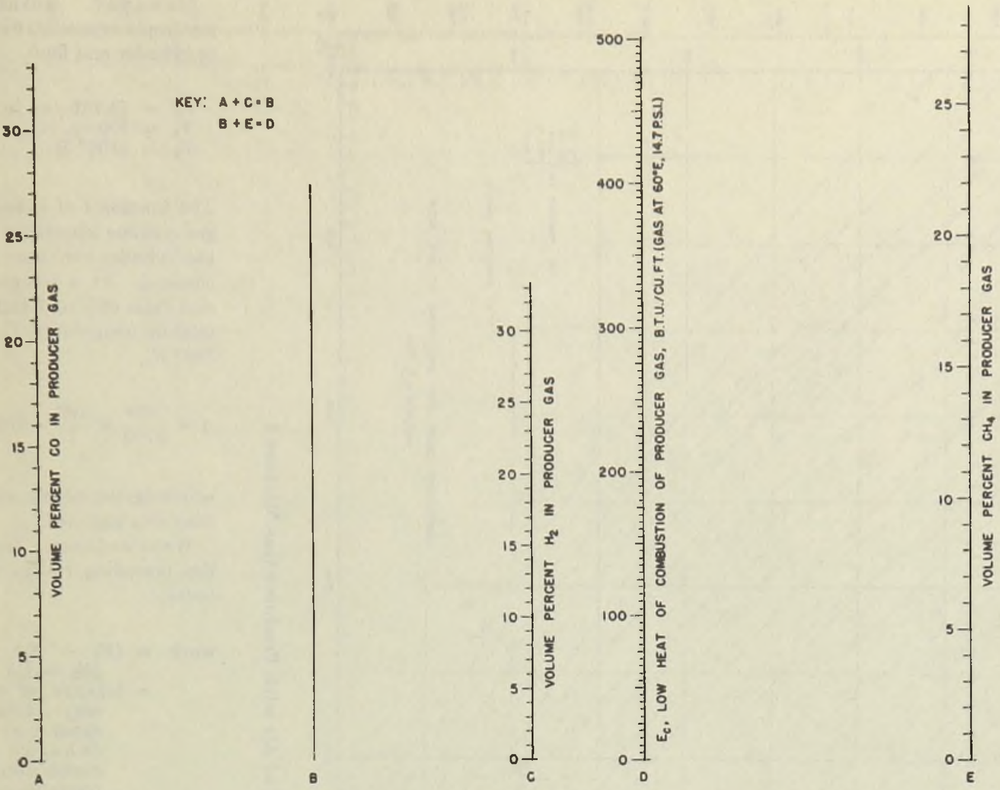

Figure 1. Nomograph for Low Heat of Combustion of Producer Gas

Internal Energy, Total. E = B.t.u. = algebraic sum of E_s and the contribution due to heats of formation involving high temperature products of reaction (CO, H_2, OH, NO, H, O), from CO_2, H_2O, O_2, and N_2

Enthalpy. H_s = B.t.u., defined by $H_s = E_s + PV$. At 520° R. its value is therefore equal to PV.

Entropy. S = B.t.u./° R. For the compression charts, zero entropy is assigned to all the individual components at 520° R. and 14.7 pounds per square inch, since no chemical reaction occurs. Entropy is defined by the equation

$$S = \int_{520}^{T} C_p \frac{dT}{T} - R \ln \frac{P}{14.7}$$

where P = partial pressure of any component

For the combustion charts the same equation holds; however, zero entropy is assigned only to CO_2, H_2O, O_2, and N_2 at 520° R. and 14.7 pounds per square inch, and the entropy of each of the remaining reactants is equal to its entropy of formation.

CALCULATION FOR GAS MIXTURE 2

The compression charts are Figures 2 and 3; those representing the equilibrium conditions after combustion are Figures 4 and 5. For illustrating the use of these charts, the following calculation of an unthrottled Otto cycle for gas mixture 2 is given. The assumed initial conditions are:

Compression ratio = 7:1
Intake temp. T = 60° F. or 520° R.
Intake pressure P = 14.7 lb./sq. in.
Fraction f of exhaust gases remaining in cylinder = 0.041 (checked at end of calculation)
Exhaust temp. T_5 = 2100° R. (also checked at end)

Intake. Calculate H_{s1} for intake conditions. The enthalpy of the mixture is the sum of the enthalpies of the fuel gas mixture and the fraction of exhaust gas, f, remaining in the cylinder. For fuel gas mixture 2, in Figure 3 at 520° R., H_{s1} is 69 B.t.u. The volume fraction of fuel gas mixture in the cylinder is $1 - f = 0.959$. For the exhaust gas in Figure 5 at 2100° R., H_s is 865 B.t.u., and the volume fraction is $f = 0.041$. Therefore, $H_{s1} = 0.959 (69) + 0.041 (865) = 100.9$ B.t.u.

Find E, V, and mixture temperature T, corresponding to H_{s1} on Figure 3. V is determined by the point at which lines for V and P (14.7 pounds per square inch) meet on the horizontal line drawn from a point corresponding to 100.9 B.t.u. on the scale for H_s:

E_1 = 23 B.t.u.
V_1 = 29.0 cu. ft.
P_1 = 14.7 lb./sq. in.
T_1 = 589° R.

Compression. The compression stroke is assumed to take place without heat exchange and therefore follows a line of constant entropy. The volume at top dead center will be:

$$V_2 = \frac{V_1}{7.0} = \frac{29.0}{7.0} = 4.14 \text{ cu. ft.}$$

Follow the constant entropy line from the intersection of P_1 and V_1 to V_2 and read P_2, T_2, and E_{s2}:

E_{s2} = 252 B.t.u.
P_2 = 290 lb./sq. in.
T_2 = 1238° R.

Combustion. This is assumed to take place at constant volume—i.e., at top dead center ($V_3 = V_2$). Add E_{s2} and E_c to obtain E_3. E_c must be multiplied by the percentage of fresh fuel added, in this case $1 - 0.041 = 0.959$.

$$E_3 = 252 + 0.959 (1667) = 1851 \text{ B.t.u.}$$

On Figure 4 find P_3 and T_3 corresponding to volume of V_3 ($= V_2 = 4.14$ cu. ft.):

P_3 = 730 lb./sq. in.
T_3 = 4485° R.

Expansion. Like compression, expansion is assumed to take place without heat exchange. Follow the constant entropy line of Figure 5 to $V_4 = V_1 = 29.0$ and read values of:

E_4 = 972 B.t.u.
P_4 = 67 lb./sq. in.
T_4 = 2910° R.

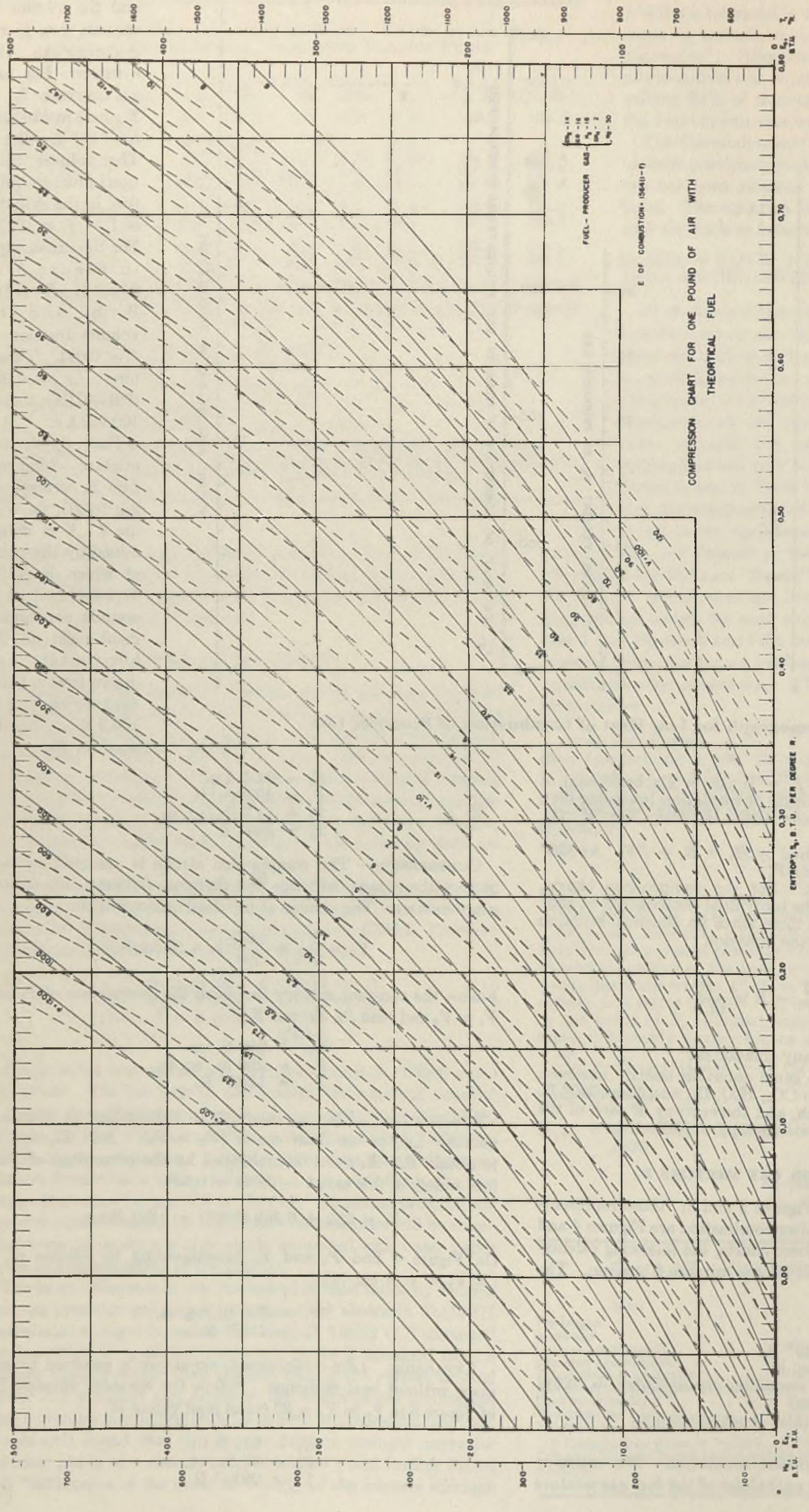

Figure 2. Compression Chart for One Pound of Air with Producer Gas Mixture 1

Exhaust. Assume isentropic expansion within cylinder and find:

$P_5 = 14.7$ lb./sq. in.
$V_5 = 100$ cu. ft.
$T_5 = 2100°$ R.

The fraction f of exhaust gas volume remaining in the cylinder can now be checked. At a compression ratio of 7 to 1 and a mixture temperature T_1 of 589° R.,

$$f = \frac{589}{2100} \times \frac{100}{7} = 0.04$$

which agrees closely with the value assumed.

Work of Cycle. From the preceding results we obtain:

$$\begin{aligned} \text{work} &= (E_3 - E_4) - (E_2 - E_1) \\ &= (\text{change of energy during expansion}) - (\text{change of energy during compression}) \\ &= (1851 - 972) - (252 - 23) = 650 \text{ B.t.u.} \end{aligned}$$

Efficiency of Cycle. The efficiency η is based on the net heat of combustion of the fuel:

$$\eta = \frac{650}{0.959 \times 1667} \times 100 = 40.7\%$$

Mean Effective Pressure. The following equation is evolved:

$$\text{m.e.p.} = \frac{\text{work}}{V_1 - V_2} = \frac{650 \times 778}{(29.0 - 4.14)144} = 141.3 \text{ lb./sq. in.}$$

To avoid all possible misunderstanding, the calculated values in this article are the limiting values obtainable under the assumed conditions; in actual practice efficiencies, mean effective pressures, and power will be much lower. The comparisons made

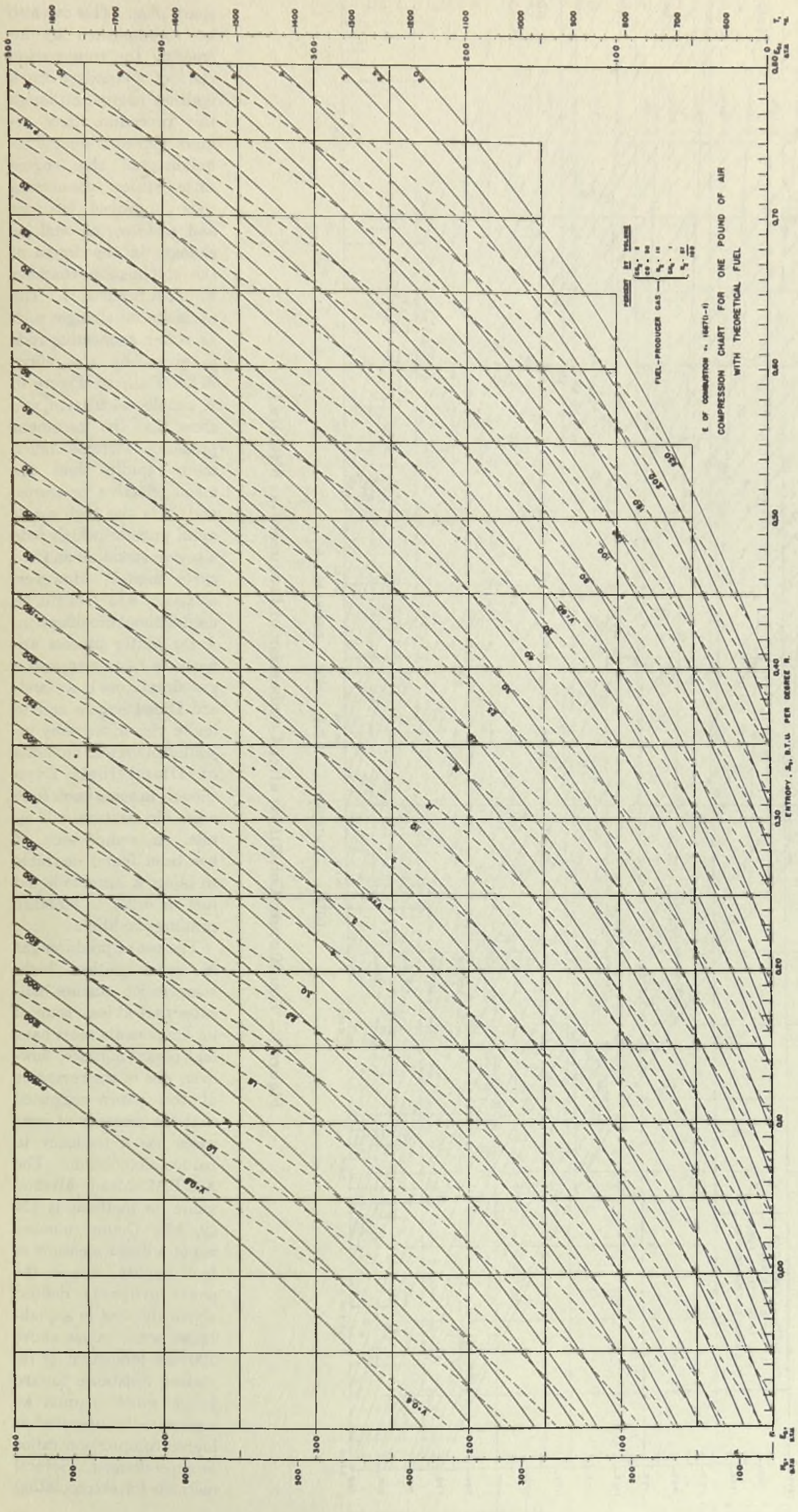

Figure 3. Compression Chart for One Pound of Air with Producer Gas Mixture 2

with operating data are therefore on a relative basis. In this connection, it should be mentioned that supercharging or raising the compression ratio may at times increase the overall efficiency of an engine to such a degree that under these conditions the percentage increase in power output will appear to be greater than the one predicted theoretically.

Figure 6 shows the influence of compression ratio on mean effective pressure, work, and thermal efficiency. Kühne (*15*), working with producer gas made from wood, states that a 9 to 1 compression ratio will give a power output of 80% of that obtainable from gasoline. Assuming for his gasoline engine a compression ratio of 7 to 1, the results in Figure 7 indicate for octane (gasoline) at atmospheric pressure a mean effective pressure of 205 pounds per square inch; the mean effective pressure for producer gas mixture 2 at a compression ratio of 9 to 1 (Figure 6) amounts to 155 pounds per square inch. The ratio (155/205) = 75.6% agrees closely with the results obtained by Kühne.

COMPRESSION RATIOS

Compression ratios as high as 16.5 to 1 (*23, 29*) have been used in connection with producer gas; such extreme compression ratios, identical with those used in a Diesel engine, are of interest in connection with the recent development of Diesel gas engines (*3, 11, 12, 18*). Several methods have been proposed. The simplest is to convert a Diesel engine to a spark ignition engine by lowering the compression ratio of a standard Diesel to possibly 10:1 and adding a

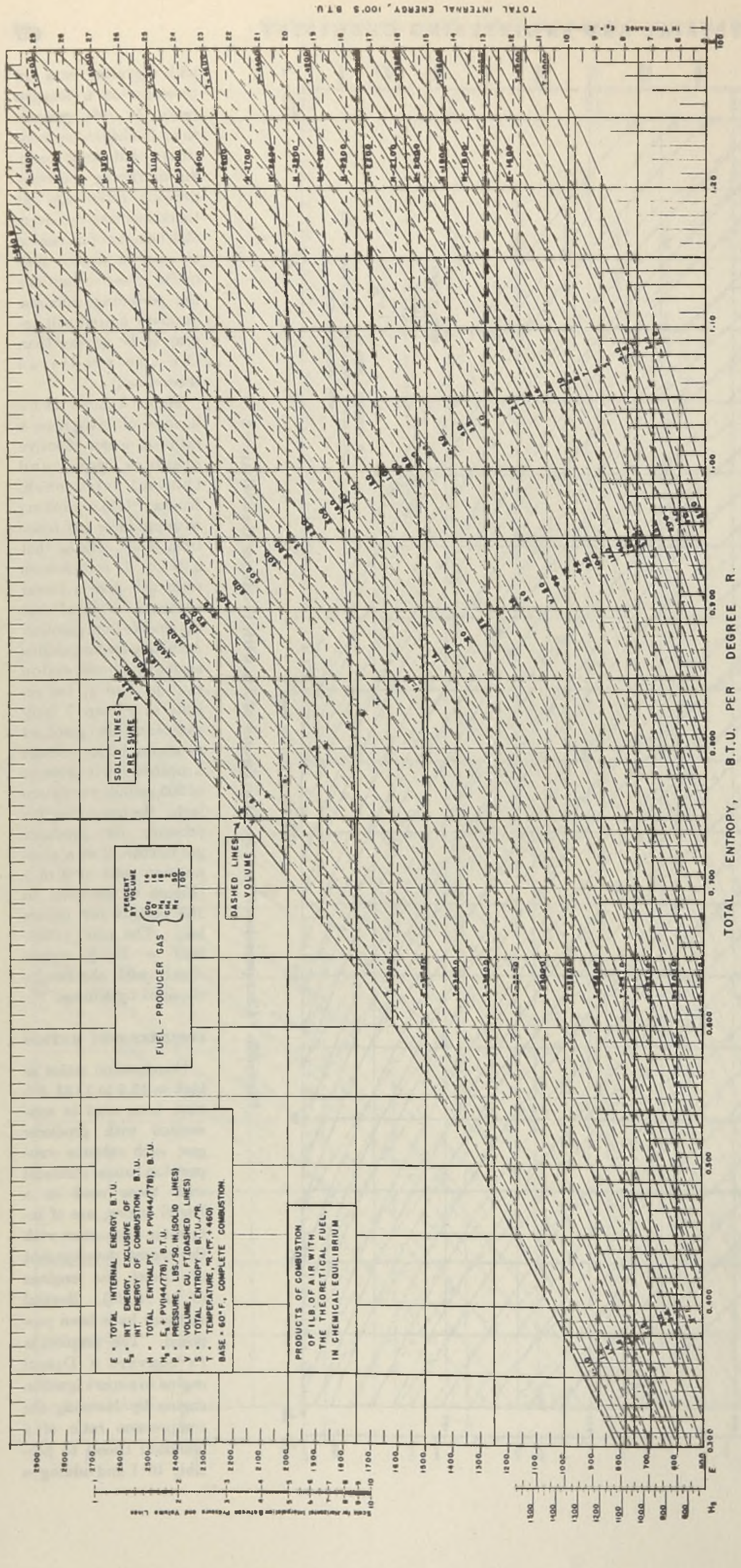

Figure 4. Equilibrium Conditions after Combustion of Producer Gas Mixture 1

spark plug. This can also be accomplished by increasing the compression ratio of a standard spark ignition engine, although this procedure may require almost complete rebuilding of the engine since stiffer connecting rods, improved bearings and pistons, as well as changes in the design of the combustion chamber would be needed (*7*). The necessity for changes such as stiffer connecting rods is given by the curve $MEP/P_{max.}$ in Figure 6. A simple calculation will show that the maximum pressures increase much more rapidly than the mean effective pressures, and it is the high maximum pressure which puts a severe strain on an Otto cycle engine. However, a ratio of 8 to 1 might be used without modification. A far better process appears to be to compress a gas-air mixture in a standard Diesel engine and to ignite this mixture by injection of various amounts of Diesel fuel. Even though in some cases such a gas-air mixture will ignite on compression, it has been found desirable to inject a suitable liquid fuel in order to stabilize running conditions.

The use of producer gas in spark-ignition high-compression engines indicates that at least some of its components must have high octane number; however, one of the reviewers of this paper suggested that the presence of inert gases has a tendency to reduce detonation. The A.S.T.M. Motor Method value for methane is 110 (*9, 22*). Octane number is not a linear measure of fuel quality, nor is the scale properly defined above 100, but in a qualitative sense values above 100 are indicative of increased resistance toward knock which permits an engine to be operated at higher compression ratios or supercharged. Several methods for extrapolating

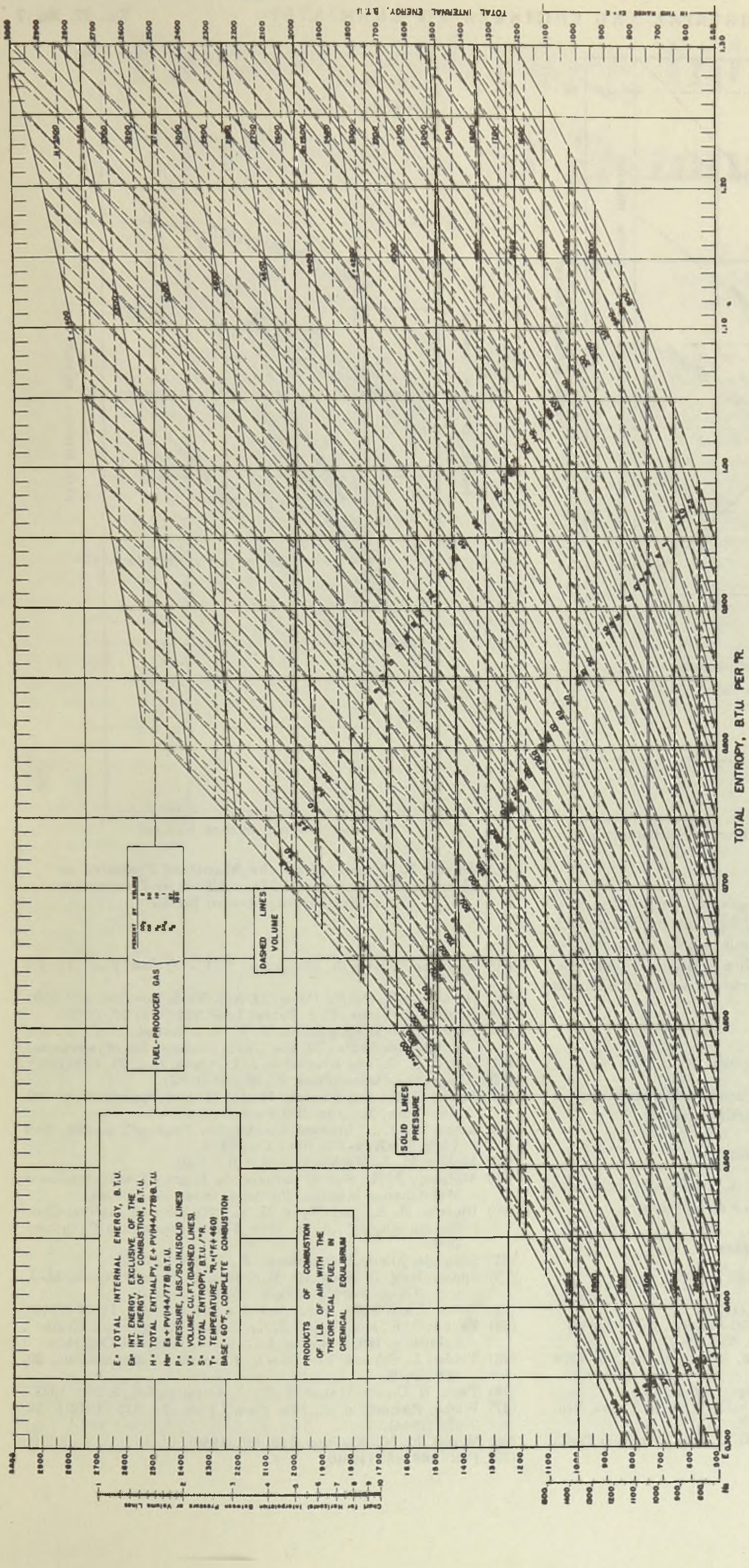

Figure 5. Equilibrium Conditions after Combustion of Producer Gas Mixture 2

octane numbers have been proposed; however, none have so far been generally accepted. According to Colwell (*7*), Graham Edgar believes that the difficulty of extending the octane number scale will be overcome in the near future, and that on the new scale the present 100 octane gasolines will have a value of 75 to 80. Recently it has been found (*4, 18, 19*) that high octane numbers and high compression ratios are no longer synonymous; instead of the fuel, the engines may become the principal variable. The heat of combustion per pound may ultimately become the sole criterion of fuels when turbine and jet propulsion are considered.

The A.S.T.M. Motor Method value for carbon monoxide is probably as high as that for methane. The octane number for hydrogen appears to be lower, which is indicated by the observation of Spiers and Giffen (*23*) that, with mixtures of high hydrogen content, detonation was encountered at compression ratios of 10.5 to 1. Pure hydrogen has been used successfully at compression ratios as high as 14 to 1 (*1*), and its exceptionally high speed of flame propagation is undoubtedly responsible for its interesting properties when employed as fuel in internal combustion engines (*1, 6, 8, 20*).

Thermal efficiency and mean effective pressure are plotted against intake manifold pressure at a fixed compression ratio of 7 to 1 in Figure 7. An intake manifold pressure of somewhat over 20 pounds per square inch absolute (not taking into account the loss from running the supercharger) gives equal power output with octane and alcohol. This checks closely with what has been found in actual practice by Branders (*5*), who stated that loss of power

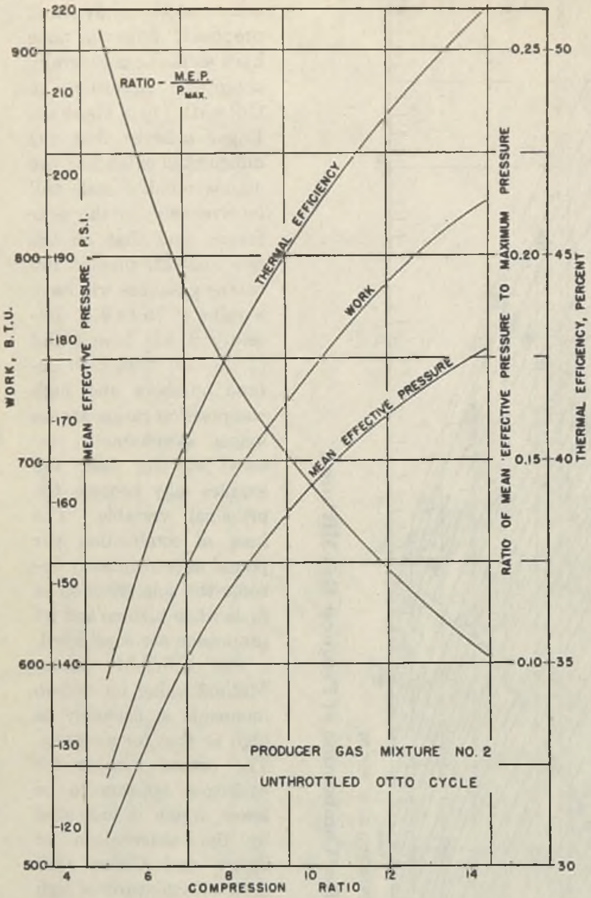

Figure 6. Effect of Compression Ratio on Mean Effective Pressure, Work, and Thermal Efficiency

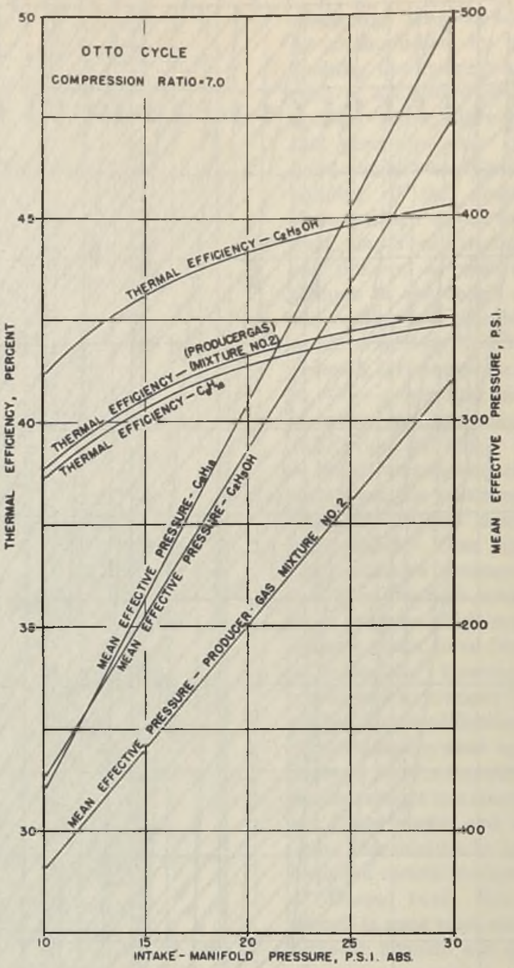

Figure 7. Effect of Intake Manifold Pressure on Thermal Efficiency and Mean Effective Pressure at a Fixed Compression Ratio

resulting from the use of producer gas can be totally compensated by a supercharging pressure of 6 pounds per square inch gage. In another instance (*2*) a six-cylinder engine with compression ratio of 4.7 to 1 was run on gasoline and on producer gas, with and without supercharging. The results are given below as brake horsepower:

Gasoline	86
Gas without supercharging	47
Gas with supercharging at 0.4 atm. (5.9 lb./sq. in.)	80

Advantages of gaseous fuels in general are better distribution of charge and elimination of the engine-starting problem.

ACKNOWLEDGMENT

We wish to express thanks to Mrs. M. E. Hodler of this laboratory for efficient help in assisting with the calculations.

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Factors Affecting Initiating Efficiency of Detonators

R. L. GRANT
Explosives Testing Section,
U. S. Bureau of Mines, Bruceton, Pa.

J. E. TIFFANY
Central Experiment Station,
U. S. Bureau of Mines, Pittsburgh, Pa.

The influence of the following factors upon the initiating efficiency of detonators was studied: base charge, priming charge, reinforcing capsule, and outside diameter of shell. The initiating efficiencies of laboratory-prepared detonators were determined by the miniature-cartridge test (*7*). Results indicated that the initiating efficiency increased in this order for the following base charges: 80 mercury fulminate–20 potassium chlorate mixture, tetryl, PETN, hexogen. The efficiency of priming compositions, as determined by minimum initiating charges, was as follows: (1) 80 lead azide–20 lead styphnate; (2) 80 lead azide–18 lead styphnate–0.5 aluminum–1.5 potassium chlorate and 60 lead azide–40 lead styphnate; (3) 100% lead azide, 80 lead azide–17 lead styphnate–3 aluminum, 40 lead azide–60 lead styphnate, and 75 DDNP–25 potassium chlorate; (4) 20 lead azide–80 lead styphnate and 80 mercury fulminate–20 potassium chlorate; (5) 100% lead styphnate. The use of a copper reinforcing capsule to enclose the priming charge increased the initiating efficiency of a detonator from one to three grades. As the outside diameter of a detonator was increased, the initiating efficiency of the detonator decreased as an approximate inverse straight-line function. Tests with the lead-plate test produced results in substantially opposite order to those of the miniature-cartridge test when the diameter of the detonator was varied. The initiating efficiency of the various kinds of detonators was calculated in terms of unit weight of explosive charge in the detonator and then systematically tabulated; detonators were thus classified according to initiating characteristics. This classification, along with selected curves, revealed that hexogen-base detonators are uniformly more efficient than detonators with other base charges. These curves also disclosed that both quantity and quality of the explosive charge in a detonator must be considered in relation to the initiating efficiency of that detonator.

THE question of what constitutes an efficient detonator is of critical importance to designers and manufacturers of detonators and to all who test and use explosives. The behavior of detonators is not clear because knowledge of the initiating characteristics of detonators is incomplete. This report studies the following four factors and their effects on the initiating efficiency of detonators: base charge, priming charge, reinforcing capsule, and diameter of detonator shell. The influence of each factor was ascertained by measuring the initiating efficiency of laboratory-prepared detonators by the routine procedure of the miniature-cartridge test (*7*). The testing of detonators has been reported in previous publications (*5, 6, 11, 26, 27*). Another purpose of this article is to present the initiating characteristics of a series of hexogen-base detonators which, although patented by Herz in 1920 (*12*), have not been described in the literature or used in practice. By the miniature-cartridge test these detonators are consistently superior to detonators containing other base charges.

The terms adopted by *Chemical Abstracts* are, for the most part, employed here for the various explosives tested. However, the common name or designation, when this is widely accepted, is also used.

The term "tetryl" is employed for the explosive chemically known as trinitrophenylmethylnitramine.

Pentaerythritol tetranitrate is commonly known in this country as PETN. This compound is variously listed in the literature as tetranitropentaerythritol, tetranitropentaerythrite, pentrite, penthrit, and niperyth.

"Hexogen" is the term used by *Chemical Abstracts* for cyclotrimethylenetrinitramine. In common usage in this country it is frequently called "cyclonite".

Lead styphnate is known chemically as normal lead trinitroresorcinate or the lead salt of styphnic acid.

DDNP refers to diazodinitrophenol. It is occasionally called dinol; *Chemical Abstracts* lists it under both "DDNP" and "benzoxdiazole, 4,6-dinitro-".

The weights of the explosive charges in the detonators described are designated by centigrams (0.01 gram). Convenient whole numbers, rather than decimal fractions, result; and weighings of the charges in the laboratory-prepared detonators are accurate to a centigram. A tendency has been noted in this country, especially in specifications, to use grains; although they provide whole numbers, "grains" are cumbersome and confusing.

The initiating efficiencies of the detonators studied were determined by the routine miniature-cartridge test (*7*). The screens used in the previous work were retained for the tests described here in order to ensure intercomparison of results.

EFFECT OF BASE CHARGE

Modern detonators are compound detonators loaded with a base charge, a priming charge, and sometimes an ignition charge (*5, 16*). The relative efficiencies of the following four base charges were studied: 80 mercury fulminate–20 potassium chlorate mixture, tetryl, PETN, and hexogen. The first was selected because it constitutes the charge of standard detonators in this country and mercury fulminate is the oldest of detonator charges. The common base charges in use today are tetryl (*17, 32*) and PETN (*3*); the latter has been introduced within the past decade. Hexogen was chosen because its high rate of detonation (approximately 8400 meters per second) indicated that it might be an effective base charge. Herz patented this compound in 1920 (*12*) and suggested it as a detonator charge (*13*). It has not been used in practical detonators, however. Its preparation and properties have been studied and described by Desvergnes (*4*), Somlo (*23*), Tonegutti (*31*), Guastalla and Raccin (*10*), Sollazo (*22*), and Stettbacher (*24*).

EXPERIMENTAL. Gilding-metal shells, of outside diameter 0.69 cm. and with the usual depressed bottoms, were used. The shells were identical to those on the market, and this particular diameter represents the most common detonator.

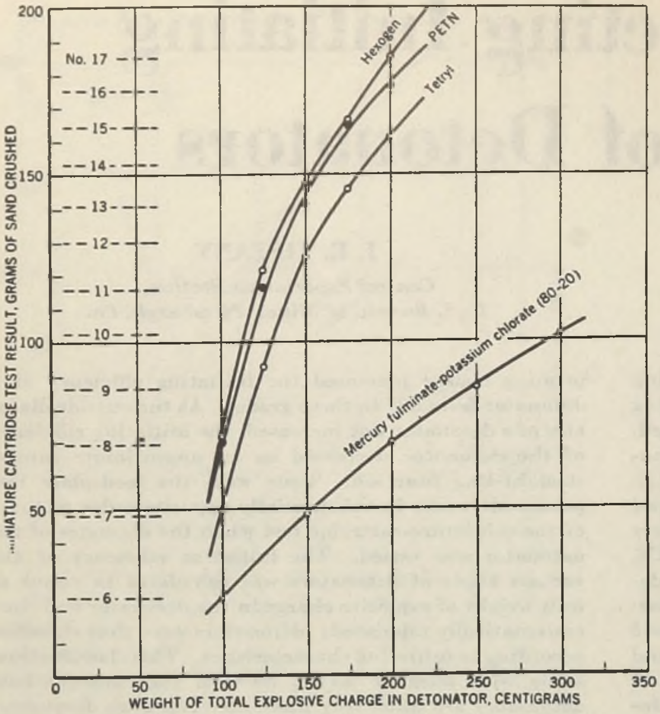


Figure 1. Effect of Base Charge on Initiating Efficiency of Detonators

For the first series of detonators containing 80–20 fulminate-chlorate, the base charge was loaded in increments of 50 cg. (0.5 gram) at a pressure of 63 kg. per sq. cm. (900 pounds per square inch). The priming charge was also 80–20 fulminate-chlorate, weighed 50 cg. for each detonator, and was pressed at 49 kg. per sq. cm. (700 pounds per square inch).

For the next three series of detonators containing tetryl, PETN, and hexogen as base charges, detonators were prepared having 25, 50, 75, 100, and 125 cg. of each base charge pressed at 98 kg. per sq. cm. (1400 pounds per square inch). The priming charge for all of these detonators was 75 cg. of 80–20 fulminate-chlorate, loaded singly and pressed at 49 kg. per sq. cm.

Figure 1 shows the results of the initiating efficiencies of the four series of detonators as determined by the routine miniature-cartridge test. Since each point represents six trials (two each for the 80–20 and 70–30 TNT–iron oxide mixtures and two for the detonator blank), the set of four curves includes a total of one hundred twenty trials.

Conclusions and Discussion. Figure 1 indicates that the order of increasing initiating efficiency for the base charges studied is: 80 mercury fulminate–20 potassium chlorate mixture, tetryl, PETN, hexogen. Furthermore, reference to tables of detonation rates reveals that the results are in the same approximate relative order as the respective rates of detonation of the base charges.

Various relations are derivable from Figure 1—for example, the relative initiating efficiencies of detonators having equal weights of total charges. By entering the graph along the 100-cg. vertical ordinate, it is found that a detonator containing, for example, 25 cg. of tetryl and 75 cg. of 80–20 fulminate-chlorate priming charge is equivalent to a No. 7 fulminate-chlorate reference detonator.

Haid and Koenen (*11*) reported results for fulminate-chlorate, tetryl-base, and PETN-base detonators that are in close agreement with those of Figure 1. They suggested that the initiating efficiency of an explosive may be expressed in terms of its brisance value, *B*, which they calculated from the following formula:

$$B = \Delta \times D \times T/273 \times V_0$$

where Δ = density
D = rate of detonation
T = absolute explosion temperature
V_0 = gas volume produced by explosive

EFFECT OF PRIMING CHARGE

The chief function of a priming charge in a detonator is to transmit full detonation to the less sensitive but usually more powerful base charge. Because the priming charge is generally a sensitive and expensive explosive, a relatively small quantity is desirable.

The common priming charges studied in this section have been selected from those used in detonators in the United States and in Europe, especially Great Britain and Germany. They include 80 mercury fulminate–20 potassium chlorate mixture, lead azide (*15*, *32*), lead styphnate (*15*, *28*), lead azide–lead styphnate mixtures (*15*, *18*), and 75 DDNP–25 potassium chlorate mixture (*1*, *3*). In addition, the effect of aluminum, alone and with potassium chlorate, when mixed with lead azide and lead styphnate, was tested.

Determination of Minimum Initiating Charge. Among the important properties of a priming composition is the minimum charge required to detonate the base explosive in the detonator. For determining this characteristic the well-known procedure of Taylor and Cope (*29*) was followed. Some details differ, however, and are noted in the following outline of the procedure used in this study.

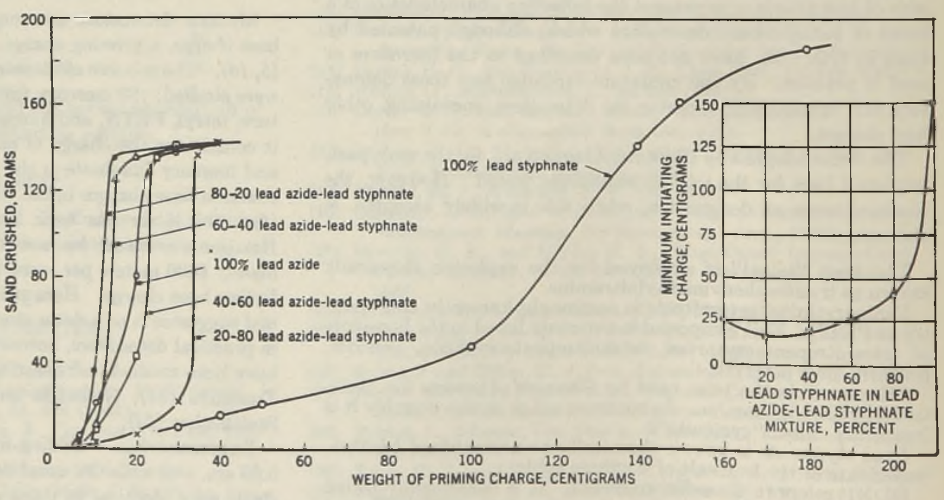


Figure 2. Determination of Minimum Initiating Charges of Lead Azide, Lead Styphnate, and Their Mixtures for 125 Cg. of Tetryl

A charge of 125 cg. was loaded in five 25-cg. increments into a gilding-metal shell having an outside diameter of 0.69 cm. Each increment was pressed at 98 kg. per sq. cm. The 125-cg. charge represents the maximum weight of base charge studied in these experiments. Varying weights of priming charge, in 5-cg. increments, were then inserted as a single charge on top of the base charge and pressed at 49 kg. per sq. cm. For these experiments no reinforcing capsule was employed. An electric match head of the copper acetylide type, obtained from Atlas Powder Company, was inserted into the detonator and the shell carefully crimped at the top. The detonator was placed in the center of 350 grams of Ottawa standard sand, introduced in portions of 100 plus 250 grams into Bureau of Mines bomb No. 2 having an inside diameter of 2 inches (*19*). The bomb was closed and fastened securely, and the detonator fired. The weight of sand crushed served as a criterion of whether the base charge detonated; it was determined by screening through a No. 30 U. S. Standard series screen (opening, 0.059 cm. or 0.0232 inch). The weight of priming charge, to the nearest 5 cg., which produced three complete detonations, without partial or incomplete detonations, was taken as the minimum initiating charge.

Table I gives the minimum initiating charges of the various priming compositions for base charges of tetryl, PETN, and hexogen. The general conclusion from these results is that hexogen is more sensitive to detonation than PETN which, in turn, is more sensitive than tetryl. If other factors are equal, a greater sensitivity to detonation is a desirable property in a base charge. The order of efficacy of the priming compositions, with the best listed first, follows:

1. 80 lead azide–20 lead styphnate
2. 80 lead azide–18 lead styphnate–0.5 aluminum–1.5 potassium chlorate and 60 lead azide–40 lead styphnate
3. 100% lead azide, 80 lead azide–17 lead styphnate–3 aluminum, 40 lead azide–60 lead styphnate, and 75 DDNP–25 potassium chlorate
4. 20 lead azide–80 lead styphnate and 80 mercury fulminate–20 potassium chlorate
5. 100% lead styphnate

Table I. Minimum Charges of Priming Compositions (to Nearest 5 Cg.) Required to Detonate 125 Cg. of Base Charge

Priming Composition	Tetryl	PETN	Hexogen
Without Reinforcing Capsule			
80 mercury fulminate–20 potassium chlorate	40	35	35
Lead azide	25	10	5
80 lead azide–20 lead styphnate	15	5	5
60 lead azide–40 lead styphnate	20	..	..
40 lead azide–60 lead styphnate	25	..	..
20 lead azide–80 lead styphnate	40	..	..
Lead styphnate[a]	150	..	..
75 DDNP–25 potassium chlorate	25	20	15
18 lead azide–17 lead styphnate–3 aluminum	25	..	..
80 lead azide–18 lead styphnate–0.5 aluminum–1.5 potassium chlorate	20	..	..
With Reinforcing Capsule			
80 mercury fulminate–20 potassium chlorate	20	15	15
80 lead azide–20 lead styphnate[b]	5	5	5

[a] Result is approximate.

[b] Small hole (diameter 0.15 cm.) in inner copper capsule; priming charge pressed under capsule at 98 kg. per sq. cm.

Lead Azide–Lead Styphnate Mixtures. Mixtures of lead azide and lead styphnate have long been used as priming charges for detonators (*9, 14, 18*) and have been employed in foreign detonators, especially those of Great Britain and Germany (*25, 30*). These mixtures, however, are not found in detonators marketed in the United States. Properties of the two constituents evidently complement each other; the low ignition temperature of lead styphnate compensates for the higher ignition temperature of lead azide, while the high initiating power of lead azide amends the low power of lead styphnate (*18, 27*).

Of the various lead azide–lead styphnate mixtures, the 80–20 is the best according to the results of Table I. It is superior to either lead azide or lead styphnate alone. As little as 5 cg. of this mixture completely detonates 125 cg. of either PETN or hexogen, whereas 35 cg. of the fulminate-chlorate mixture are required. The priming composition used by Rheinish-Westfaelische Sprengstoffe was reported to be the 40–60 lead azide–lead styphnate mixture (*21*). Figure 2 presents the relative initiating values of the lead azide–lead styphnate mixtures.

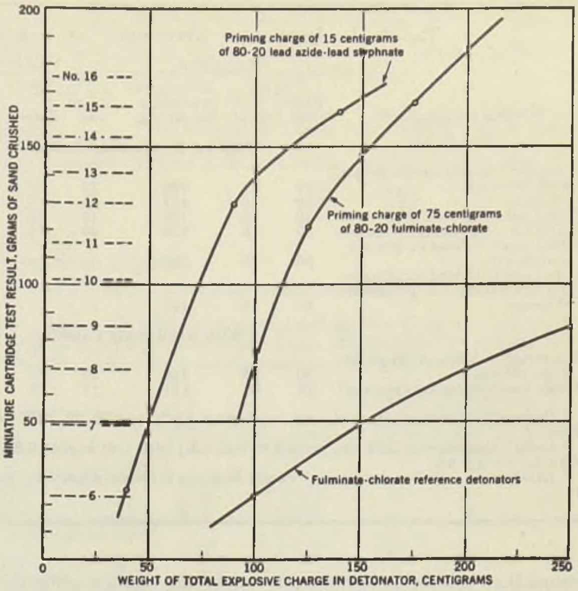


Figure 3. Effect of Priming Charge on Initiating Efficiency of Detonators

Initiating Efficiency Tests. The relative initiating efficiencies of various detonators prepared with the three base charges (tetryl, PETN, and hexogen) and the several priming compositions were determined by the routine procedure of the miniature-cartridge test. At this point the following arbitrary rule, which provided a safety factor of 2 to 3, was established and used for all subsequent detonators tested: The weight of priming charge for use in a detonator is taken as between two and three times the minimum initiating charge. These detonators were prepared like those described in the section on "Effect of Base Charge", in which the base charges were pressed at 98 kg. per sq. cm. and the priming charges at 49 kg.

Figure 3 shows two curves for hexogen-base detonators that compare the most effective priming charge with one that is relatively ineffective. The priming charges selected are the 80–20 lead azide–lead styphnate and the 80–20 mercury fulminate–potassium chlorate mixtures, respectively. Curves for the other priming charges (except for lead styphnate) will, in general, fall between these two curves, provided the same weight of the same base charge is used. Table II gives the make-up of the various detonators tested and their relative initiating efficiencies.

EFFECT OF REINFORCING CAPSULE

It is generally conceded that the use of a reinforcing or inner capsule to enclose the priming charge has the effect of producing a lower minimum charge necessary to detonate the base composition (*26, 27*). This is attributed to the additional confinement and to a focusing of the shock wave from the priming charge in the direction of the base charge. Another advantage of a reinforcing capsule is that it provides additional mechanical protection around the usually sensitive priming composition and thus improves the safety features of the detonator.

The experiments of this section consisted of obtaining the initiating efficiencies of two series of detonators made similarly,

Table II. Initiating Efficiency of Various Detonators

Priming Composition	Tetryl Base: Wt., Cg. Priming	Tetryl Base: Wt., Cg. Base	Tetryl Base: Miniature-cartridge result[a], g.	PETN Base: Wt., Cg. Priming	PETN Base: Wt., Cg. Base	PETN Base: Miniature-cartridge result[a], g.	Hexogen Base: Wt., Cg. Priming	Hexogen Base: Wt., Cg. Base	Hexogen Base: Miniature-cartridge result[a], g.
Without Reinforcing Capsule									
80 mercury fulminate–20 potassium chlorate	75	75	125	75	75	141	75	75	147
Lead azide	50	75	121	25	75	130	15	75	130
80 lead azide–20 lead styphnate	30	75	116	15	75	127	15	75	129
75 DDNP–25 potassium chlorate	50	75	129	40	75	138	30	75	134
80 lead azide–17 lead styphnate–3 aluminum	50	75	123	..	..	...	..	..	...
80 lead azide–18 lead styphnate–0.5 aluminum–1.5 potassium chlorate	40	75	128	..	..	...	..	..	...
With Reinforcing Capsule									
80 mercury fulminate–20 potassium chlorate[b]	50	75	126	50	75	138	50	75	146
80 lead azide–20 lead styphnate[c]	15	75	111	15	75	134	15	75	140

[a] Represents average grams of sand crushed by 80–20 and 70–30 TNT–iron oxide mixtures after subtraction of blank.

[b] Reinforcing capsule 0.64 cm. long, 0.64 cm. o.d., with hole having 0.25-cm. diameter; priming charge pressed at 49 kg. per sq. cm.

[c] Reinforcing capsule as given in [b] except hole has 0.15-cm. diameter; priming charge pressed at 98 kg. per sq. cm.

except that one series contained a reinforcing capsule while the other did not. The shells were the same as those described in the preceding sections. The reinforcing copper capsules were 0.64 cm. (0.25 inch) in length and 0.64 cm. in outside diameter. For the 80–20 fulminate-chlorate composition the diameter of the hole in the capsule was 0.25 cm. (0.1 inch); for the 80 lead azide–20 lead styphnate composition this diameter was 0.15 cm. (0.06 inch). The pressure for the former was 49 kg. per sq. cm., for the latter, 98 kg. It was found that a smaller hole and higher pressure were necessary to retain the lead azide–lead styphnate priming charge in the detonator.

The results of these experiments are given at the bottom of Table II and plotted as curves representing four series of detonators in Figure 4. The conclusion indicated by these results is that, in general, the use of a reinforcing capsule increases the initiating efficiency of a detonator one to three grades. The extent of the increase depends upon the degree to which the reinforcing capsule decreases the minimum initiating charge of the priming composition. From the curves of Figure 4 it is possible to determine detonators equivalent in initiating efficiency.

EFFECT OF SHELL DIAMETER

Miniature-Cartridge Test. Detonators with gilding-metal shells having the following different outside diameters were studied: 0.59 cm. (0.23 inch), 0.69 cm. (0.27 inch), and 0.79 cm. (0.31 inch). These three diameters represent a majority of the detonators marketed today in the United States in the nominal No. 6 and No. 8 grades. The shell having a diameter of 0.69 cm. was identical with those described in preceding sections and is the common diameter used for commercial electric detonators. The shells of all diameters had the usual depressions in their bottoms and were manufactured similarly by the usual shell-drawing machines. The wall thickness of all shells was the same, approximately 0.022 cm. (0.009 inch), as was the thickness of their bottoms, 0.064 cm. (0.025 inch). In loading the explosive charges, the same pressures were used as for detonators previously studied.

The results of the routine miniature-cartridge test are given in Figures 5 and 6; the initiating efficiency is seen to increase markedly as the diameter is decreased. For example, detonators containing a total weight of 90 cg. (75 of hexogen and 15 of 80–20 lead azide–lead styphnate) for the diameters of 0.79, 0.69, and 0.59 cm. are Nos. 9, 12, and 14 grades, respectively (Figure 5). In Figure 6 the outside diameter is plotted against the result obtained with the miniature-cartridge test; it is reasonable to conclude that the initiating efficiency is approximately an inverse straight-line function of the diameter of the shell for the range of diameters tested. The top curve is the result of a confirmatory experiment in which 5 grams of TNT were loaded in a miniature cartridge of 1/2 inch inside diameter at a density of 0.94 gram per cc. The four lower curves represent the results of the routine miniature-cartridge test. A possible explanation of the effect of the diameter, based upon geometrical considerations, is that for a given weight (and hence a given volume) of explosive charge the surface of the cylindrical column increases with a decrease in diameter.

Tests with Small Lead Plates. The significant effect of the diameter of the detonator on its initiating efficiency, as measured by the miniature-cartridge test, prompted experiments with the lead plate test commonly used for control work (*8*). The detonators tested were prepared exactly as in the experiments

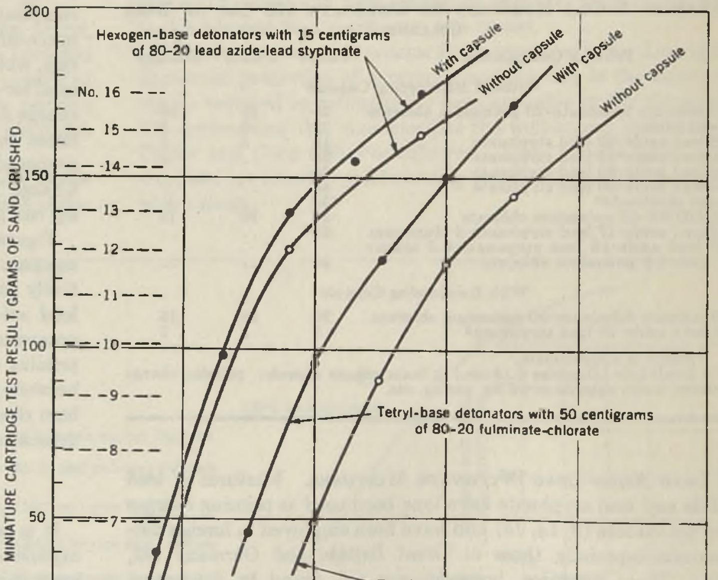


Figure 4. Effect of Reinforcing Capsule on Initiating Efficiency of Detonators

with the miniature-cartridge test and fired in the center of a 3.75 × 3.75 × 0.3 cm. (1$^1/_2$ × 1$^1/_2$ × $^1/_8$ inch) lead plate in the usual manner. The diameter of the hole produced was taken as the criterion of the detonator strength in accordance with the well known procedure. In addition, the weight of lead displaced by the explosion of the detonator was also determined. Table III gives the results obtained.

If the values in Table III for detonators of decreasing diameter are compared with the corresponding results plotted in Figure 5, it is evident that the order of results of the lead-plate test and those of the miniature-cartridge test are opposite. For the miniature-cartridge test the smallest diameter (0.59 cm.) produced the greatest initiating efficiency; this diameter gave the smallest efficiency by the lead-plate test. If it is assumed that the miniature-cartridge test is substantially satisfactory, the above experiments permit the conclusion that the lead-plate test produces erroneous results when detonators of different diameters are compared.

Table III. Results of Lead Plate Test for Detonators of Different Outside Diameters

Weights, Cg.			Diam. of Hole, in Cm., Produced in Lead Plates with Detonators Having O.D. of:			Grams of Lead Displaced by Explosion of Detonators Having O.D. of:		
Base charge[a]	Priming charge[b]	Total charge	0.79 cm.	0.69 cm.	0.59 cm.	0.79 cm.	0.69 cm.	0.59 cm.
25	15	40	1.0	1.05	0.95	0.55	0.68	0.64
50	15	65	1.25	1.2	1.05	1.20	0.97	0.68
75	15	90	1.3	1.2	1.05	1.37	0.98	0.73

[a] Hexogen.
[b] 80 lead azide–20 lead styphnate.

Table IV. Initiating Efficiencies of Various Detonators with Results of Miniature-Cartridge Test Expressed as Grams of Sand Crushed per Gram of Explosive Charge in Detonator

Priming Charge[a]	O.D. of Shell, Cm.	Reinforcing Capsule	Initiating Efficiency of Detonator Containing 75 Cg. of Base Charge of: Tetryl	PETN	Hexogen
80 mercury fulminate–20 potassium chlorate	0.69	Without	83	94	98
Lead azide	0.69	Without	97	130	145
80 lead azide–20 lead styphnate	0.69	Without	110	141	143
75 DDNP–25 potassium chlorate	0.69	Without	103	120	127
80 lead azide–17 lead styphnate–3 aluminum	0.69	Without	98	...	...
80 lead azide–18 lead styphnate–0.5 aluminum–1.5 potassium chlorate	0.69	Without	111	...	...
80 mercury fulminate–20 potassium chlorate	0.69	With	101	110	117
80 lead azide–20 lead styphnate	0.69	With	123	149	156
80 lead azide–20 lead styphnate	0.79	Without	...	...	96
80 lead azide–20 lead styphnate	0.59	Without	...	...	175
80 lead azide–20 lead styphnate	0.59	With	...	...	180

[a] Weights of priming charges are given in Table II.

EFFICIENCY EXPRESSED AS UNIT WEIGHT OF CHARGE

The data obtained in the experiments are made more instructive by calculating the initiating efficiency per unit weight of explosive charge in the detonator. This is accomplished by dividing the result of the miniature-cartridge test (average grams of sand crushed by the 80–20 and 70–30 TNT–iron oxide mixtures, after subtraction of the detonator blank) by the total weight of explosive charge in the detonator in grams. As an example, for a detonator containing a total explosive charge of 150 cg. (1.50 grams), the miniature-cartridge test result was 125 grams of sand crushed. The "sand crushed per unit weight of explosive charge in detonator" is 125/1.50, or 83 grams.

Table IV gives data derived in this manner from the data of the experiments. For all detonators represented in this table, the base charge weighed 75 cg., loaded in three equal increments as already described.

Figure 7 gives plots of eleven series of detonators selected from Figures 1, 3, 4, and 5, and recalculated to express the efficiency per unit weight of explosive charge. Each curve represents a series of detonators with a range of base charge from 25 to either 100 or 125 cg., with the exception of curve 1 which depicts a series

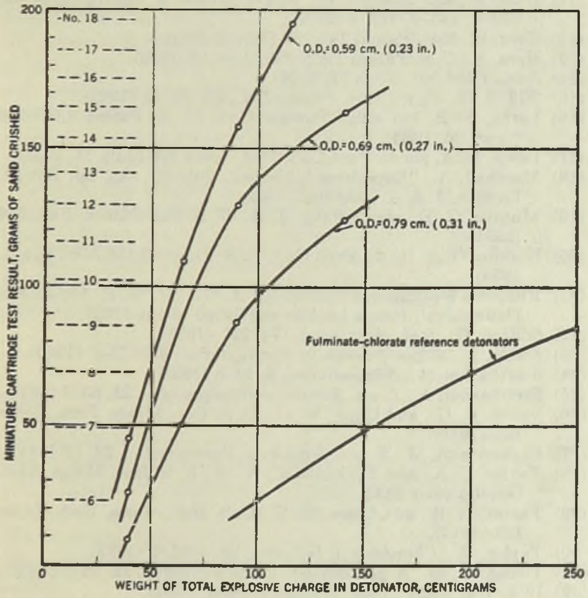


Figure 5. Effect of Diameter of Shell on Initiating Efficiency

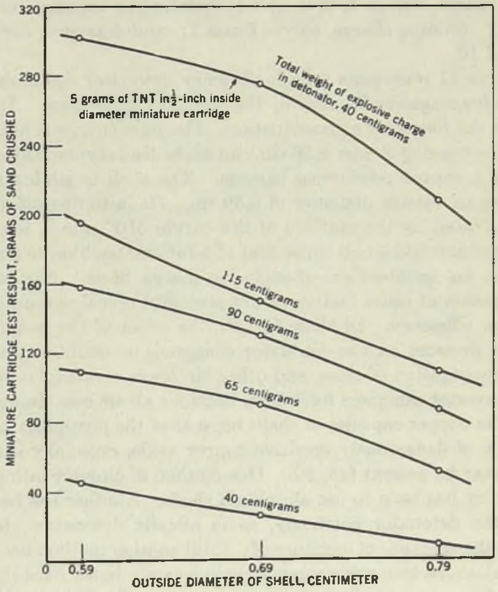
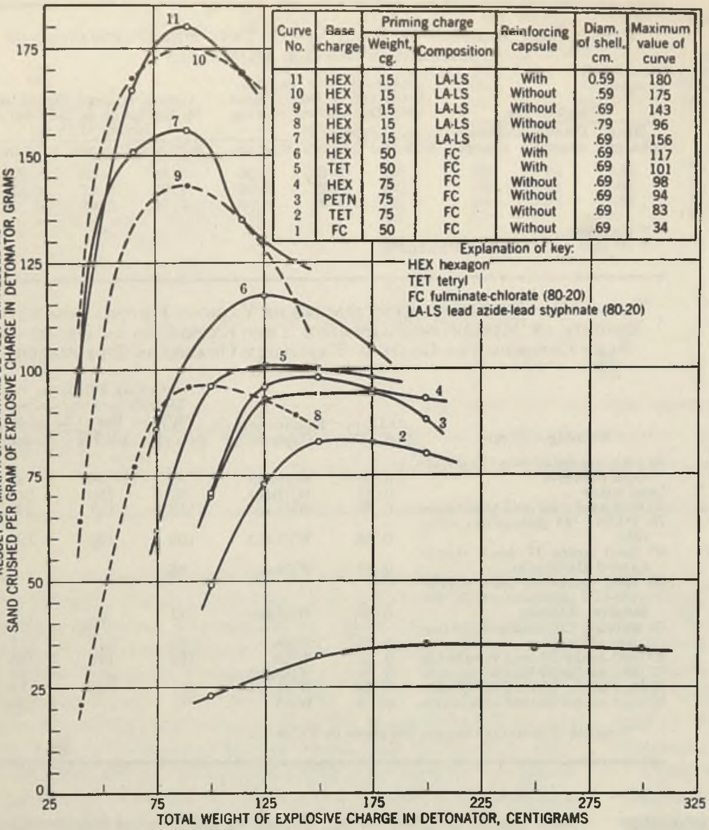


Figure 6. Effect of Diameter of Detonator Shell on Initiating Efficiency



Curve No.	Base charge	Priming charge		Reinforcing capsule	Diam. of shell, cm.	Maximum value of curve
		Weight, cg.	Composition			
11	HEX	15	LA-LS	With	0.59	180
10	HEX	15	LA-LS	Without	.59	175
9	HEX	15	LA-LS	Without	.69	143
8	HEX	15	LA-LS	Without	.79	96
7	HEX	15	LA-LS	With	.69	156
6	HEX	50	FC	With	.69	117
5	TET	50	FC	With	.69	101
4	HEX	75	FC	Without	.69	98
3	PETN	75	FC	Without	.69	94
2	TET	75	FC	Without	.69	83
1	FC	50	FC	Without	.69	34

Explanation of key:
HEX hexagon
TET tetryl
FC fulminate-chlorate (80-20)
LA-LS lead azide-lead styphnate (80-20)

Figure 7. Initiating Efficiencies of Eleven Series of Detonators Expressed as Unit Weight of Explosive Charge in Detonator

of standard fulminate-chlorate detonators. The curves were selected for Figure 7 to illustrate the influence of the factors studied in this report. The relations of the various factors affecting initiating efficiency are sharply depicted by these curves: base charge, curves 1, 2, 3, and 4; reinforcing capsule, curves 2 and 5; priming charge, curves 6 and 7; and diameter, curves 8, 9, and 10.

Curve 11 represents a high-efficiency detonator combining all the advantageous features of the previous detonators. It possesses the following characteristics: The base charge is hexogen, and the priming charge is 80–20 lead azide–lead styphnate pressed under a copper reinforcing capsule. The shell is gilding metal having an outside diameter of 0.59 cm. Its initiating efficiency, as indicated by the maxima of the curves of Figure 7, is of the order of five and a half times that of a fulminate-chlorate detonator on an equal-weight-of-explosive-charge basis. Further investigation of other factors would probably reveal detonators of greater efficiency. Of these factors, the effect of the magnitude of the pressure on the detonator charges is no doubt important. An investigation of these and other factors is contemplated.

Detonator designers have been cautious about containing lead azide in copper capsules or shells because of the possibility of formation of dangerously sensitive copper azide, especially if moisture may be present (*18, 20*). One method of circumventing this difficulty has been to use aluminum shells. Another has been to seal the detonator positively, as in electric detonators, to exclude the entrance of moisture (*2*). Still another method has been to enclose the lead azide completely in a cavity in the base charge. The detonators studied in this report were fired generally the same day they were made, thus minimizing the possibility of copper azide formation.

The maxima in the curves of Figure 7 result from the mathematical operation of subtracting the detonator blank from the total sand crushed. Curves showing the total sand crushed by the TNT–iron oxide mixture and the detonator rise to maxima and level off. The curves for the detonator blanks are essentially straight lines. Subtraction of the latter from the former produces curves with maxima as in Figure 7.

A study of Figure 7 reveals the significant fact that the initiating efficiency of a detonator depends upon both the quantity and quality of its explosive charge, and that both must be considered. Increasing the weight of charge in a mercury fulminate detonator, for example, is not nearly so effective as substituting a composition having a higher rate of detonation, such as PETN or hexogen. Another way of stating this is the generalization that a given force applied to a given area is more likely to produce initiation of an explosive than the same force applied to a larger area. Increasing the weight of charge in a detonator will increase the total force, but substituting an explosive having a higher rate of detonation will increase the force per unit area.

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Empirical Correction for Compressibility Factor and Activity Coefficient Curves

RALPH A. MORGEN AND J. HOWARD CHILDS[1]
University of Florida, Gainesville, Fla.

In determining compressibility factor z and activity coefficient f/p, correction factors for the law of corresponding states are indicated. Ethylene and nitrogen are used as the reference, and the curves of z vs. P_R and f/p vs. P_R are given for these gases. A chart (Figure 3) gives a positive correction factor for those gases ($T_R > 1$) for which the reciprocal of the compressibility factor at the critical point ($1/z_c$) is 3.35 or less; the correction factor may be neglected for those vapors ($T_R < 1$) for which the reciprocal of the compressibility factor at $1/z_c$ is 3.35 or less. A chart (Figure 4) gives a negative correction factor for those gases ($T_R > 1$) for which the reciprocal of the compressibility factor at $1/z_c$ is 4.0 or greater; Figure 4 gives a positive correction factor for those vapors ($T_R < 1$) for which the reciprocal of the compressibility factor at $1/z_c$ is 4.0 or greater. For those compounds whose $1/z_c$ values are between 3.35 and 4.0, the curve for z and f/p for ethylene and nitrogen should be used with the knowledge that values drift in the direction indicated by the correction factors.

ONE of the handiest tools in chemical engineering calculations is the use of an approximation method when empirical data are lacking. Many of these approximation methods (*3*, *4*, *5*, *14*, *15*, *16*, *18*) depend on the law of corresponding states which, in essence, says that gases and vapors the same relative distances from their critical states behave alike.

These methods have led to the use of reduced temperature, pressure, or volume relations plotted against some factor whose value is to be determined. The reduced value is defined as the actual value divided by the critical value; i.e., reduced temperature, T_R, is actual T divided by critical T in absolute units.

In using the general reduced state curves for determining z, the compressibility factor in the equation, $PV = zRT$, it has been noted (*3*, *4*, *5*) that there is a drift in the error, depending on which gases are used to make the curves. This is also true in determining f/p, the activity coefficient (*15*). The purpose of this paper is to analyze this drift and to find a general factor to correct for it. Newton (*15*) recognized that hydrogen, helium, and neon needed a correction factor and suggested that an empirical constant of +8 be added to the critical temperature and pressure of each of these gases. This is shown to be true for only a limited range.

Early in this analysis it was recognized that both z and f/p required three correction factors dependent on T, P, and V, respectively. For z the reason is obvious from its definition, $z = PV/RT$. Activity coefficient f/p is determined by evaluating Equation 1 from Lewis and Randall (*13*) by graphical integration:

$$RT \ln \frac{f}{p} = -\int_0^P \alpha \, \partial P \text{ at constant } T \qquad (1)$$

where $\alpha = RT/P - V$

Within the limits of accuracy of these correction factors, the above equation is within the modification of Tunnell's Equation 1 (*17*). If reduced values for P are plotted against f/p at constant reduced T, generalized activity coefficient curves are obtained. The error and drift of values in these curves were found to be of the same order of magnitude and direction as those for the z curves.

Preliminary calculations showed that a correction to T_R made the largest contribution to bringing the individual values onto the general curve. A correction to P_R was found to be second in importance, and a correction to V_R was, in most cases, of minor importance. The only exception is in the vicinity of the actual critical region, $T_R = 1$ and $P_R = 1$, where the correction factor for V_R becomes appreciable.

It was next observed that those substances whose critical constants were much lower than the substances for which the general curves were drawn, had deviations above the reduced temperature isotherms when T_R was greater than 1 and below the isotherms when T_R was less than 1. On the other hand, those substances whose critical constants were greater than the reference substances deviated in exactly the opposite direction.

This suggested that if a curve were plotted using the material with the lowest critical constants, helium, all the deviations would be in the same direction. However, there were insufficient reliable data to make this curve, and the correction factor would be too cumbersome for substances now satisfactorily handled with the present curves.

If the law of corresponding states were absolute, then at the critical point, $z_c = P_cV_c/RT_c$ would be the same for all substances. By plotting $1/z_c$ against T_c for various substances, there is a steady drift from $1/z_c$ for helium = 3.28 and hydrogen = 3.27 with T_c at 5.26° and 33.3° K., respectively, to $1/z_c$ for water = 4.30 and ammonia = 4.12 with T_c at 647.3° and 405.56° K., respectively. It was decided, therefore, to make a curve for a substance with an intermediate value of $1/z_c$. Ethylene (*9*, *20*), with a $1/z_c$ value = 3.58, was chosen; and in the range where data could not be obtained for ethylene, values (*10*) for nitrogen, $1/z_c$ = 3.43, were used. In the overlapping range the two check as closely as the data justify. The curves of Figures 1 and 2 were obtained.

These curves agree closely with those published by Dodge (*6*), Weber (*19*), Hougen and Watson (*7*), and Newton (*15*). However, values for the individual hydrocarbons on the family from methane (CH_4), $1/z_c$ = 3.46, to decane ($C_{10}H_{22}$), $1/z_c$ = 3.91, shift progressively from this curve with a regular deviation. The error is usually to indicate too high a value of z or f/p when T_R is 1 or more, and too low a value when T_R is less than 1. For most purposes the error is not large enough to warrant a calcu-

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[1] Present address, National Advisory Committee for Aeronautics Laboratories, Cleveland, Ohio.

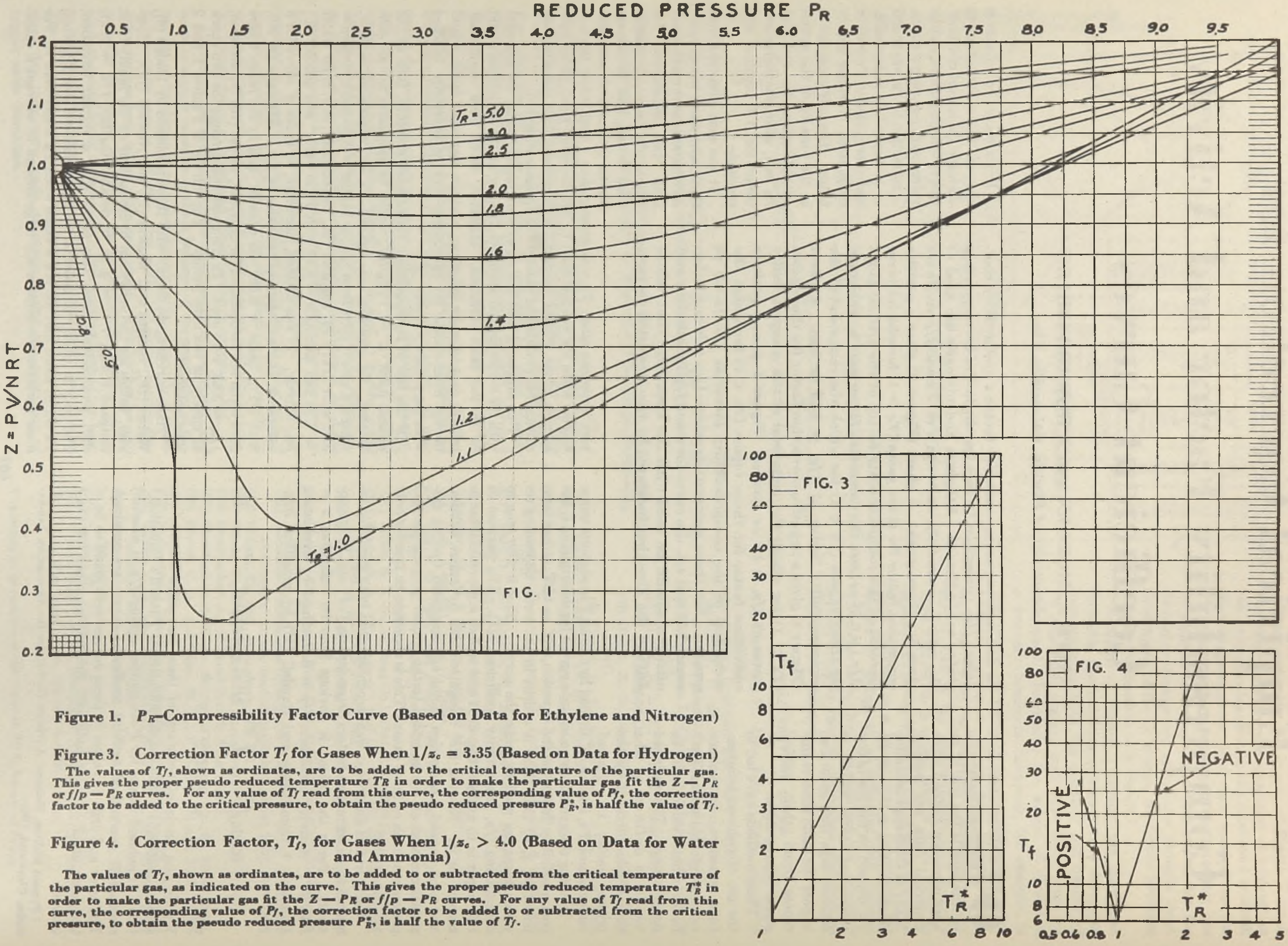

Figure 1. P_R–Compressibility Factor Curve (Based on Data for Ethylene and Nitrogen)

Figure 3. Correction Factor T_f for Gases When $1/z_c = 3.35$ (Based on Data for Hydrogen)

The values of T_f, shown as ordinates, are to be added to the critical temperature of the particular gas. This gives the proper pseudo reduced temperature T_R in order to make the particular gas fit the $Z - P_R$ or $f/p - P_R$ curves. For any value of T_f read from this curve, the corresponding value of P_f, the correction factor to be added to the critical pressure, to obtain the pseudo reduced pressure P_R^*, is half the value of T_f.

Figure 4. Correction Factor, T_f, for Gases When $1/z_c > 4.0$ (Based on Data for Water and Ammonia)

The values of T_f, shown as ordinates, are to be added to or subtracted from the critical temperature of the particular gas, as indicated on the curve. This gives the proper pseudo reduced temperature T_R^* in order to make the particular gas fit the $Z - P_R$ or $f/p - P_R$ curves. For any value of T_f read from this curve, the corresponding value of P_f, the correction factor to be added to or subtracted from the critical pressure, to obtain the pseudo reduced pressure P_R^*, is half the value of T_f.

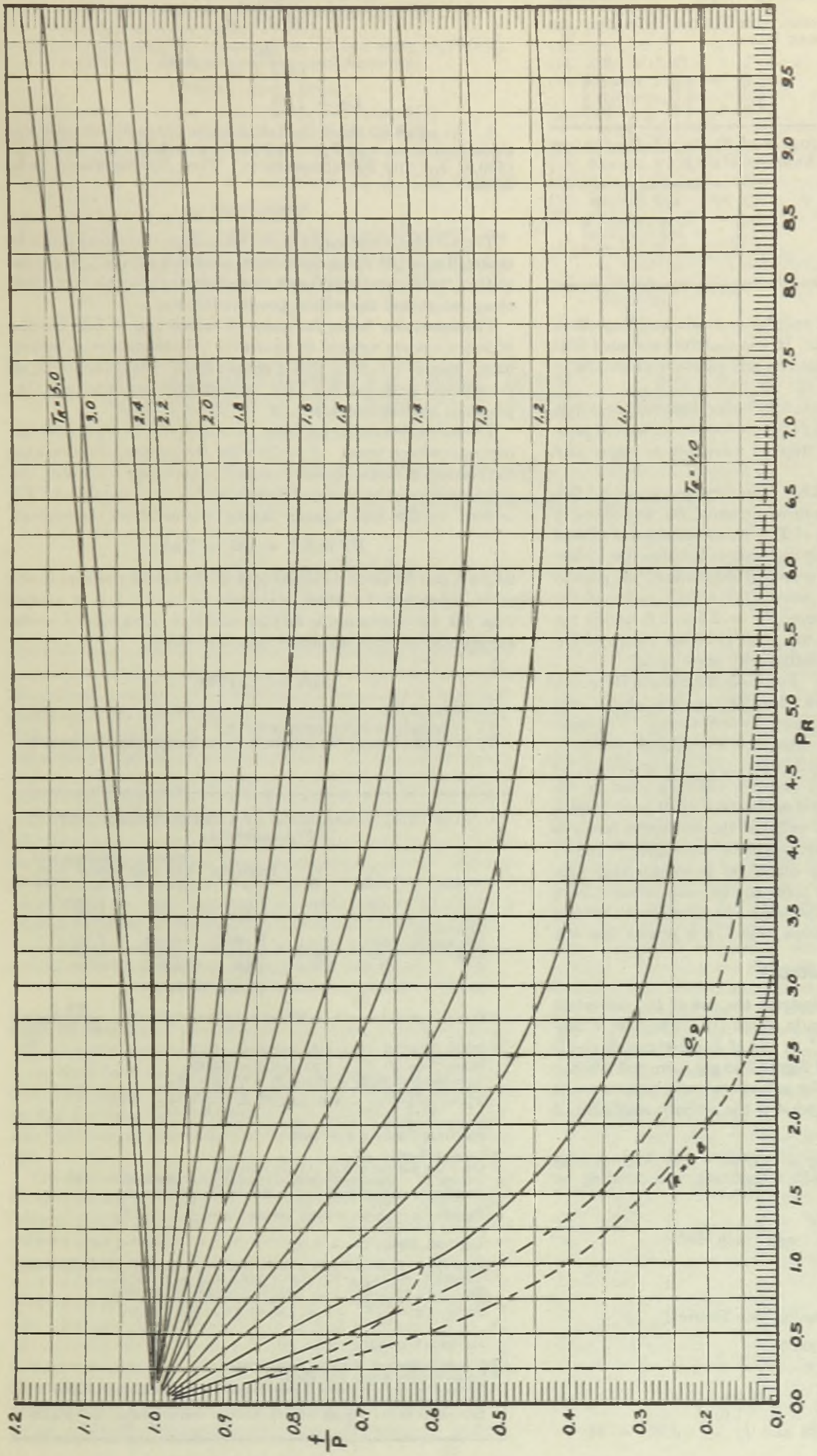

Figure 2. P_R–Activity Coefficient Curve (Based on Data for Ethylene and Nitrogen)

Dotted portions of T_R 0.8 and 0.9 lines are extrapolations for use with mixed vapors.

lated correction factor except to have a knowledge of the direction of the error. At its maximum, the deviation usually does not exceed 2 or 3%.

With water, ammonia, and other substances for which $1/z_c > 4.0$, the error at several places in the curves becomes appreciable. Two correction factors were therefore made, one for substances for which $1/z_c < 3.35$, and the other for substances for which $1/z_c > 4.0$. Since the equations of these factors are complicated, the corrections were plotted and appear as Figures 3 and 4.

CORRECTION FACTORS

TEMPERATURE T_f WHEN $1/z_c < 3.35$. Figure 3 was obtained by taking a series of PVT values for hydrogen (*8*) and adding a correction factor, T_f, of such size that a pseudo value of the reduced temperature, T_R^*, would fit the $z - P_r$ curve for ethylene and nitrogen. When plotted on logarithmic paper, these values (Table I) give approximately a straight line whose slope is 2.03 and intercepts the line for pseudo reduced temperature T_R^* = 1 at T_f = 1.05. The equation for this line is, therefore,

$$\log T_f = \log 1.05 + 2.03 \log T_R^* \quad (2)$$

or

$$T_f = 1.05\, T_R^{*2.03} \quad (3)$$

TABLE I. CORRECTION FACTORS FOR FIGURE 2 (BASED ON HYDROGEN DATA)

T_R^*	T_f	P	T_R^*	T_f	P_f
1.2	+1.5	+0.8	3.0	+10	+ 5.0
1.4	+2.5	+1.3	4.0	+17	+ 8.5
2.0	+3.5	+1.8	5.0	+28	+14.0

TABLE II. CORRECTION FACTORS FOR FIGURE 4 (BASED ON WATER AND AMMONIA DATA)

Water			Ammonia		
T_R	T_f	P_f	T_R	T_f	P_f
1.0	− 7	− 3.5	1.2	−12	− 6
1.2	−13	− 6.5	1.4	−20	−10
1.4	−21	−10.5	0.9	+10	+ 5
0.88	+12	+ 6.0			

Arbitrary values for helium and neon were chosen, and they check the use of this curve very well. It was therefore assumed that this correction factor could be used for any gases for which $1/z_c$ = 3.35 or less.

In the vapor region, $T_R < 1$, the factor becomes negative. However, the data are so meager and the temperatures and pressures so low that it was not deemed advisable to apply any correction in that range.

PRESSURE P_f WHEN $1/z_c < 3.35$. The pressure correction factor, P_f, to obtain the pseudo reduced pressure, P_R, was taken in each case as one half the value of T_f. No explanation is offered for these values except that their use makes the values for hydrogen and the other gases with low critical constants fit the general curves. Newton's correction factor (*15*) of +8 becomes the same as this method for the region T_R = 2.5 to 3.0, and is too large for lower values of T_R or too small at higher values of T_R. Arbitrary substitutions will quickly verify these facts.

T_f AND P_f WHEN $1/z_c > 4.0$. For those substances for which the correction factor is negative when T_R is greater than 1 and positive when T_R is less than 1, Figure 4 was obtained. The same method was used as that for gases with low critical constants, except that *PVT* values for both water (*12*) and ammonia (*2*) were utilized (Table II). The negative values plotted in the positive direction give a V-shaped curve made up of two straight-line segments. The numerical value of the correction factor is larger than that for Figure 3, but because of the higher T_c and P_c of these gases, the percentage correction is considerably less. The vapor correction curve is given in this case because these substances are often used in this range. It is believed that this curve can be used for all substances when $1/z_c$ is greater than 4.0.

EXAMPLES

To verify the curves and illustrate the use of the correction factors, five examples are given in Table III. The user is cautioned that the units of T_f are ° K. and of P_f are atmospheres.

One illustration of the use of Figure 2 to get corrected activity coefficients f/p using Figure 3 for adjustment, will be given. At 33.4° C. and 240 atmospheres what is the activity coefficient of hydrogen?

1. Empirically, by plotting α against P for hydrogen at 33.4° C. (306.5° K.), graphically integrating, and dividing by RT, $\ln f/p$ is found:

$$\ln \frac{f}{p} = \frac{-1}{RT} \int_0^P \alpha \, \partial P = 0.1495$$

$$f/p = 1.160$$

2. Using Figure 2 and correcting with Figure 3,

$$T_R^* - \frac{306.5}{33.2 + T_f} = \Delta$$

when T_f = 30, T_R^* = 5.25, Δ = 0.40
when T_f = 20, T_R^* = 4.30, Δ = −1.61
By interpolation T_f = 28 and P_f = $^1/_2$(28) = 14

$$T_R = \frac{306.5}{33.2 + 28} = 5.0$$

$$P_R = \frac{240}{12.8 + 14} = 8.95$$

$$f/p = 1.15$$

3. As a further check the actual value of f/p for nitrogen was calculated at its real T_R = 5.0 and P_R = 8.95—i.e., 357.3° C. (630.5° K.) and 300 atmospheres. Then f/p was found to be 1.148.

DISCUSSION

The authors were unable to obtain a single correction factor to make all gases fit the same reduced condition curves. A general shift in the values for different substances is shown as the critical temperature and the critical pressure increase.

The correction factor for gases for which $1/z_c < 3.35$ has the widest use when applied to hydrogen. Hydrogen enters into so many organic reactions that a simple method of determining its deviation is most useful. This factor is more accurate than that proposed by Newton (*15*).

The correction factor for gases for which $1/z_c > 4.0$ is interesting in showing a trend. Usually when the results justify making the correction factor for substances like ammonia and water, the actual value can be obtained just as readily from published *PVT* tables. In that case fugacity can be obtained from the relation,

$$RT \ln f/f_0 = \Delta H - T \Delta S$$

where f_0 can be assumed equal to p at the lowest pressure in the table. However for other materials for which $1/z_c$ is greater than 4.0, the correction is helpful, and this curve gives a useful approximation when empirical data are lacking.

NOMENCLATURE

f = fugacity
T_R^* = pseudo reduced temperature, ° K.
T_f = correction factor for the critical temperature to get T_R^*

TABLE III. COMPARISON OF COMPRESSIBILITY DATA CORRECTIONS

Gas	P, Atm.	T, ° K.	Empirical z	Newton Cor. and Fig. 1, z	Morgen and Childs Cor., Fig. 1, 2, 4, z
H_2	100	273.1	1.06[a]	1.09	1.065[b]
H_2	36.8	47.7	0.69[a]	0.44	0.67
50 mole % H_2 and N_2	200	273.1	1.104[c]	1.14[d]	1.11[e]
NH_3	100	548.1	0.90[f]	0.86[g]	0.90[h]
H_2O	27.2	5.9.4	0.88[i]	0.90[g]	0.89[j]

[a] From *PVT* data in International Critical Tables (*8*).

[b] T_f and P_f are obtained from Figure 3 and the relation $T_R^* - \frac{273.1}{33.2 + T_f} = \Delta$

When T_f = 30, T_R^* = 5.25 and Δ = −0.93
When T_f = 20, T_R^* = 4.30 and Δ = +0.83
By interpolation, T_f = 25 and P_f = $^1/_2\,T_f$ = 12.5

$$T_R^* = \frac{273.1}{33.2 + 25} = 4.61 \text{ and } P_R^* = \frac{100}{12.8 + 12.5} = 3.9$$

and from Figure 1, z = 1.065.

[c] Data of Bartlett (*1*).

[d] Using the method of Kay (*11*) for mixtures,
Pseudo T_c = (33.2 + 8) (0.5) + 126.1 (0.5) = 83.05° K.
Pseudo P_c = (12.8 + 8) (0.5) + 33.5 (0.5) = 27.15 atm.

$$\text{Pseudo } T_R = \frac{273.1}{83.05} = 3.29; \text{ pseudo } P_R = \frac{200}{27.15} = 7.37$$

and from Figure 1, z = 1.14.

[e] Find T_f and P_f from Figure 3 for H_2 as above = 25 and 12.5, respectively:
Pseudo T_c = (33.2 + 25) (0.5) + 126.1 (0.5) = 92.15° K.
Pseudo P_c = (12.8 + 12.5) (0.5) + 33.5 (0.5) = 29.4 atm.

$$\text{Pseudo } T_R = \frac{273.1}{92.15} = 2.96; \text{ pseudo } P_R = \frac{200}{29.4} = 6.8$$

and from Figure 1, z = 1.11.

[f] Using the data of Beattie and Lawrence (*2*).

[g] No correction factor and Figure 1.

[h] Correction factor Figure 4 (note this is a negative value) and Figure 1.

[i] Data of Keenan (*12*) and F. G. Keyes.

[j] Correction factor Figure 4 (note this is a positive value) and Figure 1.

P_R^* = pseudo reduced pressure, atmospheres
P_f = correction factor for critical pressure to get P_R^*
z = compressibility factor, PV/RT
z_c = compressibility factor at the critical state, P_cV_c/RT_c
α = $(RT/P) - v$ (deviation from perfect gas law)

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CONVERSION OF AROMATICS

Alkyl Group Transfer in the Presence of Silica-Alumina Catalysts

R. C. HANSFORD, C. G. MYERS, AND A. N. SACHANEN
Socony-Vacuum Oil Company, Inc., Paulsboro, N. J.

The conversion of alkylaromatic hydrocarbons in the presence of a typical petroleum cracking catalyst under conditions similar to those encountered in commercial catalytic cracking and reforming operations has been studied. Xylene is converted to toluene and trimethylbenzenes by disproportionation of methyl groups. Trimethylbenzenes are converted to toluene, xylene, and polymethylbenzenes, and methylnaphthalene is converted to naphthalene and polymethylnaphthalenes by the same mechanism. Diethylbenzene is converted to ethylbenzene and ethylene; no triethylbenzenes are detected in the products. In the presence of benzene, alkyl groups from alkylbenzenes are transferred to this hydrocarbon with the formation of higher yields of monoalkylbenzene than in the disproportionation reaction. Methyl groups are not, however, transferred from methylnaphthalene to benzene.

THE reactions of alkylaromatic hydrocarbons in the presence of various catalysts, particularly those of the Friedel-Crafts type, have been the subject of many investigations during the past sixty years. The primary interest in some of these investigations has been the conversion of polyalkylbenzenes to monoalkylbenzenes, as exemplified in the conversion of xylene to toluene.

The first commercial interest in this type of conversion was aroused during World War I, when the demands for larger quantities of toluene than could be obtained directly from coal carbonization forced attention to the problem of converting polymethylbenzenes to toluene. Many years prior, however, considerable work had been reported on the reactions of xylene, pseudocumene, mesitylene, and other polyalkylbenzenes in the presence of aluminum chloride. Thus, Anschütz (*1*) reported that *m*-xylene can be converted to toluene in yields as high as 25%, with the simultaneous formation of trimethylbenzenes, by refluxing with about 30% aluminum chloride for 2–3 hours. Pseudocumene was reported to yield about 20% each of xylene and toluene. The reaction of polyalkylbenzenes to form monoalkylbenzenes (or alkyl benzenes having a smaller number of corresponding alkyl groups) with the simultaneous formation of more highly alkylated benzenes is an excellent example of the type of reaction commonly termed "disproportionation".

Jacobsen (*5*) reported fair yields of toluene from xylene and of toluene and xylene from pseudocumene, through the displacement of one or more methyl groups as methyl chloride, on passing anhydrous hydrogen chloride into the refluxing polyalkylbenzene in the presence of aluminum chloride. This type of reaction is not one of disproportionation in the true sense.

Later efforts toward possible commercial conversion of polymethylbenzenes to toluene were directed mainly to the thermal cracking reaction at very high temperatures and to the transfer of methyl groups to benzene in the presence of aluminum chloride. The results reported on the latter reaction were generally negative. Boedtker and Halse (*2*) found no toluene in the reaction of xylene with benzene in the presence of aluminum chloride at the reflux temperature after 6 hours. Fischer and Niggemann (*4*) reported that the results of their investigation on this reaction were inconclusive. However, these investigators did report yields of toluene up to 12% from xylene by decomposition (undoubtedly disproportionation) at the reflux temperature in the presence of 3–4% aluminum chloride.

A high-temperature noncatalytic cracking process for the conversion of coal-tar solvent naphtha to 13–14% toluene and 8% benzene was described by Egloff (*3*).

A comprehensive review of the literature on the action of aluminum halides on alkylbenzenes, including alkylation and dealkylation reactions and intermolecular and intramolecular rearrangements, was compiled by Nightingale (*7*). More recently Pitzer and Scott (*8*) published a notable contribution on the thermodynamics and structure of benzene, toluene, and xylene. They reported equilibrium measurements on the reaction of two moles of toluene to give a mole of benzene and a mole of xylenes at 50° C., the catalyst being aluminum bromide promoted with anhydrous hydrogen bromide. Calculated equilibrium values for this reaction at 298.16° to 1500° K. are also reported in their paper.

TABLE I. CONVERSION OF *m*-XYLENE

Experiment No.	1	2	3	4	5	6
Temperature, ° C.	538[d]	538	538	538	538	538[g]
Ratio, benzene: xylene						
Molar	2:1	0:1	1:1	2:1	2:1	2:1
Weight	59.5:40.5	0:100	42.4:57.6	59.5:40.5	59.5:40.5	59.5:40.5
Space rate, vol. charged/vol. catalyst/hr.	1.09	1.05	1.04	0.36	1.05	1.13
Time on stream, min.	76	76	76	22.5	76	.....
Reaction products, wt. % of charge						
Coke	0.0	1.7	0.6	2.0	0.5	1.6
Gas	0.0	1.4	1.0	1.8	0.3	0.9
Liquid products[a]	100.0	96.9	98.4	96.2	99.2	97.5
78–95° C., C_6H_6	57.4	1.2	39.2	55.4	56.1	54.9
95–115° C., $C_6H_5CH_3$	0.4	11.7	10.0	15.2	7.6	9.9
115–135° C.	0.8	2.7	2.3	2.4	3.8	2.4
135–150° C., $C_6H_4(CH_3)_2$	40.4	66.9	38.4	19.2	31.7[f]	25.9
150–180° C., $C_6H_3(CH_3)_3$	0.0	11.8	8.5[e]	4.0[e]	.....	3.2
>180° C., residue	1.0	2.6	.....	.....	.....	1.2
Compn. of gas produced, vol. %						
Olefins	.....	10.3	10.7	8.5	15.7	12.0
Paraffins + H_2	.....	89.7	89.3	91.5	84.3	88.0
Mol. wt. of gas produced	.....	18	19	17	17	21
Benzene recovered, wt. %	97	.....	93	93	94	92
Toluene yield, wt. % on xylene charged[b]						
Per pass	0	13	19	40	23	27
Ultimate[c]	0	41	62	82	.....	83
Mole toluene produced per mole xylene						
Charged	0	0.15	0.22	0.46	0.27	0.31
Consumed	0	0.47	0.71	0.94	.....	0.95
Mole benzene consumed per mole xylene						
Charged	0	.....	0.075	0.14	0.11	0.15
Consumed	0	.....	0.24	0.28	.....	0.47
Molar ratio of toluene produced to benzene consumed	0	.....	3.0	3.4	2.5	2.1

[a] Difference between 100% and gas + coke.
[b] Based on 95–115° C. cut + half of 115–135° C. cut.
[c] Xylene only considered as recycle stock.
[d] Noncatalytic run.
[e] Total residue above 150° C.
Total residue above 135° C.
[g] Cyclic run: 15 min. on stream and 15-min. air regeneration.

Related to the present investigation are the results published by Thomas, Hoekstra, and Pinkston (*10*), who investigated the removal of side chains from aromatics with catalysts of substantially the same type as that used here. Natanson and Kagan (*6*) also used this type of catalyst in an investigation of the reaction of toluene to produce benzene and xylenes.

While the production of toluene from xylene and other polymethylbenzenes no longer represents a problem of great commercial interest, due to the availability of toluene from other hydrocarbon conversion processes and from extraction processes applied to certain straight-run and cracked gasolines, the general problem of dealkylation of polyalkylbenzenes to monoalkylbenzenes is of practical interest when applied to higher members of the series such as diethylbenzene and polyisopropylbenzenes. Moreover, a clearer understanding of some theoretical aspects of the mechanism of catalytic cracking and reforming may be obtained from a study of the reactions of the simpler alkylaromatics in the presence of usual petroleum cracking catalysts.

Earlier work (*9*) showed that a high-boiling polyalkylbenzene fraction could be converted in good yields in the presence of benzene to a lower-boiling fraction consisting entirely of simple alkylbenzenes such as toluene, ethylbenzene, and others boiling below 150° C. For example, a 150–250° C. fraction of alkylbenzenes, consisting for the most part of mono and poly isopropyl-, butyl-, and amylbenzenes, was converted at 482° C. in the presence of benzene and an activated clay catalyst to some 62% by weight of a 95–150° C. fraction of alkylbenzenes. Consumption of about 16% of benzene based on alkylbenzene charge was observed, showing a substantial transfer of alkyl groups to benzene. Under the same conditions in the absence of benzene the yield of the 95–150° C. fraction was only 25%.

These results suggested that alkyl group transfer to benzene might be effected in the presence of a typical cracking catalyst even in the case of xylene, where previous attempts with aluminum chloride catalyst had failed. A study of the transfer of ethyl groups was also made for comparison.

CATALYTIC RUNS

MATERIALS. The usual C.P. grades of benzene and *m*-xylene were used. Diethylbenzene was obtained by distillation of the polyalkylated fraction from the alkylation of benzene with ethylene. A 175–185° C. cut of this material, corresponding to the boiling points of the isomeric diethylbenzenes, was obtained by fractionation through a fifteen-plate Fenske column. The pseudocumene and α-methylnaphthalene were Eastman's Technical grade. While the purity of the Eastman materials was not determined with respect to individual isomers, physical properties (density and boiling range) indicated that they were substantially pure trimethylbenzenes and methylnaphthalenes, respectively.

A commercial synthetic silica-alumina catalyst was prepared by coprecipitation of the hydrous oxides in a ratio of about 9 to 1 by weight of silica to alumina. Its properties were similar to those of the silica-alumina catalyst described by Thomas, Hoekstra, and Pinkston (*10*).

APPARATUS AND PROCEDURE. The apparatus for processing the materials consisted of a 110-cc. stainless-steel catalyst chamber immersed in a thermostated molten lead bath; a charging system, comprising a Manzel chemical-feeder-type pump and a graduated charge cylinder; and a conventional collecting system, comprising a coil condenser, liquid-gas separator, calibrated gas receiving bottles, and wet test meter. The charge was pumped to the reaction chamber indirectly by displacement with ethylene glycol from a 500-cc. glass buret. The glycol was pumped into the bottom of the buret, and the amount of charge displaced through the top was measured by the difference in the position of the interface at the beginning and end of the run. The pressure on the reactor was maintained at 15 ± 0.5 pounds per square inch (gage) by means of a manually controlled Hoke needle valve at the exit.

Special precautions were taken to ensure accurate material balances by thermostating the buret, and by purging the system with a small amount of charge stock prior to the main run to wet the condenser walls and thus minimize drainage errors.

The initial free space in the condenser was filled with carbon dioxide in order to allow an accurate analysis of the gas produced from the reaction, when the amount of this gas was only one to two times the volume of the dead space in the condenser system. Gas analysis was made on the collected gas by Orsat absorption for carbon dioxide, oxygen, and olefins, the hydrocarbon content and weight being corrected to a carbon-dioxide-free basis. Gas densities were determined by a modified precision Schilling effusiometer.

Coke was determined by burning the catalyst, after purging hydrocarbon vapors with nitrogen, in a stream of air flowing at 500–1000 cc. per minute. The regeneration gases were passed through a hot copper oxide catalyst to convert carbon monoxide to carbon dioxide. The carbon dioxide was measured by absorption in a tared Ascarite bulb, and the equivalent carbon was calculated.

The determination of weight of gas and coke is to be considered quite accurate as compared to the experimental errors involved in measuring the recovery of liquid product. The material balance is based on the accurate determination of gas and coke and the calculation of weight of liquid product by difference. The deviation of the calculated recovery of liquid product from its experimental value was seldom greater than about 1%, which is within the experimental error.

Several experiments were made in cyclic operation; i.e., the charge was pumped to the reactor for a given time, usually 15 minutes, after which the system was purged with nitrogen and the coke deposit on the catalyst burned off in a stream of air for a time equal to the on-stream period. The charge was then pumped to the reactor for the same period, followed by regeneration, and so on for a number of such cycles. The catalyst was thereby maintained in a state of high activity, resulting in reaction conditions effectively more severe than those where the catalyst was not reactivated during a 1–2 hour run.

The synthetic crude was analyzed by careful fractionation through a fifteen-plate Fenske distillation column with total reflux–variable takeoff type head. The small residues from this distillation were further distilled through a semimicrocolumn packed with a nichrome wire spiral. Cuts were analyzed for specific gravity and iodine numbers. In all cases the latter value was zero, and the specific gravity corresponded to that of the pure compound included in the cut.

EXPERIMENTAL DATA

Table I shows the results of the investigation of methyl group transfer between *m*-xylene and benzene, and between one molecule of xylene and another at 538° C. It was found that at lower temperatures (510° C.) the rate of reaction with benzene was too slow for practicable space rates, but at 538° C. satisfactory reaction rates were obtained.

The noncatalytic run with benzene (experiment 1) shows no reaction of xylene, although according to the distillation some benzene has disappeared. It is believed that the small amounts of product boiling between 95° and 135° C. are not due to toluene formation, but rather to poor fractionation in this case. Hence, conversion of xylene to toluene under these conditions has been assigned a value of zero in the calculations.

The data listed for the next five experiments show conclusively that xylene is converted to toluene and trimethylbenzenes. It is interesting that in the absence of benzene (experiment 2) the catalytic conversion of xylene produces nearly equal molar amounts of toluene and trimethylbenzenes according to the equation:

$$2C_6H_4(CH_3)_2 \rightleftarrows C_6H_5CH_3 + C_6H_3(CH_3)_3 \qquad (1)$$

This is essentially the reaction reported by Anschütz (*1*) with aluminum chloride, showing disproportionation involving methyl group transfer between xylene molecules.

The addition of benzene to the reaction system gives rise to the competing reaction:

$$C_6H_4(CH_3)_2 + C_6H_6 \rightleftarrows 2C_6H_5CH_3 \qquad (2)$$

Experiments 3 to 6 show that transfer of methyl groups from xylene to benzene actually occurs to about as great an extent as it occurs between xylene molecules. As a matter of fact, experiment 3 shows that the molar ratio of products to reactants corresponds approximately to the sum of Equations 1 and 2. Experiment 6, on the other hand, shows a somewhat higher consumption of benzene, due possibly to a greater proportion of reaction 2.

According to Pitzer and Scott (*8*), the equilibrium constant for reaction 2 at 527° C. is calculated to be 3.3. This corresponds to the formation of 1.3 moles of toluene per mole of xylene charged in experiments 4 to 6. Even at the low space rate of experiment 4 the extent of reaction apparently has not reached more than 35% of its equilibrium value. Lower space rates than that used in experiment 4 probably would give higher yields of toluene, but side reactions leading to coke and gas formation have already become bothersome. For this reason more severe conditions of reaction time were not investigated, since any conclusions regarding the reaction equilibrium would be subject to considerable doubt.

Table II shows the results of the investigation of methyl group transfer from pseudocumene to benzene at 510° and 538° C. The same general conclusions can be drawn for the pseudocu-

TABLE II. CONVERSION OF PSEUDOCUMENE

Experiment No.	7	8
Temperature, ° C.	510	538
Ratio, benzene:pseudocumene		
Molar	2:1	2:1
Weight	56.5:43.5	56.5:43.5
Space rate, vol. charged/vol. catalyst/hr.	2.18	1.08
Time on stream, min.	75	75
Reaction products, wt. % of charge		
Coke	0.8	2.4
Gas	1.3	3.4
Liquid products[a]	97.9	94.2
78–95° C., C_6H_6	54.6	52.0
95–115° C., $C_6H_5CH_3$	1.7	3.5
115–130° C.	0.8	1.6
130–150° C., $C_6H_4(CH_3)_2$	3.9	6.6
150–160° C.	1.7	2.0
160–185° C., $C_6H_3(CH_3)_3$	32.1	25.0
>185° C., residue	3.1	3.5
Compn. of gas produced, vol. %		
Olefins	28.7	21.2
Paraffins + H_2	71.3	78.8
Mol. wt. of gas produced	24	21
Benzene recovered, wt. %	97	92
Toluene yield, wt. % on $C_6H_3(CH_3)_3$ charged[b]		
Per pass	5	10
Ultimate[c]	20	25
Xylene yield, wt. % on $C_6H_3(CH_3)_3$ charged[d]		
Per pass	12	19
Ultimate[c]	49	48
Mole toluene + xylene produced per mole pseudocumene		
Charged	0.20	0.35
Consumed	0.81	0.87
Mole benzene consumed per mole pseudocumene		
Charged	0.067	0.16
Consumed	0.28	0.40
Molar ratio of toluene + xylene produced to benzene consumed	3.0	2.2

[a] Difference between 100% and gas + coke.
[b] Based on 95–115° C. cut + half of 115–130° C. cut.
[c] Trimethylbenzenes only considered as recycle stock.
[d] Based on 130–150° C. cut + half of 115–130° C. cut + half of 150–160° C.

TABLE III. CONVERSION OF α-METHYLNAPHTHALENE

Experiment No.	9	10	11	12	13
Temperature, ° C.	538[f]	538	510	538	538
Ratio. benzene: α-methylnaphthalene					
Molar	0:1	0:1	2:1	2:1	5.5:1
Weight	0:100	0:100	54.5:45.5	54.5:45.5	75.5:24.5
Space rate, vol. charged/vol. catalyst/hr.	1.10	1.11	2.18	1.11	1.09
Time on stream, min.	75	75	70	147	260
Reaction products, wt. % of charge					
Coke	0.0	3.8	1.2	1.9	1.2
Gas	0.0	1.6	0.8	1.7	0.7
Liquid products[a]	100.0	94.6	98.0	96.4	98.1
78–95° C., C_6H_6	0.0	0.5	53.8	53.6	74.0
95–115° C., $C_6H_5CH_3$	0.0	0.0	0.0	0.2	0.0
115–200° C.[b]	0.3[g]	1.2	0.8	0.6	0.4
200–225° C., $C_{10}H_8$	0.1[g]	8.2	1.6	4.2	2.7
225–230° C.[c]	0.5[g]	2.6	0.5	0.9	0.4
$C_{10}H_7CH_3$	99.1[h]	74	37	33	19
Residue[d]	....	8.1	4.3	3.9	1.6
Compn. of gas produced, vol. %					
Olefins	....	7.3	18.6	10.6	9.8
Paraffins + H_2	....	92.7	81.4	89.4	90.2
Mol. wt. of gas produced	....	15	18	16	15
Benzene recovered, wt. %	....	...	99	98	98
Naphthalene yields, wt. % on methylnaphthalene charged[e]					
Per pass	0	10	4	10	12
Approx. ultimate	0	40	25	40	55
Molar ratio of naphthalene produced to methylnaphthalene charged	0	0.11	0.05	0.11	0.13

[a] Difference between 100% and gas + coke.
[b] Mostly alkylbenzenes.
[c] About half naphthalene.
[d] Estimated by Engler distillation of >230° C. residuum, showing about 10% heavier products in all catalytic runs.
[e] Based on 200–225° C. cut + half of 225–230° C. cut.
[f] Noncatalytic run.
[g] Liquid.
[h] Total residue above 230° C.

TABLE IV. CONVERSION OF DIETHYLBENZENE

Experiment No.	14	15	16	17	18	19	20	21	22	23
Temperature, ° C.	510[c]	510[c]	510	454[d]	454[d]	454	482	482	510	524
Ratio, benzene: diethylbenzene										
Molar	0:1	3:1	0:1	2:1	2:1	3:1	3:1	3:1	3:1	3:1
Weight	0:100	63.6:36.4	0:100	53.8:46.2	53.8:46.2	63.6:36.4	63.6:36.4	63.6:36.4	63.6:36.4	63.6:36.4
Space rate, vol. charged/vol. catalyst/hr.	1.09	1.03	1.09	1.08	1.10	1.10	1.08	2.20	1.08	1.04
Time on stream, min.	50	82	50	.....	.....	99	102	49	101	85
Reaction products, wt. % of charge										
Coke	0.0	0.0	2.0	3.0	2.3	0.5	0.5	0.4	1.0	1.3
Gas	0.1	0.2	8.4	1.3	1.5	1.0	2.2	1.4	2.7	2.7
Liquid products[a]	99.9	99.8	89.6	95.7	96.2	98.5	97.3	98.2	96.3	96.0
78–100° C., C_6H_6	0.0	61.6	3.5	49.1	49.0	58.2	59.0	59.5	60.2	60.4
100–132° C.	0.0	0.0	2.3	1.5	1.4	1.2	1.8	1.2	0.5	1.4
132–140° C., $C_6H_5C_2H_5$	0.0	0.0	23.3	13.5	14.0	10.1	14.3	11.0	15.6	11.6
140–175° C.	3.0	0.6	7.0	1.8	2.2	2.7	1.8	2.3	1.6	2.3
175–185° C., $C_6H_4(C_2H_5)_2$	91.9	35.5	39.6	25.1	22.9	23.0	17.5	21.0	15.6	15.8
>185° C., residue	5.0	2.1	13.9	4.7	6.7	3.3	2.9	3.2	2.8	4.5
Compn. of gas produced, vol. %										
C_2H_4	...	.....	41.5	43.2	41.9	46.2	54.9	61.7	53.2	34.5
Other olefins	...	.....	7.1	6.8	8.5	10.5	10.5	12.6	6.5	5.0
Paraffins + H_2	...	.....	51.4	50.0	49.6	43.3	34.6	25.7	40.3	60.5
Mol. wt. of gas produced	...	.....	28	26	30	29	32	30	20	19
Benzene recovered, wt. %	...	97	...	93	92	92	94	94	95	96
Ethylbenzene yield, wt. % on diethylbenzene[b]										
Per pass	0	0	28	33	34	33	44	35	46	37
Ultimate	0	0	49	75	71	100	90	90	84	69
Moles ethylbenzene produced per mole diethylbenzene										
Charged	0	0	0.35	0.42	0.43	0.42	0.56	0.44	0.58	0.47
Consumed	0	0	0.62	0.95	0.90	1.26	1.14	1.14	1.06	0.87
Mole benzene consumed per mole diethylbenzene										
Charged	...	.....	...	0.15	0.15	0.23	0.17	0.17	0.15	0.12
Consumed	...	.....	...	0.34	0.32	0.68	0.35	0.42	0.27	0.22
Molar ratio of ethylbenzene produced to benzene consumed	...	.....	...	2.8	2.9	1.9	3.3	2.7	3.9	4.0

[a] Difference between 100% and gas + coke.
[b] Based on 132–140° C. cut + half of 100–132° C. cut + half of 140–175° C. cut.
[c] Noncatalytic run.
[d] Cyclic run: 15 min. on stream and 15-min. air regeneration.

mene reaction as have been reached for xylene conversions. Methyl groups are readily transferred to benzene, with the formation of toluene and xylene. At the same time methyl group transfer between trimethylbenzene molecules probably occurs with the formation of tetramethylbenzenes and xylenes.

As Table III shows, methyl groups do not transfer from methylnaphthalene to benzene under the conditions investigated. However, there is apparently a transfer of methyl groups between methylnaphthalene molecules, with the formation of naphthalene and dimethylnaphthalenes. The reason for the failure of methyl groups to transfer from methylnaphthalene to benzene is not readily apparent. It is difficult to imagine that the methyl group in methylnaphthalene is more tightly bound to the bicyclic aromatic nucleus than it is to the monocyclic nucleus.

Qualitatively it appears that "activation" of a hydrogen atom of the acceptor molecule is necessary before alkyl group transfer can occur. It seems reasonable to suppose that hydrogen atoms of the naphthalene nucleus are much more readily activated than those of the benzene nucleus. The relative ease of such classical reactions as sulfonation, chlorination, and nitration of naphthalene and its homologs as compared to benzene supports such an assumption. Therefore, one might expect that the rate of methyl group transfer from methylnaphthalene to methylnaphthalene is much greater than that from methylnaphthalene to benzene. On the other hand, the apparent complete failure of methyl group transfer to benzene might be explained by steric factors involved in the adsorption of the reactants on the catalyst. Possibly the catalyst surface is preferentially covered with methylnaphthalene, effectively denying access of benzene to the surface for activation or reaction.

Table IV shows results of the investigation of ethyl group migration between diethylbenzene and benzene in the range 454° to 524° C. Similar yields of the monoalkyl derivative are obtained from diethylbenzene as from xylene, but the mechanism of the reaction appears to be somewhat different from that shown for xylene.

In the catalytic conversion of diethylbenzene in the absence of benzene, the 14% of residuum boiling above 185° C. was not principally triethylbenzenes. The specific gravity was 0.93, indicating a polycyclic structure. In the presence of benzene also, the amount of this residuum is from 3 to 7% per pass, and careful fractionation failed to show a plateau in the boiling range of triethylbenzenes. The specific gravity of the residua produced in all catalytic runs in the presence of benzene was about 0.95.

The mechanism of the diethylbenzene conversion appears to be a simple splitting out of an ethyl group to form ethylene and ethylbenzene. In the presence of benzene part of this ethylene alkylates benzene to form more ethylbenzene. A side reaction of unknown nature occurs, forming appreciable amounts of polycyclic hydrocarbons.

The dealkylation of diethylbenzene apparently does not involve any appreciable cracking of ethyl groups to methyl groups. The 3–5% intermediate fraction between benzene and ethylbenzene showed no plateau at the boiling point of toluene. The 132–140° C. fraction was examined carefully for the presence of xylenes. Oxidation gave only benzoic acid. Further confirmation of the absence of xylenes was obtained by the method of selective hydrolysis of the sulfonic acids described by White and Rose (*11*). No hydrocarbon was liberated by steam hydrolysis of the sulfonic acids between 125° and 145° C. The hydrocarbon liberated between 145° and 175° C. represented about 85% of the original oil. Its refractive index, n_D^{20}, was 1.4960, the same value as that of the original fraction.

Since the absence of dimethylbenzenes in the reaction products has been proved, it seems reasonable to suppose that ethyltoluene also is not a product of the conversion of diethylbenzene. Hence, in the calculations shown in Table IV, half of the fraction boiling between 140° and 175° C. has been assigned to the ethylbenzene yield and half to diethylbenzene. Likewise, the 100–132° C. fraction has been divided between benzene and ethylbenzene.

The absence of cracking of the side chain to one of shorter length in the case of diethylbenzene is in confirmation of the general conclusions reached by Thomas, Hoekstra, and Pinkston (*10*) that side chains of alkylbenzenes are removed intact. We are inclined to agree with this conclusion up to a certain point.

However, if the alkyl side chain is large enough, we believe that cracking to shorter chains does occur to a considerable extent. Apparently the maximum length of the side chain which is relatively unsusceptible to cracking is about C_4. In our earlier work (*9*) we found considerable amounts of toluene in the catalytically cracked products from a mixture of alkylbenzenes containing large amounts of amyl- and diamylbenzenes. Part of this toluene undoubtedly was produced by nonselective thermal cracking, since the reaction was carried out in batch operation under more severe conditions than those used by Thomas *et al.* However, in the presence of the catalyst much higher yields of toluene were produced under the same conditions.

CONCLUSIONS

The conversion of alkylaromatic hydrocarbons in the presence of a typical silica-alumina cracking catalyst, under conditions similar to those encountered in commercial catalytic cracking, consists of essentially two types of reactions, depending on the nature of the alkyl group. If the side chains are methyl groups, transfer of alkyl group occurs through bimolecular disproportionation according to the equation:

$$2\text{Ar R}_x \longrightarrow \text{Ar R}_{x-1} + \text{Ar R}_{x+1}$$

where Ar is an aromatic nucleus, R is a methyl group, and x is the number of methyl groups. If the side chains are longer than methyl, simple dealkylation of one or more alkyl groups to form the corresponding olefin and lower aromatic derivatives is the primary reaction. For example, xylene is converted selectively to toluene and trimethylbenzenes in equimolar amounts, while diethylbenzene is converted to ethylbenzene and ethylene, apparently without formation of triethylbenzenes under the conditions investigated.

The addition of benzene to the reaction system serves to double the yield of lower alkylbenzenes due to the competition of benzene for alkyl groups in both reactions. Activation of a hydrogen atom of the acceptor molecule, as well as the activation of alkyl group of the donor molecule, appears to be a necessary prerequisite for alkyl group transfer, since methyl group transfer from methylnaphthalene to benzene does not occur under the conditions of this investigation. In this case the much greater ease of hydrogen activation in the naphthalene series as compared to that in benzene, or the exclusion of benzene from the catalyst surface by methylnaphthalene, accounts for the absence of methyl group transfer to benzene.

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POLYISOBUTYLENE TANK LINING

DAVID W. YOUNG AND WILLIAM C. HARNEY

Standard Oil Company of New Jersey, 26 Broadway, New York 4, N. Y.

MANY manufacturing processes require noncorrosive ducts, containers, storage tanks, and vessels in which a wide variety of chemical reactions are conducted. Much work has been devoted to the development of corrosion-resistant linings for use in such containers. The oldest containers were enamel or tin, lead, and gold platings. Then rubber was used, and later acid-resistant stones embedded in water-glass cements were successful. Recent developments in the field of resistant coatings use high-molecular-weight synthetic thermoplastic protective agents.

A review of literature indicates that the resistance of polyisobutylene to inorganic-process liquors is being recognized. A recent paper by Krannich (*4*) states: "Polybutene represents a material with a range of corrosion resistance that is wider than that of hitherto known materials. Polybutene is one of the first materials which is simultaneously resistant to dilute and concentrated alkalies and acids, even to oxidizing acids. These excelling chemical properties, as well as the good workability, will assure a special position for polybutene in the field of corrosion prevention." Krannich reported that polyisobutylene was stable to 102 corrosive agents over a wide temperature range.

The 1939 progress report on rubber technology (*1*) states that products of Vistanex (polyisobutylene) are more resistant to extremes of heat and cold than natural rubber, but that they are attacked by oils and some chlorinated solvents. It is pointed out that they can be compounded with high proportions of fillers.

Thus, the olefinic type of polymer, such as polyisobutylene, has been recognized as a highly resistant material for several years. Its commercial utilization as a corrosion-resistant liner, however, has been dependent upon the development of a feasible method for bonding the polymer to metal. A successful bonding method has been devised, and tests on polyisobutylene-coated metal specimens indicate that this method can now be used in commercial applications for a wide variety of corrosive liquids and gases.

The objects of this investigation were to develop a process whereby polyisobutylene compounds could be bound to metal, and to determine the strength and resistance of the resulting tank lining to attack by acids and alkalies.

PREPARATION OF TANK LINING

POLYMER. The polyisobutylene was prepared by polymerizing isobutylene at −87° C. with a Friedel-Crafts type catalyst, such as boron trifluoride gas. Thomas *et al.* (*5*) reported information on the preparation and structure of the polymer. Under these conditions a polyisobutylene is produced having an intrinsic viscosity in diisobutylene at 20° C. of approximately 3.0, where

$$\text{intrinsic viscosity} = \frac{\log_e \left(\dfrac{\text{viscosity of soln.}}{\text{viscosity of solvent}}\right)}{\text{concn. of polymer (g./100 cc.)}}$$

This intrinsic viscosity value is equivalent to a molecular weight of about 95,000, or a viscosity-average molecular weight of 1,500,000 (*5*).

Such a polymer is plastic and elastic, much like slightly broken down natural rubber, and is an aliphatic hydrocarbon with a chemical inertness essentially that of other saturated hydrocarbons. Inorganic salts and their solutions are nonreactive with polyisobutylene. Similarly, alkalies and acids,

A process for the manufacture of high-molecular-weight polyisobutylene compositions is described. Available laboratory data show that such a compounded polymer would be an excellent tank lining. A method has been developed to bond the polyisobutylene lining to steel. Adhesion of the polymer film to steel is approximately 700 pounds per square inch at room temperature. High loadings of carbon black produce good adhesion or interlocking of this linear type polymer (polyisobutylene) to steel when cyclized rubber cement is applied as an intermediate bonding agent. Further data show the resistance of the lining to concentrated and dilute solutions of acids and alkalies at room temperature. Except in a few instances the compounded polymer linings show no tendency to blister at 100° C. (Wartime demand prohibits the general use of polyisobutylene except for high-priority purposes.)

or aqueous solutions of either, do not attack the polymer to any noticeable extent below temperatures of approximately 100° C. No interaction occurs between polyisobutylene and low-molecular-weight oxygenated organic solvents including alcohols, aldehydes, organic acids, or esters. Free halogens react with polyisobutylene forming substituted products. The solubility of the polymer is fairly high in the hydrocarbons and in all liquid, chlorinated hydrocarbons with dielectric constants below about 8 at room temperature (*2*).

Tank Lining. One hundred parts (400 grams) of polyisobutylene, prepared as previously described, were placed on a 6 × 18 inch laboratory mill, and 200 parts (800 grams) of carbon black were added. One part (4 grams) of paraffin wax was also added to reduce heat build-up during milling and aid in subsequent calendering. The mixed materials were removed from the mill and kneaded in a Banbury mixer until homogeneity was assured. The mixture was then transferred to a three-roll calender and sheeted at about 85° C. to a thickness of about 0.125 inch. These calendered sheets were suitable for immediate use as coatings or could be stored for considerable time before use. If immediate use is not convenient, it is desirable that the sheets be interleaved with Holland cloth or similar liner to prevent "blocking" or adhesion between layers. Dusting the sheets with talc also prevents the layers from blocking on prolonged standing.

Metal Surface. Preparatory to the application of the polymer liner, the metal surfaces are cleaned to free them from oxidized layers and all traces of grease or oil. This may best be done by thorough sandblasting or pickling in acid, until the metal surface is bright and free of all foreign matter.

APPLICATION OF LINER TO METAL SURFACE

A preliminary layer of cement is applied to the metal surface and sufficient time allowed for solvent to be evolved (about 45 minutes). Either cyclized rubber or cyclized polymethylpentadiene proved satisfactory as cementing agent. The cyclized rubber cement used was B. F. Goodrich Company's Vulcalock. Cyclized polymethylpentadiene is prepared by low-temperature polymerization of the monomer, followed by heat treatment at 100° C. for approximately 8 hours. The tank lining is then washed with a solvent to remove all foreign matter and coated with a toluene solution of the cement. After both cemented surfaces are dry, the lining is set in place against the metal surface and is rolled down under about 100 pounds per square inch pressure. The lining is preferably held in place with pressure until the cement is fully set. Some of the liners were cured at 100° C. and others at room temperature during the setting-up period. It appears that bond strength is improved slightly if the higher temperature is used. Pressure may be applied mechanically or with gas.

BOND STRENGTH OF LINER

The addition of carbon black to polyisobutylene was necessary to effect a bond with aluminum, cast iron, lead, stainless steel, and tin plate. It also stiffens the polymer and reduces cold flow. Polyisobutylene alone has a low tensile strength (about 60 pounds per square inch), and the addition of carbon black is essential to obtain a strong bond.

Adhesion strength of the liner to metal and the tensile strength of the liner itself were determined according to the Yerzley modification of A.S.T.M. Method D429-39T. Polymer to be tested is sealed to one face of a flat, circular, steel plate; precautions are taken to obtain a good seal as described before. A second steel disk is simultaneously sealed to the other side of the test specimen. Opposite faces of the metal disks, from which the liner is attached, are threaded to allow connection with a tensile test machine. The sheet of polymer separating the metal disk is 0.375 inch thick and has a surface area of 2 square inches. The machine records the maximum force required to separate the plates. Data are presented in Table I.

These results show the high strength of both the bond and the liner material to be about 700 pounds per square inch. In each test rupture occurred at least 90% within the stock and 10% at the steel, as judged by visual observation. Under the same test conditions, unloaded and slightly loaded stocks (25 to 75 parts carbon black) gave bonds too weak to test. By a similar test,

Table I. Tensile Strength Test Results

Bond to steel. Composition of tank lining: one third polyisobutylene of 95,000 mol. wt. (Staudinger) and two thirds carbon black (with a trace of wax). Adhesion material: Cyclized polymer.

Sample number	1	2	3	4	5
Time of cure of adhesion material, hr.	72	72	36	36	36
Temp. of cure, ° C.	100	100	Room	Room	Room
A.S.T.M. adhesion at room temp., lb./sq. in.	905	653	654	550	705

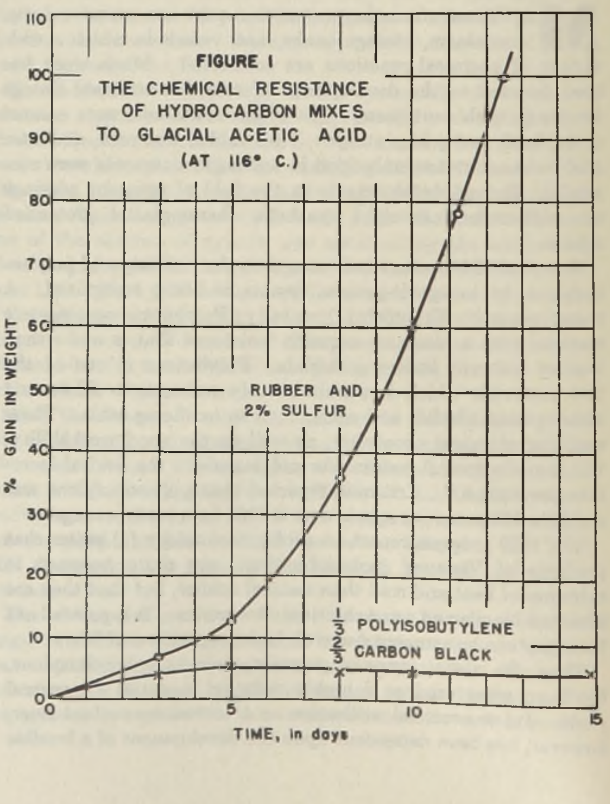
FIGURE I
THE CHEMICAL RESISTANCE OF HYDROCARBON MIXES TO GLACIAL ACETIC ACID (AT 116° C.)

Table II. Corrosion Test of Hydrocarbon Mixtures by A.S.T.M. Method D471-37T

Heavy chemical	30% H_2SO_4		45% HF		85% H_3PO_4	Glacial Acetic Acid		Mixed Acid		Mixed Alkalies		
Composition	Rubber and sulfur[a]	Polyisobutylene & C black[b]	Rubber and sulfur	Polyisobutylene & C black	Polyisobutylene & C black	Rubber and sulfur	Polyisobutylene & C black	Rubber and sulfur	Polyisobutylene & C black	Rubber and sulfur	Polyisobutylene & C black	Polyisobutylene, graphite, & C black[c]
Size of sample, in.	D.B.[d]	D.B.	D.B.	D.B.	D.B.	D.B.	D.B.	D.B.	D.B.	1 1/8 × 3 × 0.06	15/16 × 3 × 0.1	15/16 × 3 × 0.11
Gage at start of run, in.	0.073	0.107	0.076	0.111	0.106	0.073	0.107	0.074	0.106	0.06	0.10	0.11
Initial wt., grams	3.5181	6.6706	3.1169	5.7160	7.3722	2.8031	5.1391	2.9351	6.0711	3.6959	5.3576	6.8049
Final wt., grams	3.4618	6.7002	3.5240	5.7540	7.3711	6.0520	5.4489	2.6250	6.1000	3.5482	5.3620	6.9150
Total change in wt., %	−1.55	+0.443	+13.1	+0.664	−0.015	+11.6	+6.01	−10.6	+0.47	−3.99	+0.109	+1.61
Total time of run, days	14	14	14	14	15	11	15	14	14	14	14	14
Color of soln. at end (333 ml.)	Brown	Colorless	Colorless	Colorless	Colorless	Black	Very slight yellow	Colorless	Colorless	Slight yellow	Colorless	Colorless
Temp. of soln., ° C.	106–111	106–111	20–27	20–27	20–27	114–116	114–116	20–27	20–27	105	105	105
Scale formation or chips in soln.	None	None	None	None	None	Yes	None	Yes	None	None	None	None
No. of times soln. changed	2	2	0	0	2	2	2	2	2	2	2	2
Physical evaluation after run												
Tare resistance at break	106	335–35	44.5	21.5	20.5	0	39	Sample so soft that properties could not be detd.				
Elongation at break, %	650	420–330	670.0	640	620	200	610		35	44.0	....	......
Calcd. tensile, lb./sq. in.	2900	650–690	2580	775	714	0	730		520	670	500	620
Total change in tensile, %	−11.6	−13.5 (av.)	−21.5	0	−7.9	−100	−5.8		690−11.2	2580−21.5	565+3.7	714−7.9
Remarks	Sample changed from yellow to brown; no cracks	Satisfactory	Sample changed from yellow to white; cracks present; H_2S liberated	Sample unchanged	....	Sample increased in area 33.7%; very soft at end of run	Blisters presen'	Deposit of sulfur prevented material from dissolving completely	....	Sample slightly spongy and tacky; lost gloss; no cracks	Dull in color and slightly softer; no cracks or tackiness	Loss of gloss; slight loss of flexibility; no cracks or tackiness
Conclusions	Fairly resistant	Resistant	Appreciably attacked	Extremely resistant	Resistant	Attacked appreciably	Slightly attacked	Appreciably attacked	Resistant	Slightly attacked	Resistant	Resistant

[a] 2% sulfur. [b] 250 parts polyisobutylene, 500 parts carbon black. [c] 250 parts polyisobutylene, 250 parts graphite, 250 parts P-33 carbon black. [d] Dumbbell shaped. See die C in A.S.T.M. Method.

rubber is shown to have an adherence to steel of about 660 pounds per square inch when Ty-Ply R is used as a bond agent. When a rubber cement is used in addition to Ty-Ply R, bond strength rises to 815 pounds per square inch (*6*).

Since cyclized polymer cements are thermoplastic, results indicate that at temperatures above 80° C. the strength of the bond to steel decreases at a rapid rate. Tests run at this temperature in the tensile test apparatus produce bond strengths not exceeding 50 pounds per square inch; at higher temperatures the bonds were too weak to evaluate.

The liner material at these temperatures does not lose tensile strength to a large extent. A cyclized rubber cement of higher softening point or other high-temperature adhesives which are not subject to loss of strength at elevated temperatures should greatly increase the versatility of this type of tank lining.

Polyisobutylene tank linings, in addition to high tensile strength, possess the desirable property of semiplasticity after application but with an absence of cold flow property characteristic of uncompounded polyisobutylene. Shocks or direct blows to the liner do not cause cracking or fracture.

CHEMICAL RESISTANCE OF TANK LINING

A series of tests was conducted to determine the chemical resistance of polyisobutylene tank lining and cured rubber to aqueous solutions of several heavy chemicals, such as 30% C.P. sulfuric acid, mixed acid (38% sulfuric and 14% nitric), 45% C.P. hydrofluoric acid, glacial acetic acid, 85% C.P. orthophosphoric acid, and about 12% mixed alkalies (125 grams C.P. sodium hydroxide, 30 grams C.P. potassium nitrate, 5 grams C.P. potassium nitrite per liter). The tentative 1939 A.S.T.M. Method D471-37T was used in estimating the comparative ability of the polymer compositions and rubber to withstand the effects of liquids.

Table II summarizes test results. The cured rubber compounds were used as blanks. No particular effort was made to obtain a rubber composition having the highest corrosion-resistant properties, but the one used is representative of an average liner preparation of this type.

Glacial acetic acid attacks the rubber-sulfur compound vigorously. Figure 1 shows the rate of weight increase of the test hydrocarbon mixes at 114–116° C. These data indicate that polyisobutylene linings gain weight slightly during the first five days of the test. After this time, the lining is impervious to further attack. An examination of the polyisobutylene test sample revealed the presence of blisters formed on the surface. Acid was contained by each of the blisters and could be forced out with a slight pressure.

Polyisobutylene test mixtures were stable to all agents listed in Table II during a similar 15-day test at room temperature, and no blistering occurred.

Table III. Tests on Tank Linings in Nitrating Acid

Formulas				
Polyisobutylene	100	100	100	100
Rubber (crepe)	100	100	...	...
Carbon black	350	350	200	100
Graphite	...	...	...	100
Zinc oxide	5	5	...	...
Stearic acid	3	3	...	...
Sulfur	3	35	...	...
Captax	1	1	...	...
Tuads	0.5	0.5	...	...
Solux	1	1	1	1
Paraffin	...	...	...	33
Remarks	Stiff but flexible	Glossy finish; resembles ebonite	Stiff, glossy appearnace	Soft, dull, flexible
Temp. increase, ° F.[a]	+54	+26	+2	+2

[a] When 1 gram of compound is placed in 20 ml. of mixed acid.

QUALITATIVE TESTS. To determine the relative value of some of the materials, a qualitative spot test was run in which the effect of nitrating acid (15% nitric in concentrated sulfuric) was observed. Compositions containing polyisobutylene with no rubber are almost inert and undergo little change when test strips are immersed in the acid. If cured rubber is added in equal proportions to polyisobutylene, the mix is attacked vigorously by nitrating acid. This action is reduced if sulfur content is increased, but the specimen is still far less resistant to attack than are polyisobutylene compositions when no rubber is present. Rubber alone is attacked vigorously by nitrating acid. Table III summarizes the data obtained.

Blends of crepe rubber and polyisobutylene with no other compounding ingredients behave similarly in nitrating acid as do the finished liners. As the polyisobutylene content is increased, the resistance to attack is increased. In the following tests one-gram samples were placed in 20 ml. of mixed acid (85% concentrated sulfuric, 15% concentrated nitric), and the increase in solution temperature was measured:

% Polybutene in Blend	Temp. Increase of Acid, ° C.
0	49.4
20	47.2
40	38.9
60	16.1
100	0

ACKNOWLEDGMENT

The advice, encouragement, and assistance of M. D. Mann, Jr., L. B. Turner, H. G. Schneider, and H. C. Evans are greatly appreciated.

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Hydrolysis of Titanyl Sulfate Solutions

ARTHUR W. HIXSON AND RALPH E. C. FREDRICKSON[1]
Columbia University, New York 27, N. Y.

Results are presented of a fundamental study of the precipitation characteristics of titanyl sulfate solutions. The data suggest that the first step in the precipitation reaction was a rapid splitting off of half the sulfuric acid of the salt to give a basic colloidal complex in which the molar ratio of titanium oxide to sulfur trioxide was about 2 to 1. This complex then hydrolyzed more slowly to give increasingly basic complexes which finally precipitated. The oxide formed by this mechanism appeared to be easily peptized at the boiling point in weakly acid solutions. Light transmission measurements indicate that the above mechanism prevailed in solutions which were less than 1.25 to 1.5 molar in free sulfuric acid, regardless of the titanium concentration. The abnormal precipitation curves previously reported by Hixson and Plechner were found to be characteristic of solutions containing less than the above acid concentration. Their normal curves proved to be characteristic of solutions in which the acid concentration was higher than 1.5 molar.

BASICALLY the manufacture of titanium oxide pigments consists of the following steps: (*a*) solution of the titanium ore in acid, (*b*) precipitation of the titanium oxide by heating the above solution under conditions favorable to the hydrolysis of the dissolved titanium, and (*c*) calcination of the precipitated oxide whereby pigment qualities are developed. This paper is concerned with the results of a fundamental study of the second step, the hydrolysis of titanium sulfate solutions.

One of the early fundamental studies of this important reaction was reported by Hixson and Plechner (*5*). They boiled various solutions of titanyl sulfate and sulfuric acid to precipitate titanium oxide. From time to time samples were withdrawn from the boiling flask and analyzed for the amount of precipitated titanium oxide. The amounts precipitated were then plotted against time of boiling to give the curves illustrated in Figure 1.

These three typical curves were taken from series 400 of the earlier paper (*5*), in which the acid factor was 1.0:

$$\text{acid factor} = \frac{\%\,\text{total acid} - \%\,\text{acid equiv. to Ti(SO}_4)_2}{\%\text{TiO}_2}$$

Similar families of curves were obtained with other acid factors. Curve 400 (Figure 1) was obtained from a solution that was 2.45 molar in sulfuric acid and 1.34 molar in titanyl sulfate. Solution 404 was derived from 400 by simple dilution with water until the acid molarity was 1.83 and the titanyl sulfate molarity was 1.0. Solution 407 was obtained by diluting 400 to an acid molarity of 0.9 and a titanyl sulfate molarity of 0.5. Thus in all of these solutions the molar ratio of acid to titanyl sulfate was 1.83 and the acid factor was unity.

From these curves it was evident that the precipitation characteristics of titanyl sulfate solutions were a function of dilution. Further, the differences were probably not merely differences in degree. Hixson and Plechner made a number of attempts to explain these peculiar curves. Analyses of the hydrolytic products could not be correlated with the observed phenomena. Plots of density against titanium oxide concentration for solutions with a given acid factor gave no indication of any complex formation.

Parravano and Cagliotti (*8*) also observed the anomalies previously cited. They plotted refractive index against titanium oxide concentration for a series of solutions in which the molar ratio of sulfuric acid to titanyl sulfate was about 1.67. They obtained two straight lines with slightly different slopes intersecting at a titanium concentration of 1.2 molar. The corresponding acid concentration was 2.0 molar. No successful correlation of this observation with precipitation characteristics was reported.

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[1] Present address, A. E. Staley Manufacturing Company, Decatur, Ill.

Table I. Amount of $TiOSO_4.2H_2O$ Hydrolyzed at Room Temperature from pH Measurements

$TiOSO_4$, 0.12 *M*				$TiOSO_4$, 0.6 *M*				$TiOSO_4$, 1.2 *M*			
Time	pH	Molarity of H_2SO_4	% hydrolyzed	Time	pH	Molarity of H_2SO_4	% hydrolyzed	Time	pH	Molarity of H_2SO_4	% hydrolyzed
0	5.0	...	..	0	5.0	..	..	0	5.0	..	..
5 min.	1.57	0.018	15	74 min.	0.5	0.31	52	131 min.	0.18	0.65	54
10	1.38	0.029	24	86	0.5	0.31	52	166	0.18	0.65	54
21	1.15	0.061	50	116	0.48	0.32	54	211	0.16	0.65	58
26	1.1	0.070	58	119	0.48	0.32	54	56 hr.	0.16	0.69	58
31	1.1	0.07	58	184	0.48	0.32	54	92	0.19	0.64	53
36	1.09	0.072	60	54 hr.	0.59	..	..	146[a]	0.19	0.64	53
44	1.10	0.070	58	90	0.50	0.31	52				
2.5 hr.	1.08	0.086	66	144[a]	0.49	0.32	53				
21	1.02	0.086	71.5								
112	1.02	0.086	71.5								
4 mo.	0.92	0.112	92								

[a] Slight precipitate.

Hixson and Stetkewicz (*6*) attacked the problem by measuring refractive index, dispersion, density, and viscosity of a large number of titanium sulfate solutions in which the molar ratio of sulfur trioxide to titanium oxide varied from 1.001 to 3.004, and the per cent titanium oxide from 0.5 to 26%. The data were then plotted against titanium oxide concentration in the hope that irregularities in the curve might be correlated with the peculiarities in the precipitation curves. No such correlation was found. We therefore undertook a fundamental study of the hydrolysis of simple aqueous dispersions of pure titanyl sulfate in both the presence and absence of sulfuric acid. It was hoped that information so developed might be useful in explaining the data reported by Hixson and Plechner.

Titanium tetrachloride was triple-distilled over zinc amalgam and solid sodium hydroxide. The fraction boiling at 134–136° C. was collected and hydrolyzed. Sulfuric acid was then added, followed by concentration to 55–60% acid by evaporation at 30 to 60 mm. The titanyl sulfate was precipitated by boiling under reflux for 24 hours. The precipitate was washed with alcohol to remove the excess acid and then washed several times with ether. The product was air-dried for several hours and then oven-dried at 105–110° C. This procedure yielded a product whose analysis corresponded precisely to the formula $TiOSO_4.2H_2O$. The salt was chloride-free and contained less than 0.003% iron as determined with ammonium thiocyanate.

HYDROLYSIS IN ABSENCE OF SULFURIC ACID

The first experiments consisted of following the dispersion of titanyl sulfate dihydrate in water by pH measurements. The appropriate quantity of titanyl sulfate, prepared by the above procedure, was weighed into a volumetric flask. Water was added to the mark and a uniform sample of the slurry immediately placed in the measuring cell of a Beckman pH meter equipped with a glass electrode. The pH was then measured at various time intervals (Table I). Figure 2 is a plot of the data for the 0.12 molar titanyl sulfate solution. The time data were measured from the time of water addition. The sulfuric acid concentrations were derived from the pH measurements by referring them to a curve giving the relation between pH and acid molarity for pure sulfuric acid. This curve was obtained experimentally with the same pH meter used for the titanium solutions. The percentage hydrolysis of the titanium salt was then calculated from the derived acid concentration.

It was evident from these data that the dispersion of titanyl sulfate in water was accompanied by an initial rapid drop in pH during the first 20–30 minutes. Then the pH decreased slowly but did not reach a constant value. For all three solutions the amount of hydrolysis corresponding to the period in which the pH changed only slightly was about 50%. When the above measurements were being made, it was observed that the period of slow pH change set in at about the time the solutions became clear. The early section of the pH curve was, therefore, principally a measure of the rate of dispersion of the solid titanyl sulfate. The percentage hydrolysis calculated for the 5 and 10 minute points was therefore fictitious since these figures were based on the total weight of titanyl sulfate taken rather than on the amounts dissolved at those times. As a whole, however, the data indicated that the dispersion of titanyl sulfate in water at room temperatures was accompanied by rapid hydrolysis of half its sulfuric acid. The remainder of the hydrolysis seemed to occur at a much slower rate, requiring more than 4 months in a 0.12 molar solution.

To check the results of the pH measurements, the dispersion of a 0.12 molar titanyl sulfate solution was followed conductometrically. Immediately after the addition of water to the salt, a uniform slurry was placed in a conductivity cell at 25° C., and its conductivity determined at one-minute intervals. The data are presented in Figure 3. The curve marked "second difference" is the second derivative of the conductivity curve.

The conductivity data indicated the same general result as the pH data—namely, an initial rapid increase in conductivity followed by a pronounced leveling off. The minimum in the second

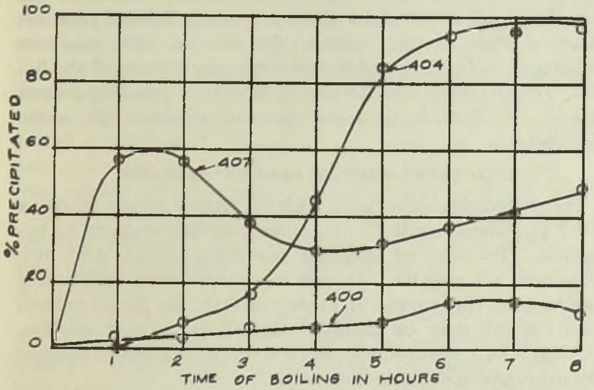


Figure 1. Amount of Titanium Oxide Precipitated at Various Times of Boiling

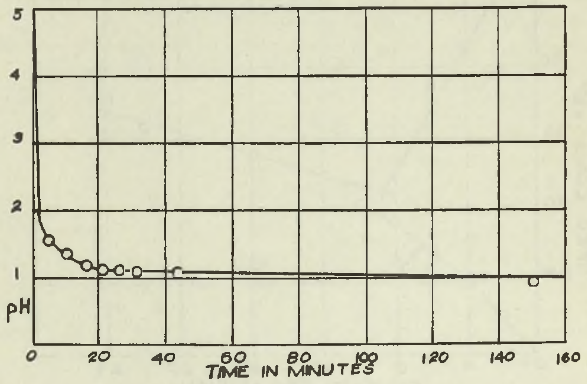


Figure 2. pH of 0.12 *M* Titanyl Sulfate Solution at Various Time Intervals

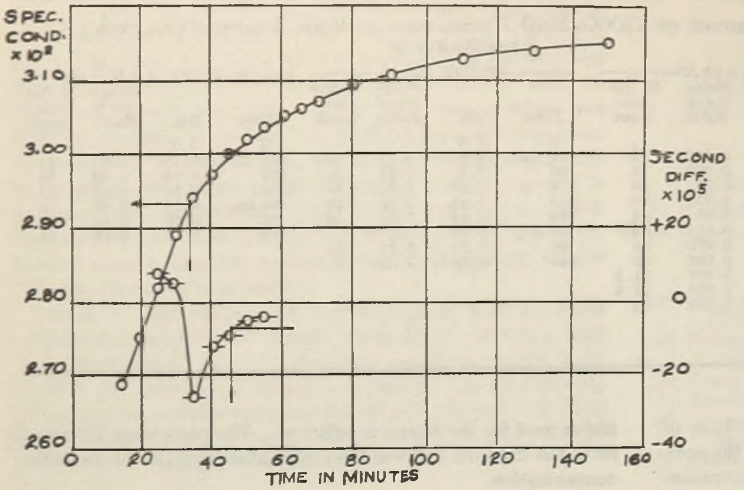


Figure 3. Conductometric Dispersion of 0.12 *M* Titanyl Sulfate Solution

difference curve (maximum numerical value) occurred about 35 minutes after the addition of water to the dry salt. This represents the point at which the variation in rate of change of slope of the conductivity time curve was a maximum. If it was assumed that the conductivity of the solution was due entirely to the sulfuric acid resulting from hydrolysis, the conductivity at 35 minutes corresponded almost exactly to 50% hydrolysis. After 150 hours the conductivity data indicated 69% hydrolysis as compared with 72% by pH measurements. Thus both conductivity data and pH data indicated that half the sulfuric acid present in titanyl sulfate dihydrate split off rapidly. This suggested the presence of a basic compound in water solutions of titanyl sulfate.

A reaction of the type,

$$2TiOSO_4 + H_2O \rightarrow 2TiO_2.SO_3 + H_2SO_4$$

would be in accord with our observations. To check this theory it seemed desirable to try to establish the existence of the basic compound by a conductometric titration. Figure 4 is a plot of the data so obtained.

The measurements were obtained by weighing 1.18 grams of titanyl sulfate into each of eight 50-cc. volumetric flasks; 20 cc. of water were then added. After the solutions were clear (about 30 minutes after the addition of water), the appropriate volume of 0.648 *N* sodium hydroxide was added to each. The flasks were then filled to the mark with water, and an aliquot was placed in the conductivity cell. The conductivities were measured at 25° ± 0.01° C. 10-12 minutes after the addition of alkali. The time specification was necessary because of the conductivity changes which occurred on standing. The salt line was calculated from the conductivities given in International Critical Tables (*7*).

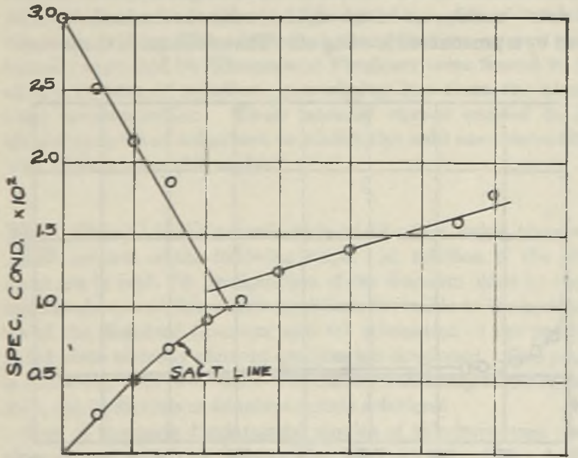


Figure 4. Results of Conductometric Titration to Establish Existence of Basic Complex $2TiO_2.SO_3$

The titration curves intersected at about 9 cc.; the salt line and the first section of the titration curve intersected at 9.4 cc. It was also observed that the precipitate which formed on addition of alkali redissolved within a few minutes in the four solutions to the left of the intersection. In the four solutions to the right of the intersection, however, the precipitate was permanent. If all of the titanium had been in the form of the basic complex, $2TiO_2.SO_3$, the curves would have intersected at 9.3 cc. The titration data therefore led to the same conclusion as our other measurements—namely, that freshly prepared aqueous dispersions of titanyl sulfate consisted essentially of a fairly well defined but unstable basic complex having the empirical formula $2TiO_2.SO_3$. We write the formula in this manner only to express the belief that the molar ratio of titanium oxide to sulfur trioxide is 2 to 1. A material of this composition has been described by Blondel (*1*), Brenek (*2*), and Wohler and Flick (*10*). Chauvenet (*4*) and Britton (*3*) reported the analogous zirconium compound.

Table II. Light Transmission at 5900 A. for Acidified Titanyl Sulfate Solutions Containing Hydrogen Peroxide

	% Transmission			% Transmission	
Time, Min.	Acidified aqueous dispersion	Acid dispersion	Time, Min.	Acidified aqueous dispersion	Acid dispersion
0	..	..	19	15.9	12.0
1	22.0	12.3	32	14.8	..
2	20.0	..	59	13.5	..
3	19.2	..	116	12.2	..
4	18.8	..	133	12.0	..
5	18.1	..	149	12.0	..
6	17.9	12.2	3 mo.	12.0	11.8
13	16.5	..			

The existence of the basic complex indicated that the hydrolysis proceeded by successive splitting off of sulfate from the titanium oxide nucleus; the hydrolysis apparently did not occur by complete cleavage of the acid in a single step.

Freshly prepared dispersions of titanyl sulfate appeared to be crystal clear to the naked eye. When a beam of blue light was passed through a 0.12 molar solution, a strong Tyndall cone was observed where the light entered the solution. The cone was completely extinguished after traversing about 1 cm. of the liquid. This indicated that the basic complex was probably present as a colloid. Further, the system probably absorbed light in the blue region.

REACTIONS WITH HYDROGEN PEROXIDE

The preceding studies were made on titanyl sulfate solutions which contained no sulfuric acid other than that produced by hydrolysis. To make up solutions containing sulfuric acid, two procedures are possible. On the one hand titanyl sulfate first may be dissolved in water and then acidified. On the other hand titanyl sulfate may be dissolved directly in the acid solution. We shall refer to the former type of solution as an acidified aqueous dispersion and to the latter as an acid dispersion.

When hydrogen peroxide was added to two solutions prepared by the above procedures, the light transmission-time data given in Table II were obtained. The time was measured from the instant the peroxide was added to the sample. The light transmission data were obtained with a Coleman spectrophotometer, type 10s, using distilled water as a reference liquid. The solutions were both 0.0928 molar in titanyl sulfate and 1.1 molar in sulfuric acid. The molar ratio of peroxide to titanium was 2.5 to 1. This peroxide ratio was chosen so as to get a reaction rate that could be easily measured.

Table III. Light Transmission–Time Data for Oxidized Aqueous Dispersions of Titanyl Sulfate Containing No Acid

Ti Concn. 0.0549 M			Ti Concn. 0.0928 M		
Time, Min.	% Transmission, at 5900 Å.	Colorimetric Ti Concn.	Time, Min.	% Transmission, at 5900 Å.	Colorimetric Ti Concn.
0	..	0.0235 M[a]	0	..	0.044 M[a]
1	57.1	0.0245	2	34.8	0.045
2	56.5	0.025	4	33.3	0.047
2.5	55.8	0.026	5	33.0	0.047
3.5	55.1	0.026	6	32.5	0.0475
4.5	54.8	0.0262	8	31.8	0.049
8.5	53.8	0.0271	11	Orange ppt.	
10	Orange ppt.				

[a] Extrapolated.

It was evident from these data that titanyl sulfate solutions which were stoichiometrically identical reacted at different rates with peroxide. The acidified aqueous dispersion required about 2 hours for full color development; in the acid dispersion the reaction was nearly complete after one minute. The only possible explanation for the above results was that the titanium entities in the two solutions were different. Further, the differences must have arisen from the manner in which the solutions were prepared. Prior to acidification the titanium in aqueous dispersion must have been present in the form of the basic micelle, $2TiO_2.SO_3$. If we could show that this material reacted slowly with peroxide, we could probably attribute the peculiar behavior of the acidified aqueous dispersion to the presence of the basic micelle. Table III gives the transmission–time data obtained when peroxide was added to two aqueous dispersions of titanyl sulfate in the absence of sulfuric acid. Such dispersions were previously shown to consist essentially of the basic micelle.

These data were similar to those previously obtained with acidified aqueous dispersions in that the light transmission changed with time. This indicated that the slow rate of reaction of peroxide with acidified aqueous dispersions was, in fact, attributable to the presence of the basic compound. This conclusion also required that the basic complex be stable in acid solutions.

Table II show that the light transmission at 5900 Å. of oxidized acid dispersions of titanyl sulfate remained constant for at least three months. It was also found that solutions prepared in this manner obeyed Beer's law. When the transmission values of Table III were referred to a Beer's law plot, the titanium concentrations given in columns 3 and 6 were obtained. When the concentration thus obtained were extrapolated back to zero time, the corresponding colorimetric titanium concentrations were found to be only 0.0235 M in one solution and 0.044 M in the other. The total titanium concentrations in these solutions were 0.0549 and 0.0928 M, respectively. It therefore appeared that only about half of the total titanium present in these solutions was capable of instantaneous reaction with peroxide. Since these solutions were previously shown to consist essentially of the basic complex, $2TiO_2.SO_3$, it also followed that only one of the two titanium atoms in the complex was able to react readily with peroxide.

Table III shows that, approximately 10 minutes after the addition of peroxide, an orange precipitate was thrown down. The question therefore arose as to whether the light transmission values correctly represented the titanium which had reacted with the peroxide. To check this, the 0.0928 molar titanium solution was allowed to stand 24 hours and then filtered free of the orange precipitate. The light transmission was then determined on the filtrate and the titanium concentration so derived (0.079 M) was compared with that determined gravimetrically (0.0797 M). It was concluded that the titanium concentrations calculated for the 10-minute interval immediately following the addition of peroxide did represent the actual amount of titanium which had reacted with peroxide. The discrepancy between the colorimetrically determined titanium concentration and the total titanium concentration in Table III was not merely the result of some effect of acidity on the light absorption coefficient of the titanium peroxide.

It is not possible from the results of this study to present a structure for the basic complex that accounts for its behavior with peroxide. It may be significant, however, that the formation of the complex apparently involved the hydrolysis of one SO_3 group from two $TiOSO_4$ molecules, leaving intact the linkage between one titanium atom and its sulfate group. The instantaneous reaction of peroxide may have occurred at this linkage since we know that peroxide reacts instantly with titanyl sulfate in acid dispersions. Only further experimental work can clarify the above question. Such work should involve, among other things, a thorough study of titanyl sulfate itself. As far as the writers are aware, no one has determined its molecular weight; the formula $TiOSO_4.2H_2O$ is probably an oversimplification.

LIGHT ABSORPTION STUDIES

It was mentioned earlier that aqueous dispersions of titanyl sulfate containing no sulfuric acid appeared to absorb light in the blue region. Figure 5 is a plot of light transmission vs. wave length for a 0.12 molar titanyl sulfate dispersion determined one hour after the addition of water to the salt. Distilled water served as the reference liquid. A Coleman spectrophotometer, type 10s, equipped with a 30-millimicron slit, was used for these and subsequent measurements.

From the curve it was evident that light absorption set in a about 4200 Å. and increased rapidly at the shorter wave lengths. A sample of spectroscopically pure titanyl sulfate prepared by Plechner in 1932 gave a similar curve. The absorption was therefore probably attributable to titanium. Rumpf (9) in 1937 observed similar behavior with dilute aqeuous dispersions of titanium tetrachloride.

Since the aqueous dispersions were colloidal, the question arose: Was the absorption true absorption or was it the result of scattering by the micelles? We believe that it was principally absorption, although some scattering undoubtedly occurred. When the solution was placed in a Raman tube and the scattered light photographed, no light below the 4047 mercury line was evident on the plate. If selective scattering had occurred in this region, the lines would have been particularly strong. Whatever

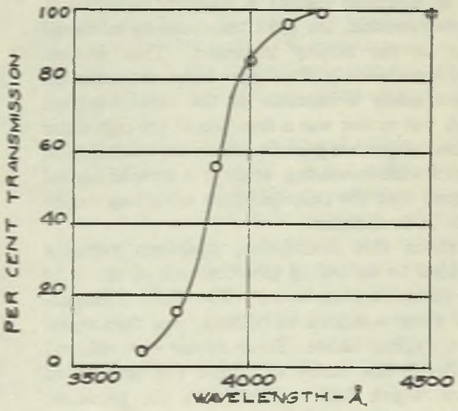


Figure 5. Light Transmission of 0.12 M Titanyl Sulfate Dispersion One Hour after Addition of Water

Table IV. Amounts of Titanium Reacting with Hydrogen Peroxide in Titanyl Sulfate Solutions of Varying Acidity

Time, Min.	Acid Concn. 0.35 *M*		Acid Concn. 0.45 *M*		Acid Concn. 0.55 *M*		Acid Concn. 0.70 *M*		Acid Concn. 1.2 *M*	
	Ti, %	TiO_2 concn.	Ti, %	TiO_2 concn.	Ti, %	TiO_2 concn.	Ti, %	TiO_2 concn.	Ti, %	TiO_2 concn.
0	..	0.073*M*	..	0.085*M*	..	0.098*M*	..	0.109*M*	..	0.113*M*
0.5	41.5	0.074	36.0	0.086	30.9	0.099	27.2	0.109	26.1	0.113
1	40.5	0.076	35.6	0.087	30.8	0.099	26.9	0.110	26.1	0.113
2	39.7	0.078	35.1	0.088	30.5	0.100	26.9	0.110	..	...
4	38.8	0.080	34.5	0.089	..	...	26.8	0.111	..	...
5	38.6	0.080	34.5	0.089	30.1	0.101	26.7	0.111	26.0	0.114
10	37.3	0.083	33.3	0.092	29.8	0.102	..	...	..	...
54 hr.	25.0	0.117	25.0	0.117	25.0	0.117	25.0	0.117	25.0	0.117

Table V. Effect of Aging on Light Transmission of Titanyl Sulfate Solutions

(Solution A = acidified aqueous dispersion, solution B = acid dispersion composition: $TiOSO_4$, 0.0928 *M*; H_2SO_4, 1.12 *M*)

Wave Length, Å.	% Transmission after:									
	3 Hr.		20 Hr.		120 Hr.		12 Days		73 Days	
	A	B	A	B	A	B	A	B	A	B
3600	..	..	5.5	68.8	38.5	75.3	46.3	77.2	48.9	76.0
3800	41.3	92.2	51.5	93.1	83.2	94.8	86.2	96.5	86.6	95.0

Table VI. Comparison of Transmission Characteristics of Solutions A, Oxidized and Decolorized A, and B

Wave Length, Å.	% Transmission		
	Original soln. A	Oxidized and decolorized A	Dispersion B
3500	3.6	54.4	54.0
3600	5.5	68.0	68.8
3700	20.7	81.0	82.9
3800	51.5	90.8	93.1
3900	79.2	95.5	97.5
4000	92.8	97.3	98.8
4100	97.5	98.0	99.0

is the correct interpretation of the absorption, the important fact was that below 4200 Å. increasingly less light got through the solution. For purposes of discussion we shall refer to the phenomenon as absorption.

The titanyl sulfate solutions obeyed Beer's law at 4000 Å. up to a concentration of about 0.6 molar. Beyond this concentration they deviated widely; i.e., a mole of titanium in a concentrated solution absorbed less light than a mole of titanium in a dilute solution.

Figure 6 is a plot of light transmission at 3800 Å. against acid concentration for several series of solutions. In each series the titanyl sulfate concentration was constant and the sulfuric acid concentration varied. These solutions were prepared by dissolving the salt in acids having the indicated molarities. The salt was therefore acid-dispersed since the entire dissolving process occurred in an acid medium.

Several facts were revealed by these curves. First, in solutions having a constant titanyl sulfate concentration, the light transmission increased rapidly as the acidity increased. This demonstrated conclusively that the light transmission was not solely a function of the total titanium present, but rather was a function of the particular titanium compounds present. Since the transmission increased with increasing acidity, it seemed logical to assume that the principal light absorbing entity was the basic complex.

To check this assumption, hydrogen peroxide was added to several of the solutions of the 0.12 molar titanyl sulfate series. The light transmission of these solutions at 6100 Å. was then measured at various times. These values were referred to a Beer's law curve to obtain the amount of titanium which had reacted with the peroxide. The data are given in Table IV.

The columns labeled "TiO_2 concentration" represent the concentration of titanium which had reacted with the hydrogen peroxide at the indicated times. The values at zero time were obtained by extrapolation of the measured values. The values at zero time increased from 0.073 to 0.113 molar as the acidity increased from 0.35 to 1.2 molar. After standing 54 hours, all of the solutions transmitted 25% of the incident light, which corresponded to a titanium concentration of 0.117 molar. This indicated complete reaction between titanium and peroxide, since the total titanium concentration after dilution of the 0.12 molar solution with the reagent was 0.117 molar. The equality of the 54-hour values also conclusively demonstrated that the concentration values at zero time were not due to some effect of acidity on the absorption coefficient of titanium peroxide. We therefore concluded that the concentration of the basic complex $2TiO_2 \cdot SO_3$ decreased with increasing acidity. Since the light absorption decreased similarly, we also concluded that the basic complex was the principal light-absorbing entity at 3800 Å. in weakly acid solutions.

The data of Table II showed that hydrogen peroxide reacted slowly with acidified aqueous dispersions of titanyl sulfate and rapidly with acid dispersions. The difference was attributed to the presence of the basic complex in the aqueous dispersion. This involved the assumption that the basic complex formed on dispersing the salt in water did not immediately disappear on subsequent acidification. If we accept the conclusions of the last paragraph, it should be possible to measure the stability of the complex in acid solutions by light transmission measurements. Table V gives the results of light transmission measurements on portions of the original solutions of Table II—i.e., solutions which contained no peroxide.

Comparison of A and B values reveals that the acidified aqueous dispersion transmitted much less light than the acid dispersion. This confirmed our previous conclusion that stoichiometrically identical titanyl sulfate solutions prepared in one case by aqueous dispersion and in the other by acid dispersion had different properties. The difference in light transmission persisted for more than 73 days and established the fact that, once the colloidal basic complex was formed, it disappeared only slowly on standing at room temperature.

Table II indicated that approximately 2.5 hours were required for complete reaction of solution A with peroxide. This suggested that the basic complex was much less stable in solutions containing peroxide. To check this point, a portion of solution A

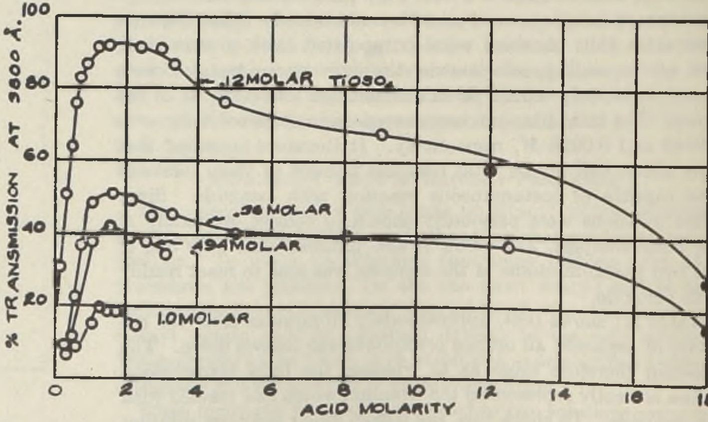


Figure 6. Light Transmission at 3800 Å. for Solutions of Varying Sulfuric Acid Concentration

that had been treated with peroxide was allowed to stand 4 hours and then decolorized with sulfur dioxide. Table VI compares the transmission data for solutions A, oxidized and decolorized A, and B.

The data reveal that the light transmission of the acidified aqueous dispersion after treatment with peroxide and sulfur dioxide was practically identical with that of the acid dispersion. The results also demonstrated that peroxide and acid were much more effective than acid alone in destroying the basic complex. This solvent effect has long been utilized to aid in the solution of titanium oxide. The data of Table VI are also in accord with our previous conclusion that the principal light-absorbing entity in weakly acid titanyl sulfate solutions is the basic complex.

Figure 6 shows that the light transmission reached a maximum at an acid molarity of 1.25 to 1.5, regardless of the titanium concentration. In addition to showing maximum light transmission, solutions in this acidity range were characterized by the following properties:

1. They reacted instantly with hydrogen peroxide.
2. They exhibited only a faint Tyndall cone; the titanium diffused completely through a cellophane membrane.
3. The unoxidized solutions followed Beer's law at 3800 Å. up to a titanium concentration of at least 1 *M* except for the 0.12 *M* solution. The data from this solution fell about 10% above the line determined by the more concentrated solutions.
4. The solutions remained crystal clear on standing at room temperature for several months. Solutions containing less acid deposited sediment on similar standing. The rate of deposition and amount of sediment increased as the acidity decreased.

It thus appeared that the location of the transmission maxima was of fundamental significance. It seemed to define the acidity below which the basic complex was not formed from titanyl sulfate. This at once suggested that a correlation might exist between the peculiar precipitation characteristics reported by Hixson and Plechner and the transmission maxima.

HYDROLYSIS IN PRESENCE OF SULFURIC ACID

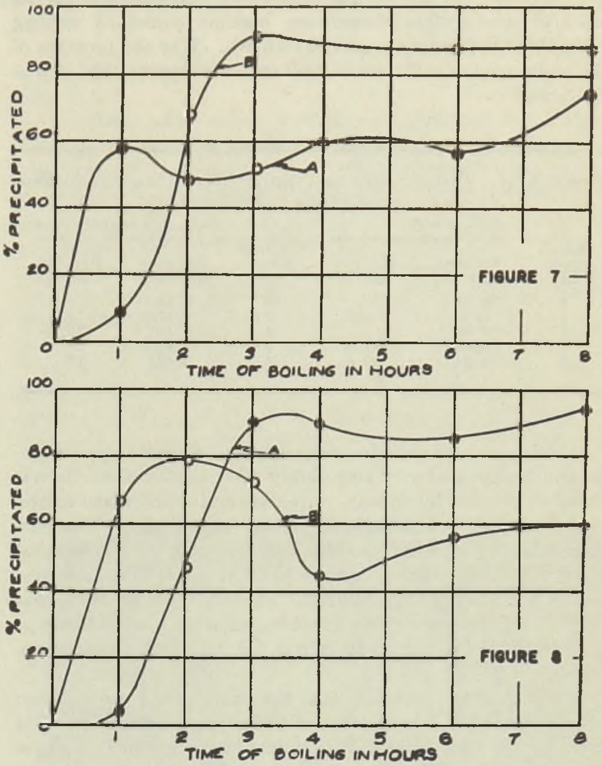
The precipitation curves of Hixson and Plechner were of three types: (*a*) normal curves characterized by a low initial rate of precipitation and high yield of titanium oxide; (*b*) abnormal curves characterized by a high initial rate of precipitation, followed by an apparent reversal of the precipitation reaction with a low final yield of titanium oxide; and (*c*) strong acid type curves in which mixtures of titanium oxide and titanyl sulfate were precipitated on boiling. The present discussion will be limited to the first two.

Table VII. Summary of Hixson and Plechner Data

Solns. Showing Normal Pptn.				Solns. Showing Abnormal Pptn.			
No.	Acid factor	$TiOSO_4$ concn.	Acid concn.	No.	Acid factor	$TiOSO_4$ concn.	Acid concn.
201	0.1	1.46*M*	1.55*M*	200	0.1	1.63*M*	1.73*M*
202	0.1	1.32	1.40	204	0.1	0.98	1.04
				205	0.1	0.81	0.86
				206	0.1	0.65	0.69
				207	0.1	0.49	0.52
102	0.52	1.35	1.92	105	0.52	0.84	1.19
103	0.52	1.18	1.63	106	0.52	0.67	0.95
104	0.52	1.02	1.45	107	0.52	0.51	0.73
				108	0.52	0.34	0.49
403	1.0	1.16	2.13	406	1.0	0.65	1.2
404	1.0	1.0	1.83	407	1.0	0.50	0.9
405	1.0	0.83	1.53				

Hixson and Plechner attempted to correlate precipitation phenomena with the acid factor of the solutions. Upon recalculating their data to a mole basis, the results in Table VII were obtained. The acid concentrations were taken as the difference between the total acid and that combined as $TiOSO_4$ so as to conform with the system adopted throughout this paper. This differs from Plechner's practice in which the free acid represented the total acid minus that combined as $Ti(SO_4)_2$.

It is evident that the acid concentration of all solutions which precipitated normally were located at, or slightly above, the concentration corresponding to the transmission maxima. Of the eleven solutions which precipitated abnormally, ten fell on the low acid side of the maxima. The sole exception was solution 200. We have no explanation for this discrepancy. Nevertheless, it appeared that for titanium solutions up to a least 1.46 molar our transmission maxima defined the boundary between normal abnormal solutions. As a further check on this correlation, several hydrolysis experiments were performed. The results are given in Figures 7 and 8. These solutions were acid-dispersed.



Figures 7 and 8. Results of Hydrolysis Experiments Showing Normal and Abnormal Titanium Solutions

Curve *A* of Figure 7 represents the data for a solution which was identical with Plechner's solution 407 and was therefore on the low-acid side of the maxima. Obviously the precipitation was abnormal. Curve *B* represents the data for a solution of the same titanium concentration as *A* but an acid concentration of 1.51 molar so as to bring it to the high-acid side of the maxima. The precipitation was normal.

Plechner's solution 404 was 1 molar in titanyl sulfate and 1.83 molar in acid and precipitated normally. If our correlation was correct, a solution of the same titanium concentration but 1.51 molar in acid should likewise precipitate normally. Figure 8*A* confirms this. On the other hand, if the acidity were reduced below that at the maxima to, say, 0.9 molar, the precipitation should be abnormal. Figure 8*B* confirms this. We therefore concluded that the narrow range of acid concentration corresponding to the transmission maxima was the zone of demarcation between normal and abnormal precipitation. The reasons for the differences in precipitation characteristics of the two types of solutions were not clear, however.

Table VIII gives the electrical conductivity of the centrifugal filtrates of solutions *A* and *B*, Figure 7, after various boiling times.

It was clear from these data that the electrical conductivity increased with boiling time for both solutions even though the amount of precipitated titanium oxide in solution *A* decreased after about 4 hours of boiling. We therefore suggest that the abnormal curve was not the result of any reversal of the hydrolysis reaction, simply the result of peptization of the initially precipitated titanium oxide. The peptized titanium oxide was not separated from the mother liquor in the centrifugal operation which preceded the analysis; hence the amount of precipitated titanium oxide so determined was not a measure of the extent of hydrolysis.

The foregoing naturally led to the question of the reasons for the difference in peptizability of the oxides precipitated from the two solutions. It has been demonstrated that solutions on the low-acid side of the transmission maxima contained varying amounts of the basic complex, $2TiO_2.SO_3$. Was the presence of the basic complex sufficient in itself to determine the type of precipitation?

Table VIII. Comparison of Conductivity Changes during Normal and Abnormal Precipitation

Normal (7*B*)			Abnormal (7*A*)		
Boiling time, hr.	Sp. conductivity	Hydrolysis, %	Boiling time, hr.	Sp. conductivity	Hydrolysis, %
0	0.49	..	0	0.35	..
1	0.55	..	2	0.473	72.0
2	0.60	..	3	0.477	74.5
6	0.638	81.5	4	0.480	78
8	0.643	89.5	6	0.482	78

It will be recalled that the basic complex formed by aqueous dispersion disappeared only very slowly after acidification. It was therefore possible by aqueous dispersion and acidification to prepare a solution on the high-acid side of the maxima, which contained substantial amounts of the basic complex. A solution that was 0.494 molar in titanyl sulfate and 1.51 molar in sulfuric acid was so prepared and hydrolyzed. The precipitation curve was normal. It therefore followed that the mere presence of the basic complex in the initial solution was not sufficient to cause abnormal precipitation.

The possibility then arose that the two types of precipitation curves were the result of different hydrolytic mechanisms. The following table shows the change in light transmission of the above dispersion during the first few minutes of heating and before any change in appearance was noted. The sample was placed in a water bath at room temperature and heated to boiling in 4 minutes. It was held at that temperature an additional 4 minutes, followed by rapid cooling under the cold water tap. The light transmission was then immediately determined and compared with an acid dispersion of the same composition:

Wave Length, Å.	% Transmission of Dispersions		
	Aqueous, no heat	Aqueous, boiled	Acid, no heat
3800	5.6	23.4	41.3
3900	26.6	51.5	68.5

From the increase in transmission with heating, it was clear that in an aqueous dispersion on the acid side of the transmission maxima, the initially present basic complex decreased prior to precipitation. This led to the conclusion that the basic complex was probably not an intermediate in the hydrolysis of solutions on the acid side of the transmission maxima.

The following table shows the results obtained by the above procedure on a solution that was 0.117 molar in titanyl sulfate and 0.51 molar in acid. This solution was prepared by acid dispersion and was located on the low-acid side of the transmission maxima. The solution was heated from room temperature to boiling in 5 minutes and then immediately cooled, and its transmission determined:

Wave Length, Å.	% Transmission of Acid Dispersions	
	No heat	Boiled
3700	27.2	12.0
3800	57.6	39.0

The decrease in transmission on heating indicated an increase in the amount of basic complex prior to precipitation. We therefore concluded that the basic complex was an intermediate in the hydrolysis of all solutions located on the low-acid side of the transmission maxima. Ease of peptization seemed to be characteristic of the products of this mechanism; the solutions therefore gave abnormal precipitation curves. We have no information as to why the products of this mechanism were easily peptized but suggest that this property may be closely linked with stepwise hydrolytic processes.

Solutions on the high-acid side of the transmission maxima apparently hydrolyze by some other mechanism, perhaps by direct cleavage of the titanium oxide and sulfuric acid. For some unknown reason the products of this mechanism are not easily peptized. Such solutions therefore give normal precipitation curves.

CONCLUSIONS

1. In the absence of sulfuric acid the first step in the hydrolysis of titanyl sulfate solutions appeared to be the formation of a basic complex in which the molar ratio of titanium oxide to sulfur trioxide was 2 to 1.
2. About half the titanium of this complex seemed to react instantaneously with hydrogen peroxide; the remainder of the titanium reacted much more slowly.
3. The basic complex was not entirely destroyed even after standing 73 days in 1 molar sulfuric acid. This made it possible to prepare stoichiometrically identical titanyl sulfate solutions which showed different light transmission characteristics and which reacted at different rates with hydrogen peroxide.
4. Light transmission at 3800 Å. of sulfuric acid solutions of titanyl sulfate increased with acidity to a maximum at 1.25 to 1.5 molar acid. Solutions on the low-acid side of the maxima gave abnormal precipitation curves on boiling. Solutions at the maxima or on the high-acid side gave normal precipitation curves.
5. Abnormal precipitation appeared to result from peptization of the hydrolytic products.
6. Easily peptized products were believed to result from a hydrolytic mechanism in which the basic complex was an intermediate. This mechanism appeared to be characteristic of all solutions lying on the low-acid side of the transmission maxima.
7. The hydrolytic products from solutions on the high-acid side of the maxima were resistant to peptization, hence gave normal precipitation curves. These products were apparently the result of some mechanism which did not involve the basic complex as an intermediate.

ACKNOWLEDGMENT

It is a pleasure for the authors to express their appreciation to the Titanium Pigments Division of the National Lead Company for the fellowship which made this study possible.

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Artificial Bristles from Proteins

T. L. McMEEKIN, T. S. REID, R. C. WARNER, AND R. W. JACKSON

Eastern Regional Research Laboratory, U. S. Department of Agriculture, Philadelphia, Pa.

A method is described for producing coarse fibers from casein by extruding a heated mixture of casein and water through a suitable die. When the fiber is stretched and hardened, under tension, with quinone, a bristle material is obtained, which is being tested in certain types of brushes.

METHODS for the conversion of amorphous proteins into fibers have long been known. In 1898 Millar (*3*) prepared protein fibers by extruding heated protein-water mixtures into air. A few years later Todtenhaupt (*6*) made casein fibers by extruding an alkaline solution of casein into an acid bath. Recent improvements in the latter process have resulted in the commercial development of a textile fiber from casein. Early in the development of protein fibers, it was found that the durability of the fiber was markedly increased by treatment with formaldehyde and other tanning agents. These substances decrease water absorption and bacterial decomposition of protein fibers and make them more flexible. Water absorption of the treated protein fiber is not completely eliminated, however, and loss in strength and shape of the fibers in the presence of water limits their use.

The present shortage of pig bristles and other coarse animal hair, such as horsehair, suggested the development of a protein fiber having the size and properties of these natural hairs. In the following method for preparing such fiber, heated isoelectric protein mixed with water is extruded into air; it is then stretched and hardened, under tension, with quinone alone or quinone followed by formaldehyde.

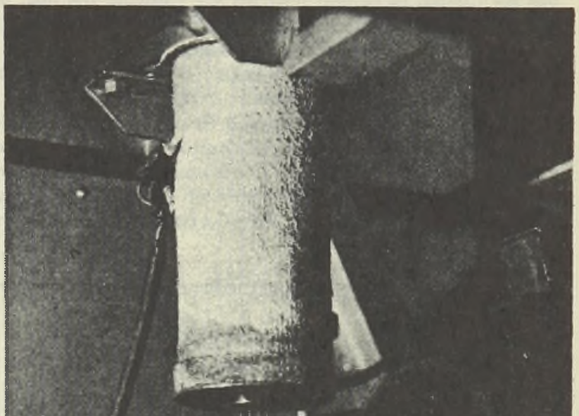
PREPARATION OF FIBERS

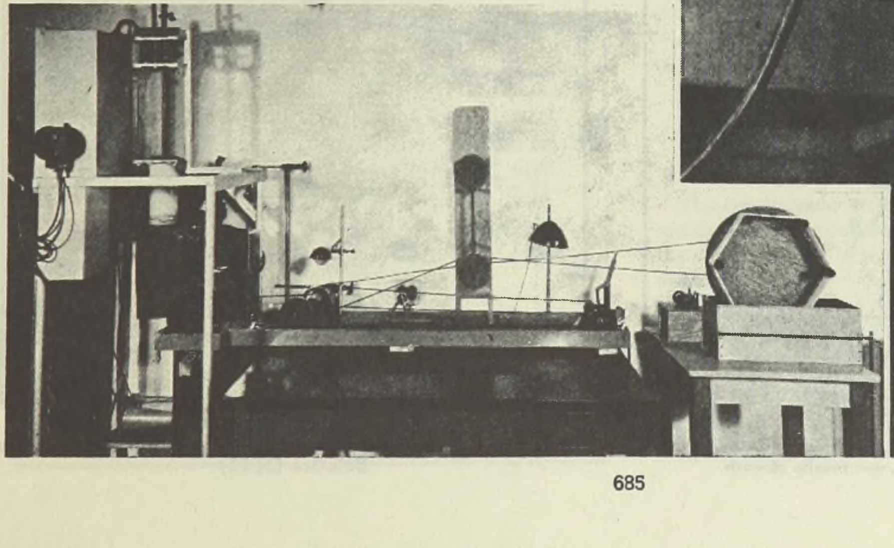
A number of proteins, including casein, soybean, gelatin, zein, edestin, arachin, and glutenin, have been converted into fibers by extrusion. However, casein was used entirely in the development of fibers suitable for bristle material as described in this report. Several commercial acid-precipitated caseins were found to be suitable for fiber extrusion. Purification of the better commercial caseins did not materially improve the quality of the fiber. The quality of the casein, however, is of importance for making fiber. To be suitable for the production of fiber, a casein should be free from lactose and other whey constituents, be soluble in borax solution, and yield an aqueous extract having a pH near the iso-electric point of 4.7.

In making casein fiber, 40-100 mesh commercial acid-precipitated casein containing approximately 9% moisture is mixed with 70% of its weight of water, and the mixture is allowed to stand for an hour. The hydrated casein is placed in a discontinuous press of the cylinder type with a volume of 370 cc. (Figures 1 and 2) and heated slowly to about 95° C. to remove air and form a plastic mass. Fibers are formed by forcing the heated casein-water mixture through a die with holes of a suitable diameter, usually from 0.3 to 0.6 mm. A finely woven stainless steel screen or breaker plate is placed in back of the die to assist in the removal of air and foreign material from the casein before the fiber is formed. To minimize sticking, the fibers are passed rapidly by means of rotating drums through a solution, at a pH of about 4.7, containing 2% formaldehyde, 0.1% naphthalene sulfonate, and 10% sodium sulfate. The fibers are collected on a suitable reel,

Figure 1 (*Below*). Press and Accessory Equipment for Spinning Casein Fibers

Figure 2 (*Right*). Close-up View of Fiber Formed by Extrusion of Heated Casein-Water Mixture through the Four-Hole Die into Air





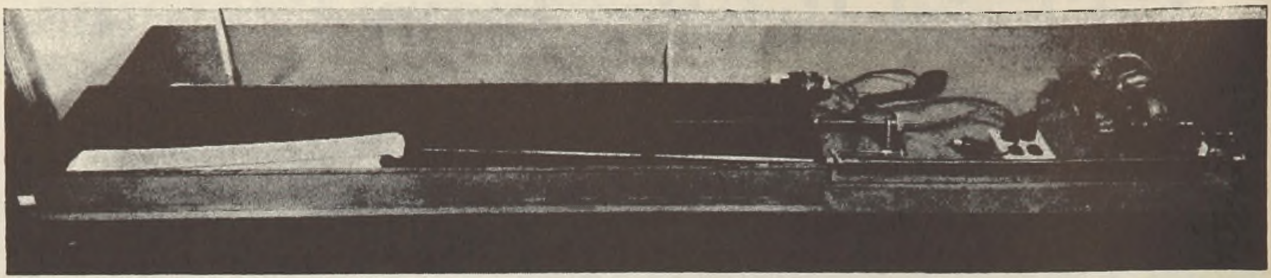


Figure 3. Motor-Driven Machine for Stretching Skein Casein Fiber during Hardening with Quinone

as shown in Figure 1. Fiber can also be made by extruding casein mixed with only 37% of its weight of water. In this case sticking is so much reduced that the fibers are extruded directly in air without the bath.

The extruded fiber, in the form of a skein of continuous filaments, is placed in the stretching bath (Figure 3) and is passed through two stirrups. One of these is stationary while the other is gradually pulled along the length of the tank by a motor mechanism. When a saturated solution of quinone is employed at room temperature, the fiber is stretched at the rate of 1% of the original length per minute until the original length has been doubled; the time required is 1 hour and 40 minutes. When higher temperatures are used, the rate of stretching must be increased. After stretching is completed, the fiber remains under tension in the quinone bath (room temperature) for at least 24 hours; further hardening and attendant reduction of water absorption may be obtained by allowing it to stand under tension in a 2% formaldehyde solution for another 24 hours. Hardening has been found to be best near pH 4.7. Finally the fiber is removed from the bath, washed, and dried at room temperature under sufficient tension to keep it straight.

The effect of variations in degree of stretching on tensile strength and flexibility is shown in Figure 4. The testing was done at 65% relative humidity and 70° F. on a standard Scott inclined-plane serigraph-2 testing machine. The tensile strength of a fiber with a loop tied in it was employed as a measure of flexibility (curve *C*). As the degree of stretching is increased, tensile strength increases. However, a point is reached where an increase in the degree of stretching reduces flexibility. Consequently, stretching is not carried to the greatest possible extent in making bristlelike casein fibers. Instead the fibers are stretched only to twice their original length in the quinone bath in order to obtain the highest strength consistent with greatest flexibility Stretching also increases the wet strength and slightly decreases water absorption. This treatment results in a casein bristle with a dry strength of 0.7–0.8 gram per denier under standard conditions and a wet strength of 0.3–0.4 gram per denier after immersion in water for 4 hours at 70° F. (Table I).

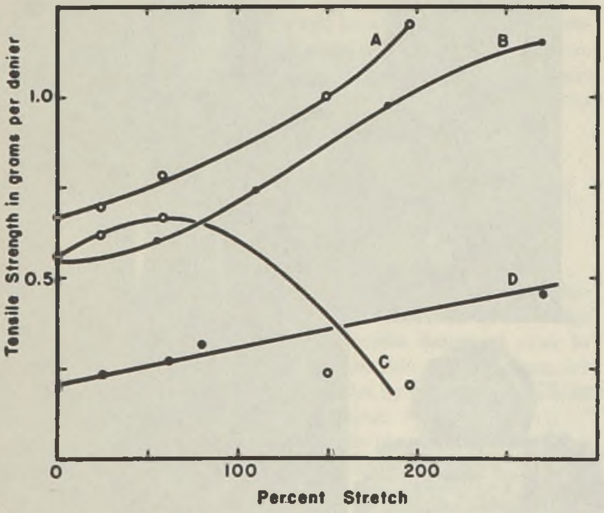


Figure 4. Influence of Degree of Stretching on Properties of Fiber (300–1000 denier)

A and *B*, dry tensile strength; *C*, tensile strenth of fiber with a loop tied in it (flexibility); *D*, wet tensile strenth

PROPERTIES AND USES OF ARTIFICIAL BRISTLES

The stretched and quinone-hardened casein fibers are cylindrical (Figure 5) and black. Figure 6 shows samples of experimental brushes made with casein bristle fiber. The stiffness of the fiber varies with the diameter. Fibers with a diameter of 0.6 mm. (3312 denier) are quite stiff; fibers with a diameter of 0.2 mm. (368 denier) are soft and pliable. Experimental paint brushes made with this fiber have been prepared in considerable numbers. Since heating hardened casein fibers above 100° C. for several hours produces brittleness, ordinary methods of setting natural bristles such as that involving the vulcanization of rubber for several hours at 140° are unsuited for artificial bristles made from casein. This difficulty has been overcome by vulcanizing with rubber at lower temperatures and also by using a setting ma-

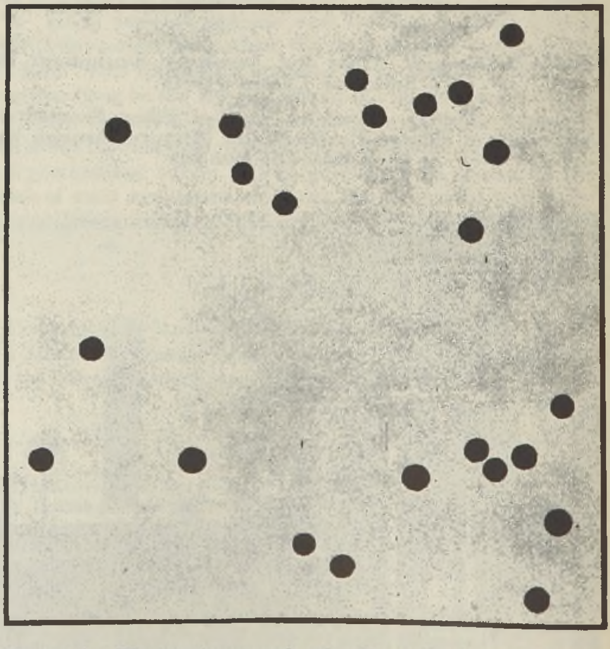


Figure 5. Photomicrograph of a Cross Section of Casein Bristles (× 11)

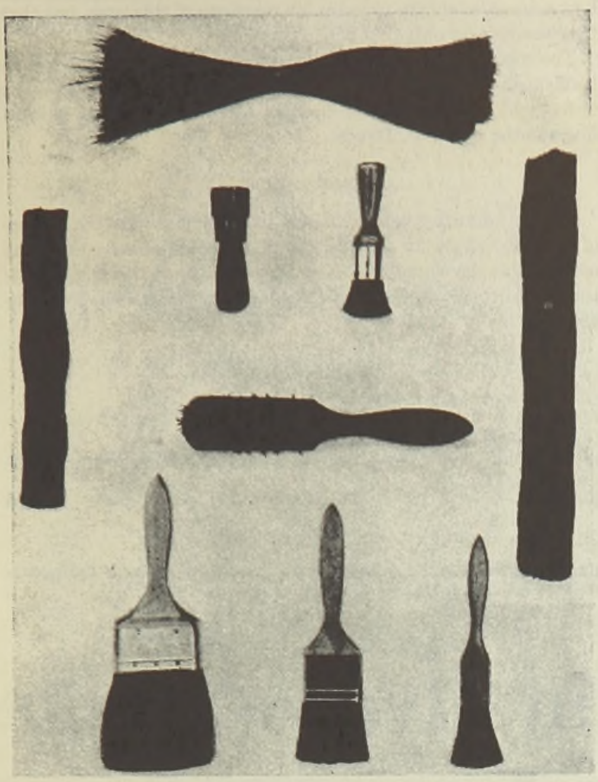


Figure 6. Casein Bristle and Experimental Brushes Made from Artificial Fiber

terial, made of urea-formaldehyde and alkyd types of synthetic resin, that hardens at 80° C. These paint brushes, although made of untapered bristles, have good paint-carrying capacity, make smooth films, and have good wear resistance. The bristles are resistant to oils and fat solvents, but soften when allowed to stand in water.

Although the dry tensile strength of the casein bristles is not so great as that of natural bristles, the strength is adequate for most brushes not subject to wetting with water. In water the casein bristles absorb about 18% water, become soft, and have a tensile strength of only about half their dry tensile strength; this makes them unsuited for use in water. Table II compares casein bristles with natural bristles.

Table I. Strength of Standard Casein Bristles Stretched to Twice Their Original Length

Expt. No.	Denier	Tensile Strength, G./Denier[a] 65% r.h., 70° F.	Tensile Strength, G./Denier[a] 4 hours in water
40	214	0.84	0.36
		0.78	0.48
		..	0.33
67	470	0.85	0.44
		0.76	0.42
		0.76	0.37
104	425	0.71	0.47
		0.79	0.40
		0.86	0.45
388	507	0.71	
		0.71	
		0.73	
443	421	0.73	
		0.80	
		0.82	

[a] Grams per denier can be converted to pounds per square inch by multiplying by the factor 16,630 since the fiber has a density of about 1.3. [Sieminski, M.A., *Rayon Textile Monthly*, 24, 63 (1943)]. Denier = weight in grams of 9000 meters of fiber.

Casein bristles are stable in air under ordinary conditions and have been kept for two years without deterioration. Even after long heating at 60° C., the physical properties of the fiber were changed only slightly when subsequently conditioned at room temperature.

Table II. Comparison of Casein Bristles with Natural Bristles

Material	Tensile Strength, G./Denier 65% r.h., 70° F.	Tensile Strength, G./Denier Single knot	Tensile Strength, G./Denier 4 hr. in water	% Water after 24 Hr. in Water (22–25° C.)
Casein bristle	0.7–0.8	0.6–0.65	0.35–0.45	18.5
Pig bristle	1.0–1.2	0.8–0.9	0.9–1.2	20
Horsehair	1.2–1.4	0.9–1.0	1.0–1.3	21

DISCUSSION

The batch process described for the production of casein bristles is adequate for many purposes. For large-scale economic production, however, a continuous process would be highly advantageous, and it has been found that the fiber can be extruded with a commercially available screw-type extruder. The process described here, involving hardening for 24 hours at room temperature, produces a fiber containing approximately 10% quinone. This amount of quinone is required to make the fiber durable and resistant to water. The influence of temperature on the rate of uptake of quinone is shown in Figure 7. In order to obtain approximately 10% quinone in the fiber in 10 minutes, it is necessary to use a temperature of 60° C.

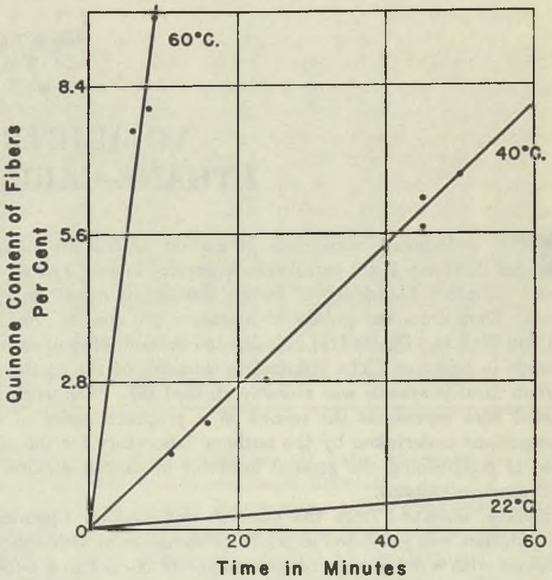


Figure 7. Influence of Temperature on Uptake of Quinone (Fiber Diameter 0.3–0.5 Mm. or 828–2301 Denier)

The simultaneous stretching and hardening of the fiber in a relatively short period requires further investigation. To increase the tensile strength of the fibers, the stretch must be applied at a definite time during hardening. Considerable stretch can be applied to the fiber as it emerges from the orifice of the extruder while it is in the air and still at an elevated temperature. However, no added strength is given the fiber by the maximum stretch that can be applied in this manner. It is necessary to have a certain minimum degree of hardening in order to increase the strength by stretching. If the hardening has progressed too far, however, the fiber can be stretched comparatively little before it breaks. There is thus an optimum amount of hardening for permitting the maximum effective stretch to be applied. This was shown by an experiment in which the maximum degree of stretch that could be applied to the fibers was determined at 5-minute intervals after immersion in a quinone solution under various conditions. The maximum extension of about 300% was attained in 30 to 45 minutes at 22°, 15 to 35 minutes at 35°, and 10 minutes at 50° C. in 1% quinone, but it was attained in less than 5 minutes at 50° in 2% quinone. Stretch should be applied under any of these combinations of temperature and time to be of most benefit. If the fiber is to be stretched not more than 100%, however, there is considerable latitude in the time at which stretch may be applied.

The reaction of quinone with casein appears to be irreversible in neutral solutions. Casein fiber hardened with quinone is superior to formaldehyde-hardened fiber with respect to brittleness and resistance to water. Quinone hardening was most effective near the isoelectric point of casein. Although the nature of the reactions is still unknown, quinone has been found to react with proteins and many amino compounds (*1*, *2*); most of these reactions proceed readily in aqueous solution at room temperature. It has been found (*4*, *5*) that deaminized collagen (hide powder) fixes about 60% of the amount of quinone fixed by untreated collagen in 24 hours. It is thus probable that the ε-amino groups of lysine are available in proteins for reactions of this type, but that they account for only part of the reaction.

The modification of casein by acetylation, deamination, or esterification, as well as the addition of small quantities of quinone or formaldehyde, markedly decreases the ability of casein to form fibers in the presence of water.

ACKNOWLEDGMENT

The authors are greatly indebted to R. Hellbach and N. J. Hipp of this laboratory for designing and constructing the equipment used in this development. Also they wish to record their gratitude to Alice Wolferd, Helen Dearden, and Edith Polis for valuable aid.

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Presented at a meeting sponsored by the American Society for Testing Materials, Philadelphia District Committee, September, 1943.

Phase Equilibria in Hydrocarbon Systems

VOLUMETRIC BEHAVIOR OF ETHANE–CARBON DIOXIDE SYSTEM

THE widespread occurrence of carbon dioxide in natural gas mixtures from petroleum reservoirs makes desirable a more complete knowledge of carbon dioxide–hydrocarbon systems. Data from the published literature are sparse. Sander (*9*) and Wan and Dodge (*11*) investigated the solubility of carbon dioxide in benzene. The volumetric behavior of the methane–carbon dioxide system was recently studied (*6*). The work reported here represents the second of a proposed series of investigations undertaken by the authors' laboratory for the purpose of establishing the general behavior of carbon dioxide in hydrocarbon systems.

Ethane, obtained from the Carbide and Carbon Chemicals Corporation, was subjected to triple fractionation at atmospheric pressure with a reflux ratio of approximately 50 to 1 in a 4-foot, vacuum-jacketed column packed with glass rings. Initial and final cuts amounting to 10% of the charge in the kettle were discarded in each fractionation. The overhead was condensed in vacuo at liquid air temperatures with continuous removal of any condensable gases which might have accumulated during the condensation process. The purity of the material so obtained was verified by the constancy of its vapor pressure. At 80° F. the observed bubble-point and dew-point pressures differed by less than 0.3 pound per square inch.

Carbon dioxide was prepared by the thermal decomposition of reagent-grade sodium bicarbonate. The gas was dried at atmospheric pressure by passage in succession through a water trap at 32° F., a tube packed to a depth of 12 inches with calcium chloride, and a similar tube packed with barium perchlorate. The dried gas was then condensed in vacuo at liquid air temperatures with continuous evacuation of noncondensable gases. The resulting material had a vapor pressure at 32° F. which differed from that of pure carbon dioxide by less than 0.1 pound per square inch.

EQUIPMENT AND PROCEDURE

A detailed description of the apparatus has been published (*8*). No changes in the equipment were necessary for the present work.

The components of the mixtures were introduced gravimetrically into the volumetric apparatus from small steel sample bombs which could be weighed directly upon an analytical balance. Great care was exercised in preparing the mixtures. The equilibrium cell and connecting lines to the sample bombs were evacuated to an absolute pressure of 10^{-4} mm. of mercury before admitting the sample. Residual gas left in the connecting lines was condensed back into the sample bomb by means of liquid air. The change in the weight of the sample bomb was determined upon an analytical balance using the method of tares and

H. H. REAMER, R. H. OLDS, B. H. SAGE, AND W. N. LACEY
California Institute of Technology, Pasadena, Calif.

TABLE I. COMPRESSIBILITY FACTORS FOR MIXTURES OF ETHANE AND CARBON DIOXIDE

Pressure, Lb./Sq. In. Abs.	Compressibility Factor at 100° F. with Mole Fraction Ethane as Follows: 0.1777	0.3313	0.5132	0.6763	0.8280
0	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.9398	0.9380	0.9336	0.9268	0.9181
400	0.8725	0.8678	0.8567	0.8404	0.8205
600	0.7951	0.7863	0.7655	0.7371	0.6994
800	0.7030	0.6894	0.6549	0.6085	0.5347
1,000	0.5896	0.5718	0.5207	0.4387	0.3157
1,100	0.5190	0.5020	0.4460	0.3602	0.3005
1,200	0.4360	0.4245	0.3799	0.3331	0.3046
1,250	0.3929	0.3934	0.3623	0.3307	0.3100
1,300	0.3587	0.3682	0.3517	0.3311	0.3154
1,400	0.3225	0.3454	0.3459	0.3364	0.3279
1,500	0.3152	0.3395	0.3488	0.3455	0.3420
1,600	0.3161	0.3428	0.3558	0.3568	0.3568
1,700	0.3220	0.3494	0.3659	0.3694	0.3721
1,750	0.3261	0.3539	0.3717	0.3761	0.3800
2,000	0.3500	0.3797	0.4026	0.4114	0.4192
2,250	0.3779	0.4087	0.4345	0.4478	0.4590
2,500	0.4069	0.4394	0.4677	0.4842	0.4985
2,750	0.4360	0.4707	0.5017	0.5209	0.5380
3,000	0.4651	0.5017	0.5360	0.5574	0.5773
3,500	0.5235	0.5644	0.6041	0.6307	0.6546
4,000	0.5819	0.6270	0.6725	0.7031	0.7310
4,500	0.6401	0.6891	0.7400	0.7741	0.8061
5,000	0.6973	0.7509	0.8066	0.8440	0.8803
6,000	0.8107	0.8732	0.9362	0.9810	1.0265
7,000	0.9221	0.9911	1.0630	1.1159	1.1711
8,000	1.0306	1.1070	1.1884	1.2473	1.3124
9,000	1.1376	1.2212	1.3132	1.3762	1.4497
10,000	1.2412	1.3333	1.4383	1.5038	1.5821

Pressure, Lb./Sq. In. Abs.	Compressibility Factor with Mole Fraction Ethane as Follows: 0.1777	0.3313	0.5132	0.6763	0.8280	0.1777	0.3313	0.5132	0.6763	0.8280	0.1777	0.3313	0.5132	0.6763	0.8280
	160° F.					280° F.					400° F.				
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.9565	0.9551	0.9523	0.9479	0.9420	0.9776	0.9757	0.9734	0.9706	0.9676	0.9883	0.9871	0.9855	0.9838	0.9820
400	0.9111	0.9078	0.9016	0.8921	0.8797	0.9546	0.9512	0.9465	0.9409	0.9349	0.9768	0.9746	0.9714	0.9679	0.9644
600	0.8632	0.8582	0.8464	0.8315	0.8117	0.9316	0.9271	0.9201	0.9117	0.9026	0.9654	0.9623	0.9578	0.9530	0.9476
800	0.8127	0.8053	0.7868	0.7654	0.7368	0.9088	0.9031	0.8938	0.8829	0.8711	0.9539	0.9508	0.9447	0.9385	0.9316
1,000	0.7586	0.7495	0.7246	0.6953	0.6553	0.8865	0.8804	0.8691	0.8554	0.8409	0.9433	0.9394	0.9329	0.9250	0.9170
1,250	0.6893	0.6779	0.6499	0.6110	0.5607	0.8594	0.8535	0.8401	0.8236	0.8062	0.9308	0.9269	0.9191	0.9100	0.9006
1,500	0.6204	0.6109	0.5828	0.5449	0.4996	0.8342	0.8288	0.8148	0.7961	0.7757	0.9196	0.9155	0.9071	0.8966	0.8865
1,750	0.5597	0.5584	0.5403	0.5123	0.4834	0.8114	0.8062	0.7931	0.7732	0.7518	0.9087	0.9060	0.8965	0.8855	0.8757
2,000	0.5207	0.5285	0.5234	0.5097	0.4941	0.7916	0.7876	0.7753	0.7561	0.7349	0.8996	0.8976	0.8880	0.8771	0.8671
2,250	0.5039	0.5202	0.5262	0.5232	0.5165	0.7746	0.7728	0.7620	0.7452	0.7258	0.8917	0.8912	0.8818	0.8717	0.8616
2,500	0.5040	0.5269	0.5410	0.5449	0.5453	0.7616	0.7622	0.7540	0.7398	0.7240	0.8852	0.8863	0.8782	0.8688	0.8600
2,750	0.5152	0.5424	0.5616	0.5710	0.5766	0.7524	0.7564	0.7510	0.7400	0.7288	0.8809	0.8835	0.8770	0.8686	0.8608
3,000	0.5317	0.5621	0.5852	0.5990	0.6090	0.7473	0.7555	0.7535	0.7453	0.7390	0.8781	0.8825	0.8778	0.8701	0.8646
3,500	0.5727	0.6085	0.6393	0.6581	0.6748	0.7479	0.7633	0.7703	0.7692	0.7714	0.8771	0.8854	0.8861	0.8819	0.8794
4,000	0.6193	0.6591	0.6961	0.7190	0.7415	0.7601	0.7826	0.7980	0.8038	0.8113	0.8831	0.8949	0.9009	0.9003	0.9030
4,500	0.6675	0.7119	0.7531	0.7813	0.8085	0.7838	0.8088	0.8326	0.8447	0.8573	0.8944	0.9113	0.9213	0.9240	0.9325
5,000	0.7176	0.7665	0.8113	0.8439	0.8753	0.8123	0.8411	0.8705	0.8893	0.9067	0.9100	0.9318	0.9466	0.9530	0.9660
6,000	0.8187	0.8732	0.9297	0.9697	1.0073	0.8784	0.9161	0.9555	0.9838	1.0096	0.9527	0.9809	1.0062	1.0224	1.0416
7,000	0.9180	0.9793	1.0439	1.0920	1.1370	0.9526	0.9969	1.0462	1.0807	1.1151	1.0040	1.0386	1.0744	1.0978	1.1258
8,000	1.0177	1.0851	1.1580	1.2122	1.2650	1.0305	1.0802	1.1377	1.1790	1.2204	1.0620	1.1029	1.1467	1.1772	1.2106
9,000	1.1129	1.1893	1.2714	1.3310	1.3911	1.1089	1.1656	1.2293	1.2766	1.3252	1.1230	1.1706	1.2206	1.2579	1.2966
10,000	1.2059	1.2948	1.3838	1.4456	1.5144	1.1861	1.2500	1.3186	1.3748	1.4278	1.1848	1.2395	1.2947	1.3400	1.3844
	220° F.					340° F.					460° F.				
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.9683	0.9670	0.9642	0.9608	0.9566	0.9836	0.9822	0.9803	0.9782	0.9758	0.9918	0.9910	0.9897	0.9884	0.9869
400	0.9358	0.9330	0.9277	0.9202	0.9113	0.9673	0.9648	0.9608	0.9565	0.9519	0.9838	0.9823	0.9797	0.9772	0.9743
600	0.9030	0.8986	0.8903	0.8783	0.8649	0.9512	0.9477	0.9418	0.9355	0.9285	0.9760	0.9739	0.9702	0.9664	0.9623
800	0.8697	0.8639	0.8529	0.8362	0.8184	0.9354	0.9310	0.9234	0.9152	0.9062	0.9684	0.9658	0.9612	0.9563	0.9511
1,000	0.8370	0.8299	0.8156	0.7952	0.7721	0.9197	0.9151	0.9064	0.8960	0.8858	0.9613	0.9585	0.9526	0.9471	0.9408
1,250	0.7965	0.7890	0.7701	0.7468	0.7185	0.9008	0.8967	0.8862	0.8741	0.8619	0.9527	0.9501	0.9431	0.9367	0.9293
1,500	0.7579	0.7505	0.7315	0.7047	0.6729	0.8836	0.8796	0.8683	0.8550	0.8422	0.9451	0.9425	0.9350	0.9277	0.9191
1,750	0.7222	0.7165	0.6985	0.6719	0.6400	0.8679	0.8650	0.8534	0.8393	0.8259	0.9382	0.9358	0.9281	0.9206	0.9116
2,000	0.6914	0.6886	0.6742	0.6503	0.6231	0.8547	0.8523	0.8411	0.8273	0.8144	0.9318	0.9308	0.9223	0.9149	0.9059
2,250	0.6675	0.6695	0.6589	0.6412	0.6213	0.8430	0.8420	0.8319	0.8187	0.8057	0.9265	0.9264	0.9184	0.9113	0.9031
2,500	0.6504	0.6584	0.6538	0.6438	0.6290	0.8336	0.8345	0.8260	0.8138	0.8020	0.9223	0.9231	0.9160	0.9098	0.9025
2,750	0.6420	0.6555	0.6575	0.6533	0.6447	0.8271	0.8296	0.8230	0.8136	0.8016	0.9192	0.9215	0.9156	0.9095	0.9037
3,000	0.6412	0.6587	0.6676	0.6679	0.6642	0.8229	0.8278	0.8241	0.8163	0.8064	0.9179	0.9215	0.9168	0.9118	0.9079
3,500	0.6568	0.6810	0.6971	0.7095	0.7140	0.8212	0.8314	0.8342	0.8308	0.8276	0.9190	0.9253	0.9241	0.9216	0.9211
4,000	0.6837	0.7137	0.7405	0.7574	0.7697	0.8291	0.8455	0.8524	0.8539	0.8595	0.9251	0.9340	0.9374	0.9379	0.9421
4,500	0.7185	0.7533	0.7885	0.8094	0,8272	0.8430	0.8650	0.8787	0.8847	0.8950	0.9347	0.9479	0.9565	0.9590	0.9681
5,000	0.7573	0.7974	0.8375	0.8621	0.8855	0.8634	0.8879	0.9094	0.9211	0.9350	0.9481	0.9644	0.9795	0.9842	0.9967
6,000	0.8418	0.8885	0.9368	0.9697	1.0031	0.9170	0.9479	0.9791	1.0016	1.0246	0.9822	1.0103	1.0324	1.0433	1.0622
7,000	0.9303	0.9825	1.0391	1.0799	1.1204	0.9790	1.0175	1.0567	1.0865	1.1167	1.0277	1.0616	1.0916	1.1105	1.1345
8,000	1.0199	1.0779	1.1419	1.1890	1.2367	1.0465	1.0905	1.1403	1.1753	1.2106	1.0780	1.1175	1.1558	1.1814	1.2124
9,000	1.1060	1.1723	1.2437	1.2975	1.3516	1.1159	1.1662	1.2225	1.2646	1.3064	1.1305	1.1785	1.2233	1.2557	1.2929
10,000	1.1906	1.2653	1.3440	1.4057	1.4653	1.1852	1.2420	1.3038	1.3547	1.4024	1.1837	1.2412	1.2928	1.3307	1.3757

substitution weighing. Air buoyancy corrections were applied to the stainless steel weights, which had been calibrated against a 100-gram weight certified by the National Bureau of Standards. Comparison of the sample weight measured by addition at the start of a test and by withdrawal at the end of a test indicated that this quantity was known with an uncertainty of 0.01 gram in a total sample weight of 100 grams.

The volume of the sample was determined by the volume of mercury displaced from the equilibrium cell. The specific volume of mercury at the pressures and temperatures involved in the experimental observations was computed from the values given in the Smithsonian Tables for mercury at atmospheric pressure with corrections for the compressibility of mercury in accordance with the data of Smith and Keyes (*10*). It is estimated that the volume occupied by the sample was measured with an uncertainty not exceeding 0.2%.

The equilibrium cell was immersed in a rapid-circulation oil bath whose temperature was maintained with a maximum fluctuation of 0.05° F. by electronically controlled thermostats. The temperature was measured by a platinum resistance thermometer calibrated against a similar instrument certified by the National Bureau of Standards. The resistance of the thermometer was measured with a Mueller bridge, and the corresponding temperature was computed from interpolations between calibration points on the basis of the Callendar equation (*3*). It is believed that the absolute temperature in terms of the international temperature scale was known with an uncertainty less than 0.1° F.

Pressure was determined with a rotating cylinder and piston hydraulic balance. The balance was calibrated against a mercury manometer at pressures up to 50 pounds per square inch absolute and against the vapor pressure of pure carbon dioxide at 32° F. using Bridgeman's value of 505.56 pounds per square inch

Five mixtures of ethane and carbon dioxide were studied with regard to their volumetric properties in the temperature interval from 100° to 460° F. at pressures up to 10,000 pounds per square inch. The results are tabulated in terms of compressibility factors and molal volumes.

Table II. Molal Volumes for Ethane–Carbon Dioxide

Pressure, Lb./Sq. In. Abs.	Molal Volume with Mole Fraction Ethane as Follows:														
	0.1777	0.3313	0.5132	0.6763	0.8280	0.1777	0.3313	0.5132	0.6763	0.8280	0.1777	0.3313	0.5132	0.6763	0.8280
	100° F.					220° F.					340° F.				
14.696	406.99	406.95	406.85	406.67	406.44	495.22	495.16	495.07	494.96	494.81	583.29	583.22	583.14	583.05	582.95
200	28.23	28.17	28.04	27.83	27.57	35.32	35.27	35.17	35.04	34.89	42.21	42.15	42.07	41.98	41.87
400	13.102	13.031	12.865	12.620	12.321	17.065	17.014	16.918	16.781	16.618	20.754	20.701	20.615	20.522	20.424
600	7.960	7.872	7.663	7.379	7.002	10.978	10.925	10.824	10.678	10.515	13.606	13.556	13.471	13.381	13.281
800	5.278	5.176	4.917	4.569	4.015	7.930	7.877	7.777	7.624	7.462	10.035	9.988	9.906	9.818	9.722
1,000	3.541	3.435	3.128	2.635	1.8963	6.105	6.054	5.949	5.801	5.632	7.893	7.854	7.779	7.690	7.602
1,250	1.8880	1.8904	1.7410	1.5891	1.4896	4.648	4.604	4.494	4.358	4.193	6.185	6.157	6.085	6.001	5.918
1,500	1.2622	1.3595	1.3967	1.3835	1.3695	3.686	3.650	3.557	3.427	3.272	5.056	5.033	4.968	4.892	4.819
1,750	1.1193	1.2147	1.2758	1.2909	1.3043	3.010	2.987	2.912	2.801	2.668	4.256	4.242	4.185	4.116	4.050
2,000	1.0512	1.1404	1.2091	1.2356	1.2590	2.522	2.511	2.4589	2.3718	2.2726	3.668	3.657	3.609	3.550	3.495
2,250	1.0088	1.0911	1.1599	1.1954	1.2253	2.1640	2.1705	2.1361	2.0787	2.0142	3.216	3.212	3.173	3.123	3.073
2,500	0.9776	1.0557	1.1237	1.1634	1.1977	1.8977	1.9211	1.9076	1.8785	1.8353	2.862	2.865	2.836	2.794	2.753
2,750	0.9523	1.0281	1.0958	1.1378	1.1751	1.7029	1.7387	1.7440	1.7329	1.7101	2.581	2.589	2.568	2.539	2.502
3,000	0.9312	1.0045	1.0732	1.1160	1.1559	1.5591	1.6016	1.6232	1.6240	1.6150	2.3541	2.3681	2.3576	2.3352	2.3069
3,500	0.8984	0.9686	1.0367	1.0824	1.1234	1.3688	1.4193	1.4528	1.4787	1.4881	2.0137	2.0387	2.0455	2.0372	2.0293
4,000	0.8738	0.9415	1.0099	1.0558	1.0977	1.2468	1.3015	1.3504	1.3812	1.4036	1.7789	1.8141	1.8289	1.8321	1.8441
4,500	0.8544	0.9198	0.9878	1.0333	1.0760	1.1647	1.2211	1.2781	1.3120	1.3409	1.6078	1.6497	1.6758	1.6873	1.7069
5,000	0.8377	0.9021	0.9690	1.0139	1.0575	1.1048	1.1633	1.2218	1.2577	1.2918	1.4820	1.5240	1.5609	1.5810	1.6049
6,000	0.8116	0.8742	0.9372	0.9821	1.0276	1.0234	1.0802	1.1389	1.1789	1.2195	1.3117	1.3559	1.4005	1.4327	1.4656
7,000	0.7912	0.8504	0.9121	0.9575	1.0049	0.9694	1.0238	1.0828	1.1253	1.1675	1.2003	1.2475	1.2956	1.3321	1.3691
8,000	0.7738	0.8312	0.8923	0.9365	0.9854	0.9299	0.9828	1.0412	1.0841	1.1276	1.1227	1.1699	1.2233	1.2609	1.2987
9,000	0.7592	0.8150	0.8764	0.9185	0.9675	0.8964	0.9501	1.0080	1.0516	1.0955	1.0641	1.1121	1.1658	1.2059	1.2458
10,000	0.7455	0.8009	0.8639	0.9033	0.9503	0.8685	0.9230	0.9804	1.0254	1.0688	1.0172	1.0659	1.1190	1.1626	1.2036
	160° F.					280° F.					400° F.				
14.696	451.12	451.08	450.99	450.86	450.67	539.28	539.21	539.12	539.02	538.90	627.26	627.20	627.13	627.05	626.97
200	31.81	31.76	31.67	31.52	31.32	38.80	38.73	38.64	38.52	38.41	45.59	45.54	45.46	45.38	45.30
400	15.148	15.093	14.990	14.832	14.626	18.945	18.877	18.784	18.673	18.554	22.530	22.480	22.406	22.325	22.244
600	9.568	9.512	9.382	9.216	8.997	12.326	12.266	12.173	12.062	11.942	14.845	14.797	14.728	14.654	14.571
800	6.756	6.695	6.541	6.363	6.125	9.018	8.961	8.869	8.761	8.644	11.001	10.965	10.895	10.823	10.744
1,000	5.045	4.985	4.819	4.624	4.358	7.037	6.989	6.899	6.790	6.675	8.703	8.667	8.607	8.534	8.460
1,250	3.667	3.607	3.458	3.251	2.983	5.458	5.420	5.335	5.230	5.120	6.870	6.841	6.784	6.717	6.647
1,500	2.751	2.709	2.584	2.4159	2.2151	4.415	4.386	4.312	4.213	4.105	5.656	5.631	5.579	5.515	5.453
1,750	2.1270	2.1221	2.0533	1.9469	1.8371	3.681	3.657	3.598	3.507	3.410	4.791	4.777	4.726	4.668	4.617
2,000	1.7315	1.7574	1.7404	1.6949	1.6430	3.142	3.126	3.077	3.001	2.917	4.150	4.141	4.096	4.046	4.000
2,250	1.4894	1.5376	1.5553	1.5465	1.5267	2.733	2.727	2.688	2.629	2.561	3.656	3.654	3.616	3.574	3.533
2,500	1.3407	1.4017	1.4392	1.4495	1.4506	2.4183	2.4202	2.3942	2.3491	2.2989	3.267	3.271	3.241	3.206	3.174
2,750	1.2459	1.3117	1.3582	1.3809	1.3944	2.1719	2.1835	2.1679	2.1361	2.1038	2.955	2.964	2.942	2.914	2.888
3,000	1.1787	1.2461	1.2973	1.3279	1.3500	1.9774	1.9991	1.9939	1.9722	1.9555	2.701	2.714	2.700	2.676	2.659
3,500	1.0882	1.1562	1.2148	1.2505	1.2822	1.6963	1.7312	1.7471	1.7446	1.7496	2.3121	2.3340	2.3358	2.3247	2.3182
4,000	1.0297	1.0958	1.1573	1.1954	1.2328	1.5085	1.5531	1.5837	1.5952	1.6101	2.0369	2.0641	2.0780	2.0766	2.0828
4,500	0.9865	1.0521	1.1130	1.1547	1.1949	1.3827	1.4268	1.4688	1.4901	1.5123	1.8338	1.8684	1.8889	1.8944	1.9119
5,000	0.9545	1.0195	1.0791	1.1225	1.1642	1.2897	1.3354	1.3821	1.4119	1.4395	1.6792	1.7194	1.7467	1.7585	1.7825
6,000	0.9075	0.9679	1.0305	1.0748	1.1165	1.1622	1.2121	1.2642	1.3016	1.3358	1.4650	1.5083	1.5472	1.5721	1.6017
7,000	0.8722	0.9304	0.9918	1.0375	1.0802	1.0803	1.1305	1.1864	1.2256	1.2646	1.3233	1.3689	1.4161	1.4469	1.4838
8,000	0.8460	0.9021	0.9627	1.0077	1.0516	1.0226	1.0719	1.1289	1.1699	1.2110	1.2248	1.2720	1.3225	1.3576	1.3962
9,000	0.8224	0.8788	0.9395	0.9835	1.0279	0.9781	1.0281	1.0843	1.1260	1.1689	1.1512	1.2000	1.2513	1.2895	1.3292
10,000	0.8020	0.8611	0.9203	0.9614	1.0072	0.9416	0.9923	1.0468	1.0914	1.1334	1.0931	1.1436	1.1945	1.2363	1.2773

Pressure Lb./Sq. In. Abs.	Molal Volume at 460° F. with Mole Fraction Ethane as Follows:				
	0.1777	0.3313	0.5132	0.6763	0.8280
14.696	671.21	671.17	671.10	671.03	670.96
200	48.95	48.91	48.84	48.78	48.70
400	24.276	24.238	24.174	24.113	24.041
600	16.055	16.021	15.960	15.897	15.830
800	11.948	11.916	11.859	11.798	11.734
1,000	9.488	9.460	9.402	9.348	9.286
1,250	7.523	7.502	7.447	7.396	7.338
1,500	6.219	6.202	6.152	6.104	6,048
1,750	5.292	5.279	5.235	5.192	5.141
2,000	4.598	4.594	4.552	4.515	4.471
2,250	4.064	4.064	4.029	3.998	3.962
2,500	3.641	3.644	3.616	3.592	3.563
2,750	3.299	3.307	3.286	3.264	3.243
3,000	3.020	3.032	3.016	3.000	2.987
3,500	2.592	2.609	2.606	2.599	2.598
4,000	2.2837	2.3047	2.3131	2.3143	2.3247
4,500	2.0501	2.0791	2.0979	2.1034	2.1234
5,000	1.8716	1.9037	1.9336	1.9428	1.9675
6,000	1.6157	1.6620	1.6983	1.7162	1.7473
7,000	1.4491	1.4969	1.5392	1.5658	1.5997
8,000	1.3300	1.3787	1.4260	1.4576	1.4958
9,000	1.2398	1.2924	1.3416	1.3771	1.4179
10,000	1.1683	1.2251	1.2760	1.3134	1.3578

absolute (*2*). The balance was sensitive to pressure changes of 0.1 pound per square inch. The uncertainty in pressure measurement is estimated to be less than 0.1%.

The experimental procedure consisted in compressing to 10,000 pounds per square inch the mixture under consideration and permitting several hours to elapse for the attainment of thermal equilibrium before making the first observation. Then, while isothermal conditions were maintained, a series of 15 or 20 volumes was measured at arbitrarily chosen pressures ranging from maximum to approximately 800 pounds per square inch. Observations were taken at 30-minute intervals with the system continuously agitated by a magnetically driven impeller within the equilibrium cell. This process was repeated for each of the seven temperatures experimentally studied. Thus, for the system of five mixtures more than six hundred equilibrium states were observed.

RESULTS

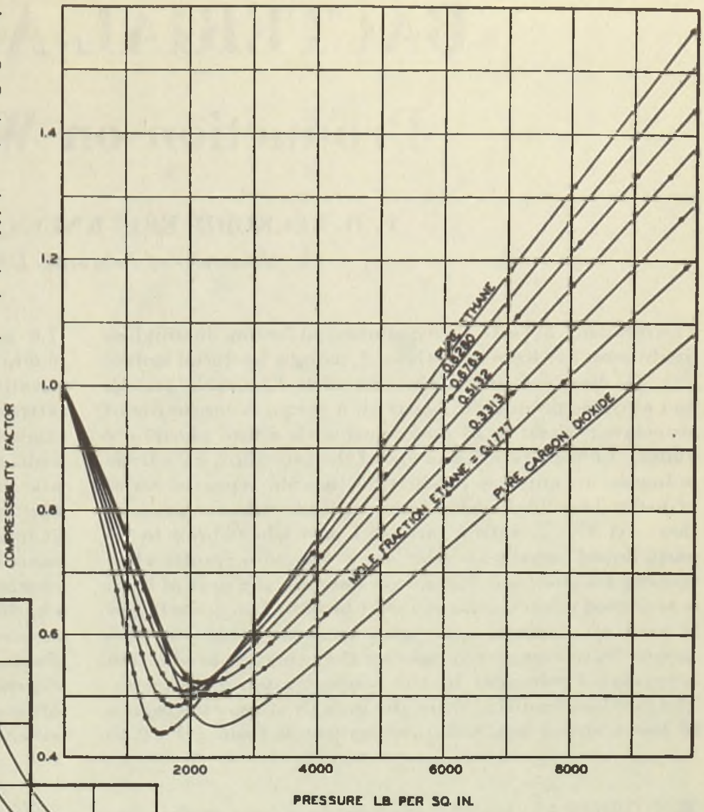
Molal volumes and compressibility factors were computed from the experimental data and plotted against pressure on 50 × 75 cm. sheets of millimeter coordinate paper. Smooth curves were drawn through the isothermal points, and values at even pressures were obtained by interpolation. The results are presented as compressibility factors in Table I and molal volumes in Table II. In the tabulation of compressibility factors at 100° F. the density of the data at pressures between 1000 and 2000 pounds per square inch has been augmented in order to facilitate reconstruction of the compressibility-pressure isotherms in the region where curvature is greatest. The following numerical constants were employed in the calculations: molecular weight of carbon dioxide, 44.010; of ethane, 30.069; universal gas constant, 10.732 (pounds per square inch) (cubic feet per pound mole) per °Rankine; and absolute zero of thermodynamic temperature, −459.69° F. The compressibility factor was assumed to approach the value unity at infinite attenuation of the system, and for finite volumes it was computed from the relation:

$$Z = PV/\mathbf{R}T$$

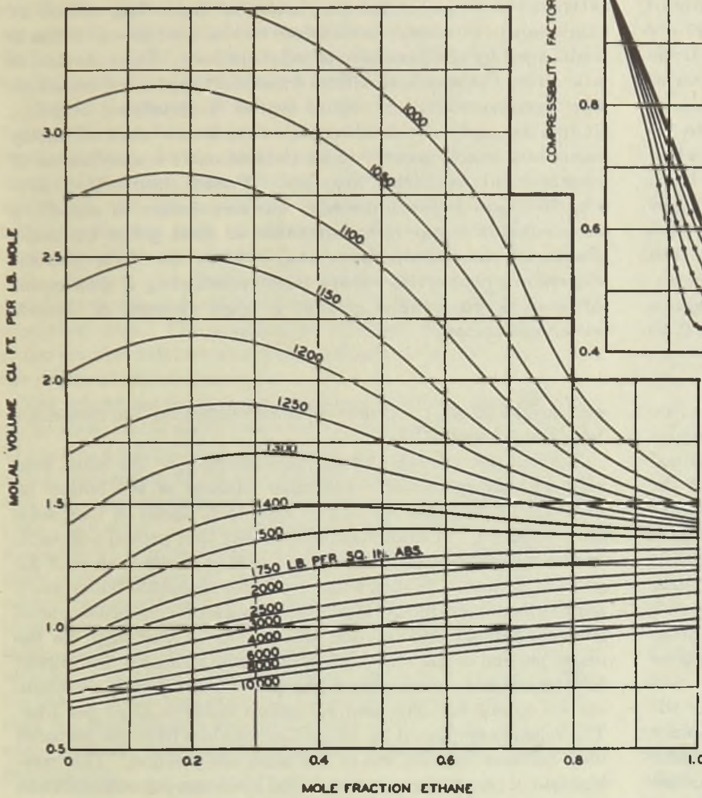
where P = pressure, lb./sq. in. abs.
$\mathbf{R}$ = universal gas constant
T = thermodynamic temperature, ° R.
V = molal volume, cu. ft./lb. mole
Z = compressibility factor

The consistency of the results was tested by cross plotting values from the smooth curves with respect to composition. The isobaric-isothermal curves of volume *vs.* composition were found to extrapolate nicely to the limiting values representing the volumetric behavior of the pure components. For the volumetric behavior of pure carbon dioxide the data of Michels and Michels were used (*4*, *5*). The volumetric properties of pure ethane were obtained from data published by Beattie, Su, and Simard (*1*) and from the results of a recent investigation by the authors (*7*). The scales used in plotting the data were carefully chosen so as to permit a precision of at least 0.1% in smoothing and interpolating. A thorough graphical examination of the experimental results indicates that the reported volumetric data are descriptive of actuality with an uncertainty probably not exceeding 0.5%.

Figure 1 shows the relation between the compressibility factor and pressure at 160° F. for the pure components and the five experimentally studied mixtures. The experimental values are represented by circles, and the curves are drawn in accordance with the final smoothed results obtained by cross plotting the experimental data with respect to temperature and composition. It may be noted that the minimum values of the compressibility factor of the pure components are less than those of the mixtures, and the curves of the family describe a saddle-shaped surface in the neighborhood of their minima.



↑ **Figure 1. Compressibility Factor for Mixtures of Ethane and Carbon Dioxide at 160° F.**



← **Figure 2. Molal Volume of Ethane–Carbon Dioxide System at 100° F.**

Figure 2 gives isobaric curves relating molal volume and molal composition at 100° F. For the most part each of these curves lies above a straight line joining its extremities. This indicates that, in general, the mixing of the components under isobaric, isothermal conditions results in a total volume which is greater than the sum of the volumes of the components before mixing. In fact, Figure 2 shows that the actual volume of a mixture may exceed that predicted on the basis of ideal mixtures by as much as 20%.

As in the case of the methane–carbon dioxide system (*6*) the volumetric behavior of the ethane–carbon dioxide system deviates most widely from that of an ideal mixture in the region of high concentrations of carbon dioxide, and these deviations become increasingly large as the critical temperatures and pressures of the components are approached.

ACKNOWLEDGMENT

This work represents part of the activities of Research Project 37 of the American Petroleum Institute. The financial support and encouragement of that organization are gratefully acknowledged. The cooperation of H. A. Taylor and E. S. Turner in connection with the experimental operations and the assistance of Louise Reaney in the calculations and preparation of figures are appreciated.

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BACTERIAL AMYLASES

Production on Wheat Bran

L. D. BECKORD, ERIC KNEEN, AND K. H. LEWIS[1]

University of Nebraska, Lincoln, Nebr.

The influence of various environmental factors on amylase production has been investigated, using a bacterial isolate (No. 23) classified as *Bacillus subtilis*. Favorable growth and amylase production occur on a medium consisting of autoclaved wheat bran moistened with dilute phosphate buffer. Concentration and age of the inoculum have little influence on amylase production, nor do repeated serial transfers in a fluid wheat bran medium enhance production. At 37° C., with a ratio of 1 part wheat bran to 2.5 parts liquid, maximum amylase production results after 48-hour incubation. Maximum amylase per unit of bran is produced when a ratio of 1 part bran to 1.75 parts liquid is used as medium. However, enzyme yields over the range of ratios employed indicate that amylase production is regulated primarily by the concentration of nutrient. The amylase resulting from the growth of selected isolate 23 has a starch dextrinization optimum from pH 7.0 to 7.6 and a starch saccharification optimum from pH 6.6 to 7.0. The amylase is most resistant to thermal inactivation at about pH 7.0. It has the characteristic ability, attributed to bacterial amylases, of degrading starch at high temperatures. Resistance to thermal inactivation is enhanced by the presence of calcium ions. Degradation of starch by the amylase differs from that typical of commercial preparations. At equal starch dextrinizing activity, it has an early saccharification rate below that of barley malt but much greater than that of malt α-amylase or of commercial bacterial amylase. Postdextrinization saccharification is pronounced; the conversion of starch to fermentable sugar is comparable to that given by malt. Bacterial amylases, then, vary widely in their starch-degrading properties—from those producing a minimum of sugars to others giving a high degree of starch saccharification.

IN GENERAL, bacterial amylases have been produced on liquid-type media. Boidin and Effront (*4, 5*) recommended extracts of proteinaceous materials, either of vegetable or animal origin, as liquid media for the production of amylases by the growth of *Bacillus subtilis* or *Bacillus mesentericus*. These workers reported unfavorably on the applicability of solid media such as soybean cake with 1 to 2 parts of water. Additional emphasis was given to the utilization of soybean extracts by Wallerstein (*17*) and Schultz, Atkin, and Frey (*15*). On the other hand, Tilden and Hudson (*16*) employed media prepared from potatoes, rolled oats, and corn meal for the production of amylases by the growth of *B. macerans* and *B. polymyxa*.

A solid or semisolid material as culture medium offers an advantage since the resulting active product can be air-dried rapidly and stored for future use. Soybean meal, potato meal, alfalfa meal, and wheat bran were investigated. Although amylase was produced by bacterial growth on semisolid media formed from all these materials, wheat bran proved to be the most satisfactory for laboratory manipulation. This report presents the technical details of the production of bacterial amylase on wheat bran and a preliminary description of the properties of the amylase.

EXPERIMENTAL METHODS

General Culture Procedure. The stock culture collection of the various bacterial isolates was maintained on beef extract–peptone–agar slants. The only exception was strain No. 51 (*Aerobacillus polymyxa*) which was maintained on Difco corn meal–agar slants. Subcultures were made from stock cultures to fresh slants and incubated for 24 hours at 37° C. The agar slant growth was either suspended in sterile distilled water and transferred to the autoclaved (1 hour at 15 pounds pressure) wheat bran medium, or was subcultured in a liquid bran medium before final inoculation. The containers for the bran cultures were either screw-capped French squares (6 × 6 × 14 cm.) or 64-ounce capacity cotton-plugged round bottles (diameter 11.5 cm., height 20 cm.). Unless otherwise indicated, the incubation temperature was 37° C.

To facilitate growth and amylase production, the moist bran medium was spread over the inner surfaces of the bottles by vigorous shaking and the bottles were then placed on their sides for incubation. A bran mash consistency that proved adaptable to this technique was obtained by 1 part of wheat bran with 2.5 parts of diluent. As shown later, a dilute phosphate buffer was a more satisfactory diluent than distilled water for the promotion of bacterial growth and amylase production. Accordingly, for the major portion of the work, unless otherwise indicated, the diluent for preparing the media was a phosphate buffer solution containing 1.5 grams KH_2PO_4 and 3.5 grams $K_2HPO_4.3H_2O$ per liter. The solution employed for extracting amylase from the prepared bran cultures likewise was of the same composition. This combination of phosphates gave an initial hydrogen-ion concentration in the bran mash of approximately pH 6.0, and the extracts of the bran cultures likewise approximated pH 6.0.

After an appropriate incubation period, usually 48 hours, the bran was either extracted for activity determinations or removed from the container and air-dried at room temperature. Neither drying nor storage of the dried material for several months appreciably decreased amylase activity. The dried bran cultures were much darker in color than the original material and retained a characteristic offensive odor.

Clarification of Extracts from Bran Cultures. Water extracts of bran cultures contain suspended material that resists removal by centrifugation or filtration and obscures the end point in the iodine test for dextrinization. To eliminate this difficulty, the bran culture was extracted for 1 hour at 30° C. with the described phosphate buffer solution. One milliliter of a 20% $CaCl_2.2H_2O$ solution per 40 ml. of buffer was then added. The resulting precipitate was centrifuged out with the bran, leaving a clear extract undiminished in amylase activity.

Evaluation of Amylase Activity. The characteristics of bacterial amylases are reported to be those of an α-amylase type (*3, 9*); i.e., they hydrolyze gelatinized starch to the low-molecu-

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[1] On leave for service with the armed forces.

lar-weight dextrins that give essentially no color with iodine. Accordingly, a dextrinization procedure was used for routine evaluation. Dextrinizing activity is expressed as dextrinization time—i.e., the time, in minutes, required to convert 20 ml. of 1% boiled soluble starch to the point where the "red-brown" color described by Sandstedt, Kneen, and Blish (*14*) is given with iodine. The reaction temperature was 30° C. and a 10 ml. aliquot of a 1 to 50 extract[3] of "bacterial bran" was used throughout. The starch was buffered to approximately pH 6.0 with 50 ml. of stock phosphate buffer solution (4.0 grams KH_2PO_4 and 0.84 gram $K_2HPO_4.3H_2O$ per liter) per liter of starch suspension. Occasionally (as indicated) a 20-ml. aliquot of 2% starch was employed as the substrate for activity determinations.

It was not deemed advisable to translate the dextrinization times to arbitrary units. The time required for dextrinization of the starch was inversely proportional to the amount of active amylase present. This permitted accurate evaluation of relative activity; e.g., a solution with a dextrinization time of 10 minutes was twice as active as one giving a time of 20 minutes.

Two other methods were used for final evaluation of the bacterial amylase. Both were designed to evaluate the conversion of starch to sugar. In one, aliquots were withdrawn at appropriate intervals from the same reaction mixture employed for dextrinization, and the content of reducing substances was determined by heating with an alkaline ferricyanide reagent as described by Blish and Sandstedt (*1*) and modified by Sandstedt (*12*). Enzyme and starch blanks were subtracted, and a maltose-ferricyanide reduction relationship was established for the conditions used. For comparative purposes the reducing value of the reaction mixture was calculated as maltose and, from this the degree of starch conversion.

The second saccharification procedure involved an evaluation of the fermentable sugar produced by amylase action on starch. The reaction mixture was composed of 15 ml. of 4% boiled soluble starch (containing 25 ml. of stock phosphate buffer per liter, pH 6.0), 0.5 gram of baker's compressed yeast, 0.5 gram of dried yeast "activator" (*2*), and sufficient enzyme solution (plus water if necessary) to give a final volume of 20 ml. Fermentation of sugar was measured by the evolution of carbon dioxide as recorded manometrically in a closed system using the pressure meter described by Sandstedt and Blish (*13*). Readings were taken hourly for the first few hours and at other appropriate intervals for 24 hours. The enzyme aliquot was adjusted so that the rate of conversion of starch to fermentable sugar did not exceed the fermentation capacity of the yeast; thus, the rate of carbon dioxide evolution likewise was a measure of starch saccharification.

SELECTION OF ORGANISM

From some sixty cultures of aerobic bacilli obtained from various sources, sixteen that were known to hydrolyze starch were tested for amylase production on wheat bran. A ratio of 1 part bran to 2.5 parts phosphate buffer solution was used. The bran was placed in the culture vessels, the liquid added, and the whole autoclaved for 1 hour at approximately 121° C. before inoculation. The classification of the organisms, their origins, and the amylase activities after 48-hour incubation on wheat bran at 37° C. are given in Table I. The activities ranged from levels below the practical limits of measurement (180+ minutes) to the dextrinization time of 15 minutes found for isolate 23. On the basis of this and other investigations isolate 23 was selected for further study. The characteristics of this organism indicate that it belongs to the *Bacillus subtilis* group. The microorganisms are rod-shaped. In hanging drop preparations from 24-hour-old broth cultures, their dimensions are 4 to 5 microns in length and 1 to 1.25 microns in width. The rods are actively motile by means of flagella. Endospores are formed in cells grown on nutrient agar slants. The endospores are small ovoid bodies which do not exceed a maximum diameter of 0.8 micron and do not cause swelling of the sporangium. The vegetative cells are Gram-positive when stained by Hucker's modification of the Gram stain. Colonies on agar plates are circular or slightly irregular, flat, and creamy white, with a somewhat uneven surface which may be glistening or dull. Streaks on nutrient agar slants are usually echinulate, flat, grayish white, and translucent or opaque, with a dull uneven surface. Broth cultures produce a surface pellicle with a slightly flocculent turbidity and sediment. Nutrient gelatin stab cultures show saccate liquefaction which progresses to completeness in about two weeks. In litmus milk cultures the indicator is reduced and a soft curd is formed which is slowly peptonized. Acid is produced from glucose and sucrose but not from lactose, trehalose, or sorbitol. Starch is hydrolyzed. Acetylmethylcarbinol is produced from glucose. Nitrite and ammonia are formed in nitrate broth. In tryptone broth ammonia, but not indole, is formed. Growth occurs in the synthetic medium of Burkholder and McVeigh (*6*).

AMYLASE PRODUCTION BY ISOLATE 23

COMPARISON OF PHOSPHATE BUFFER AND DISTILLED WATER AS MASH DILUENTS. Bran mashes were prepared with 1 part of bran to 2.5 parts of diluent. Water was compared with phosphate buffer as the diluent; the mashes were inoculated with isolate 23 and incubated at 37° C. for 48 hours. A dextrinization time of 23 minutes was obtained with the phosphate buffer and 50 minutes with water. It is apparent that the use of phosphate buffer rather than distilled water as a diluent resulted in greatly enhanced amylase production; more than twice as much amylase activity was obtained with phosphate buffer as with distilled water.

CONCENTRATION OF INOCULUM. To determine the concentration of inoculum for maximum production, the growth on a number of 18-hour slant cultures was suspended in sterile water to give a concentrated inoculum. The latter was diluted to give five suspensions each; agar plate counts showed a final concentration of approximately 2, 4, 8, 16, and 32 million organisms per ml., respectively. Bottles containing 10 grams of wheat bran and 25 ml. of phosphate buffer solution were inoculated with 2.5 ml. of the suspensions and incubated for 48 hours at 37° C. The dextrinization times for the products (average of triplicate runs) were 15, 14, 15, 16, and 14 minutes. Since 2.5 ml. of inocula were used in each instance, these activities resulted from approximate initial inoculations of 5, 10, 20, 40, and 80 million organisms per 10 grams of wheat bran, respectively. The amylase activities of the bran cultures after 48-hour incubation were essentially equal; at least over the range employed, the concentration of inoculum was not a critical factor in the production of amylase.

TABLE I. AMYLASE PRODUCTION ON WHEAT BRAN BY SELECTED CULTURES

Strain or Isolate No.	Species	Source	Dextrinization Time, Min.
1	Bacillus subtilis	Potato	180+
8	B. subtilis (Marburg)	Univ. of Nebr.	180+
11	B. graveolens	Univ. of Nebr.	180+
14	B. mycoides	Univ. of Nebr.	180+
17	B. mesentericus	Soil	180+
20	B. mesentericus	Soil	50
23	B. subtilis	Corn meal mash	15
39	B. mesentericus	Soybean	71
40	B. mesentericus	Soybean	89
41	B. subtilis	Peanut	44
42	B. mesentericus	Peanut	55
43	B. mesentericus	Peanut	43
47	B. subtilis (231 N.R. Smith)	Natl. Inst. Health	74
49	B. vulgatus (237 N.R. Smith)	Natl. Inst. Health	47
50	B. aterrimus (230 N.-R. Smith)	Natl. Inst. Health	180+
51	Aerobacillus polymyxa (510)	No. Regional Research Lab.	180+

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[3] A "1 to 50 extract" means the solution obtained by adding extractant, either water or dilute phosphate buffer solution to bring the final ratio to 1 part of dry bran (original weight) per 50 parts of extractant.

Age of Inoculum. The degree to which age of inoculum influenced amylase production was determined. Five suspensions with approximately the same concentration of organisms in each were prepared from agar slant cultures previously incubated at 37° C. for 12, 18, 24, 42, and 180 hours. From each suspension a 2.5-ml. aliquot was introduced into a bottle containing 10 grams of wheat bran and 25 ml. of phosphate buffer solution. Incubation was for 48 hours at 37° C. The dextrinization times of the products (average of duplicate runs) were 20, 21.5, 22.5, 21.5, and 25.5 minutes, respectively. This indicates that over the range tested the age of the inoculum had little influence on the resulting amylase activity. The most active product was obtained when inoculum cultured for the shortest period (12 hours) was used, but the variation from 20 to 22.5 minutes—i.e., the variation in activity of the cultures with 12 to 42 hour inocula—is within the experimental error. The dextrinization time of 25.5 minutes for the oldest inoculum (180 hours) may be significant as indicating that cultures of this age are not quite so satisfactory.

Table II. Influence of Solid-Liquid Ratio (Wheat Bran-Phosphate Buffer) on Amylase Production by Isolate 23

Wheat Bran (*A*), Grams	Phosphate Buffer (*B*), Ml.	Ratio, *A*:*B*	Dextrinization Time, Min.[a]
40.0	60.0	1:1.5	19
36.4	63.6	1:1.75	15
33.4	66.8	1:2.0	19
28.6	71.4	1:2.5	18
25.0	75.0	1:3.0	26
22.2	77.8	1:3.5	27
16.7	83.3	1:5.0	24

[a] Calculated on the basis of 0.2 gram of dry wheat bran introduced (average of triplicate runs).

Subculturing (Serial Transfers). Growth of an organism in a medium of essentially the same composition as that employed for final culture has been demonstrated as an effective means of enhancing a desired property (*4*). Serial transfers for inocula were made every 48 hours, initially from the agar slant and subsequently from a fluid wheat bran mash (3 grams of wheat bran plus 60 ml. of phosphate buffer solution). Thus a comparison was obtained with inocula taken directly from the agar slant, from the first subculture in fluid bran mash for 48 hours (slant to bran), from the second subculture in fluid bran mash for 48 hours (slant to bran to bran), and from the third subculture in fluid bran mash for 48 hours (slant to bran to bran to bran). A 2.5-ml. aliquot of each subculture was used for inoculation of a mash containing 10 grams of bran and 25 ml. of phosphate buffer solution. The final bran cultures obtained after 48-hour incubation at 37° C. showed dextrinization times of 15 minutes when the inoculum was taken directly from the agar slant, 12 minutes when the inoculum was from the first subculture, 13.5 minutes when it was from the second subculture, and 12.5 minutes when the third subculture was used. Subculturing for 48 hours on a medium similar to the final material apparently had a beneficial effect. Subculturing more than once in fluid mash had no significant influence on the potentialities of the inocula.

Period of Incubation. To determine the influence of incubation period on the activity of the bran culture, duplicate bottles containing 10 grams of wheat bran and 25 ml. of phosphate solution were inoculated from agar slants. Samples withdrawn aseptically from each bottle at the end of 1, 2, 3, 5, and 8 days of incubation at 37° C. gave dextrinization times (average of duplicate runs) of 121, 15, 17, 15, and 14 minutes, respectively. These results show that essentially maximum activity was attained by 2-day incubation. The marked increase in activity between 1 and 2 days should be noted; the 2-day culture was almost ten times more active than the 1-day culture.

Temperature of Incubation. The incubation temperature used throughout the investigation was 37° C. No temperature data were obtained with a semisolid bran medium. However, the same isolate (No. 23) was grown on liquid medium at 25°, 30°, 37°, 40°, and 45° C. Following a 5-day incubation period, the dextrinization times for 10-ml. aliquots of the liquids were 22 minutes at 25°, 9 at 30°, 6 at 37°, 7 at 40°, and 23 minutes at 45° C., respectively. The production of amylase was lower at both 30° and 40° than at 37°; pending further investigation, 37° C. was selected as a temperature suitable for incubation of this isolate.

Solid-Liquid Ratio (Wheat Bran-Phosphate Buffer Solution). The degree to which the solid-liquid ratio influenced amylase production was determined by culturing the organism in bran mashes ranging from "just moist" (1 part bran to 1.5 parts buffer) to "fluid" (1 to 5). Bottles containing a final combined weight of 100 grams of bran and phosphate buffer were each inoculated with 8-ml. portions of a fluid mash inoculum (subcultured from slants) and incubated at 37° C. for 48 hours. Dextrinization times were determined with aliquots from clarified 1-hour extracts made at 30° C. with phosphate buffer solution. For comparison, all results were recalculated (on an equal weight basis) so that the dextrinization time represents in each case the activity of an equal weight of wheat bran. Specifically, a dextrinization time represents the activity of 10 ml. of a 1 to 50 extract of moisture-free bran—in other words, the total activity of 0.2 gram of the moisture-free bran initially used to prepare the different mashes.

As Table II shows, the greatest yield of amylase per unit of bran was given when a medium composed of 1 part of bran to 1.75 parts of liquid was used. Somewhat lower, but of the same order, were the yields with ratios of 1 to 1.5, 1 to 2.0, and 1 to 2.5. Amylase yields in those media containing a higher proportion of liquid per unit of bran (1 to 3.0, 1 to 3.5, and 1 to 5.0) were still lower but again of the same order. It is notable that the variation in amylase activities per unit of bran was not greater than Table II indicates. Apparently the production of amylase was regulated primarily by the concentration of nutrient present. However, there is a limit below which the ratio of liquid to solid cannot be reduced without greatly decreasing amylase production; other data (unpublished) indicate that the ratio of 1.5 parts of liquid to 1 part of bran represents about the lowest that can be employed with satisfactory results.

PROPERTIES OF AMYLASE FROM ISOLATE 23

From a comparative study of a purified commercial preparation of bacterial amylase and an α-amylase made from barley malt, Hopkins and Kulka (*9*) concluded that their starch-degrading properties were similar. The principal difference was that the bacterial amylase functioned at higher temperatures than did malt α-amylase. The resemblance of commercial bacterial amylase to malt α-amylase likewise was pointed out by Blom, Bak, and Braae (*3*). However, Effront (*8*) found it possible to produce bacterial preparations of much greater saccharifying activity than that typical of malt α-amylase.

Starch Saccharifying Activity. Two different methods were employed to evaluate the starch saccharifying activity of the bacterial amylase of isolate 23. By means of the ferricyanide method, the starch saccharifying activity was compared with that of barley malt and malt α-amylase. The bacterial amylase was an extract of the dried bran culture and the malt was an extract of ground barley malt. The malt α-amylase was prepared by the Kneen, Sandstedt, and Hollenbeck modification (*11*) of the familiar Ohlsson technique. The extracts were adjusted to comparable dextrinizing activities; for 10-ml. aliquots the dextrinization times were 20 minutes for the bacterial, 22 for the malt, and 20 for the malt α-amylase. Aliquots were withdrawn from the reaction mixtures at intervals over a 6-hour period. The reducing values obtained were calculated as maltose, and apparent starch conversion was evaluated upon that basis. Figure 1 shows the data.

Saccharification (Figure 1) by the bacterial amylase was dissimilar to that of either malt α-amylase or of the mixture of α- and β-amylases represented by barley malt. In the early stages of starch degradation the bacterial amylase was intermediate in action between α-amylase and malt. With time the bacterial preparation proved to be a better saccharifying agent, per unit of dextrinizing activity, than malt. Malt α-amylase exhibited the customary low production of sugar. Owing to the supplemental dextrinizing activity of β-amylase, considerably less α-amylase was present in the malt extract than in either of the other two extracts. At the end of 6 hours of action, apparent conversions were 94% for the bacterial amylase, 84% for the malt, and 54% for the malt α-amylase.

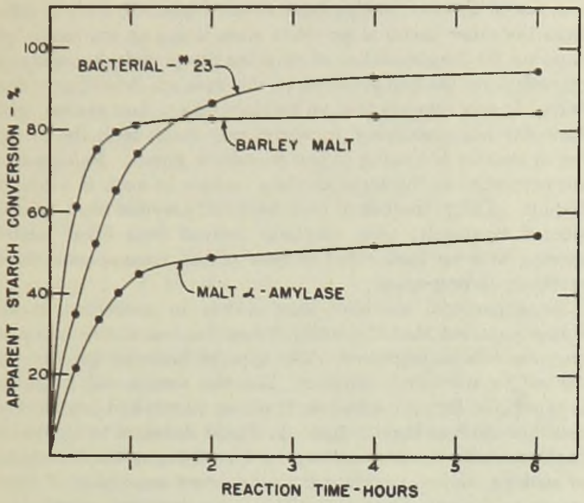

Figure 1. Apparent Conversion of Starch to Maltose at 30° C. by Bacterial Amylase 23, Barley Malt, and Malt α-Amylase

The reducing compounds produced by enzymic hydrolysis of starch are predominantly maltose but include reducing dextrins and, on occasion, glucose. The production of fermentable sugar from starch was used as the second method for evaluation of saccharifying power. Here the saccharifying activity of the amylase of isolate 23 was compared with the barley malt and malt α-amylase described above and, in addition, with a purified commercial bacterial amylase preparation from Wallerstein Laboratories[3]. All of the enzyme aliquots were adjusted to a dextrinization time of 15 minutes. Gas production in the pressure meters by yeast fermentation was measured in millimeters of mercury. Readings were taken hourly for 5 hours, and then again at the end of 8, 12, 20, and 24 hours (Figure 2).

The data of Figure 2 support and emphasize those found for the production of reducing groups. The amylase of isolate 23 was intermediate in action between barley malt and malt α-amylase during the early stages, but was the most efficient one in the final conversion of starch. Further, the relative starch saccharifications by barley malt and by the amylase of isolate 23 were similar to the results obtained by Kneen (*10*) when barley malt and fungal amylase were compared. Figure 2 shows that in saccharifying properties the commercial bacterial amylase preparation was not like isolate 23 but, as found by other investigators (*3*, *9*), more nearly resembled malt α-amylase. Malt α-amylase, however, was more efficient in the final stages of starch conversion than was the commercial bacterial amylase. At the end of the 24-hour fermentation period, the pressures produced were 407 mm. for isolate 23, 390 mm. for barley malt, 171 mm. for malt α-amylase, and 98 mm. for the purified commercial bacterial preparation.

Table III. Comparison of Starch Conversion at 75° C. by Bacterial Amylase and Malt α-Amylase

	Dextrinization Time, Min.		
		At 75° C.	
Amylase	At 30° C.[a]	With calcium	Without calcium
Bacterial (isolate 23)	85	16	21
Malt α-amylase	60	27	180+

[a] With or without added calcium.

Relative Thermostability. The ability to hydrolyze starch in the temperature range causing starch gelatinization is considered to be a desirable industrial property of amylases. It is well known that commercially prepared bacterial amylases show this property to a greater degree than most other amylase preparations. That the amylase of bacterial isolate 23 likewise has a high degree of resistance to thermal inactivation was demonstrated by comparing its dextrinization rate at 75° C. with that of barley malt α-amylase at the same temperature. In every respect but temperature and enzyme concentration, the conditions were the same as outlined for the determination of dextrinization time at the lower temperature of 30° C.; the enzyme solutions were diluted in order to extend the times at 75° C. to a measurable range. Since calcium ions have been reported to stabilize amylases against thermal inactivation (*11*), the reactions were carried out both with and without added calcium ions (4 mg. of $CaCl_2.2H_2O$ per ml.). Table III gives the results.

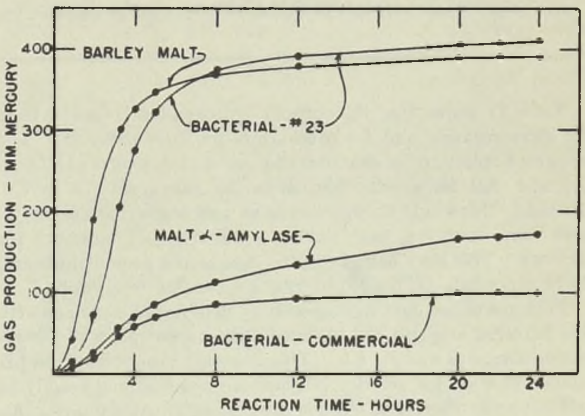

Figure 2. Conversion of Starch to Fermentable Sugar at 30° C. by Bacterial Amylase 23, Commercial Bacterial Amylase, Barley Malt, and Malt α-Amylase

Table III shows that the bacterial amylase was much more resistant to heat than was malt α-amylase. Without the benefit of added calcium ions the bacterial amylase showed a dextrinization time at 75° C. of 21 minutes, whereas the malt α-amylase was so reduced in activity that dextrinization was not achieved after 3 hours of action. The malt α-amylase originally had a higher activity (60 minutes at 30° C. as compared to 85 minutes for the bacterial amylase). In the presence of added calcium ions, dextrinization rates at 75° C. were measurable for both preparations, but the bacterial amylase still retained its activity

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[3] We are informed that this preparation is more highly refined than those available in commercial quantities, and further, that it is designed specifically for the liquefaction and dextrinization of starch pastes. That it is very active in this respect is evidenced by the fact that only 0.0033 gram was required to give dextrinizing activity equal to that provided by the equivalent of 0.3 gram of barley malt or 0.25 gram of bacterial bran.

to a greater degree. Both preparations were stabilized by the added calcium ions. It is apparent that, like commercial bacterial amylases, the amylase of isolate 23 had the ability to hydrolyze starch at elevated reaction temperatures. Further, this faculty was similarly enhanced by the presence of calcium ions.

Preliminary data were obtained which indicate that the hydrogen-ion concentration best suited to the retention of bacterial amylase activity at high temperatures is similar to that previously found for malt α-amylase. Aliquots of a bacterial preparation were adjusted to pH 6.0, to pH 7.0, and to pH 8.0, and then heated comparably for 1 hour at 60° C. After cooling and determination of the remaining dextrinizing activity it was found that 44% of the activity was retained at pH 6.0, 52% at pH 7.0, and 37% at pH 8.0. As with malt α-amylase (*11*), hydrogen-ion concentrations in the neighborhood of pH 7.0 seem to be most favorable for stability of the bacterial amylase.

OPTIMUM HYDROGEN-ION CONCENTRATION FOR ACTIVITY. To determine the influence of hydrogen-ion concentration on the activity of the bacterial amylase, a series of citrate buffers was used to prepare starch substrates varying from pH 5.4 to pH 8.1. Two types of activity determinations were made. One was the customary dextrinization procedure except that 2% starch was used; the second was a determination of the reducing groups resulting from a 15-minute action on 2% starch. The reaction temperature was 30° C. in both instances. The data are listed in Table IV. The pH values are those found in the reaction mixtures.

TABLE IV. INFLUENCE OF HYDROGEN-ION CONCENTRATION ON STARCH CONVERSION BY BACTERIAL AMYLASE FROM ISOLATE 23

pH	Dextrinization Time, Min.[a]	Saccharification, %[b]	pH	Dextrinization Time, Min.[a]	Saccharification, %[b]
5.4	56	23.2	7.0	34	26.7
5.7	53	25.0	7.6	34	23.2
6.3	42	25.0	8.1	40	17.5
6.6	39	26.8			

[a] Dextrinization time on 2% starch at 30° C.

[b] Apparent starch conversion to maltose in 15 minutes of action on 2% starch at 30° C.

Table IV shows that the optimal hydrogen-ion concentrations for dextrinization and for saccharification were different. The apparent optimum for dextrinization was in the region pH 7.0 to 7.6 and that for saccharification in the range pH 6.6 to 7.0. Normally this would be regarded as an indication that two amylases were operative, each having a different pH optimum for activity. This may have been the case in the present instance, but further data are needed to substantiate this observation.

For most of the dextrinizing-activity determinations made with the bacterial amylase, the hydrogen-ion concentration of the reaction mixtures was pH 6.0. This is considerably below the pH value optimum for activity. Wheat bran is buffered readily to pH 6.0, and culturing at this pH proved highly satisfactory. Although at a hydrogen-ion concentration lower than the bacterial optimum and higher than the cereal and fungal optima, a starch substrate buffered at pH 6.0 proved to be adequate for preliminary comparisons of these various amylases. A further consideration influencing the selection of pH 6.0 for routine studies was that many of the processes utilizing amylases are conveniently carried out in the proximity of this hydrogen-ion concentration.

DISCUSSION

The investigations reported here appear to have considerable significance, with respect to both production and characterization of bacterial amylases. While culturing of the organism in a liquid medium in many instances may be the method of choice for amylase production, the demonstrated applicability of solid or semisolid media permits an alternate procedure. The use of wheat bran with a minimum of liquid has certain advantages. A large surface area is provided to facilitate growth of the organism. When the growth period is terminated, the material may be dried rapidly in a current of air to give a relatively stable, enzymically active preparation.

Based on previous reports (*3*, *7*, *9*), commercial bacterial amylases have been considered typically "α-amylase"; i.e., they are capable of liquefying and dextrinizing starch with a minimum of sugar production. From the data reported here, the properties of bacterial amylases are not necessarily those of the α-amylase type. The starch-degrading actions of commercial preparations are well understood and frequently assumed to be those characteristic of bacterial amylases in general, or at least characteristic of preparations from the *Bacillus subtilis-mesentericus* group. The amylase of *B. macerans* has been shown repeatedly (*16*) to differ from the other bacterial amylases since it has an extremely low capacity for the production of reducing compounds during starch degradation; the end products in this case are Schardinger dextrins. It now appears that an amylase, or amylase system, with high starch-saccharifying properties may result from the culturing of isolates belonging to the *B. subtilis* group. Reference to the properties of "bacterial amylase" cannot be made in a general fashion. The properties of each bacterial amylase must be considered separately, since amylases derived from other related species, or even from other isolates of the same species, differ markedly in properties.

Since bacterial amylases vary widely in properties, it becomes apparent that the industrial utilization of this group of enzymes can be expanded. The type of bacterial amylase described in this communication, like the commercial products, is capable of liquefying and dextrinizing starch, and has marked resistance to heat inactivation. It should therefore be applicable in the thinning of corn mashes prior to and during the first stages of cooking, and so facilitate the subsequent conversion of cornstarch to fermentable sugar. This same property, starch conversion at elevated temperatures, is of value in other industries; the sizing and desizing operations associated with textile processing frequently are facilitated by the use of a thermostable amylase. In addition, the ability of certain bacterial amylases to convert starch readily to fermentable sugars indicates another property of value to industry. Used either alone or in conjunction with other saccharifying amylases such as those of barley malt or certain fungal preparations, they may be of value not only as thinning agents but also in the final saccharification of starch.

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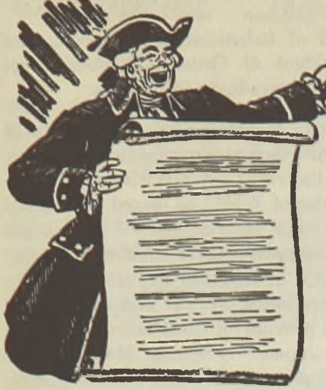
THIS work was supported in part by a grant from the Nebraska Chemurgy Project. Published with the approval of the Director as Paper 367, Journal Series, Nebraska Agricultural Experiment Station.



JUNE'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ JUNE 1. Representatives of management, labor, and War Manpower Commission agree at meeting in Washington that manpower controls should be lifted "in a manner consistent with war production needs".~~Chairman Avery of Montgomery Ward sends letter to Secretary of War Stimson demanding that War Department immediately return possession of a subsidiary property, the Hummer Mfg. Co., Springfield, Ill.

¶ JUNE 2. War Production Board imposes new controls on the use of tin.

¶ JUNE 3. Senator Pepper says Reconstruction Finance Corp. has approved a $7,500,000 loan to U. S. Sugar Corp. for starch plant at Clewiston, Fla.~~Bradley Dewey, A.C.S. President-elect and chairman of award committee, announces $1000 American Chemical Society Award in Pure Chemistry, provided by Alpha Chi Sigma, has been awarded to Frederick T. Wall, University of Illinois.~~A.C.S. announces $1000 Borden Co. award in the chemistry of milk has been made to Ben H. Nicolet, Bureau of Dairy Industry, U. S. Department of Agriculture, Beltsville, Md., and the $1000 Eli Lilly & Co. prize for outstanding achievement in biochemistry has been awarded to Max A. Lauffer, University of Pittsburgh.

¶ JUNE 5. James E. Markham, Alien Property Custodian, says every effort will be made to prevent return to German hands of German-controlled corporations and patents, seized during the war.~~Glass manufacturers meet in Hotel Biltmore, New York, to plan organization of Glass Container Manufacturers Institute to replace Glass Container Association of America dissolved early this year by order of U. S. Supreme Court.

¶ JUNE 6. Winthrop W. Aldrich, president International Chamber of Commerce, addressing Canadian Manufacturers Association, submits four-point world-trade program which opposes cartels and commodity agreements.

¶ JUNE 7. Documents from files of I. G. Farbenindustrie introduced as court evidence show that I. G. transferred complete control and title to all patents it sold to Standard Oil of N. J.

¶ JUNE 8. Senate Finance Committee turns down Administration's request for additional tariff authority.~~U. S. Circuit Court of Appeals upholds Government in seizure December 28, 1944, of Montgomery-Ward facilities in Chicago and six other cities.~~War Mobilization and Reconversion Director Vinson lifts all restrictions on use of carbon black in tires and rubber products and disbands Special Interagency Committee on Carbon Black.~~President Truman signs Executive Order 9568, providing for release of scientific information for publication[1].

¶ JUNE 9. Montgomery Ward files motion in Circuit Court of Appeals for a stay of its mandate following Army announcement that it will make effective War Labor Board's directives granting retroactive back pay of $1,342,000 to CIO Union employees.

¶ JUNE 11. WPB allots 100,000,000 pounds aluminum a quarter to industry for civilian production.~~Government indicates it and Montgomery Ward seeks early Supreme Court decision in legality of Army seizure and operation of plant.~~WPB says pulpwood production during first quarter of 1945 was so far below 1944 levels as to be a "grave" national concern.~~Supreme Court denies Wisconsin Alumni Research Foundation petition asking review of decision which held invalid three patents relating to production of vitamin D.~~War Mobilization Director Vinson testifies before Mead Senate War Investigating Committee that last week he authorized disbandment of Interagency Committee on Carbon Black after being advised production had been increased by more than 43% in past 4 months.~~B. F. Goodrich Co. announces longer, more uniform tire life through use of new synthetic rubber GR-S-10.

¶ JUNE 12. Mr. Humphrey, chairman committee on taxation, National Association of Manufacturers, at a meeting of 300 southern California business leaders, asks 10% income tax cut from 1946 to stimulate production and create jobs.

¶ JUNE 13. WPB sends detailed memorandum to manufacturers allowing them to place orders now for unlimited amounts of controlled materials.~~WPB officials say Government is studying Russian request for prompt resumption of shipments of industrial alcohol to Soviet Union.~~WPB releases aluminum for civilian uses immediately or 18 days ahead of date set for general open ending of controlled materials.~~United States Rubber announces that flameproof, waterproof upholstery is being made available for the first time for civilian use.~~Reynolds Metals Co. announces extensive postwar building and research program is being planned for its plastics division.~~Harry C. Markle, area director War Manpower Commission, says for at least 3 years after war ends there will be no unemployment problems in the Akron rubber industry area.

¶ JUNE 14. WPB lifts all restrictions on use of zinc.~~Lammot du Pont, chairman, executive committee, E. I. du Pont de Nemours, takes stand in cartel plot case in which Du Pont is codefendant with Rohm & Haas.

¶ JUNE 15. Battelle Institute, with the installation of a new electron microscope, begins long-range program of industrial research, according to Director Clyde Williams.~~Acting Secretary of State Grew confirms 2-way oil exchange agreement between the U. S. and Argentina whereby U. S. will get vegetable oil for United Nations in exchange for supplying fuel oil.~~WPB allows purchase of copper raw materials up to a 30-day inventory supply without authorization by the agency.~~B. F. Goodrich says postwar automobile will ride on rubber springs which eliminate part of the noise and all lubrication and repair of present steel springs.

¶ JUNE 16. Howard S. Fritz, director of research, B. F. Goodrich, says increasing output of synthetic tires will bring lower cost.

¶ JUNE 18. Supreme Court decides that labor union cannot be sued under antitrust law for action resulting in destruction of

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[1] *Chem. Eng. News*, 23, 1089 (June 25, 1945).

an employer's business.∼∼Supreme Court rules that the Associated Press, in passing on applicants for membership, must disregard possible competitive effects on existing members, thus upholding a lower court ruling that AP's membership bylaws violate Sherman Antitrust Law.∼∼Petroleum Administrator for War Ickes announces that a group of expert technologists is in Germany under auspices of Petroleum Administration for War studying refinery and oil production methods.

¶ June 19. J. Edgar Pew, chairman, Petroleum Institute's Committee on Petroleum Reserves and vice president Sun Oil Co., Philadelphia, tells Special Senate Committee investigating petroleum resources that this country has sufficient oil reserves to meet its requirements for generations to come.∼∼Cartel conspiracy trial involving Du Pont, Rohm & Haas, Lammot du Pont, and five other officers and executives of the two companies goes to jury.∼∼President Truman directs Secretary of War to seize and operate plants of Diamond Alkali Co., at Painesville, Ohio, where 2000 workers are on strike.∼∼Senate approves President's request to reduce tariffs 50% under Jan. 1 rates when negotiating trade agreements with other nations.∼∼WPB restores controls on atabrine.∼∼House approves H.R. 3266 providing for certification of drugs composed wholly or partly of penicillin.

¶ June 20. Du Pont, Rohm & Haas, and six executives of two corporations acquitted of cartel charges.∼∼WPB says three government-owned magnesium plants have resumed operations or stepped up production.∼∼Aluminum Co. of America officials say orders for 12,000,000 pounds of aluminum sheet have been placed by Quartermaster Corps for construction of shelters in Pacific area.∼∼War Department cancels contract for $20,000,000 toluene plant at Lake Charles, La., WPB says.∼∼Since April WPB says it has approved 754 applications for preference ratings for reconversion construction and equipment.

¶ June 21. Assistant Attorney General Wendell Berge says Department of Justice has not decided on its course following cartel verdict, acquitting E. I. du Pont de Nemours, Rohm & Haas, and six individuals.∼∼WPB and Rubber Reserve Co. say America has developed better synthetic rubber than Germany according to a report from a technical mission that went to Europe to study rubber developments there.∼∼Operations at Diamond Alkali seized by War Department June 19 are slowly returning to normal.

¶ June 22. Assistant Secretary of the Interior Michael V. Straus announces that Bureau of Mines is making synthetic fuels and gasoline which will drive internal combustion engines.∼∼WPB says production of magnesium, allowed to drop during past two months, must be increased to meet urgent new military demand.∼∼New England Council at quarterly meeting in Boston appeals to Congress to grant deferments to scientific technical students to correct a situation "which has already placed this country at a disadvantage compared with other Allied Nations and promises, if continued, to be destructive to postwar prosperity".∼∼Edward G. Budd Manufacturing Co. announces that as soon as materials and manpower are available it will build 59 stainless steel railroad passenger coaches for operation between New York and Miami.∼∼Bernard M. Baruch calls for economic destruction of Germany's heavy industries and cartels and warns that vigilant controls must be maintained on all German scientific research and technological growth.

¶ June 23. Governor Dewey says a $765,000 materials and soil testing laboratory for the New York State Department of Public Works will be erected at Syracuse University as soon as building material priorities can be obtained.∼∼Massachusetts Institute of Technology gets $450,000 from two alumni: Alfred P. Sloan, Jr., chairman of board of General Motors, gives $350,000 to endow professorship in field of industrial management, and Gerard Swope, retired president of General Electric, gives $100,000 to endow a group of postgraduate fellowships.

¶ June 24. Chemical allotment report of WPB for first time in six months indicates that definite increases in allotments of many chemicals have been made to individuals.∼∼WPB asks that interregional recruitment facilities of WMC be placed at disposal of rubber companies to end labor shortages.∼∼WPB officials tell Zinc Industry Advisory Committee the estimated 1945 zinc supply will be only about 95% of essential requirements.∼∼WPB restates policy on cancellation of war contracts in an amendment to Directive 40 to provide for cancellation as rapidly as possible after victory over Japan.∼∼Senator Mead asks for immediate survey of iron ore deposits in New York State by state and federal agencies.∼∼WPB extends policy rules for handling war contract cancellation after the fall of Japan.∼∼Petroleum Administration for War asks oil industry for new high production rate of 5,213,100 barrels daily of all petroleum liquids during July.

¶ June 25. WPB is forming committee to study and distribute technical information gathered from enemy countries, the group to be known as Enemy Technical Reports Committee. Donald B. Keyes, director of WPB's office of production, research and development, will be chairman of new committee.∼∼Industry Advisory Committee asks WPB for an additional 50,000 tons of steel for steel shipping container industry in third quarter.∼∼WPB frees cane alcohol for beverage purposes.∼∼State Department reveals plan to clamp controls throughout the world on German efforts to regain economic position.∼∼R. S. Reynolds, president, Reynolds Metal Co., reveals Defense Plant Corporation will expand aluminum extrusion plant at Louisville, Ky., at a cost of $2,000,000.∼∼WPB says retention of controls on allocation of sodium phosphate for at least four more months has been recommended by sodium phosphate manufacturers industry advisory committee.

¶ June 26. WPB says current softwood plywood is insufficient even to meet military requirements.∼∼Tennessee Eastman Corp. announces that it has begun construction of plant additions for making cellulose esters and acetate rayon.

¶ June 27. Board of Directors of the Associated Press announces a petition for rehearing Government's antitrust case against the AP will be filed with Supreme Court on or before September 1.∼∼Charles Rayner, State Department's petroleum adviser, tells Senate committee studying petroleum problems, that U. S. may have to import oil after the war as consumption is rising while discoveries of new resources are declining.∼∼Senate passes and sends to House legislation to extend life of antitrust suits.

¶ June 29. War Food Administration places all supplies of castor oil under complete allocation.∼∼Mathieson Alkali expands dry ice output 50% with completion of a $400,000 addition to its Saltville carbon dioxide plant, according to George W. Dolan, president.∼∼OPA bans use of fuel oil for production of paving products, dust palliatives, or for surfacing or maintaining roads.∼∼WPB eases control on off-grade pyrethrum.∼∼Attorney General Biddle in report to Congress urges continuance after the war of western steel-making operations to end dominating influence of big eastern producers.∼∼Interim tax bill, for return of 5.5 billion dollars in tax credit to business, passes House Ways and Means Committee.∼∼Lend-lease to Russia for machine tools cancelled and priority transferred to France and Belgium.

¶ June 30. Department of Commerce offers a three-point plan for full employment after war.∼∼Stabilization Extension Act, renewing price control laws, passes Congress.∼∼Clarification of DPC rental terms for war plants is asked by Allis-Chalmers Mfg. Co.

Current Developments in

EQUIPMENT AND DESIGN

Mass-production precision machining by gages has helped make V-E day possible.

Discussed by Charles Owen Brown

LAST month's column reported briefly how a quartz optical flat is prepared. We now describe one of the most important uses of optical flats—namely, the inspection and calibration of the gages needed in large numbers for fine machine work. These gages are not new. They have been employed for many years, but the simplicity of their theory and application is still remarkable, in view of the important results obtained. The gage really consists of a small block of special steel, having a definite accurate dimension between two practically parallel sides. The idea and application of these gages are attributed to a Swedish craftsman named Johannson, but the perfection and skill with which they are made on a production basis with 0.000001 inch accuracy can be credited not only to Swedish, but also to American workmen. Gage blocks are made by fine grinding pieces of steel with precision machines, using fine abrasive wheels and a lubricant. The same surface is then machine-lapped with progressively finer abrasives until a high degree of smoothness is obtained. The blocks are sorted into two grades, rigidly inspected for accuracy, stabilized, and given several final inspections. President Harrington of the Savage Tool Company has contributed materially to reductions in cost and improvements in usefulness and accuracy of these instruments.

In use they are grouped together to make a synthetic gage merely by the selection of blocks whose dimensions add up to the dimensions required. By wringing the blocks together or sliding one surface carefully over the next surface, any combination can be made to adhere into a unit which is used as desired. Figure 1 shows a typical unit gage with tungsten carbide wear blocks on each end. The combination consists of a gage, having a dimension across the parallel faces of 0.650 inch, wrung to one having a dimension of 0.500 inch, together with several smaller gage blocks plus a wear block on each end. Tungsten carbide is not used for the gage blocks themselves because its thermal coefficient of expansion is unsatisfactory and the cost is unnecessarily high. Furthermore, it is not known how to make tungsten carbide gage blocks as permanent and stable as a carbon steel gage block properly heat-treated.

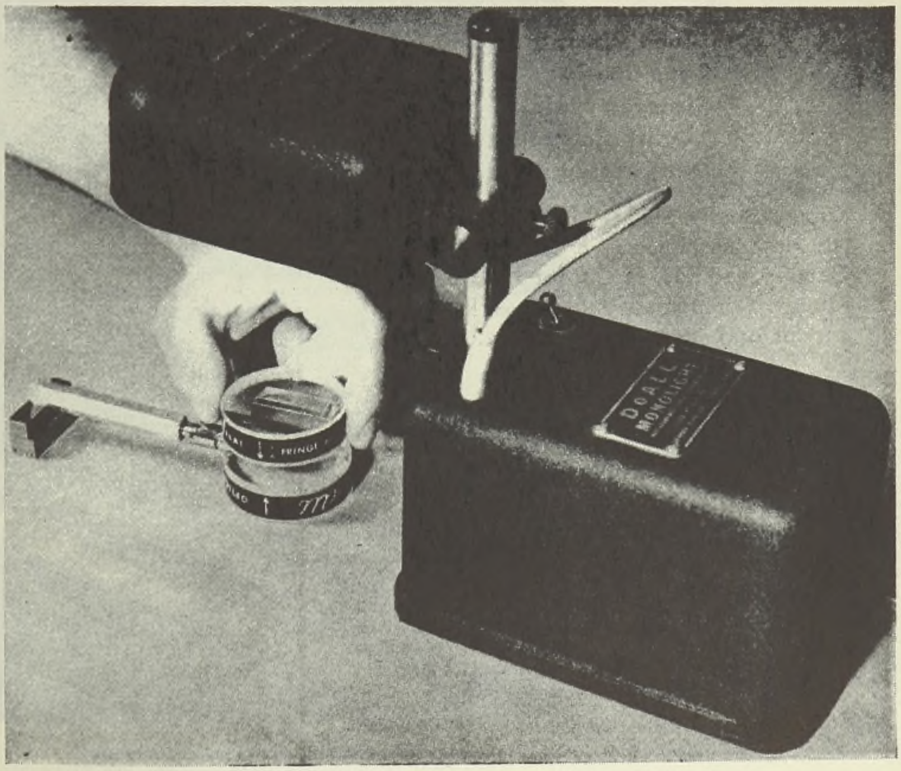
Manufacture of these gage blocks in hundreds of different sizes, each one standardized, calibrated, and certified, is a triumph for American methods of mass production. Figure 2 shows a gage block, made by the DoAll Company, being used to calibrate a plug gage between optical flats. The gage block is nearest the operator's hand. The fringes, or light and dark bands, on the gage block not on the plug, are used to calculate the deviations in the diameter of the plug from the known dimension of the gage block by means of the angle between the top optical flat and the surface of the gage block, or the "wedge of air".

Gage blocks are not limited to checking line dimensions only; they can also be used to measure an angle down to 1–3 seconds of arc. Such measurements are useful in certifying the angle of a bevel gear or the taper on a key. It is accomplished with the aid of simple trigonometry. Whenever two lines intersect at less than a right angle, a right triangle can be formed by erecting a perpendicular to either line and extending it to meet the other line. The ratio of the length of this perpendicular to the length of the line it meets is called the "sine of the included angle". From the known length of two sides of the triangle and a table of sines, the value of the included angle can be determined. Measuring the angle of a bevel gear is just as simple. The triangle is built of a DoAll sine bar

(*Continued on page 66*)

Figure 1 (*Below*). A Typical Unit Gage with Tungsten Carbide Blocks

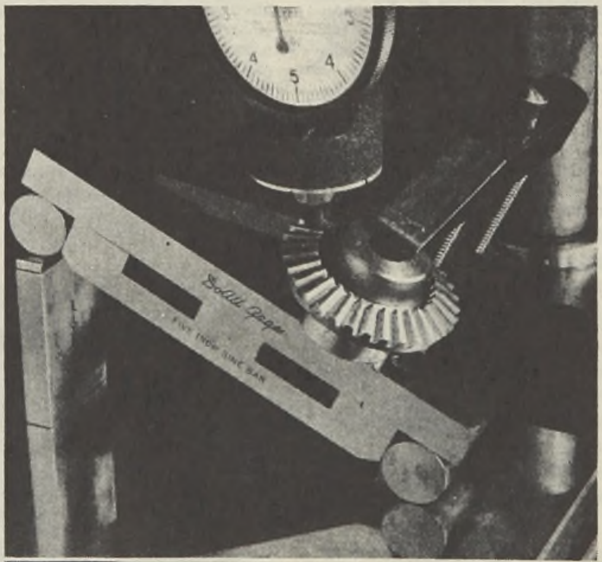
Figure 2 (*Right*). Helium-Light Lamp Measuring Diameter of a Plug Gage



5 inches long, and a flat master face plate is used for a foundation; a perpendicular of known length with millionth of an inch accuracy is built of DoAll gage blocks. The work to be checked is clamped to the sine bar, as Figure 3 shows. The length of the sine bar is 5 inches ± 0.000001. The perpendicular composed of gage blocks also has a definite length accurate to 1 or 2 millionths of an inch. Since the sine of 1 second of arc for a radius 1 inch long is 4 micro inches, the sine of the 5-inch DoAll bar would be 20 micro inches for each second of arc, making it possible to estimate 1 second accurately. Figure 3 shows the deviation of the tooth face from the true angle being determined by a comparator gage.

Figure 4 shows a case of holders used to support gage blocks in combination with trammel points for layout work, or in combination with parallel straight edges to make a caliper gage or a snap gage. The possibilities of these gage blocks, suitably mounted in a holder, for constructing fixed special gages are limitless and can be assembled rapidly. For the production of fifty or a hundred small threaded bushings containing one shoulder, with all dimensions accurate to 0.0001 inch, the probable cost of fixed gages to inspect this small number of pieces might well exceed the cost of the work and require many weeks to build. With DoAll holders, parallel edges, and gage blocks, the required gage can be constructed in a few minutes, with millionths of an inch accuracy.

Figure 3. Sine Bar in Use



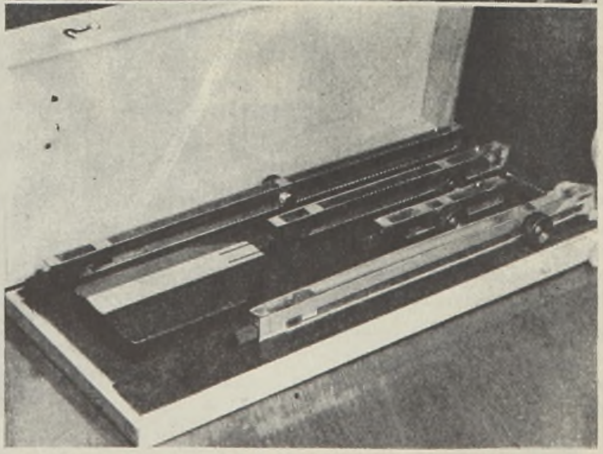


Figure 4. Holders to Support Gage Blocks

Current Developments in
INSTRUMENTATION

A new infrared gas analyzer and a new high-speed visible recording polarograph share the spotlight this month.

Discussed by Ralph H. Munch

Everyone concerned with instrumentation in the chemical industry should read the series of papers on "Analytical Control for Ammonia Synthesis", in the Analytical Edition of Industrial and Engineering Chemistry for May. Earl H. Brown and co-workers, of the Tennessee Valley Authority, describe methods devised to obtain continuous automatic analyses of process materials at a number of critical points.

For various reasons, chiefly to obtain sufficient sensitivity and also freedom from interference by other constituents of the mixtures to be analyzed, it was necessary to combine chemical methods with standard instruments. In only one case (the photometric method for recording the concentration of Cu^{++} in the ammoniacal copper scrubbing solution) was it possible to make the measurement by a method not involving chemical operations. Use of chemical methods required complicated and fragile glass reaction trains and absorption-conductivity cells. Large quantities of reagents were also used. For these reasons and to facilitate maintenance, it was necessary to locate the equipment in the control laboratory under the direct supervision of a properly trained technician.

There is little doubt that one of the greatest needs in the field of automatic control of chemical processes is for instruments which can perform continuous analyses. We have a wide variety of highly developed instruments to control such process variables as temperature, pressure, flow rate, and liquid level, but all too few which can indicate the composition of a process stream. Two instruments which have excellent possibilities in this field are the infrared gas analyzer and the visible recording polarograph.

Baird Associates, Cambridge, Mass., are now producing infrared gas analyzers designed to detect and measure gases having absorption bands in the infrared region of the spectrum. These instruments may be described as filter type infrared photometers. Because of the wide variety of gases with infrared absorption, these photometers should have many applications in the chemical and petroleum industries. Such gases as carbon dioxide, carbon disulfide, ammonia, hydrogen chloride, and various hydrocarbons can be determined in gas mixtures where all the constituents are known. Gases such as oxygen, nitrogen, and hydrogen which do not absorb infrared radiation cannot be detected. The sensitivity varies with the application. In the case of carbon dioxide in air, less than 1 part in 10,000 can be detected with the control type analyzer. Figure 1 shows the gas analyzer, complete with recorder.

Figure 2 is a diagram of the optical system of the simplest unit. Radiation from source S is focused by two concave mirrors, M_1 and M_2, onto the two arms of bolometer B which are part of a Wheatstone bridge. When equal amounts of radiation fall on the two arms of the bolometer, their resistances are equal and the bridge is balanced. When gas, absorbing in the wave length region transmitted by F_2 but not transmitted by F_1, enters the absorption cell, less light reaches the lower bolometer arm and thus unbalances the bridge. The unbalance voltage is amplified and recorded to indicate the concentration of the absorbing gas. This simple unit serves where a single, highly absorbing impurity is to be measured in a nonabsorbing gas such as air. Where more selectivity is required, the filters are replaced by cells; one

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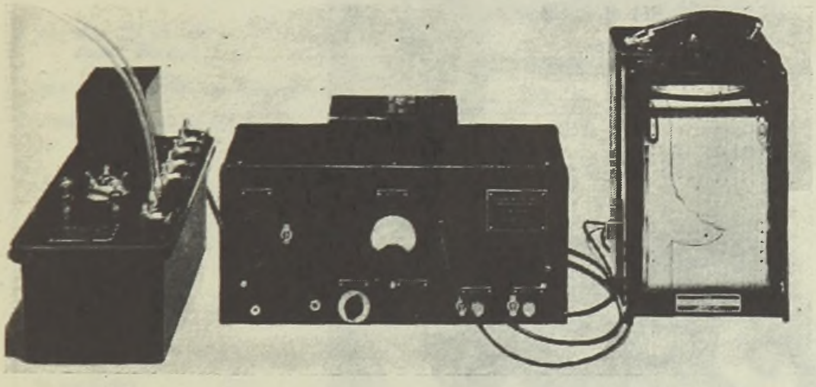


Figure 1. Photograph of Recording Infrared Gas Analyzer of Baird Associates

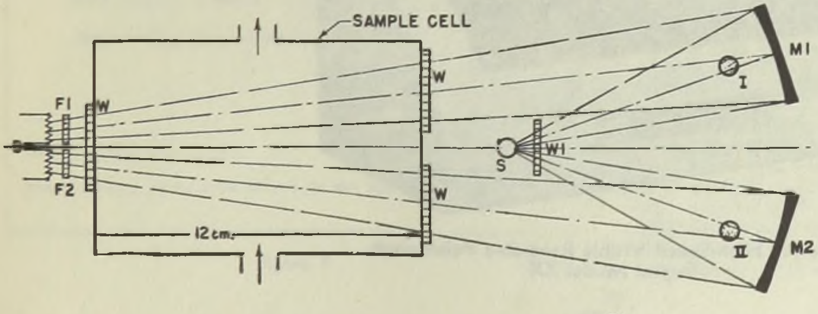


Figure 2. Diagram of Optical System of Model A Infrared Gas Analyzer

B. Bolometer arms
F_1, F_2. Differential filters
S. Infrared source
I, II. Light trimmers
W_1. Optional window
M_1, M_2. Front-surface concave mirrors
W. Windows, silver chloride, lithium fluoride, quartz, or sodium fluoride

contains the gas to be detected, the other serves as a compensator to maintain the symmetry of the optical system. This system makes the analyzer sensitive only to the gas in the filter cell and any others which have absorption in common with it. For complicated gas systems containing constituents with overlapping absorption bands, a filter of the interfering gases is inserted in both beams to give the instrument high discriminating power.

A new high-speed visible recording polarograph has just been announced by E. H. Sargent & Company, Chicago 11, Ill. Figure 3 is a photograph of the instrument. Basically, it consists of a dropping mercury electrode, a polarizing circuit which supplies electrolyzing voltage to the cell, and a recording unit for measuring the current voltage characteristics of the solution. The recorder is a continuous-balance electronic strip-chart instrument, which avoids difficulty from vibration.

The polarizing circuit and chart are synchronized so that the chart displacement is a linear function of the voltage applied to the cell. Since the displacement of the pen across the chart is a linear function of the current through the dropping mercury electrode cell, the pen plots the current as a function of the applied voltage. The polarizing circuit and chart are driven by separate motors so that it is possible to make a continuous record of the concentration of a reducible ion as a function of time. This technique may be used to study reaction kinetics, rates of corrosion, rates of polymerization, etc. Provision is made so that the current voltage curve may be started at any voltage. It is also possible to adjust the voltage span covered by the polarizing bridge.

In many cases it is necessary to determine a small amount of one constituent in the presence of a much larger amount of another which is more readily reduced. Here it is desirable to be able to balance out the diffusion current of the more abundant constituent so that the wave for the minor constituent can be recorded on a scale large enough to measure accurately. The Model XX polarograph is provided with a compensator. In many cases compensation makes a chemical separation unnecessary. Another feature of the instrument is the damping circuit provided to minimize the characteristic oscillations in the polarogram which occur each time a drop falls.

Figure 3. High-Speed Visible Recording Polarograph, Sargent Model XX

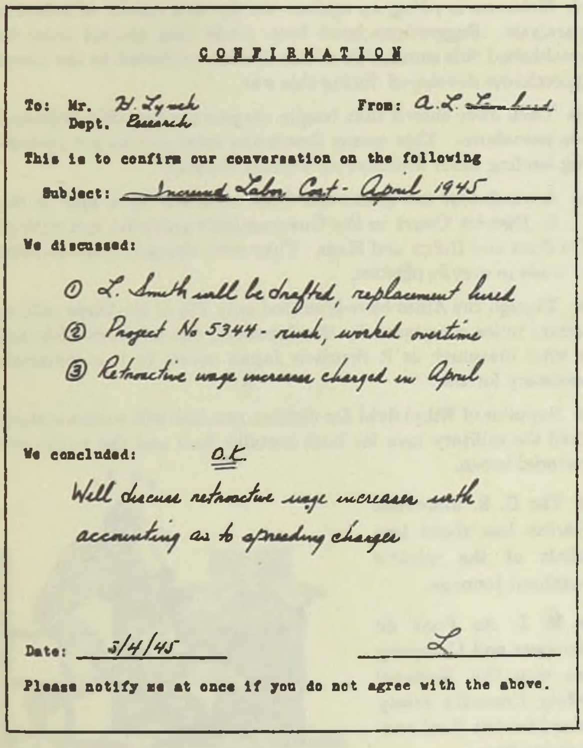
Current Developments in
PLANT MANAGEMENT

Intraplant means of communication by production executives are discussed.

Discussed by Walter von Pechmann

The selection of means of communication available to plant executives is important. On it depends the speedy execution of business, the correct transmission of information down the line, and, although often not realized, the spirit of cooperation prevailing in an organization. A study of the various methods used by executives in chemical plants to communicate among themselves will reveal that information of the same nature is transmitted in many ways. It also will show that the manner in which executives communicate with one another usually changes with management. Recently I spent some time discussing this matter with men who know how to handle production problems. The many valuable suggestions are reported here so that others may share the benefit of their experience.

Executives generally consider the manner in which they communicate with one another their own affair. Depending upon their personalities, they are inclined to manage their plants either on a personal or a "strictly business" basis. Management controls to a certain degree the manner prevailing in the plant since the top executives' ways of doing business are generally accepted as company policy. It may be of considerable advantage for an executive entering a new organization to keep this in mind, since a departure from accepted standards in office routine can cause considerable confusion throughout the plant.



CONFIRMATION

To: Mr. H. Lynch
Dept. Research

From: A. L. [illegible]

This is to confirm our conversation on the following

Subject: Increased Labor Cost - April 1945

We discussed:

① L. Smith will be drafted, replacement hired
② Project No 5344 - rush, worked overtime
③ Retroactive wage increases charged in April

We concluded: O.K.

Will discuss retroactive wage increases with accounting as to spreading charges

Date: 5/4/45

L

Please notify me at once if you do not agree with the above.

Figure 1

Many plant executives insist that the standard of courtesy in private life cannot be followed in business because it causes unnecessary waste of time. In my opinion this disregard of the human factor is dangerous to the morale of an organization; it will usually result in unnecessary discussion or letter writing and thus practically eliminate the advantage gained by time-saving short cuts. Consideration of the feelings and wishes of one's colleagues does not mean that we cannot come quickly to the point of our discussion or that we have to write lengthy intraplant letters. It does mean, however, that "time saving" is no excuse for rudeness, and that a few minutes spent in listening to other people's problems can be considered a good investment in promoting good will.

Proper organization of one's own work can be considered the first step in efficiently communicating with others, since the time saved makes it possible to choose a system of communication which may consume more time but is better suited for specific needs. It is surprising how many production executives who are experts in laying out work for others are mismanaging their own time. In fact, most executives admit that they are guilty to some degree of working inefficiently. (On one occasion I asked my secretary for a report on my previous day's activities. Reading it, I realized that I had wasted considerable time; analysis revealed that I could have saved two hours. Ever since, I have planned my work for the following day.) Occasionally, concerns dealing in communication systems or the sale of printed matter for transmitting intraplant information are inclined to convey the impression that all business transactions in production can be handled in one way. Nothing is farther from the truth. The spoken word (by direct conversation, telephone, or other electrical devices), letter writing on printed forms, or bulletin board announcements, all have their specific uses. To determine if and when to utilize one or the other, we must know their usefulness and their limitations.

Problems requiring communication between two people are most satisfactorily solved by direct verbal contact. It gives both parties an opportunity to express their points of view and come quickly to a solution. The argument is often brought up that such an approach should not be used if important decisions are at stake because verbal agreements cause difficulties. Verbal agreements can be put in writing with little effort. One executive conducts most of his business by direct contact. He has in front of him a self-designed duplicate form pad (Figure 1) on which he makes notes when talking. After the conversation is finished, he retains the original and sends the duplicate to the person with whom he talked. He claims that this method saves himself and others considerable time for the following reasons: (1) It reduces correspondence throughout the plant; (2) when referring to this writing the executive can quickly gain knowledge of its content without having to go through a lengthy description often found in memorandums; (3) this writing can be filed in his desk with little effort and is ready for quick reference when needed; (4) because each slip covers only one subject, the usual confusion arising from having two subjects covered in one memorandum is eliminated; (5) the writing of the slips does not require extra time because it usually takes place when a conversation is in progress.

The majority of executives seem to agree that problems involving only two persons can be settled on a verbal basis if provisions are made that important conclusions are put in writing.

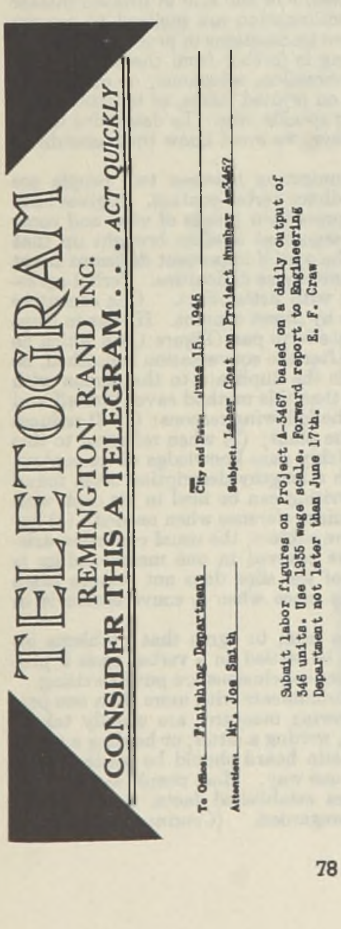
Where it is necessary to communicate with more than one person, one or more of the following measures are usually taken: announcing by bulletin board, writing a letter, or holding a meeting. Announcement by bulletin board should be made only if information has to be carried one way. Most people assume that the bulletin board announces established facts, and requests for answers are frequently disregarded. (*Continued on page 78*)

Plant Management

Intraplant communications by letter should be short and to the point, and contain only one subject. Many concerns have successfully standardized letter headings which usually contain a space for the entry of the subject under discussion. In some instances, complete standardization was attempted by issuing instructions describing in detail how to write plant correspondence. One manager makes it a practice to study letters written by his staff in order to assure himself that the contents can be readily understood by every one. Such attempts at standardization have some merit; if carried too far, however, they may reduce initiative because the writer feels unable to express his personality. One of the headaches in almost every plant is how to transmit written information requiring immediate attention. The words "rush", "special", and "at once" are used too frequently to have any value. A unique approach to this problem is employed by Remington Rand, Inc., which prints letterheads in the form of a telegram (Figure 2). Provided its usage is properly controlled, this form should find successful use in many plants.

In regard to holding staff meetings, an economically minded executive remarked that if management had to approve beforehand the money which is spent to arrive at conclusions, staff meetings would be almost nonexistent. Meetings are necessary, especially if a majority opinion of the staff members is to be known, or if one problem involves the cooperation of various department heads. Meetings, however, need not take much time if the presiding official has the ability to confine the conversation to the subject under discussion and proceeds immediately to the next issue as soon as a conclusion on one phase of the problem has been reached. It has been suggested that all persons scheduled to attend a meeting be notified of the subject in advance so that they can acquaint themselves with it. One executive is able to conduct meetings in a very short time because he submits questions beforehand to those who will attend.

The conduct of meetings by telephone is a rather new idea. One plant manager has the telephones of his department heads interconnected at predetermined times each day. After announcements of general interest, he asks every department head to give his report. The other members quickly obtain a picture of affairs throughout the plant, and are able to contact one another in the event they feel it necessary to obtain additional information. Communication devices, such as loud-speakers, vacuum tube transmission, electric writing devices, etc., are of considerable aid in conducting business quickly and efficiently. Because no one device or method can solve all communication problems, it is important that plant executives acquaint themselves with every available facility. I should like to recommend for a study on this subject the book "Getting Things Done in Business" by E. Wilson (McGraw-Hill Book Company).



TELEGRAM
REMINGTON RAND INC.
CONSIDER THIS A TELEGRAM . . . ACT QUICKLY

To Office: Finishing Department
City and Date: June 15, 1945
Attention: Mr. Joe Smith
Subject: Labor Cost on Project Number A-3467

Submit labor figures on Project A-3467 based on a daily output of 346 units. Use 1935 wage scale. Forward report to Engineering Department not later than June 17th.
E. F. Craw

Figure 2

Last-Minute Flashes
FROM THE EDITOR'S DESK

Wood pulp allocations for the third quarter will mean more paper for civilians. Pulp for that period will total 2,718,000 tons, or 4.5% more than the second quarter.

★ DDT will get its supreme test shortly—against the New Jersey mosquito. In this work extermination officials will cooperate with the entomology department of Rutgers University.

★ Natural rubber will soon be trickling in from the Dutch East Indies. The Rubber Reserve Company is gearing its machinery to handle this business as the eastern areas are liberated.

★ Farmer cooperatives surprised everyone in Washington when they came out definitely against further involvement of the Government in fertilizer production and distribution.

★ The prolonged litigation over the Steenbock Vitamin D patents finally came to an end when the Wisconsin Alumni Research Foundation lost its appeal in the Supreme Court.

★ Commerce Department, quoting an authority, places research expenditures during the war at from $500,000,000 to $750,000,000. In more peaceful days private business spent, in some years, $275,000,000 to $300,000,000 annually on industrial research.

★ Two chemical trade developments point to the return of the good old days. Mercury has been coming in from Spain, and Norway is once more offering her cod liver oil to importers in the fine chemical market.

★ A severe coal shortage is retarding recovery in Europe. France is making steel at only 17% of her 1938 monthly average; rayon at 25%, paper at 11%, and carloadings are only 25% of the prewar level.

★ A German industrial organization, the "Phrix" group, was discovered by the TTT (Target) Force to have had a daily output of 250 tons of synthetic wool made from straw and wood pulp.

★ Evidence is piling up against the fly as a carrier of infantile paralysis. Suggestions have been made that control areas be established this summer in which flys are subjected to the latest insecticides developed during this war.

★ Tests have shown that fragile cargoes can be safely delivered via parachute. This means that many communities not possessing landing fields will have air express anyway.

★ A verdict of not guilty has been returned by a jury in the U. S. District Court in the Government's antitrust suit against Du Pont and Rohm and Haas. They were charged with restraint of trade in acrylic plastics.

★ Though the Allies have liberated only 7% of the three million square miles conquered by the Japanese, the territory liberated is vital inasmuch as it deprives Japan access to raw materials necessary for war.

★ Supplies of Ethyl fluid for civilian gasoline will continue short until the military uses for both metallic lead and the antiknock material lessen.

★ The U. S. Merchant Marine has about two thirds of the world's merchant tonnage.

★ E. I. du Pont de Nemours and Company has won the National Safety Council's safety award for the third consecutive time.