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The Nitrate Muddle

IN THESE troublesome times when many ships seem to be drifting rudderless, few muddles have appeared more complicated than that in which fixed nitrogen now finds itself. The nitrate cartel, initiated last year with a blare of trumpets and including all important world factors save the United States, has now gone to pieces. One conference after another seemed only to give rise to additional points of difference. The Belgians refused to accept the license system proposed by German interests. France, the Netherlands, and Denmark declined to prohibit or restrict imports of Chilean nitrate of soda on a plan proposed by Germany. France insisted that her nitrate production quota be based, not on commercial requirements, but on the government's theoretical military needs as a world power. This proposal would not even be discussed by the others. The recent application by Germany of high duties on nitrogenous materials was interpreted by Chile as an attack upon Chilean nitrate. The failure of the nitrate cartel has added to the financial troubles of Chile. Another result was an immediate break in sulfate of ammonia prices, which were cut to $27.50, a decline of $4.50 per ton. Later, sulfate of ammonia was imported in quantities at such prices as to indicate possible dumping, into which the Government has been asked to look. Concurrently, representatives of the cotton states have expressed opposition to the application of the antidumping provisions of the tariff act to imports of sulfate. Of course cotton growers want cheap fertilizers, just as some others are pleased with low-priced cotton. The law defines dumping as sales made here at prices lower than in the country of production, and detrimental to our competing industry. If the case is proved, the provisions of the law must apply, regardless of the consumer's identity.

The breaking up of the cartel has already tended again to focus the attention of various countries on producing within their own borders adequate supplies of fixed nitrogen for domestic uses. In computing requirements, military rather than industrial and agricultural needs dictate. A big expansion of the nitrate industry in Russia is said to be planned, though it remains to be seen whether the unit about completed can be successfully operated without the importation of high-priced technicians from other lands.

It will take some one wiser than the proverbial Philadelphia lawyer to predict how the nitrate muddle will be untangled. Wisdom would surely dictate the avoidance of any price war, and yet the enormous stocks on hand, the capacity for production so greatly in excess of consumption, and the highly competitive state of the industry may make that impossible. The price of Chilean nitrate has just been cut and may well be the opening gun. In the United States we already have manufacturing facilities sufficient to meet, not only the entire demand for nitrogenous fertilizers, but any possible industrial and military needs. The market has been such that the greatest unit for the production of synthetic nitrate has been operating recently at not more than 25 per cent capacity. Present prices of farm products and the oversupply will suggest to few, if any, farmers the advisability of investment in even low-priced fertilizers, sold on the basis of increasing production.

Into this highly complex situation our old friend Muscle Shoals has been injected. The President has appointed three members to a commission, upon which others represent Alabama and Tennessee as the two states primarily concerned in the wise disposition of the Muscle Shoals property. The commission hopes to make recommendations to the President which he, in turn, can send to Congress with his approval, in the hope that Congress may adopt the suggestions and get Muscle Shoals settled and out of perennial politics. After a meeting held at Muscle Shoals early in August and gathering together the data that have been compiled during the years, this latest Muscle Shoals commission has asked between one hundred and twenty-five and one hundred and fifty concerns to make "informative bids." In this manner it is hoped to ascertain the attitude of any interested parties, and while the commission has no power to make awards to any of the chemical, power, farm, and other organizations included in the list, the attitude of these firms and organizations can be learned.

The most interesting stipulation is that the property must be operated in the interest of fertilizer production and of agriculture. We have frequently pointed out that, if Muscle Shoals is to be helpful to agriculture, it will be in the manufacture of something other than nitrogenous fertilizers. With a world oversupply, with prices on basic nitrogenous fertilizer materials about one-half pre-war values, with facilities in our own country great enough to more than meet agricultural needs in fixed nitrogen, the present state of agriculture and the fertilizer business, we certainly do not need power at Muscle Shoals for the fixation of atmospheric nitrogen. A reduction in the cost of available phosphoric acid and of potash would be worth discussing, but the plant facilities at Muscle Shoals are unsuited to any present methods of preparing these plant foods. It will be a courageous corporation indeed which will offer an acceptable bid for Muscle Shoals under the terms that have been promulgated. It should be said, however, that the commission is seeking all possible advice and suggestions and some one of the concerns which may respond to its invitation may offer a plan that will show the way out. A careful study of the "informative bids" should yield real information. In event the plants are leased, no avenues should be left open for subsequent grafts on the public treasury to assist failing operations.

If the commission should finally recommend the destruction of all but the power plants at Muscle Shoals, we should raise no voice in opposition. As is well known, it was a war measure, and doubtless as potent as many other undertakings in leading to the war's termination. The wooden cargo fleet has been burned, many of the steel freight ships have been sold for junk, and who knows but perhaps sale for salvage and junk may be today the most rational solution of the Muscle Shoals problem?

The New American Chemical Society Award

WHEN A. C. Langmuir proposed that a new award be made by the AMERICAN CHEMICAL SOCIETY, he generously offered the initial financing. He stressed, among others, four principal points.

First, the award is in the nature of a tribute from applied to pure chemistry. It is an indication that industry appreciates and values the efforts constantly being made by thousands of men and women to increase our store of knowledge.

Second, it is to be given to a young man or woman not yet thirty-one years of age.

Third, only original work in pure chemistry is to be considered in choosing the recipient. In this, one must be careful to distinguish between work in pure chemistry and equally meritorious research, even if conducted in a university but done in the field of industrial or applied chemistry. In making a nomination, therefore, one should ask himself, has the research advanced the science of chemistry? Has it brought out a new chemical law or theory, or perhaps cleared up obscurities in existing laws? Have theoretically interesting substances been produced, unrelated facts correlated, or new tools or methods of research been provided? One might do outstanding research in applying to industry the results achieved in such pure research and still not be eligible under the terms of this award.

Fourth, the candidate must have shown independence of thought and originality in conducting his research, and the work should have been done in the laboratories of an educational institution.

In accepting Doctor Langmuir's plan the SOCIETY undertook a certain obligation for the future. With that obligation there goes the opportunity to amend and make such improvements in the plan as may seem best, but for the immediate present at least the above points remain cardinal in its administration.

What does the award accomplish? It encourages young men who are willing to devote themselves to pure science rather than to industrial gain. It helps to confirm their faith in the importance of what they have undertaken and assures them that there is merit in the discovery of truth without immediate reference to gainful application. It serves to direct attention to meritorious work and indicates to the university where it has been done that the research is appreciated by the peers of the recipient. It enables us each year, by means of publicity given the award, to call again to the attention of industry its debt to pure science and its obligation to help foster it. It emphasizes to the university its duty to further pure research and to center its efforts upon adequate facilities, that others may be well trained for it.

The recipient of the award for 1931 is Linus Pauling, of California Institute of Technology, who fully meets the specifications. He celebrated his thirtieth birthday in February. His work has been purely scientific and of exceptional merit. It shows independence of thought and originality—stressed in defining for what the award is to be given. His work has been done in a university.

Although so recently established, this award of one thousand dollars in cash has disclosed that there is a very considerable amount of first-class work in pure chemistry being done in American colleges and universities by men and women under thirty-one years of age. The Committee of Award has been able to select a man who has not only done outstanding work showing independence of thought and originality, but who has worked solely in the field of pure chemistry. The award will serve to fasten the eyes of the chemical world upon a young man who, notwithstanding the large amount of work already accomplished, is nevertheless just beginning his scientific career. What he does will be followed with keen interest by old and young, and they in turn will be directly helped by the increase in attention which the public will pay to such work.

The award, quite appropriately in cash, is presumably to be used by the recipient in furthering his career. There is no medal, but in its stead a certificate, to remain as evidence of the honor conferred even after the cash has done its work.

Nominations for the 1932 award will soon be in order. Turn to page 100 in the NEWS EDITION for April 10, 1931, or to page 37 of the Proceedings for May, 1931, and again become familiar with the preliminary rules which have been established for this award. Watch the NEWS EDITION for September 10, 1931, for any change made by the Council at Buffalo, and then send nominations for 1932 to the Secretary of the SOCIETY. Consider carefully the requirements, and call to the attention of the committee, through our Secretary, the capabilities of some young man or young woman who meets the specification. A complete record of work done is all that is required. Attempted overemphasis and the pressure of influence hinders rather than helps.

We have in this new A. C. S. award an excellent opportunity to do much for our science in America. It may be confidently expected that after a few years we can point to particularly bright spots in its progress, where stimulation, encouragement, and even inspiration may be credited to this award, initiated by A. C. Langmuir.

Reciprocal Courtesy

IN TIMES past occasional complaints reached us that those announcing situations open made no replies to unsuccessful candidates who sent in their qualifications and made application for the place. It has not been difficult to show employers that men who take the trouble to answer advertisements are at least entitled to an acknowledgment of their application and the return of data laboriously compiled for their consideration.

It is equally important that those who announce themselves as available for new places courteously acknowledge letters received from those who offer employment. A manufacturer has recently called to our attention the failure of three different chemists to respond to his letters. It is difficult to understand such a situation, particularly in these days. In any case, courtesy should be reciprocated. We insist upon manufacturers acknowledging the receipt of applications. We equally insist upon members showing a similar courtesy to employers.

Official

THROUGH a misunderstanding, there was recently attributed as official a release of the A. C. S. News Service based upon an article in the August issue of INDUSTRIAL AND ENGINEERING CHEMISTRY dealing with methanol used in antifreeze mixtures. In many parts of the country the release appeared as a pronouncement of the AMERICAN CHEMICAL SOCIETY, or as a warning issued by the SOCIETY. Members of the SOCIETY realize that the only official statements are those voted by the Council, by the Council's Committee on Policy when the Council is not in session, or by the Directors of the SOCIETY. In common with all other publications, those of the AMERICAN CHEMICAL SOCIETY do not assume any responsibility for statements made by authors and, while their papers are often reports made to the SOCIETY, they carry no official sanction without authoritative votes.

Why Be Idle?

ONE is impressed by the frequency with which he finds students of the depression pointing an accusing finger at science as one of the major contributing factors. "Technological unemployment" has become a familiar phrase. Scientists and engineers have appropriated the word "creative," and when the world is puzzled and befogged it is not strange that many turn toward them in the hope of finding the way out. Times like these do try men, and in too many cases scientists have appeared as "fair weather" creators and, like the rest of the human family, fearful and panic-stricken at the first approach of serious trouble.

A few minutes' conversation with occasional chemists now out of employment reveals that some of them hold the belief that the world owes them a living. In their eyes the long years spent in their training have only increased the debt. They overlook their own great debt to society—one which they can only hope to repay by using to the best possible advantage their God-given and college-trained talents. A man who has received an education is directly in debt to the state and to philanthropic individuals who have assisted the educational process by endowments and other forms of support. Notwithstanding his own expenditure of energy and money, every graduate owes more than he can repay merely as a laborer or a hireling performing assigned tasks, no matter how adept or accomplished he may be or become.

The planless discouragement of most unemployed technical men at the present time is appalling. There is nothing creative in their attitude, but rather the mere seeking of a job where they can work like any laborer, depending on others to supply the motivating force of creative thought. Such are to be classed with laborers rather than with artists, with stonemasons rather than with sculptors, with bricklayers rather than with architects.

There are many cogent reasons why a particular chemist may be out of employment, but is there any good reason why one worthy of a place in his profession need be idle? The immediate past has made its contributions to today's psychological causes of idleness among professional men. The most potent of these originates in the comfortable ease of getting employment during the past decade. There have been many creative minds at work providing for thousands of jobs calling for a minimum of mental effort. Regular incomes have been forthcoming without the travail of creating truly original thinking, and this has pampered numbers of fertile intellects into a pleasant dream of security, which has been hard to interrupt. Let this type of mental idleness be stopped!

In the profitable years of the later twenties most of us were pampered, too, with splendidly equipped laboratories, plants, and work shops of sundry kinds. So complete has been our kit of tools that some have come to depend less upon their own ingenuity and more upon labor- and thought-saving devices, so that they are in danger of losing touch with themselves. Yesterday the workman, whether manual or professional, took pride in making his own tools, as well as in using them. Today many are so unable to provide themselves with the tools on which they have relied too fully that they are lost without them. Do we forget the great discoveries of science and engineering which were feats of mind based on experiments with the crudest apparatus? John Dalton with his ink bottles on the back of the kitchen stove, Charles Goodyear with his frying pan, Joseph Priestley with an ordinary burning glass—these and others have demonstrated that logical thinking is often capable of bridging the physical deficiencies of experimental equipment.

Great industries of today have sprung from the original experiments carried out in somewhat simple or crude equipment by such individual workers as Hall, Acheson, Baekeland, Hyatt, Perkin, Frasch, and others. A genius could find in the stock of an average Five and Ten Cent Store materials with which to assemble extensive trains of apparatus. The kitchen stove can still be brought into use and some of the kitchen utensils. There can be no adequate excuse for idleness based on equipment if a man really wants to do things.

Then, too, we become accustomed to accepting the judgment of others on our own ideas and it is hard for us to evaluate them ourselves. A period of unemployment relieves the restraint of routine and offers an unequaled opportunity to call up for review one's discarded or half-formed ideas to determine whether or not they were rightly laid to one side. We know that the waste heaps of one generation often provide the wealth of the next. The same is as true of the intangible waste heaps of ideas. Dig into them now!

The old home town may be full of opportunities for those who seek them. One is not forced to go far to apply sound principles of science and engineering. This can be made to yield valuable results anywhere. Near-by small industries frequently offer better opportunities for applied science than the distant larger ones which are slower to move. It is ridiculous to be always overlooking opportunities at hand and seeking the remote apparently greener fields, the brightness of which always fades upon closer approach.

The rapid growth of the merger system in its responsibility for much unemployment is likely to overawe us with mere physical size. That immensity is necessary to success is an idea in danger of becoming too fixed in our minds. Nothing, no matter how great, was born huge. A single idea can be discovered at the foundation of every enterprise.

An essential point is to study what people want and need. Doubtless there are many ideas, recorded and forgotten because they were ahead of their time, which, if revived, might stimulate hundreds of industries. The real problem is one of selection and requires even more research into human desires than into things to do. Many lists of needed discoveries and improvements have been printed. Who will provide a really first-class fuel for cigaret lighters? Or a convenient can opener? Much time and effort have been spent to make people buy what they do not want. A little originality mixed with a lot of practical psychology and applied with diligence is the best foundation for tomorrow's fortune.

To cite an instance recently, a young man with ideas was removed from his customary payroll. His work had been in the analysis of metals and their treatment. In conversation regarding his problem it developed that he had some thoughts on several methods for producing new artistic effects through the fabrication and treatment of certain metals. In the daily routine his employer had been uninterested in these thoughts, which had no immediate application to the business in hand. Unemployed and with idleness threatening, this man began actively to develop these discarded ideas. He went to work with a most meager equipment in a garage and is now within sight of several processes of wide usefulness and of a potential value far greater to him than that of his former engagement.

We know that unemployment under present circumstances may very well be excusable. We realize that no general panacea can be prescribed. But we know there are unemployed men with energy and ideas. There is even unoccupied space in industrial and other laboratories that might be put at their disposal on some mutually satisfactory basis. It would pay those with idle space and facilities to consider seriously some form of grubstake for men with ideas. Idleness among the trained members of the creative profession of chemistry is not only inexcusable but little short of criminal. Idleness of scientific equipment is likewise inexcusable. Their responsibility to society is clearly defined and the gain of those who will do their best to discharge it is parallel therewith.

Effect of Heat and Light on Nitrocellulose Films[1]

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Plasticized nitrocellulose films were subjected to the action of heat and light, and the effects of these agents on mechanical properties, water permeability, viscosity of the film material, acidity development, and nitrogen content of the films were determined. Heat is shown to produce softening and a gradual lowering of viscosity and moisture resistance; its effect on mechanical properties seems more pronounced with increasing amounts of plasticizer in the film. The added effect of light is to impart brittle properties to the film, to lower its viscosity and moisture resistance rapidly, and to accelerate the development of acidity; its action is principally on the nitrocellulose in the film.

The data indicate that the effects of heat are general, while those of light are localized at the surface exposed.

SUNLIGHT is the agent most destructive to the protective properties of nitrocellulose lacquer. Not only does it subject the protecting film to the stresses incidental to normal temperature change, but it also promotes photochemical changes in the film itself. A study of the effects of light and of radiation, in general, upon the physical and chemical nature of the film should thus prove of value in developing nitrocellulose lacquer for all-round uses.

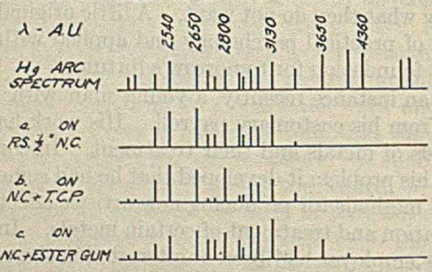
Treatment of Films with Ultra-Violet Light

Not all of the wave lengths present in sunlight are effective in promoting this photochemical decomposition. DeVore, Pfund, and Cofman (*1*) have shown that the wave lengths greater than 3130 Å. have much lower quantum efficiencies than those below this length and that this particular wave length showed the highest quantum efficiency of the range investigated. With the sun at the zenith on a clear day, these efficient wave lengths (2900–3250 Å.) carry 0.24 per cent of the total solar radiation, 0.86 per cent being transmitted by the range 3250–3500 Å., while 2.8 per cent is borne by the range 3500–4000 Å. (*2*).

FIG. 1

EFFECT OF LIGHT ON NITROCELLULOSE FILM

INTENSITY INDICATED BY HEIGHT OF LINE



Some idea of the extent of the decomposition obtained when a nitrocellulose film is irradiated by ultra-violet light is given by Figure 1*a*. Light from a Uviarc is directed through a Hilger E-26 quartz spectrograph, and is focused on a nitrocotton film spun on clear glass, in the plate holder. After an exposure of 24 hours the film is removed and is immersed for 2 minutes in a 2:1 volume mixture of water and acetone. Upon drying, the film areas attacked by the various wave lengths show up as white lines whose position is easily determined by reference to a spectrum of the mercury arc. According to DeVore, Pfund, and Cofman, who reported the method (*1*), this whitening is due to the increased sensitivity of the decomposed areas to water, with consequent precipitation of any undecomposed nitrocellulose. Later results will be presented which are obtained by exposing films containing various lacquer ingredients in this manner. Figure 1*b* shows such a picture of a 10 to 7.5 R.S. ½-second tricresyl phosphate film.

It is seen that the practical absorption limits of a film containing nitrocellulose only, as shown by this method, lie between 3340–2400 Å. The upper limit must lie close to the true absorption limit, for experience in this laboratory has shown that the Uviarc discoloration of nitrocellulose films takes place at half the usual rate when the wave lengths below 3130 are screened out by ordinary window glass. The lower wave length given is that of the lowest mercury-arc line of sufficient intensity to affect the film; as such low wave lengths are not present in sunlight, the lower limit seems of little practical importance.

Further, these lines are a direct evidence of water sensitivity. To show the effect of radiation on water sensitivity, the water permeability of films given different treatments was measured on an R.S. 4-second nitrocellulose, of 12.0 per cent nitrogen content. The film composition was 10 parts nitrocotton and 7.5 parts tricresyl phosphate, dissolved in a 50–50 butyl acetate–toluol mixture.

With films of equal thickness, a form of Fick's diffusion law should apply:

$$\frac{dn}{dt} = Kq\frac{dc}{dx}$$

where $\frac{dn}{dt}$ = water vapor penetrating in grams per hour
K = diffusion or permeability constant
q = area of film, square centimeters
$\frac{dc}{dx}$ = concentration gradient of water vapor prevailing in film, assuming it uniform for present purpose

Permeability can thus be measured by separating a saturated and a completely dry atmosphere by a film, maintaining a constant temperature, and measuring the weight of water passing through the film in a known time.

This was done by putting water in vessels sealed with nitrocellulose films and placing them in a phosphorus pentoxide desiccator at 25° C. Weighings were made and phosphorus pentoxide recharged daily. A convenient vessel for such work was found to be the top of a small-mouth 12-ounce (354-cc.) bottle, cut off about one inch (2.5 cm.) below the flare, and inverted, thus giving a goblet-like cup. The mouth was closed with a clean rubber stopper and the cup filled with mercury to within 0.5 inch (1.27 cm.) of the top. Films 0.01 cm. thick were laid down on this surface from the above solutions and aged a week, and the mercury was removed from the bottom by suddenly pulling the stopper. Ten cc. of water were then added and the top again stoppered, weighed, and placed in the desiccator at 25° C.

Table I gives the results of this work with irradiated films. It is seen that 4 hours of radiation at a temperature of 70° C.

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[1] Received April 14, 1931. Presented before the Division of Colloid Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

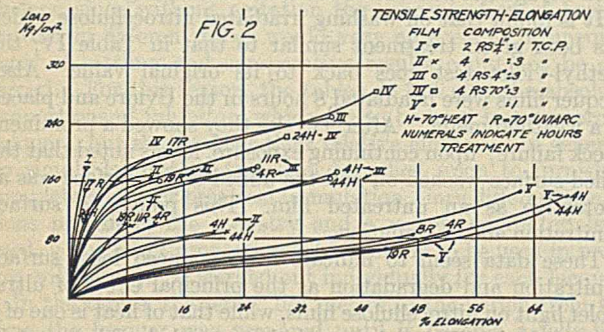
has the same effect on permeability as 24 hours' heating, while 8 hours of irradiating nearly doubles the permeability.

Table I—Water Permeability of Films

10 R.S. 4-second nitrocellulose, 7.5 tricresyl phosphate

Treatment	K
	Grams/cm./hr./cm.²
None	1.09×10^{-4}
4 hours' irradiation, 70° C.	1.54
8 hours' irradiation, 70° C.	2.89
24 hours' irradiation, 70° C.	1.53

From these results it is evident that the idea of the destructive radiations given by the method of development used is a correct one, aside from the fact that they point out a distinct effect of ultra-violet light on film properties.



Due to the fact that films of nitrocellulose alone become very brittle after short periods of Uviarc irradiation, tensile properties together with the corresponding chemical changes were measured on films plasticized with tricresyl phosphate. A series of nitrocelluloses containing 12.00 ± 0.03 per cent nitrogen, and varying in viscosity, was used.

The effect of ultra-violet irradiation on the tensile strength of films made from nitrocellulose of the foregoing nitrogen content was measured on 1/4-second, 4-second, and 70-second types, plasticized with tricresyl phosphate in various ratios. The change in viscosity of these films is shown in Table II together with their composition.

Table II—Change in Viscosity of Nitrocellulose

Film Composition	Original Viscosity	Viscosity at 70° C. after Treatment Below				Treatment
		8 Hrs.	14 Hrs.	24 Hrs.	48 Hrs.	
	Cp.	Cp.	Cp.	Cp.	Cp.	
10 R.S. 1/4-sec.	10.2	8.5	6.0	5.8	...	Rayed
7.5 Tricresyl phosphate		9.2	..	7.4	...	Heated
10 R.S. 4-sec.	56.1	25.6	19.8	12.1	...	Rayed
10 T.C.P.		33.8	..	32.0	...	Heated
10 R.S. 4-sec.	52.9	20.6	20.7	18.8	...	Rayed
7.5 T.C.P.		...	..	44.2	37.0	Heated
10 R.S. 4-sec.	57.2	25.2	20.9	14.4	...	Rayed
5 T.C.P.		...	..	46.4	31.8	Heated
10 R.S. 70-sec.	335.5	...	..	202.8	141.5	Heated
7.5 T.C.P.		157.5	68.0	50.3	...	Rayed

The films were laid down on mercury to a thickness of 0.01 cm. from solutions that contained 10 per cent nitrocellulose in a 50–50 butyl acetate–alcohol solvent. After drying for 10 days, the required test strips were cut and given the treatments outlined in Table II.

It was desired to obtain the effect of both heat and light on films, so the materials were exposed to radiation in a cylindrical drum, 20 inches (50.8 cm.) in diameter and closed at the ends, in the axis of which was placed a horizontal Uviarc, operating 4–5 amperes and 160–170 volts across the terminals. The temperature inside the drum varied from 70° to 75° C. The test strips were laid on asbestos strips along the circumference of the drum and irradiated for the various times together with 4 by 4 inch (10.2 by 10.2 cm.) strips for the viscosity work. Similar sets were given heat treatment in a 70° C. oven. Stress-strain measurements were made, using the New Jersey Zinc machine (3), 14 days after laying down the films. Nitrogen and viscosity data were taken immediately after the completion of the exposures listed above.

The viscosity change was obtained by dissolving untreated and treated film in the butyl acetate–alcohol solvent to a 6 per cent nitrocellulose concentration, and determining the viscosity on a capillary tube viscometer. On some of the irradiated films it was found necessary to add the alcohol first to thoroughly wet the material and then the butyl acetate in order to get solution. Films that required this method of solution always gave small portions of insoluble matter easily seen in solution but not in sufficient volume to be examined for nitrogen content, etc.

The results of the stress-strain test are shown in Figure 2. Irradiated films in most cases gave a curve only slightly below that of the original but with a marked decrease in breaking elongation. Films, given heat treatment only, showed a marked loss in tensile strength and an equally distinct increase in breaking elongation.

Relative Effect of Heat and Light

To compare the relative effect of heat and light, it was considered preferable to compare these properties for a series of films treated by both agencies to the same viscosity in the solvent. From Table II it is seen that 4 hours of radiation at 70° C. produces a viscosity reduction very near to that given by 24 hours' heating at 70° C. A series of films as shown in Table III was given such treatment. The tensile strength data are shown in Figure 3. The nitrogen content was determined by the modified Gunning method, analyses being made on treated and untreated films. It was impossible to use the more rapid nitrometer method owing to side reactions with the plasticizer.

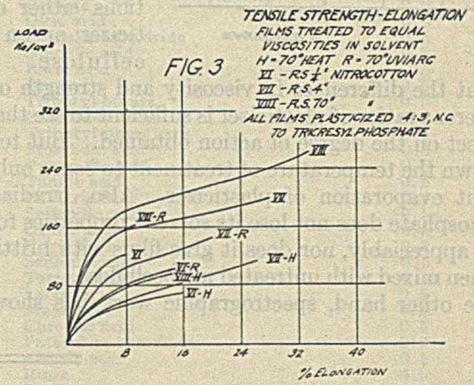


Table III—Change in Nitrogen Content of Films Treated to Equivalent Viscosity

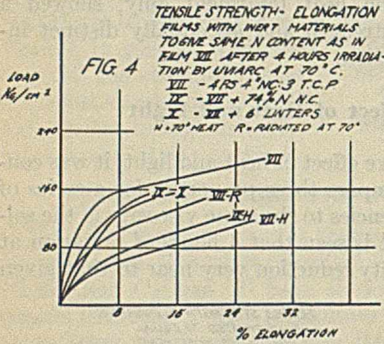
Film Composition	Treatment, 70° C.	Viscosity	Nitrogen	Difference
		Cp.	%	
10 R.S. 1/4-sec.	None	9.2	6.48	..
7.5 T.C.P.	4 hours, ray	8.6	5.96	0.52
	24 hours, heat	7.7	6.06	0.42
10 R.S. 4-sec.	None	52.9	6.5	..
7.5 T.C.P.	4 hours, ray	36.0	6.04	0.46
	24 hours, heat	43.8	6.10	0.40
10 R.S. 70-sec.	None	335.5	6.47	..
7.5 T.C.P.	5 hours, ray	192.	..	
	24 hours, heat	203.	6.39	0.08

Another point of great interest in this matter of relative stability is the effect of such treatments on the methyl-violet stability test. Table IV gives the methyl-violet tests shown by various nitrocelluloses on exposing them to heat or light when spread out in thin layers in weighing dishes, 60 by 30 mm.

Table IV—Change in Methyl-Violet Test of Various Nitrocelluloses after Heat and Light Exposures

Viscosity of Nitrocotton	Original Methyl Violet	Methyl Violet at 70° C. after 48 Hours	
		Heat only	Rayed
Sec.	*Min.*	*Min.*	*Min.*
1/4	57	60	30
1/2	63	60	24
4	77	70	27
70	70	55	16

It is well to point out the differences between the effects of heat and light as found thus far. Heat at 70° C. does cause marked changes in viscosity, tensile properties, and nitrogen content; the added effect of ultra-violet light is to cause much more rapid loss of nitrogen and viscosity, to increase the acidity development as shown by the methyl-violet test, and, of greatest significance, to alter the tensile properties of the heated film remarkably and in a manner directly opposite to the softening produced by heat.



In Figure 3 the treated films of each type are of approximately the same viscosity in solvents, yet the irradiated samples show this same characteristic in spite of the discrepancy in times of treatment. The brittleness shown can be due to the actions either on plasticizer or on nitrocellulose. Merely looking at the differences in viscosity and strength obtained with different ratios of plasticizer is sufficient to see that it has some effect on the degree of action obtained. But tests here have shown the temperature of treatment to cause only an insignificant evaporation of plasticizer. Also, irradiated tricresyl phosphate does not lose its solvent properties for nitrocellulose appreciably, nor does it give films with brittle properties when mixed with untreated nitrocellulose.

On the other hand, spectrographic work has shown that nitrocellulose is changed upon exposure to light. The nature of this change leads to the conclusion that ultra-violet light causes a local denitration wherever a correctly energized quantum strikes the film, and this gives rise to insoluble bodies in the colloid owing to denitration and degradation. Polarized light does not bring out such particles, however.

The effect of denitrated cellulosic bodies, visible at low magnifications and showing distinct orientation in polarized light, on the stress-strain curve is shown in Figure 4. Here finely comminuted low-nitrogen nitrocotton and low-viscosity cotton linters were incorporated in a formula to give the same nitrogen and solids as the irradiated 4-second film in Figure 3. The decrease in elongation due to these particles is distinct, even though not as much as occurs on irradiating.

It is found that on washing irradiated nitrocellulose which has been given treatment similar to that in Table IV, the methyl-violet test goes back to its original value. Also, lacquer films were irradiated 8 hours in the Uviarc and placed in a weatherometer. After 9 cycles they showed a prominent check failure; upon continuing exposure, it was noted that the failed surface washed off and the dulled under-surface was as protective as an untreated film. This points to surface denitration and degradation.

These data seem to indicate a pronounced local surface denitration and degradation as the principal effect of ultraviolet light on nitrocellulose films, while that of heat is one of a general denitration and degradation, coupled with a certain amount of continued colloiding action of the solvent plasticizer on the nitrocellulose, this softening becoming more pronounced with increasing plasticization.

Acknowledgment

The author wishes to express his appreciation of the helpful advice and stimulating criticism of his colleagues at the Experiment Station.

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Prevention of Gelling of Bronze Lacquers[1]

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Gelling of lacquers containing copper bronze can be prevented or greatly delayed by the use of certain acids and salts, such as boric, citric, malic, tartaric, and lactic, in the proportion of 0.25 to 1.0 per cent. Boric acid is preferable to all the others on account of its low price, minimum darkening and tarnishing effect, and great uniformity of behavior. Proportions of inhibitor necessary depend on the grade and concentration of the bronze powder, on the purity and age of the nitrocellulose, on the presence and proportions of resins, and on the degree of protection desired.

THE rapid gelling effect of copper bronzes on nitrocellulose solutions has been known since the earliest uses of such lacquers as coating materials and has led to the practice of supplying the liquid vehicle and the bronze in separate containers and mixing the two just before use. In many cases even this remedy has been found insufficient, as some such mixtures gel appreciably in a few hours or overnight and any portion of the lacquer unused at the time of gelling is irrevocably lost. The lacquer trade has, therefore, long been interested in finding some means of preventing, or at least delaying, the occurrence of this gelling.

There is practically no information on this subject available in the literature. Worden (*2*) states that cellulose nitrate bronzing lacquers containing aluminum tend to develop acidity and coagulate, especially if kept in metal cans. He describes a patent where the addition of 8 ounces of sodium carbonate per gallon is recommended in cellulose acetate lacquers. The absurdly high proportion of salt used is commented upon, but the matter is not discussed further. No mention is made of the gelling of nitrocellulose lacquers. Wilson (*1*) states that free acid is detri-

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mental to copper bronzes, causing them to turn green and gelatinize.

The work to be described was done with the main object of finding materials satisfying practical requirements for anti-gelling agents in bronze lacquers.

Experimental Procedure

The method used was as follows:

> To portions of nitrocellulose stock solutions in the appropriate solvents were added gums, plasticizers, inhibitors, etc., and, finally, bronze powder. Test tubes containing these mixtures were placed in a pebble-mill holder and rotated end over end to keep the bronze powder well dispersed.

This procedure has the disadvantage of introducing a factor not encountered in actual practice. It was adopted nevertheless, since without agitation the concentration of bronze powder in different tubes would vary on account of unequal rates of settling and comparative results could not be obtained. For this reason, the tables do not give the absolute proportions of inhibitors which are to be used in commercial lacquers, but show rather their relative efficacy. In general, no simple laboratory tests can be relied upon to furnish a complete guide for practical formulation, since different conditions prevail in the industry and a variety of materials is used. The exact proportions of inhibitors to be used in practice will have to be worked out individually for each lacquer.

In the tables, the term "life" refers to the period from the time the lacquer was prepared until it became a jelly-like material with definite cleavage surfaces when broken or cut. A few of the lacquers thickened slightly soon after preparation, but did not really gel until much later. In such cases the early thickening was disregarded in view of the fact that it could be easily corrected by thinning. When the lacquers really gelled, however, it was impossible to restore them to their original state by adding more of the same solvent mixture. The experiments were discontinued, the lacquer in several cases was still in good condition. As a rule the experiments were stopped when they had run long enough to give the desired result. In frequent cases, however, they came to a premature end when the test tubes broke in the shaking operation.

The bronze powders used in the tests were: A, U. S. Fresco Decorators Palegold; B, U. S. Helius Palegold Brilliant; and C, U. S. Vernis Martin.

Effect of Tests on Gelling of Bronze Lacquers

Various Materials—Table I shows results obtained by the addition of various materials to lacquers containing bronze powders. Series A gives preliminary tests in which several weak acids and alkalies were used to check the impression gained from the literature that gelling is connected with the acidity of the lacquer. Several other materials, such as glycerol and gelatin, were included as they were rumored to have some effect on reducing or delaying gelling. Series B was obtained mainly in a study of the effect of acids. Several salts and other compounds were included in the tests. Many of the results in Table I were obtained by duplicate tests, although these are not indicated.

The results of series A show clearly that the gelling phenomenon is not due to high acidity, but rather that the contrary is true. Certain polybasic acids, such as oxalic, tartaric, and citric, delay the gelling greatly, whereas urea and zinc oxide, which are weakly basic, have no such power. Comparing tests 6 and 7 of series A1, urea is seen definitely to reduce the anti-gelling effect of tartaric acid and might in this case be said to promote rather than delay gelling.

The presence of ethyl alcohol is apparently conducive to gelling, as is seen from tests 6 and 7 of series A2 where the life of the lacquer dropped from 168 hours in test 6 to 30 hours in test 7. This point, however, should be checked by further tests.

Table I—Effect of Various Materials on Gelling of Bronze Lacquers

Stock solution:	Series A	Series A
n-Butyl acetate	40%	15%
Ethyl acetate	—	10%
Butanol	—	10%
Ethyl alcohol	—	10%
Toluene	60%	55%
1/2-second nitrocellulose	10 grams/100 cc.	10 grams/100 cc.
Bronze concentration	B, 5 grams/100 cc.	C, 5 grams/100 cc.

Test	Material Added	Concentration *Grams/100 cc.*	Life *Hours*
	SERIES A		
	(1)		
1	Blank	...	6
2	Urea	0.25	12
3	Zinc oxide	3.0	4
4	Pyridine	0.25	4
5	Hydroquinone	0.25	30
6	Urea Tartaric acid	0.25 0.25	24
7	Tartaric acid	0.25	168
8	Rosin	2.0	24
9	Stabilisal A	0.25	72
10	Malic acid	0.50	72
11	Gelatin	0.50	4
	(2)		
1	Blank	...	16
2	Lactic acid	0.25	16
3	Citric acid	0.25	120
4	Benzoic acid	0.25	16
5	Oxalic acid	0.25	120
6	Tartaric acid	0.5	168
7	Tartaric acid Ethyl alcohol	0.5 20.0	30
8	Butyl tartrate	5.0	16
9	Glycerol	5.0	30
10	Stannous chloride	0.5	16
11	Litharge (no bronze)	5.0	16
12	Copper oxide (no bronze)	5.0	168[a]
	SERIES B		
1	Blank	...	48
2	Benzoic acid	0.5	15
3	Oleic acid	0.5	30
4	Phthalic anhydride	0.5	15
5	Salicylic acid	0.5	15
6	Boric acid	0.5	1000[a]
7	Borax	0.5	1000[a]
8	Tributyl borate	0.5	75[a]
9	Phosphoric acid	0.5	15[b]
10	Tributyl phosphate	0.5	30
11	Molybdic acid	0.5	15
12	Pyrogallic acid	0.5	24[c]
13	Tannic acid	0.5	48[c]
14	Fumaric acid	0.5	23[c]
15	Sulfanilic acid	0.5	20
16	Oxalic acid	0.5	48
17	Citric acid	0.5	1000[a]
18	Sodium citrate	0.5	225[d]
19	Tartaric acid	0.5	300[a]
20	Lactic acid	0.5	1000[a]
21	Malic acid	0.5	800[a]
22	Chromic acid	0.5	500[d]
23	Potassium chromate	0.5	48[d]
24	Formic acid	0.5	63
25	Rosin	6.0	15
26	Shellac	6.0	15
27	Linseed oil	5.0	15
28	Stabilisal A	1.0	1000[a, e]

[a] Lacquer in good condition at end of experiment.

[b] Decomposition set in at once.

[c] Lacquer darkened considerably.

[d] Results obtained in different set of tests, but as life of blank (not shown) was 48 hours, as in main set, results considered comparable with other data above.

[e] Vehicle turned slightly green.

Stabilisal A, a German product whose composition is unknown to us, is advertised as a gel preventer. It is quite effective, though possibly less so than tartaric acid.

Hydroquinone has moderate gel-inhibiting properties.

Ordinary coarse copper oxide does not cause gelling. Litharge is a bad gelling agent. In line with this result is the authors' observation that lead-lined cans cause rapid gelling of lacquers.

In series B the gel-inhibiting effect is largely limited to polybasic acids and several of their salts. Lactic acid is the only monobasic acid which showed the property, in contrast to its behavior in series A.

It is interesting to note that two of the three salts of polybasic acids that were tested are of the same order of gel-inhibiting effectiveness as the acids themselves. This should be of considerable practical importance, as it may permit the use of mixtures of acids and salts and thus reduce the danger of rust formation which may result from the use of high proportions of the former, or of discoloration due to the use of certain salts, like borax.

Stabilisal A is found to be very effective, though not more so than the best acids and salts. Its high price militates somewhat against its use.

Of the acids in series B, boric is the most promising for the following reasons:

(1) It is the cheapest, costing only 3 to 5 cents per pound.
(2) It has the smallest tendency to cause darkening of the lacquers.
(3) It is not surpassed by any other compound in anti-gelling effect.

Consequently, boric acid was used as standard in most of the following experiments.

Borax cannot be given quite as unqualified a recommendation as boric acid. While it gives good results in the presence of gold bronze, it has a rapid gelling effect on nitrocellulose solutions in the absence of bronze, owing to its strong alkaline reaction.

Citric, malic, and lactic acids in concentrations below 1 per cent are not precipitated from solution during evaporation of the film. In the case of boric acid, however, only about 0.25 per cent is thus tolerated in most lacquers, the excess being deposited in the dry film as a cloudy dispersion or as a precipitate, depending upon the concentration. While this is fully masked by the bronze, and no effect on the gloss or appearance results, it is probably best not to exceed the proportion of 0.25 per cent of the acid.

Tartaric, malic, and lactic acids, and Stabilisal A, while effective as inhibitors, are somewhat more erratic in their behavior than boric acid. Moreover, lacquers containing these materials have a slight tendency to darken, which is not the case with boric acid.

SOLVENTS—Table II shows the effect of solvent formulation on the behavior of bronze lacquers.

Table II—Effect of Solvents

($^1/_2$-second nitrocellulose, concentration: 10 grams per 100 cc.; bronze: 5 grams per 100 cc.)

TEST	SOLVENT	LIFE Bronze A	LIFE Bronze B
	SERIES A		
1	Acetone	12 days	15 days
2	*n*-Butyl acetate	36 hours	48 hours
3	Ethyl lactate	20 hours	20 hours
4	*n*-Butyl acetate, 40% Butanol, 60%	..	36 hours
5	*n*-Butyl acetate, 40% Toluene, 60%	5 hours	6 hours
	SERIES B		
1	*n*-Butyl acetate	1 day	1 day
2	*n*-Butyl acetate, 40% Butanol, 60%	1 day	1 day
3	*n*-Butyl acetate, 40% Toluene, 60%	8 hours	8 hours
4	Acetone, 40% Toluene, 60%	1 day	1 day
5	Ethyl acetate	60 days	25 days
6	Butyl acetate, 50% L. D. naphtha, 50%	1 day	8 hours
7	*n*-Butyl acetate, 80% Toluene, 20%	1 day	3 days
8	*n*-Butyl acetate, 100% Bronze powder extracted with toluene and dried before using	..	2 days

Note—The two series in this table, while similar in many respects, were started on different days, and nitrocellulose used may not have been same in both cases. Tests are therefore reported separately, each with its blank.

It is seen that in general the more powerful the solvent or solvent mixture, the less likely is gelling to occur. A notable exception to this rule is the behavior of ethyl lactate solutions, but here the early failure may have been caused by the presence of impurities in the solvent.

High proportions of toluene are distinctly conducive to gelling as is seen from test 5 in series A and tests 3 and 4 in series B. It was thought that this might be due to the toluene dissolving off the waxes with which the bronze is often coated in the polishing operation, thereby increasing the degree of contact between the bronze proper and the nitrocellulose solution, and also increasing the gelling tendency. The point was checked in test 8, series B. It is seen that the removal of the wax does not affect the gelling behavior appreciably. Incidentally, this also disposes of the idea that wax might be the agent largely responsible for the gelling phenomenon.

VARIOUS BRANDS OF BRONZE—Table III gives the results obtained with thirteen commercial brands of bronze powders.

Table III—Effect of Various Grades of Bronze

(Stock solution: *n*-butyl acetate, 40 per cent; toluene, 60 per cent; and $^1/_2$-second nitrocellulose, 7 grams per 100 cc. Bronze concentration: 15 grams per 100 cc.)

TEST	BRONZE POWDER	LIFE (DAYS) Boric acid $^1/_4$ *gram/100 cc.*	LIFE (DAYS) Boric acid $^1/_8$ *gram/100 cc.*
1	U. S. Venus Vernis Martin	23^a	8^a
2	U. S. Helius Palegold Brilliant	23^a	23^a
3	U. S. Venus Fresco Decorators Palegold	23^a	23^a
4	Electro Patent Brown	9	9
5	Illinois Citron	14^a	20^a
6	Illinois Copper Lining	20^a	15^a
7	Illinois Orange	23^a	11^a
8	Illinois Fire	23^a	23^a
9	Illinois Statuary	13	3
10	Leo Uldfelder Superior Quality Vernis Martin	14^a	20^a
11	Crescent Vernis Martin	23	23^a
12	U. S. Venus Statuary	1^b	$9^{a,c}$ $9^{a,d}$ 7^e

[a] Lacquer in good condition at end of experiment.
[b] Without boric acid.
[c] Boric acid, 1 gram per 1000 cc.
[d] Tartaric acid, 1 gram per 100 cc.
[e] Stabilisal A, 1 gram per 100 cc.

The only solutions showing gelling within the period of the test were those containing dark bronze powders. In all the other cases the boric acid prevented the effect. Tartaric acid and Stabilisal A were similarly effective in the few tests made with them. Somewhat higher concentrations than those used would perhaps overcome the strong gelling tendency in the case of the dark bronzes. The difference in behavior of the light and dark powders may be due to a variation in the amount of oxide present on the surface of the particles.

ALUMINUM BRONZES—The lacquers indicated in Table II, series B, were also mixed with two samples of aluminum powder. None of them gelled within 60 days. Apparently the gelling action of the aluminum powder is much slower than that of the copper bronzes although, even with the former, long contact with the lacquer is harmful, as the aluminum tends to lose its valuable leafing properties. This probably is due to too thorough wetting by the vehicle.

CONCENTRATION OF BRONZE POWDER—In these tests a solution was used having the same solvent and nitrocellulose composition as that described later under Resins. With one bronze B, $^1/_4$ gram of boric acid per 100 cc. of solution was used; with the other bronze, C, $^1/_8$ gram per 100 cc. was used. With bronze concentrations of from 5 to 50 grams per 100 cc. no gelling was noted in the observation periods which ranged from 6 to 25 days. One exception in eight tests may be neglected. With 100 grams of bronze, on the other hand, gelling had occurred in each case after 6 days.

Therefore it would appear that lacquers containing the highest proportion of bronze powder ordinarily used (60 grams per 100 cc.) are stable enough for practically all purposes, the outstanding exception being where shelf goods are involved. The packaging of gold-bronze lacquers ready mixed for retail sales is probably still impracticable, since the bronze powder soon settles to the bottom of the container, causing an abnormally high concentration there so that gelling probably sets in sooner than it would if the lacquer were stirred from time to time. In such a case, or in any other case where the concentration of bronze powder is very high, the gelled mass, instead of being rubbery, is stiff and granular and disintegrates readily when stirred. The effect is such as to decrease the hiding power of the bronze tremendously and give a granular appearance to the film. It seems probable, however, that, if a much higher proportion of boric acid were incorporated in the lacquer, the resistance to gelling would be great enough to permit of storage in cans for a year or more.

Resins—Eight resins—namely, ester gum, dammar gum, rosin, rezyl 12, rezyl 33, Syntellac E. W., and Syntellac C—were tested as gel inhibitors. The solutions were composed of mixtures of 15 per cent n-butyl acetate, 10 per cent butanol, 10 per cent ethyl acetate, 10 per cent ethyl alcohol, and 55 per cent toluene in which were dissolved 10 grams of $^{1}/_{2}$-second nitrocellulose and 3.75 grams of resin per 100 cc. The concentration of the bronze B used was 16 grams per 100 cc. Ester and dammar gums had a marked effect in inhibiting gelling, a solution containing the former being in good condition after 600 hours where the blank had gelled after 48 hours, while the dammar solution began to gel only after about 300 hours. The other resins had no decided effect.

Nature of Nitrocellulose—Tests on the effect of various types of nitrocellulose were made with the following materials: 12-second dope cotton (an old sample), $^{1}/_{2}$-second R.S., 4-second R.S., $^{1}/_{2}$-second A.S., $^{1}/_{2}$-second bronzing. The lacquer consisted of mixtures of 40 per cent n-butyl acetate and 60 per cent of toluene to which were added 7.5 grams of nitrocellulose, 0.25 gram of boric acid and 15 grams of bronze C per 100 cc.

The 12-second dope cotton was the only sample that gelled in the presence of boric acid, after 2 days. The sample was rather old, and decomposition may have set in before the experiment was started, rendering the cotton more susceptible to gelling than a fresh sample would have been. In general old samples of nitrocellulose are probably more prone to gel than fresh ones.

The other nitrocellulose samples had not gelled, when boric acid was present, within the period of observation (8 to 26 days.) Where boric acid was absent, $^{1}/_{2}$-second R.S. nitrocellulose gelled in 8 hours, while 40-second bronzing nitrocellulose had not shown this effect after 10 days. In these last tests the nitrocellulose concentration was 5 grams instead of 7.5 grams per 100 cc.

Cellulose Acetate—Solutions of cellulose acetate in several solvents were mixed with gold and with aluminum bronze. No gelling occurred in 75 days.

Proportion of Gel Inhibitor—In Table IV are tabulated experiments in which varying proportions of boric, lactic, and tartaric acids were used in bronze lacquers.

Table IV—Effect of Various Proportions of Acid Inhibitors

(Stock Solution: n-butyl acetate, 15 per cent; butanol, 10 per cent; ethyl acetate, 10 per cent; ethyl alcohol, 10 per cent; toluene, 55 per cent; $^{1}/_{2}$-second nitrocellulose, 7 grams per 100 cc.; and bronze B concentration, 15 grams per 100 cc.)

Test	Acid	Concentration *Grams/100 cc.*	Life *Days*
1	Tartaric	1.0	ca. 30
2	Tartaric	0.5	ca. 25
3	Tartaric	0.25	ca. 25
4	Tartaric	0.12	ca. 20
5	Tartaric	0.06	ca. 20
6	Tartaric	0.03	3
7	Boric	1.0	25[a]
8	Boric	0.5	25[a]
9	Boric	0.25	25[a]
10	Boric	0.12	ca. 15
11	Boric	0.06	ca. 10
12	Boric	0.03	5
13	Lactic	1.0	ca. 30
14	Lactic	0.5	ca. 15
15	Lactic	0.25	ca. 8
16	Lactic	0.12	ca. 10
17	Lactic	0.06	7
18	Lactic	0.03	7

[a] Lacquer in good condition at end of experiment.

A consideration of the table leads to the conclusion that within limits the degree of the lacquer's resistance to gelling increases with the concentration of acid added. Boric acid seems to be the most effective of the three acids tested.

A second series of tests with boric and tartaric acids, using a different solvent formula, gave erratic results for the tartaric acid.

Several lacquers containing 0.5 per cent of boric acid were stored in tin cans. Gelling took place in most cases in from 8 to 10 weeks, although several lacquers were still in good condition after 9 months.

Tarnishing of Metal Surfaces

To lacquers of the same solvent formula as indicated in Table III and containing 10 grams of nitrocellulose per 100 cc. were added 1 gram of boric and of tartaric acid per 100 cc. The lacquers were then applied to thoroughly cleaned brass and steel plates and allowed to dry. In the case of boric acid the metal surfaces showed no effect, in the case of the tartaric acid the steel plate was slightly tarnished.

Summary

(1) The gelling of lacquers containing copper bronze can be prevented or greatly delayed by the use of certain acids and salts in the proportion of 0.25 to 1.0 per cent. Boric, citric, malic, tartaric, and lactic acids as well as some of their salts are effective.

(2) Boric acid is preferable to all the others on account of its low price, minimum darkening and tarnishing effect, and greatest uniformity of behavior. When used in proportions greater than 0.25 per cent, part of it is precipitated in the film on drying, but this does not appear to affect the appearance or gloss of the finish.

(3) The effect of solvent variations is minor. While very rich solvent mixtures are superior to lean ones, the difference is small in comparison with the effect of traces of the inhibitors given in (1). Ethyl alcohol in moderately large proportions is distinctly injurious and the nitrocellulose used should therefore preferably be moistened with butanol.

(4) The proportions of inhibitor necessary depend on the grade and concentration of the bronze powder, on the purity and age of the nitrocellulose, on the presence and proportions of resins, and finally, on the degree of protection desired. One-tenth to one-quarter per cent is sufficient for most industrial uses, but more may have to be used occasionally.

(5) Dark-colored bronzes tend to cause earlier gelling than light-colored ones.

(6) Resins have moderate gel-inhibiting qualities.

(7) Bronzing cotton is superior to the ordinary grades of dope and $^{1}/_{2}$-second cotton.

(8) The gelling phenomenon has no simple relation to the acidity or alkalinity of the nitrocellulose solution.

(9) In shelf goods the concentration of bronze reaches a very high value at the bottom of the can, due to settling, while the degree of protection necessary is the maximum, as a non-gelling life period of several years may be desirable. It is not known whether the inhibitors found in the experiments described will meet these rigorous conditions fully. The main use for the inhibitors is in the industrial fields.

(10) Aluminum bronzes do not cause gelling readily.

(11) Boric acid, in the proportions necessary to prevent gelling, does not tarnish brass or steel surfaces.

(12) The few cellulose acetate solutions tested containing copper or aluminum bronze did not gel in 75 days.

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Combating the Corrosion Problem with Lubricated Valves[1]

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The various factors are analyzed which enter into the selection of valves for industrial applications where corrosion is important. The problem is briefly outlined as to the selection of materials and selection of valve design. In a great many cases where the use of high-priced metals is not economically justified, lubricated plug cocks manufactured of iron or steel will successfully handle the problem. This results from making use of the well-known natural advantages of the plug-cock design for resisting corrosion combined with the practical solution of their operating weaknesses by means of pressure lubrication.

The subject is developed by pointing out the adaptability of the plug-cock design to pressure lubrication and the resulting advantages of ease of operation, ability to hold high pressures without leakage, and increased resistance to corrosion. The importance of proper distribution of the lubricant in the valve and the factors affecting selection of a lubricant are pointed out. Examples are given of the lubricant requirements on several valve services.

THE immense field of the process industries entails to a large degree the transportation of various fluids through piping and apparatus under a great variety of conditions. The control of these fluids is effected principally by means of valves. Therefore, the part played by valves is of direct interest to all persons concerned with the technical phases of the process industries. Coincident with the flow of these various fluids through valves, there arises the problem of corrosion and erosion. This problem can be attacked from two directions: (1) from the standpoint of the materials used in the construction of the valves and (2) from the standpoint of the design of the valves employed.

Materials Used in Valve Construction

Many alloys are available for the construction of valves and, lacking past experience, the selection of the proper materials for the problem in hand is best determined by the trial-and-error method, first in the laboratory and then under actual conditions as nearly as possible. Careful analysis of the problem will show that the resistance to corrosion is not the only factor in the selection of materials. There must also be considered the cost of the material, its availability in castings or in other forms which may be required, and its adaptability to foundry and machine-shop technic. Its physical properties must be considered, such as requisite strength at working temperatures, resistance to shock, and freedom from galling. Aside from the effect of corrosion in determining the length of valve service, there is the matter of contamination of the product being handled through the valve. If the corrosion of the valve metal imparts an undesirable taste or color to the product, this may justify the use of some other more expensive alloy. To properly fix upon a justifiable expenditure for a valve aside from its original cost, there must also be included: the cost of operation; the cost of frequent shutdowns for repairs to the valve; estimate of the probable cost of the hazards connected with the operation of the valve, with consequent destruction of property or human life; and the loss through stoppage of production in other units of the plant, including the cost of investment charges during a shutdown.

In reaching a decision as to the maximum cost of valve materials which may be economically feasible, the factors cited should be carefully weighed in their proper importance, and it is quite evident that no fixed set of rules can be followed in reaching this decision. Likewise, no two engineers are agreed as to the exact valuation to be placed upon these various factors. It would obviously be folly to build a valve of platinum or some other costly metal merely because it happened to be 100 per cent resistant in a service where the degree of corrosion is comparatively slight and where the products handled have a relatively low value. The great majority of valve services are such that from an economic standpoint the metals available for the fabrication of the valves are limited to iron or steel or the commoner forms of nonferrous alloys, such as ordinary brasses and bronzes. In certain instances where heavy corrosion is present, special metals, such as the stainless steels or complex copper alloys, may be economically desirable.

One of the commoner methods of meeting the valve-corrosion problem, without going to the expense of employing special high-priced alloys throughout for the valve construction, is the use of special metal trim or the use of specially treated parts at points where the greatest corrosion or erosion is experienced. If the design of the valve is such as to permit replacement of these special parts, this offers an additional method of bringing the valve cost in line with the maximum cost the service will bear.

There are many valve services in which the corrosion problem can be satisfactorily solved by the use of ordinary cast iron or cast steel as materials of construction for the valves, and by the judicious selection of a suitable design of valve. These are found in high-pressure gas distribution, oil refining and production, the manufacture of chemicals and explosives, the steel and cement industry, and the mining industry. A great many valve services occur in the above fields in which the selection of the valves depends primarily upon their ability to afford a simple, reliable shut-off when wanted, in combination with easy and quick operation. The problem of corrosion enters into this selection chiefly in so far as it involves the matter of maintaining a tight shut-off, not only when the valve is new, but after long service with either frequent or infrequent operating of the valve during that time.

Advantages of Plug-Cock Design

The engineer has a wide variety of valves from which to select the type best suited for his particular problem. They include plug cocks, gate-and-globe type valves, needle valves, angle valves, and many others, all of which have certain advantages and disadvantages, depending upon the nature of the service. However, from the standpoint of resisting corrosion, the plug-cock type of valve (Figure 1) possesses inherent advantages not accorded the others. In this type of valve, when fully opened, no part of the machined surfaces of the valve is exposed to the corrosive or erosive action of the line fluid. When in the closed position, while a portion of the plug is exposed to the action of the line fluid, this area of the plug does

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not form a part of the machined surfaces which must be brought in contact to effect a shut-off. In all other common forms of valves, when the valve is opened, the line fluid passes over the machined portions of the valve, which later must be brought into contact in order to effect a shut-off of the valve. Naturally these portions, when subjected to corrosion or erosion, rapidly lose their efficiency, and to just such a degree they are rendered ineffective in maintaining the primary function of a valve to provide a means of stopping the passage of fluids through the pipe line.

Another advantage of the plug-cock design is the fact that it offers a smooth passageway through the port with no opportunity to collect pipe scale, etc., in the seat as is the case with a gate valve. The effectiveness, however, of the unlubricated plug cock in combating corrosion and erosion is largely theoretical unless means are provided to prevent the entry of the line fluid between the machined surfaces or into other portions of the valve where it may exert an unfavorable influence. Because of the fact that the plug cock is the only common form of valve in which the contact surfaces are not exposed to the action of the line fluid, this type also lends itself admirably to the idea of pressure lubrication. The plug cock then, is a form of valve which, because of its design, offers the most effective natural resistance to corrosion and erosion, and which is ideally suited to the application of pressure lubrication. Without lubrication, however, the use of the plug cock is limited principally to small sizes because of the practical difficulty of operating the large plug cocks, especially when exposed to corrosive influences. To the operator in the field, this is evinced simply by a rusting and consequent sticking of the plug.

Adaptability of Plug-Cock Design to Pressure Lubrication

It is assumed that a lubricant is available which is adequately resistant to the chemical action of the line fluid and to the temperature to which it will be subjected, and is of sufficient viscosity to make it effective as a sealing medium. This offers an effective means, when properly applied under pressure in the plug cock, of combating corrosion in the valve, of reducing the friction incidental to the operation of the valve, of sealing the valve against leakage, and of freeing the plug, in case it is stuck, by employing the lubricant as in a hydraulic jack on the base of a tapered plug. By means of pressure lubrication, not only are the smaller sizes of plug cocks made more easy of operation, but the manufacture of plug cocks in large sizes, formerly considered impracticable, is made more practicable. Today there are in operation on a number of gas lines, 30-inch (76.2-cm.) plug cocks which may be operated with all the ease of a small plug cock.

The opinion has been advanced that the somewhat lower hydraulic efficiency of the conventional form of plug cock with rectangular port, as compared with that of the gate valve, is a disadvantage. However, it may be easily shown that the hydraulic loss incurred by any form of valve is generally a very small or fractional percentage of the hydraulic loss incurred in other parts of the pipe line or system. This is particularly true when handling gas or vapors under high pressures, or when handling liquids under a high static head. This lower hydraulic efficiency is easily offset by the greater reliability and inherent ruggedness of the lubricated plug cock. The cost of the lubricated plug cock when compared with a gate valve is generally less in the smaller sizes, but in the larger sizes the spread turns somewhat in favor of the gate valve. This comparison, however, does not hold strictly when other factors are taken into consideration, such as the use of more expensive metals and also the application of valves of reduced port area where the greater hydraulic loss through the use of such a reduced area valve is a negligible part of the total head lost either in pumping through a long length of pipe line or against a high static pressure.

Pressure lubrication as applied to a plug cock has advantages other than merely offering ease of operation of the valve by means of a reduction of friction. The ability to renew the lubricant offers a means of sealing the valve against leakage by renewing the seating surface after it has become worn, or in the event that corrosion or erosion has progressed to the point of rendering ineffective the metal-to-metal contact of the plug and seat. To a large extent, also, the lubricant protects the seating surfaces by preventing ingress of the line fluid to these parts. The injection of a lubricant of high viscosity between the closely adjacent metallic surfaces offers a means of combating leakage in a very simple and effective way. Lubricant can be forced into these parts by pressure many times greater than the pressure of the line fluid, but it requires the application of only a small torque applied to the lubricant screw or grease gun.

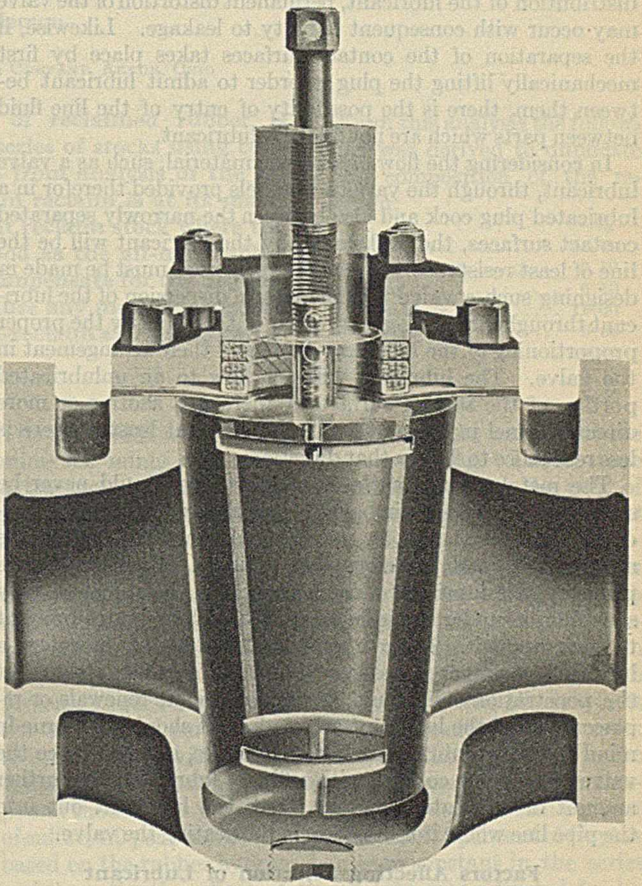

Figure 1—Plug-Cock Type of Valve

In one form of the lubricated plug valve the lubricant under pressure is used to free the plug in case it is stuck by means of a multiplied hydraulic pressure applied at the base of the plug according to Pascal's law. In the case of the tapered plug cock this is equivalent to separating the contact surfaces by a normal lifting action rather than by sliding the one surface across the face of the other. The movement of the plug under the action of the lubricant pressure takes place against the counter thrust of a flexible or resilient packing, which forces the plug again into its seat upon dissipation of the lubricant. This also secures an effective distribution of the lubricant over the contact surfaces, which is also of great importance in securing a tight valve. If the lubricant is not effectively distributed, the line fluid will take the path of least resistance and percolate through the unlubricated interstices between the surfaces. It is quite obvious, of course, that the arrangement of the lubricant ducts in the plug cock must be such that when the lubricant is forced in under pressure, it will at no time be dissipated directly into the pipe line. This is accomplished by an arrangement of lubricant ducts or grooves in such a manner that these are at no time exposed to the direct pressure of the line fluid. If this precaution were not taken, it is quite evident that the line pressure would find access to the atmosphere through the lubricant channels when the lubricant screw is removed from the valve. As an additional protection a ball check is generally incorporated within the lubricant channel.

Importance of Proper Lubricant Distribution

The uniform dispersion of the lubricant over the contact surfaces of the valve is quite evidently of great importance. Of equal importance is the necessity of securing this distribution without distortion of the valve body by means of excessive lubricant pressures. If this means is relied upon for distribution of the lubricant, permanent distortion of the valve may occur with consequent liability to leakage. Likewise, if the separation of the contact surfaces takes place by first mechanically lifting the plug in order to admit lubricant between them, there is the possibility of entry of the line fluid between parts which are not filled by lubricant.

In considering the flow of a plastic material, such as a valve lubricant, through the various channels provided therefor in a lubricated plug cock and also between the narrowly separated contact surfaces, the path taken by the lubricant will be the line of least resistance. Therefore, provision must be made in designing such a valve for the uniform dispersion of the lubricant throughout the necessary parts of the valve by the proper proportioning of the lubricant ducts and their arrangement in the valve. The lubricant will not flow to an unlubricated portion of the seating surfaces if there is a shorter or more direct channel in some other direction, or at least if there is less resistance to flow in that direction.

The metal contact surfaces of the valve should never be separated without their being concurrently filled with lubricant. Also, it should be remembered that these lubricants are plastics, and therefore lack rigidity. Because of this property, the lubricant must be regarded as subject to very slow motion under the influence of the high pressures brought to bear upon it. From a practical standpoint, however, a lubricant of proper viscosity will be found to adequately resist the penetration of line fluid, assuming periodic renewals or replacements of the lubricant are made. It should be borne in mind that over-lubrication is not desirable, and that once the valve surfaces are covered with a film of lubricant, any further amount of lubrication merely forces the lubricant out into the pipe line where it is of no use in lubricating the valve.

Factors Affecting Selection of Lubricant

The problem of valve lubrication is quite different from the problem of ordinary cup-grease lubrication, such as is found in the usual lubricated bushings or bearings. Valve lubricants must possess characteristics suitable for adequately supporting heavy loads and are required to operate only under a low velocity of rotation. They must be able to successfully withstand wide fluctuations of temperature, be resistant to solubility in the line fluids, and must be able to retain a proper degree of viscosity for sealing purposes under operating conditions. They must not pack in the valve lubricant ducts and must be readily displaceable by fresh lubricant when inserted in the valve. The matter of reducing friction is therefore only one of a number of requirements of a good valve lubricant. Valve lubricants are commonly supplied in the form of plastic sticks which may be easily inserted in the hollow shank of the valve when the lubricant screw is removed. They may also be supplied in bulk form in order to meet the requirements of grease-gun lubrication. The particular form of application of the lubricant to the valves is largely a matter of individual preference of the engineer, or is determined by local conditions.

It is not necessary to insert a large quantity of lubricant each time the valve is lubricated. The preferable method is to lubricate at more frequent intervals and inject only sufficient lubricant for renewing or replacing that dispersed through ordinary operation of the valve. This is on the assumption, of course, that the lubricant is not being dissipated by dissolving in the line fluid or lost from other causes.

A little reflection will soon indicate the importance of the lubricant in the successful operation of a lubricated valve; in fact, it has been said that a lubricated valve is no better than its lubricant. For this reason, a great deal of care should be exercised in selecting a suitable lubricant for the service at hand. In selecting a suitable lubricant, not only the physical and chemical character of the fluid being handled must be taken into consideration but also all the limiting conditions of the service. This includes factors, such as the temperature of the service, variation in climatic conditions, the possible handling of several different materials in sequence, the frequency of operation of the valves, the line pressures, and the size of the valve which has to be lubricated.

As an example, consider the acid-agitator service in an oil refinery. Here the conditions to be met by the valve lubricant are: (1) it must be resistant to the chemical attack of both acid and alkali; (2) it must be able to withstand a temperature variation of from atmospheric to 175° F. (79.44° C.); (3) it must be insoluble both in water and hydrocarbon distillates; (4) it must be a plastic of high enough viscosity to act as a good seal in valves more or less subject to heavy corrosion and yet be capable of ready application to the valves under considerable climatic temperature variation; and (5) it must act as a lubricant in reducing the operating torque of the valves. Many plastics possess one or more of these attributes, but it is a rather difficult problem to combine all of them in a single material suitable for valve lubrication. Such a lubricant will generally be composed of a mixture of insoluble soaps and blended wax. While not 100 per cent resistant, such a plastic possesses sufficient permanence to render satisfactory service. Such a service will require more frequent lubrication than others having less stringent requirements.

A condition difficult to meet is the handling of oleums and mixed acid for nitrating purposes. These require lubricants which are not subject to carbonizing as is the case with most organic materials. Here a great deal depends upon the temperature. There are various chlorinated hydrocarbon waxes available which are relatively inert, but these lack certain desired characteristics of a valve lubricant, such as a low temperature–viscosity coefficient and good load-carrying ability. By combining certain waxes of different melting points, a composite plastic of satisfactory physical characteristics may be obtained.

Another difficult lubrication problem is that of providing a lubricant suitable for high-pressure manufactured or natural-gas transmission lines. Here the problems to be contended with are a gas drip containing both aqueous and organic solvents, considerable temperature at places near compressor stations, and the difficulty of holding valves tight against high gas pressures. In certain parts of the transmission lines there is a very pronounced drying action consequent to expansion of the gas and reduction of pressure during its travel through the line.

Where it is not possible to combine all the desired characteristics in a single valve lubricant, a number of lubricants may be necessary. The extent to which the desirable properties of oils, fats, waxes, synthetic hydrocarbons, and other plastics may be incorporated in a valve lubricant determines, to a large extent, the efficiency of a lubricated valve.

Temperature plays a large part in determining the efficiency of a lubricant. The most desirable lubricant, other things being equal, is one which has a very flat viscosity curve; in other words, it is one which possesses the same viscosity at high temperatures as at the temperature at which the lubricant is inserted in the valve. This condition, however, is only approximated, and, as a result, lubricants are seldom as efficient on high-temperature services as they are on low. Generally speaking, satisfactory lubricants are available for temperatures up to 500° F. (260° C.).

It will thus be seen that an efficient lubricant plays a large part in resisting corrosion. There are also certain services which are quite beyond the range of a lubricated valve; at least until suitable lubricants can be devised to handle very high temperatures. It is likewise apparent that where conditions are beyond the ability of a lubricant to withstand them, the lubricated valve is no more effective against corrosion than a non-lubricated valve. On the many services, however, where suitable lubricants are available, the lubricated plug valve offers an effective means of successfully combating this corrosion, both through the means of pressure lubrication and the natural ability of the plug-cock type of valve to handle corrosive services.

Value of Rubber Hydrocarbon in Reclaimed Rubber[1]

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The rubber hydrocarbon of reclaimed rubber is evaluated by road tests in a series of stocks using constant composition as derived from analysis of the reclaim. The hydrocarbon from reclaim is at its maximum value in the 100 per cent reclaim stock where the abrasion is 50 per cent as good as the all-new rubber stock. It is not possible to compensate for the degrading effect of the reclaim because any method proposed can also be applied to the non-reclaim stock with corresponding improvement.

THE investigation reported in this article is concerned with the evaluation of the rubber hydrocarbon of reclaimed rubber as measured by resistance to road wear in a tire tread stock. The work is a confirmation by road tests of that reported by Vogt (*5*) under this same subject and is similar to previous work by the author (*4*). The method of constant composition as used by Vogt was employed in this work. However, the series was carried from 0 to 100 per cent reclaimed rubber hydrocarbon, instead of from 0 to 60 per cent as in Vogt's work.

Experimental Tests

The reclaim used was whole-tire alkali reclaim, and in order to get an average material the lot used was prepared by selecting daily samples over a period of about 3 months and then blended. Mixed with 5 per cent sulfur and cured 17 minutes at 141.5° C. it gave:

Tensile strength	55 kg. per sq. cm.
Elongation	437 %

The chemical analysis of the reclaim was as follows:

	%
Sp. gr.	1.155
Moisture	0.46
Alkalinity (4 hrs.)	0.008
Alkalinity (48 hrs.)	0.007
Acetone extract	7.12
Chloroform extract	28.24
Alcoholic potash extract	1.08
Free sulfur	0.07
Combined sulfur	2.47
Free carbon	11.18
Ash	18.55

The analysis of ash was:

	%
Silica	2.42
Iron and aluminum oxide	2.60
Calcium oxide	1.37
Magnesium oxide	1.10
Zinc oxide	9.00
Sulfates (SO_3)	1.21

From this analysis the following was derived to duplicate the composition of the reclaim:

	%
Rubber	55.00
Mineral rubber	6.10
Pine tar	6.10
Carbon black	11.00
Zinc oxide	9.00
Clay	6.50
Whiting	4.10
Sulfur	2.20

The insolubles were assumed as clay and the balance of the minerals, minus the zinc oxide, as whiting. The acetone extract was increased by 50 per cent to allow for the part of mineral rubber not extracted and was assumed to be 50 per cent mineral rubber and 50 per cent pine tar.

The starting point for the series of stocks used was the 100 per cent reclaim compound. It was derived by adding as much carbon-black loading as the stock would stand and still be capable of processing in the factory. No zinc oxide was used in this compound, as it had been found by previous work that its presence in such a compound adds neither to the physical tests nor to the road performance. The composition of this stock (9 in Table I), taking into consideration the ingredients in the reclaim with the exception of the sulfur, was then used to compound the series as given in Table I. Three and a half per cent of sulfur, 4.0 per cent of stearic acid, and 0.75 per cent of Captax based on the rubber hydrocarbon were constant in the series and the activating effect of the reclaim was adjusted for by using litharge in the low reclaim stocks. The black was added as a 60–40 master batch with rubber and as a 75–25 master batch with reclaim. The stocks were judged to have a uniform optimum technical cure at 60 minutes at 126.4° C.

Physical Tests

Standard methods of testing, as recommended by the Physical Testing Committee, were used except as noted. The tests were made on samples taken from tubed treads.

Tensile Strength—The tensile tests were made with the Goodyear autographic machine. Table II shows the tensile, elongation, and moduli (load at 300 per cent and 500 per cent elongation).

The relative values (non-reclaim stock, 100) are shown on Figure 1. The noteworthy fact is that the tensile properties do not fall off until over 15 per cent reclaimed rubber hydro-

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[1] Received April 6, 1931.

Table I—Composition of Series

Stock	1	2	3	4	5	6	7	8	9
Rubber	100	95.0	90.0	85.0	80.0	75.0	50.0	25.0	0
Reclaim	0	9.1	18.2	27.3	36.4	45.5	91.0	136.5	182.0
Carbon black	49.2	48.2	47.2	46.2	45.2	44.2	39.2	34.2	29.2
Zinc oxide	16.38	15.56	14.74	13.92	13.10	12.29	8.19	4.10	0
Clay	11.56	10.98	10.40	9.83	9.25	8.67	5.78	2.89	0
Whiting	7.46	7.09	6.71	6.34	5.97	5.60	3.73	1.87	0
Mineral rubber	10.50	9.98	9.45	8.93	8.40	7.88	5.25	2.63	0
Pine tar	10.50	9.98	9.45	8.93	8.40	7.88	5.25	2.63	0
Litharge	0.60	0.40	0.20	0.10	0.10	0.10	0	0	0
Sulfur	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Stearic acid	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Captax	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Total	214.45	214.54	214.60	214.80	215.07	215.37	216.65	218.07	219.45

Table II—Results of Tensile Tests

RECLAIMED RUBBER HYDROCARBON	TENSILE STRENGTH	ELONGATION	LOAD	
			At 300%	At 500%
%	*Kg./sq. cm.*	%	*Kg./sq. cm.*	
0	226	590	75	178
5	222	580	80	180
10	230	560	80	178
15	225	565	80	174
20	190	520	88	170
25	180	515	82	
50	150	470	88	
75	118	485	78	
100	84	325	78	

carbon is reached, this being in direct contrast to the road results.

ABRASION—Laboratory abrasion tests were carried out by two methods: the Goodyear, called method A by Vogt (*5*), and the Du Pont abrader. The results are shown in Table III.

Table III—Results of Abrasion Tests

RECLAIMED RUBBER HYDROCARBON	LOSS BY GOODYEAR	DU PONT
%	*Cc.*	*Cc./hp-hr.*
0	19.5	402
5	19.3	377
10	20.3	359
15	21.7	456
20	22	481
25	23.9	413
50	28.8	562
75	34.4	685
100	37.1	856

The Goodyear abrasion results (relative) are shown on Figure 1. They check fairly well with the road tests except that here again the results on the 0 to 25 reclaimed rubber hydrocarbon are too high. The Du Pont abrader results between 0 and 25 are very erratic and are not plotted.

Road Test

The stocks were run on a tubing machine and built into two-way treads for 4.50–21 tires. The comparisons were made as follows: 1 *vs.* 2, 2 *vs.* 3, 3 *vs.* 4, 4 *vs.* 5, 5 *vs.* 6, 6 *vs.* 7, 7 *vs.* 8, 8 *vs.* 9, also 1 *vs.* 4, 4 *vs.* 6, and 6 *vs.* 8. The tires were run in general service, the majority being on Ford cars. The tests were run over a period extending from March to December, 1930. The rating was determined by design height measurements on an average of eight tires per test.

Table IV—Results of Road Test

RECLAIMED RUBBER HYDROCARBON	RATING	SECONDARY RATING
%		
0	100	100
5	92	
10	87	
15	86	86
20	81	
25	79	78
50	65	
75	56	57
100	50	

The results are quite consistent and the secondary comparison checks the main series. The results are shown graphically on Figure 1.

Discussion of Results

Using the method of Vogt (*5*) for interpreting the results,

Let A = value of abrasion resistance of new rubber hydrocarbon with assigned value of 100 units
B = value of reclaim hydrocarbon in same units
C = experimentally determined values for abrasion resistance (based on new rubber stock = 100) of various stocks
Y = amount of new rubber hydrocarbon as decimal fraction
$1.00\ Y$ = amount of reclaim hydrocarbon as decimal fraction.

Then $AY + B\,(1.00 - Y) = C$, on assumption that qualities of two types of hydrocarbon are additive.

Solving
$$B = \frac{C - AY}{1.00 - Y}$$

Using the road values, Table V is obtained.

Table V—Values of Reclaimed Hydrocarbon

RECLAIM HYDROCARBON	*B* VALUE
%	
0	
5	Neg.
10	Neg.
15	7
20	4
25	16
50	30
75	41
100	50

These results check very well with Vogt's (*5*) conclusion—namely, "The value of the reclaimed rubber hydrocarbon varies from 0 when substituted in small percentages, up to a maximum of 50 per cent of the value of new rubber when compounded in large percentages." There is a close similarity between these results and those obtained in the previous work by the author, even though in that series the composition was not constant.

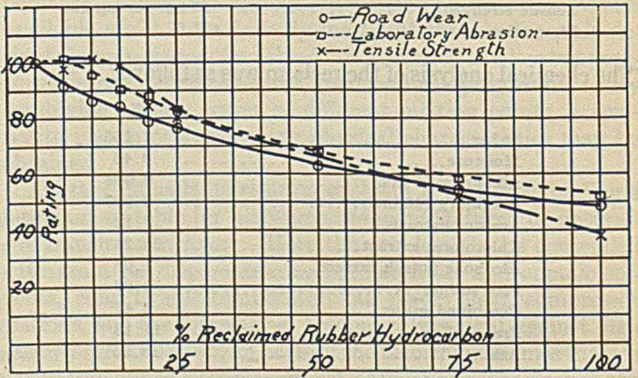

Figure 1—Evaluation of Reclaimed Rubber Hydrocarbon

The relative road abrasion value of the rubber hydrocarbon in the reclaim having been shown, the next question is, what does this value mean when used in practical tread compounding? Bierer and Davis (*1*), while perfectly clear on the fact that the rubber hydrocarbon from reclaim is inferior to new hydrocarbon, attempted to show that this could be overcome or compensated for, when substituting reclaim for rubber, by taking diluents or excess filler from the rubber stock and by adding reënforcing material to the reclaim stock. They failed to realize that the same measures which would improve the reclaim tread could be applied to the base stock.

If it were true that, due to the plasticizing effect of the reclaim, it would be possible to carry higher black loading in the reclaim tread stock with the same ease of handling, there would be some weight to the argument that the reclaim can be compensated for by adding black. Factory practice does not show this to be the case. On the contrary, the added black must be considerably reduced to keep the same handling conditions. If it were possible to process the reclaim stock with higher black, then it would also be possible to add more black to the non-reclaim stock and keep the differential in road wear. Since this is the case, if the non-reclaim tread stock is taken with no diluent or excess zinc oxide and with as much black loading as can be processed, then it is not possible to make compensation for the effect of the reclaim. These facts were put forth very clearly by Cranor (*2*), who states that "A better tread can be made without reclaim than can possibly be made with it."

The series in the present paper was not designed primarily to show the extent to which wear will fall off with the use of reclaim in a series of practical tread stocks. However, since no compensation for its effect is possible, the wear in such a series would fall off even faster than in the series in this paper, for in the latter diluent materials were added to the non-reclaim stock. Therefore, it can be said that up to 20 per cent, the use of reclaim will cut down the resistance to road wear by approximately the percentage used. This is essentially the conclusion reached by Holt and Wormeley (*3*). Their method was severely criticized by Bierer and Davis, but considering that their base stock was as stiff and tough as was considered practical at the time, this criticism was not justified and their conclusions were essentially in line with the facts.

Acknowledgment

The writer wishes to express his appreciation to W.W. Vogt for valuable suggestions and criticism.

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Extraction of Potash from Polyhalite

II—Production of Syngenite and By-Product Magnesia[1]

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A discussion is presented of data concerning the conversion of polyhalite ($K_2SO_4.MgSO_4.2CaSO_4.2H_2O$) to syngenite ($K_2SO_4.CaSO_4.H_2O$) and the production of by-product magnesia by way of the precipitation and subsequent thermal decomposition of $MgCO_3.(NH_4)_2CO_3.4H_2O$. Processes are suggested for the production of either syngenite or K_2SO_4 or both.

PUBLICATIONS by Wroth (*7*), Storch (*3*), and Storch and Clarke (*4*) have indicated the commercial possibilities in the production of K_2SO_4 from Texas–New Mexico polyhalite and have given the results of experiments on the calcination and subsequent leaching with water at 100° C. In this paper it is desired to present a discussion of the results of experiments concerning the conversion of polyhalite to syngenite, and the production of by-product magnesia. The detailed, tabulated data upon which this discussion is based have already been presented by the authors (*5*).

The equilibrium diagram at 25° C. (*2*) for the system $K^+-Mg^{++}-Ca^{++}-SO_4^{--}-H_2O$ indicates that syngenite (potassium calcium sulfate monohydrate) is stable in the presence of a concentrated $MgSO_4$ solution, the K_2SO_4 concentration being comparatively low (2.6 per cent). Hence, it is to be expected that, when calcined[2] polyhalite is leached with water at 25° C., a mixture of syngenite and gypsum will constitute the solid phase. If, however, a leach liquor containing sufficient K_2SO_4 to combine with the gypsum is used instead of water, practically pure syngenite is obtained. The liquid phase contains practically all of the $MgSO_4$ from the polyhalite as well as any soluble impurities, such as NaCl. The solid phase will also contain any natural anhydrite and other insoluble materials present in the polyhalite, since the former material reacts only very slowly with K_2SO_4 solutions.

The rate of solution of $MgSO_4$ from minus 30-mesh polyhalite calcined at 500° C., using a 10–11 per cent K_2SO_4 solution as leach liquor, is fairly rapid, being practically complete at the end of 3 hours. The rate of drop of K_2SO_4 to the equilibrium value is much slower, about 6 hours being necessary to obtain a 3 per cent K_2SO_4 concentration in the mother liquor. The solid phase at the completion of the reaction is a very finely divided powder. Its composition depends upon the percentage of natural anhydrite present in the polyhalite, but if it is possible to obtain industrial quantities of polyhalite containing not more than 5 per cent anhydrite,[3] the syngenite product would contain about 50 per cent K_2SO_4, 5.2 per cent H_2O, and 44.8 per cent $CaSO_4$. The potash content of this product is completely water-soluble, and it should be a desirable potash fertilizer, as the $CaSO_4$ is a common constituent of mixed fertilizers. Some mixing tests conducted on 5-pound to 10-pound batches of syngenite by the laboratories of one of the largest mixed-fertilizer companies indicate that this product is suitable for the production of mixed fertilizers.

Production of K_2SO_4 from Syngenite

In one of the processes to be described below, K_2SO_4 is produced by the conversion of calcined polyhalite to syngenite, and subsequent leaching of the latter with 3 per cent

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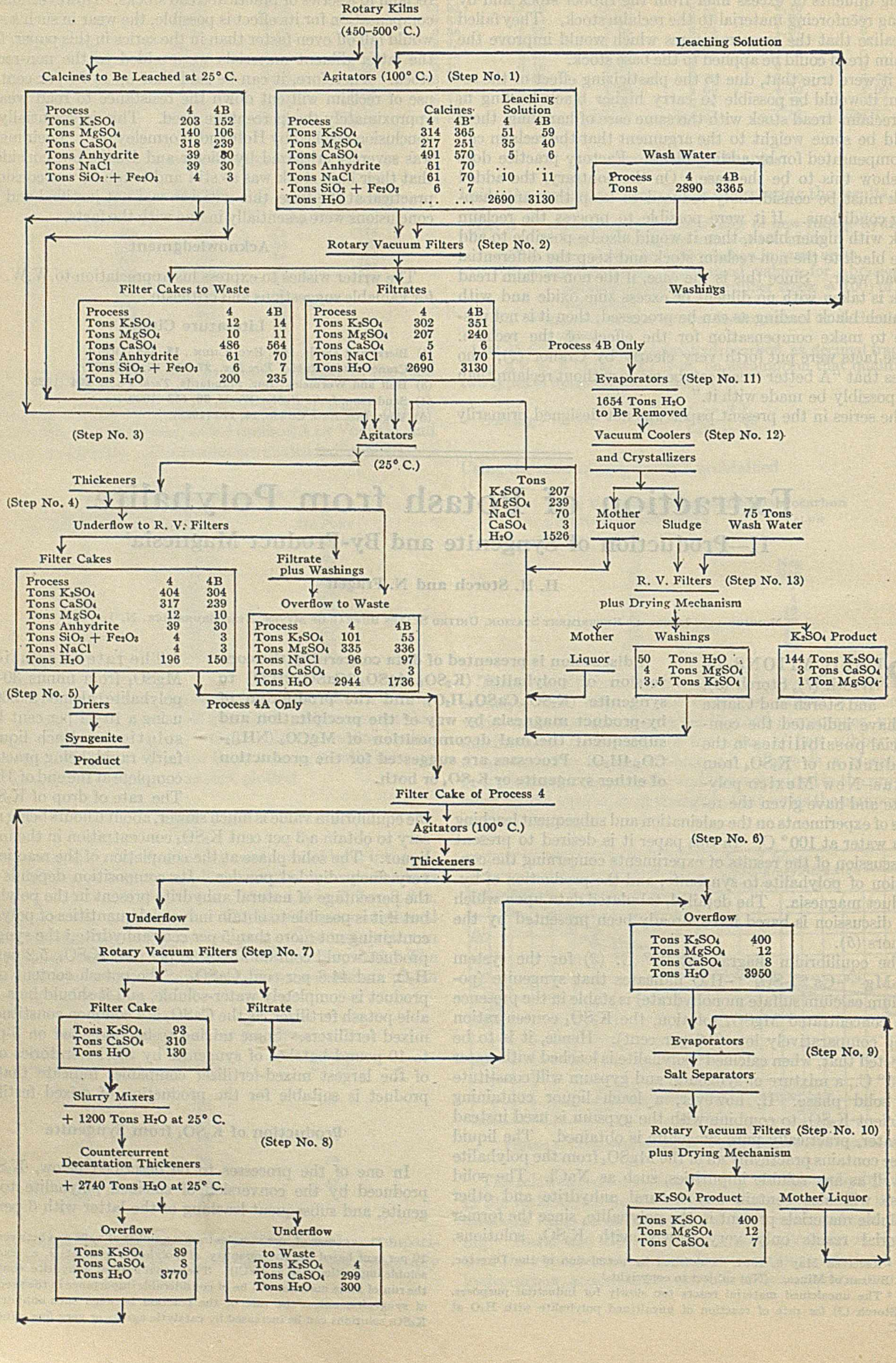
[1] Received May 6, 1931. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] The uncalcined material reacts too slowly for industrial purposes. See Storch (*3*) for rate of reaction of uncalcined polyhalite with H_2O at 25° C.

[3] The average of core samples from a number of wells was between 5 and 10 per cent based on the quantity of polyhalite present (i. e., excluding soluble impurities such as NaCl). The actual natural anhydrite content of the run of mine material will be of considerable importance in the production of syngenite, unless the rate of the reaction between such anhydrite and K_2SO_4 solutions can be increased by catalytic agents or very fine grinding.

Figure 1—Flow Diagram for Processes 4, 4A, and 4B



Process	4	4B
Tons K_2SO_4	203	152
Tons $MgSO_4$	140	106
Tons $CaSO_4$	318	239
Tons Anhydrite	39	30
Tons NaCl	39	30
Tons $SiO_2 + Fe_2O_3$	4	3

	Calcines		Leaching Solution	
Process	4	4B	4	4B
Tons K_2SO_4	314	365	51	59
Tons $MgSO_4$	217	251	35	40
Tons $CaSO_4$	491	570	5	6
Tons Anhydrite	61	70	..	..
Tons NaCl	61	70	10	11
Tons $SiO_2 + Fe_2O_3$	6	7	..	..
Tons H_2O	...	...	2690	3130

Process	4	4B
Tons	2890	3365

Process	4	4B
Tons K_2SO_4	12	14
Tons $MgSO_4$	10	11
Tons $CaSO_4$	486	564
Tons Anhydrite	61	70
Tons $SiO_2 + Fe_2O_3$	6	7
Tons H_2O	200	235

Process	4	4B
Tons K_2SO_4	302	351
Tons $MgSO_4$	207	240
Tons $CaSO_4$	5	6
Tons NaCl	61	70
Tons H_2O	2690	3130

Tons	
K_2SO_4	207
$MgSO_4$	239
NaCl	70
$CaSO_4$	3
H_2O	1526

50 Tons H_2O
4 Tons $MgSO_4$
3.5 Tons K_2SO_4

144 Tons K_2SO_4
3 Tons $CaSO_4$
1 Ton $MgSO_4$

Process	4	4B
Tons K_2SO_4	404	304
Tons $CaSO_4$	317	239
Tons $MgSO_4$	12	10
Tons Anhydrite	39	30
Tons $SiO_2 + Fe_2O_3$	4	3
Tons NaCl	4	3
Tons H_2O	196	150

Process	4	4B
Tons K_2SO_4	101	55
Tons $MgSO_4$	335	336
Tons NaCl	96	97
Tons $CaSO_4$	6	3
Tons H_2O	2944	1736

Tons K_2SO_4	93
Tons $CaSO_4$	310
Tons H_2O	130

Tons K_2SO_4	89
Tons $CaSO_4$	8
Tons H_2O	3770

Tons K_2SO_4	4
Tons $CaSO_4$	299
Tons H_2O	300

Tons K_2SO_4	400
Tons $MgSO_4$	12
Tons $CaSO_4$	8
Tons H_2O	3950

Tons K_2SO_4	400
Tons $MgSO_4$	12
Tons $CaSO_4$	7

K_2SO_4 solution at 100° C. Syngenite reacts with boiling water to form a K_2SO_4 solution leaving a solid phase which is pure potassium pentacalcium sulfate ($K_2SO_4.5CaSO_4.H_2O$, referred to hereafter as pentasulfate). The following equation presents the optimum conditions for this leaching operation:

$$5K_2SO_4.CaSO_4.H_2O + 375.3H_2O \longrightarrow K_2SO_4.5CaSO_4.H_2O + 4K_2SO_4 + 379.3H_2O$$

The mother liquor contains 10.2 grams K_2SO_4 per 100 grams H_2O. This reaction is slow, requiring about 5 hours for completion.

The recovery of the 20 per cent of the total potash which remains in the pentasulfate residue from the above reaction is readily accomplished by taking advantage of the fact that this compound is decomposed by water at 25° C., yielding a 3 per cent K_2SO_4 solution, the solid phase being gypsum. This reaction is a very slow one, requiring about 18 hours for completion. The 3 per cent K_2SO_4 solution may be used for the hot (100° C.) leaching of another batch of syngenite, the same maximum concentration of K_2SO_4—viz., 10.2 grams per 100 grams H_2O being obtained. This figure is about 10 per cent higher than the equilibrium concentration (*2*) for the system K^+-Ca^{++}-SO_4^{--}-H_2O at 100° C.

Processes Producing Syngenite and K_2SO_4

Figure 1 presents flow diagrams for three processes—viz., process 4 producing syngenite, 4A producing K_2SO_4 by way of the conversion of calcined polyhalite to syngenite, and 4B producing both K_2SO_4 and syngenite. In process 4 the polyhalite, after calcination in rotary kilns, is divided into two portions. One portion (1.54 parts) is extracted in a system of agitators and thickeners with water at 100° C. so as to yield a solution containing 11.2 grams of K_2SO_4 and 7.8 grams of $MgSO_4$ per 100 grams of H_2O; and the second portion (1.0 part) is mixed with the cooled (to 25° C.) and filtered liquor from the extraction of the first portion. Contact time of about 6 hours is essential for the complete conversion of the calcine to syngenite. The liquor obtained as the thickener overflow from this step, containing 3.6 grams of K_2SO_4 and 15.6 grams of $MgSO_4$ per 100 grams of H_2O, is wasted or sent to the MgO recovery plant.

The syngenite sludge, obtained as the underflow from the thickener system, is filtered, washed, and dried. The composition of the product is given in Table I. The over-all yield of potash is 78.1 per cent. This yield would be considerably increased if the end liquors from the 25° C. leach could be used for the extraction at 100° C. of K_2SO_4 from a second portion of calcined polyhalite. Experiments on this point have thus far indicated that this may not be feasible, a decreased hot-extraction yield being obtained which more than offsets the gain involved in sending less K_2SO_4 to waste in the end liquors. These experiments are, however, not conclusive, and further research may disclose a set of conditions which will make such recirculation feasible.

In process 4A the syngenite product of process 4 is not dried, but is mixed with 3 per cent K_2SO_4 solution and sent to agitators where leaching at 100° C. takes place, resulting in a solution containing 10.2 grams of K_2SO_4 per 100 grams of H_2O. Contact time of about 5 hours is necessary. The leach liquor is evaporated practically to dryness, the K_2SO_4 crystals being separated from the bulk of the mother liquor with the aid of salt traps and subsequently filtered and dried on salt-type rotary vacuum filters equipped with a drying mechanism. The residue from the 100° C. leach (of the syngenite) is leached with water at 25° C. for about 18 hours, and the resulting 3 per cent K_2SO_4 solution returned for extraction of another batch of syngenite. The over-all yield of process 4A is about 77.4 per cent.

In process 4B, 2.4 parts of calcined polyhalite are leached at 100° C. to yield a solution containing 11.2 grams of K_2SO_4 and 7.8 grams of $MgSO_4$ per 100 grams of H_2O. This liquor is evaporated until the $MgSO_4$ concentration is about 16.5 grams of H_2O. It is then cooled to 25° C. and the K_2SO_4 crystals separated from the mother liquor. The latter is mixed in agitators with 1.0 part of calcined polyhalite at 25° C. Contact time of about 6 hours in the agitators and thickeners is essential for this step. The remainder of process 4B is identical with process 4. Process 4B would produce 4.2 tons of syngenite for every ton of K_2SO_4 produced. The over-all yield of this process is 86.2 per cent.

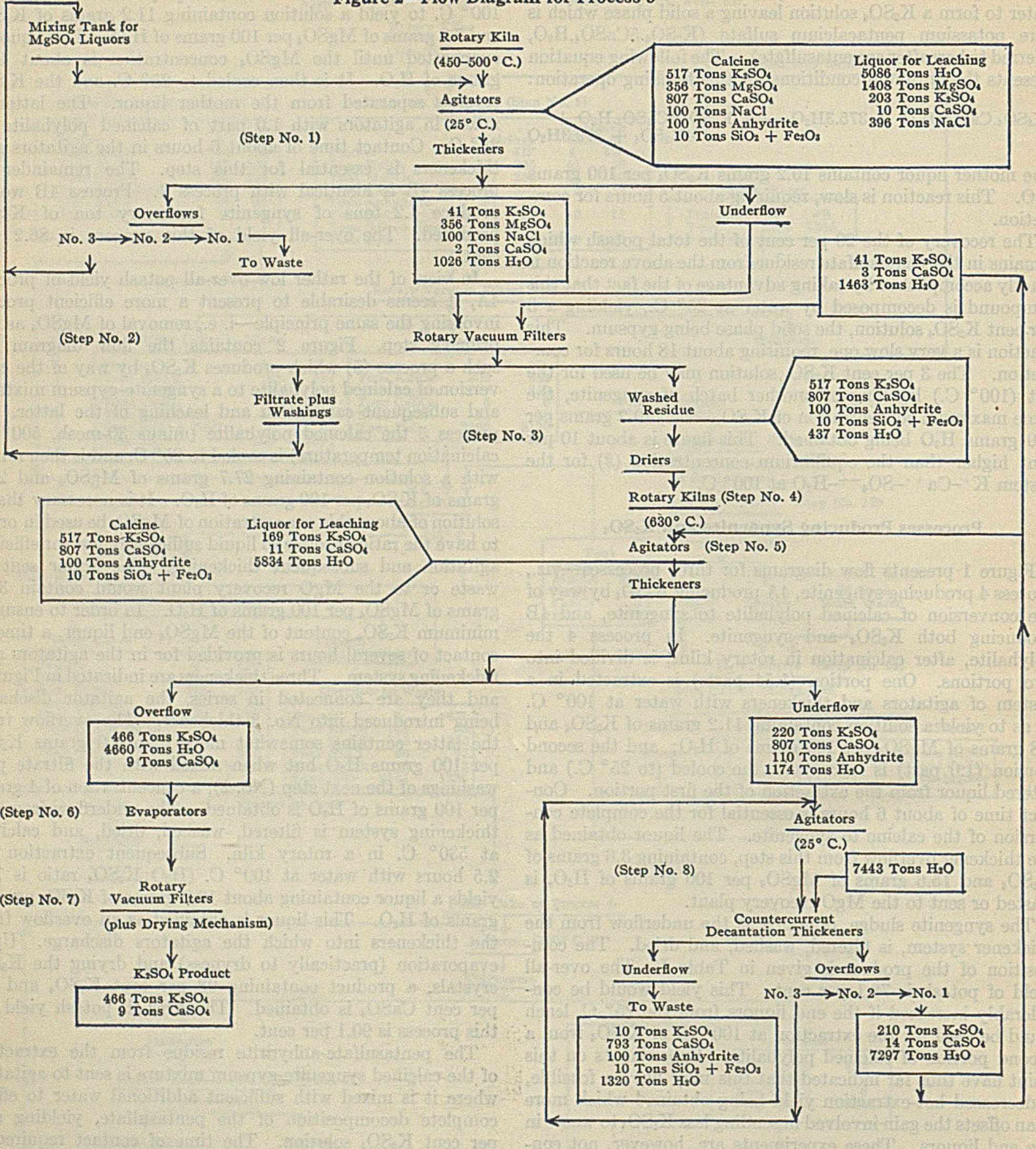
In view of the rather low over-all potash yield of process 4A, it seems desirable to present a more efficient process involving the same principle—i. e., removal of $MgSO_4$ as the primary step. Figure 2 contains the flow diagram for such a process (5) which produces K_2SO_4 by way of the conversion of calcined polyhalite to a syngenite-gypsum mixture, and subsequent calcination and leaching of the latter. In process 5 the calcined polyhalite (minus 30-mesh, 500° C. calcination temperature) is cooled to 25° C. and is then mixed with a solution containing 27.7 grams of $MgSO_4$ and 2.35 grams of K_2SO_4 per 100 grams of H_2O. It is necessary that a solution of about this concentration of $MgSO_4$ be used in order to have the ratio of solids to liquid sufficiently low for efficient agitation and subsequent thickening. The liquor sent to waste or to the MgO recovery plant would contain 34.7 grams of $MgSO_4$ per 100 grams of H_2O. In order to ensure a minimum K_2SO_4 content of the $MgSO_4$ end liquor, a time of contact of several hours is provided for in the agitators and thickening system. Three thickeners are indicated in Figure 2 and they are connected in series, the agitator discharge being introduced into No. 3 thickener. The overflow from the latter contains somewhat more than 4.0 grams K_2SO_4 per 100 grams H_2O but when mixed with the filtrate plus washings of the next step (No. 2), a concentration of 4 grams per 100 grams of H_2O is obtained. The underflow from the thickening system is filtered, washed, dried, and calcined at 530° C. in a rotary kiln. Subsequent extraction for 2.5 hours with water at 100° C. (H_2O:K_2SO_4 ratio is 7.2) yields a liquor containing about 10.2 grams of K_2SO_4 per 100 grams of H_2O. This liquor is obtained as an overflow from the thickeners into which the agitators discharge. Upon evaporation (practically to dryness) and drying the K_2SO_4 crystals, a product containing 98 per cent K_2SO_4 and 2.0 per cent $CaSO_4$ is obtained. The over-all potash yield for this process is 90.1 per cent.

The pentasulfate-anhydrite residue from the extraction of the calcined syngenite-gypsum mixture is sent to agitators where it is mixed with sufficient additional water to effect complete decomposition of the pentasulfate, yielding a 3 per cent K_2SO_4 solution. The time of contact required is about 18 hours. This dilute K_2SO_4 solution is returned for use in washing the syngenite-gypsum mixture, the resulting wash waters being then sent to the $MgSO_4$ liquor-mixing tank.

Attempts to obtain a solution containing about 10 grams K_2SO_4 per 100 grams of H_2O combined with a 65–70 per cent potash extraction by leaching the uncalcined syngenite-gypsum mixture have thus far been unsuccessful. Further research may, however, disclose a set of conditions which will dispense with this calcination step.

Table I shows the tonnages and composition of the products obtained in processes 4, 4A, 4B, and 5, assuming a plant using 2000 tons per day of polyhalite containing 25.85 per cent K_2SO_4, 17.8 per cent $MgSO_4$, 45.35 per cent $CaSO_4$, 5.0 per cent NaCl, 5.5 per cent H_2O, and 0.5 per cent $SiO_2 + Fe_2O_3$, etc. Detailed cost estimates for these processes have been

Figure 2—Flow Diagram for Process 5



made, but it is considered undesirable to publish these until chemical engineering tests which are now in progress have been completed. For the purposes of this paper it will suffice to state that these processes appear to be economically feasible and that process 4B is selected by the authors as the best one of these here presented.

Table I—Composition and Tonnage of Products in Processes 4, 4A, 4B, and 5[a]

Process	Character	Tons per Day	K_2SO_4	$CaSO_4$	$MgSO_4$	NaCl	H_2O	SiO_2 + Fe_2O_3, etc.
			%	%	%	%	%	%
4	Syngenite	822	49.1	43.4	1.4	0.5	5.1	0.5
4A	K_2SO_4	420	95.2	1.7	2.9	...	0.2	...
4B	K_2SO_4	148	97.0	2.1	0.7	...	0.2	...
	Syngenite	620	49.1	43.4	1.4	0.5	5.1	0.5
5	K_2SO_4	476	97.9	1.9	...	...	0.2	...

[a] Based on use of 2000 tons per day of polyhalite containing 25.85 per cent K_2SO_4.

Possible Production of By-Product Magnesia

In the first paper (*3*) of this series and in the preceding sections of this paper, five processes were suggested for the production of K_2SO_4, or $K_2SO_4.CaSO_4.H_2O$, or both from polyhalite. In all except one (No. 3) of these processes, end liquors containing 15–35 grams of $MgSO_4$ and 4–6 grams of K_2SO_4 per 100 grams of H_2O are produced. When these end liquors are treated at 25° C. with 3.5 to 4 moles of $2NH_3 + CO_2$ gas, a double salt—namely, $MgCO_3.(NH_4)_2CO_3.4H_2O$, is obtained as small well-formed orthorhombic crystals about 0.5 × 1 × 0.1 mm. in size. Ninety-eight to ninety-nine per cent of the $MgSO_4$ is thereby removed from solution, and about 2 per cent of the K_2SO_4 is occluded in the magnesium ammonium carbonate crystals.

Engel (*1*) reported in 1899 that the product obtained by slow decomposition of this double salt, using a current of dry air and a maximum temperature of 130–140° C., was normal magnesium carbonate. He did not, however, present any analytical data in support of his statement. A large number of experiments were made in this laboratory attempting to produce normal magnesite by the thermal decomposition of $MgCO_3.(NH_4)_2CO_3.4H_2O$, but in all cases the CO_2 content of the products was between 30 and 40 per cent. Since the theoretical CO_2 content of normal magnesite is 52.4 per cent, it is apparent that a mixture of $MgCO_3$ and $Mg(OH)_2$ was obtained. After decomposition at 130–140° C. in a current of dry air the products obtained contained about 43 per cent MgO, 4 per cent K_2SO_4, 1 per cent $(NH_4)_2SO_4$, and 32 per cent CO_2. Calcination tests on this product showed practically complete evolution of CO_2 in 10 minutes of heating at 500° C., but the H_2O required a considerably higher temperature (800–900° C.) for complete removal.

It is apparent that the by-product magnesia produced in the manner indicated above (decomposition of $MgCO_3.(NH_4)_2CO_3.4H_2O$ at 130–140° C. in a current of dry gas, followed by calcination at 500° C.) would contain 65–80 per cent MgO, 5–6 per cent K_2SO_4, less than 1 per cent $(NH_4)_2SO_4$, and 12–30 per cent H_2O. It is probable that most of the K_2SO_4 could be removed by leaching with water prior to the calcination, but this procedure would undoubtedly result in a higher H_2O content of the final product. It would perhaps be more satisfactory to wash the calcined material free from K_2SO_4 and subsequently dry (or recalcine if necessary) the product, which might then be salable as caustic calcined magnesite. An alternative procedure would consist in recalcination at 800–900° C. of the washed product calcined at 500° C. so as to produce dead-burned magnesite for use as a refractory.

The recovery of the excess $NH_3 + CO_2$, present in the liquor from the magnesium ammonium carbonate precipitation, is a problem that must receive considerable laboratory study before detailed flow diagrams can be prepared. The bulk of this excess would be driven off in the first effect of the evaporator system and according to Terres and Weiser (*6*) would probably be admixed with about three volumes of steam per volume of NH_3, leaving approximately a 3 per cent $(NH_4)_2CO_3$ solution to be recovered from the steam traps. The presence of this large volume of noncondensable gases in the steam chest of the second effect would result in very low heat-transfer coefficients. In order to secure normal triple-effect economy in evaporation, it would probably be necessary to provide the second effect with a much larger area of heating surface than is usually employed.

The discussion indicates that the $MgSO_4$ end liquors of processes 1, 2, 4, 4A, 4B, and 5 might be treated for recovery of MgO and the production of $(NH_4)_2SO_4$ containing a small amount of K_2SO_4. It will, however, be noted from the flow diagrams for these processes, that the $MgSO_4$ end liquors contain appreciable amounts of NaCl. Hence upon evaporation of the mother liquors from the magnesium ammonium carbonate crystallization, the potassium and ammonium salts obtained would be mixed with varying amounts of NH_4Cl, Na_2SO_4, $(NH_4)_2SO_4.Na_2SO_4.4H_2O$, and NaCl. This introduces either a difficult fractional-crystallization problem, or (if the liquor is simply evaporated practically to dryness, and the solids obtained are thoroughly mixed) the expense of freight on the sodium and chlorine content of the product. It is, however, unlikely that a mixture of $(NH_4)_2SO_4$, K_2SO_4, and appreciable quantities of Na and Cl (25 per cent for process 5) could be successfully marketed. It will therefore be necessary to base the MgO recovery processes upon the elimination of the NaCl contained in the polyhalite by washing the latter (crushed through 4 mesh) with one part of water at atmospheric temperatures. Laboratory experiments indicate that practically complete removal may be obtained in a contact time of 10 minutes, a loss of 4.5 per cent of the total potash in the polyhalite accompanying the extraction of the NaCl.

It has, however, been found that practically NaCl-free (i. e., about 0.2 per cent NaCl) calcined polyhalite will not yield as high a concentration upon extraction as is obtained when 5 per cent NaCl is present. Thus a maximum of about 10.5 grams of K_2SO_4 per 100 grams of H_2O is obtained, using NaCl-free material, whereas 11.4 grams K_2SO_4 per 100 grams H_2O is reached if 5 per cent NaCl is present. In the case of the NaCl-free material it is also necessary to use a much lower ratio of H_2O to K_2SO_4 in the extraction and to modify the procedure used in washing the residues. Hence the flow diagrams given for processes 1, 2, 4, 4A, 4B, and 5 would require some modification if MgO recovery is contemplated. The over-all yields would, however, not be appreciably altered.

Acknowledgment

The authors wish to express their appreciation of the critical suggestions made by L. Clarke, assistant chemist at this station.

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Europeans Experimenting with Transparent Wrapping Paper

The varied uses and growing potentialities of transparent wrapping paper, as evidenced by the development of cellulose sheeting of this type, are attracting greater attention on the part of the European paper industry, which is now developing a number of paper impregnating processes with the object of maximum transparency, according to a report received in the Commerce Department.

Impregnation, as a paper converting process, has developed very rapidly in Europe during recent years, although it has by no means attained the importance and proportion that it has in the United States. The more common processes, such as waxing, oiling, and asphalting, have been known for years, but the use of such papers, compared to the American consumption, is quite in its infancy in Europe. On the other hand, certain processes have been developed there, notably in the manufacture of transparent papers, and are more extensively used than in the United States. European trade leaders state that advantages of transparency in wrapping materials have always been obvious, but never to such an extent as with the development of transparent cellulose sheeting. Because of the investment necessary in its manufacture, and possible patent infringement litigation, there have been comparatively few competitive developments, except in cheaper imitations. Some of these are gelatin and others impregnating processes. Impregnating is the least expensive, of course, requiring comparatively simple equipment. The solutions used seem to have a varnish base, although the actual composition is the secret of the manufacturer, and analysis is difficult. There has been a gradual improvement in the quality of these types of paper, most of which are produced from a tissue paper base, but the perfection of transparent cellulose sheeting has not been reached, according to European trade opinion.

The vogue for transparent wrappings has also been taken up by vegetable parchment manufacturers. So-called silver parchments have appeared on the market in Germany.

Occurrence of Fluorides in Some Waters of the United States[1]

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INVESTIGATORS of the dental defect known as mottled enamel seem to agree on two points: the defect occurs in certain geographical areas, and the causal factors seem to be associated with the water supply of those areas. Reference to the complete bibliography on the subject compiled by Kempf and McKay (*2*) shows that no specific common characteristic of the waters from affected areas has been discovered. Following the publication just mentioned, A. W. Petrey of this laboratory spectrographically discovered the presence of fluorides in deep-well water from Bauxite, Arkansas. These deep wells were formerly the source of water used by individuals who show the characteristic dental defect known as mottled enamel. Several months prior to the investigation covered in the report of Kempf and McKay the deep-well supply at Bauxite was abandoned in favor of another supply which has since been found to be free from fluorides.

The presence of fluorides was first revealed by means of the spectrograph. Substances containing both calcium and fluoride show a characteristic spectral band which has its head at 5490 Å. and which is degraded towards the infra-red end of the spectrum (*4*). The spectrum obtained from Bauxite deep-well water is shown in Figure 1. The definite and specific character of the 5490 Å. band of calcium fluoride is given in Figure 2 which shows the spectra obtainable from a variety of calcium salts. Only those salts which contain both calcium and fluoride show the characteristic band indicated by the limiting lines in the cases of the spectra of calcium fluoride and that of a mixture of calcium oxide and aluminum fluoride.

Figure 1—Spectrum of Deep-Well Water

Following the discovery of fluorides in Bauxite deep-well water, the author secured samples of water from other localities where the defect occurs. These localities were Colorado Springs, Col., a well near Kidder, S. D., a well near Lidgerwood, N. D., and Oakley, Idaho. Spectrograms of the water from these localities are shown in Figures 3 and 4. The presence of fluorides is definitely shown in all cases. When the residues from these waters, after evaporation, were tested qualitatively for fluorides by etching methods (*5*) positive tests resulted in all cases. While the etching produced in some cases is slight, nevertheless in all cases it was demonstrably positive.

Quantitative estimation of fluorine is fraught with difficulty. In the author's opinion, determinations for fluorine even with the best available methods tend to give low results. For the determination of fluorine in the samples herein considered recourse was taken to a method of Fairchild (*1*). Since this method was worked out for particular use on phosphate rock, it was necessary to adapt it to the analysis of water. The method, as finally used in the work covered in this paper, follows:

Pipet 100 cc. of water into a 250-cc. glass-stoppered Erlenmeyer flask, add 1 drop of methyl red, and 1.0 *N* hydrochloric acid drop-

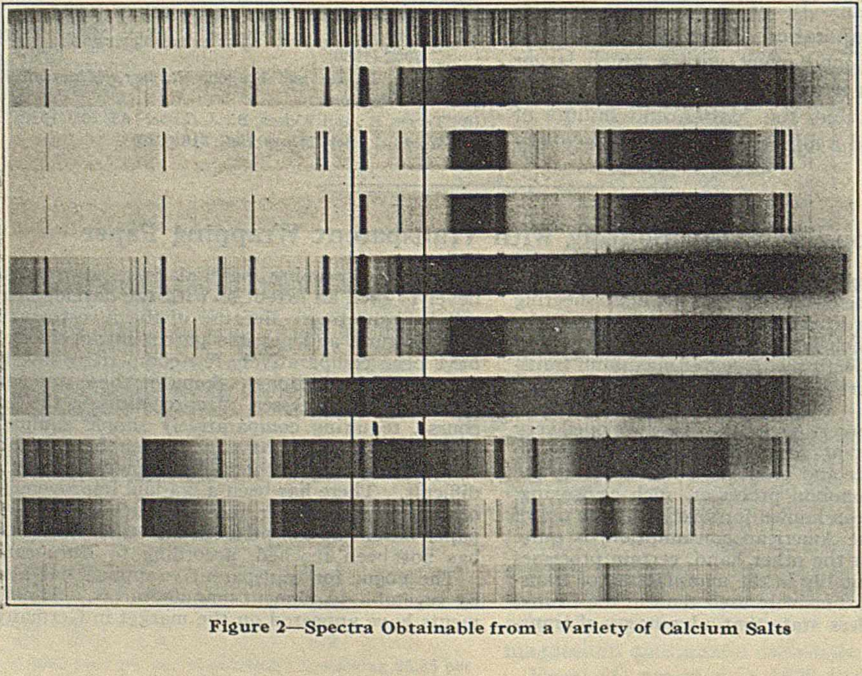

Figure 2—Spectra Obtainable from a Variety of Calcium Salts

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[1] Received May 19, 1931.

Figure 3—Spectrogram of Spring Water

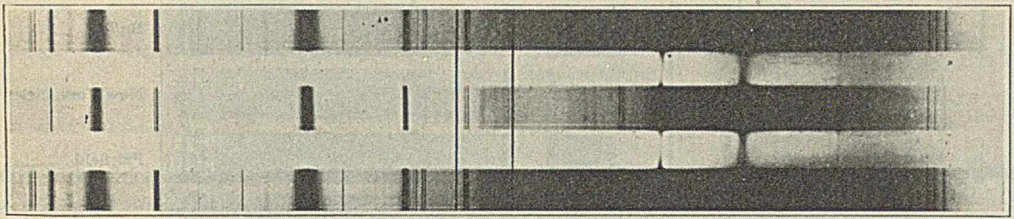

Figure 4—Spectrograms of Various Waters

wise until acid. Add 10 cc. of 20 per cent sodium chloride solution. Filter, wash, and discard any precipitate. Add an excess of 0.08 *M* ferric chloride over that required for completion of the reaction,

$$FeCl_3 + 3NaF = FeF_3 + 3NaCl$$

5 cc. is the proper amount for fluorine content from 0.001 to 0.0100 gram. Add 2 cc. of 1.0 *N* hydrochloric acid and 10 cc. of 5 per cent potassium iodide solution, and stopper the flask. Immerse it in a water bath at a temperature of 38 ± 1° C. and allow it to remain in the bath 30 minutes. Iodine is liberated by the ferric chloride in excess of that required to react with the fluorine present. Quickly cool the flask, and titrate the iodine with standard thiosulfate solution, using starch as indicator. Simultaneously carry through a control sample with 100 cc. of distilled water and the quantities of reagents used in the analysis. The difference in thiosulfate consumption between the control and the sample represents the ferric chloride consumed in the reaction with fluoride. If the thiosulfate solution contains 4.354 grams of the crystallized salt per liter, it will be equivalent to 0.001 gram fluorine per cubic centimeter.

If the fluorine content shown by the analysis is very low, repeat the analysis, with a larger sample. Evaporate this to 100 cc. in platinum. Do not allow the solution to become strongly concentrated during the evaporation, lest hydrofluoric acid be lost.

Application of this method to various samples from endemic areas yielded the following results:

LOCATION OF SAMPLE	FLUORINE AS FLUORIDE *P. p. m.*
Deep Well, Bauxite, Ark.	13.7
Colorado Springs, Colo.	2.0
Well near Kidder, S. D.	12.0
Well near Lidgerwood, N. D.	11.0
Oakley, Idaho	6.0

It is well to emphasize the fact that no precise correlation between the fluoride content of these waters and the mottled enamel has been established. All that is shown is the presence of a hitherto unsuspected common constituent of the waters from endemic areas. However, it is of interest to note that apparently the relative severity of the defect in these various areas seems to follow the fluoride concentration.

Since the occurrence of fluorides in potable waters has apparently not been widely studied, a survey of some mu-

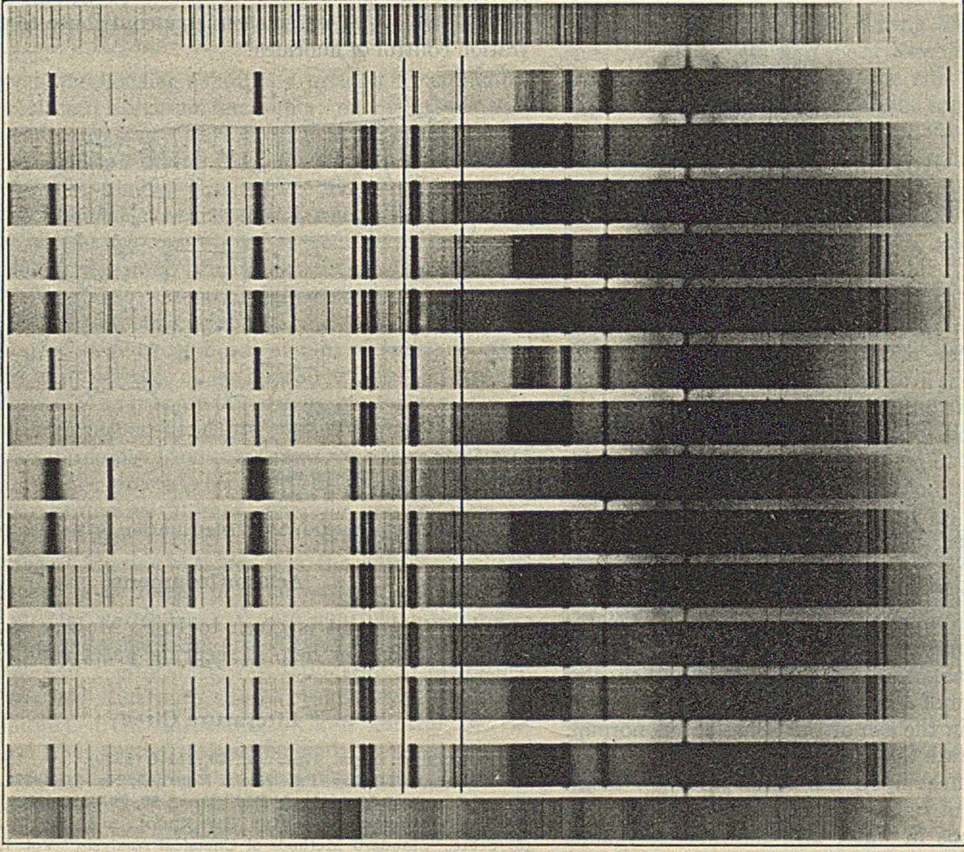

Figure 5—Spectrograms of Various Waters

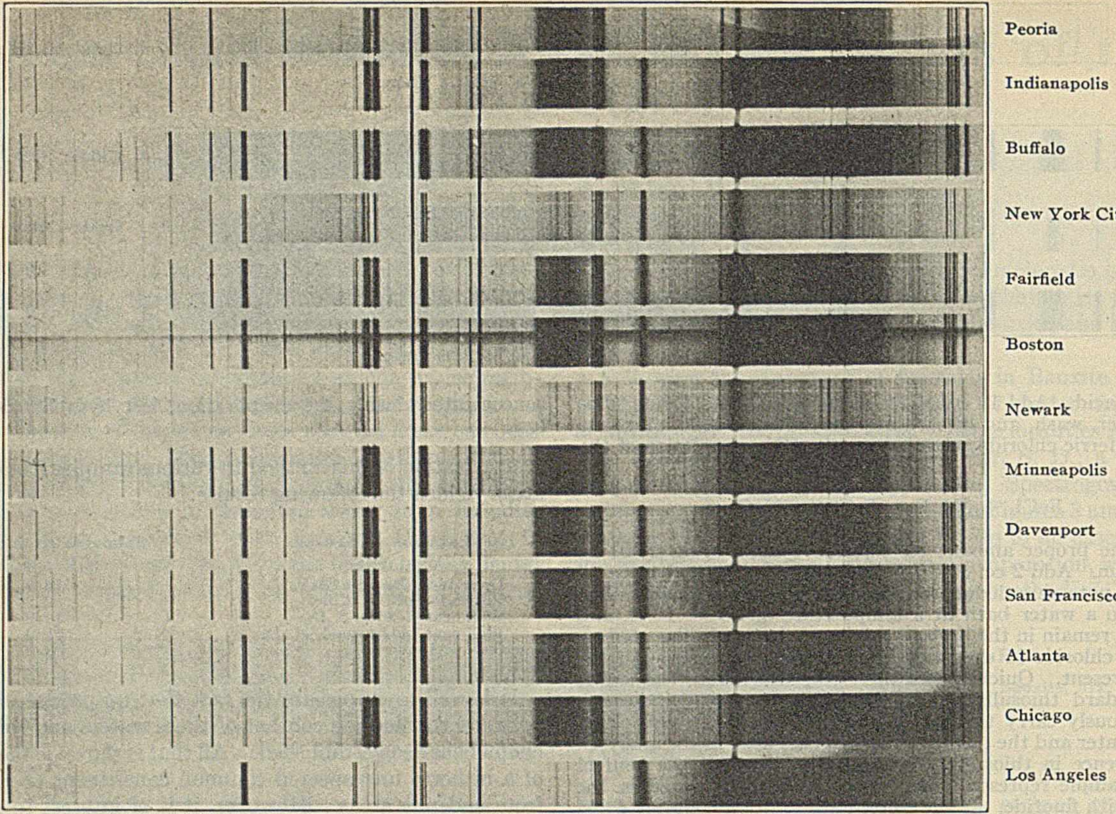

Figure 6—Spectrograms of Various Waters

nicipal supplies in the United States was undertaken with the results as shown in Table I.

Table I—Distribution of Fluorides in Water

Present	Not Present
Cincinnati, Ohio	Philadelphia, Pa.
Milwaukee, Wis.	Washington, D. C.
Birmingham, Ala.	Albany, N. Y.
Pittsburgh, Pa.	Fairfield, Conn.
E. St. Louis, Ill.	New York, N. Y.
Kansas City, Mo.	Boston, Mass.
Toledo, Ohio	Newark, N. J.
Cleveland, Ohio	Chicago, Ill.
Detroit, Mich.	Dallas, Texas
Peoria, Ill.	Atlanta, Ga.
Indianapolis, Ind.	
Buffalo, N. Y.	
Davenport, Iowa	
San Francisco, Calif.	
Minneapolis, Minn.	
Los Angeles, Calif.	

Figures 5 and 6 show spectrograms of the various waters. Quantitative examination of the waters covered in Table I shows the fluorine content in all cases to be less than 1.0 p. p. m.

The geographical distribution of the waters tested is shown in Figure 7, which brings out the interesting fact that traces at least of fluorides are to be expected west of the Appalachians. In no case were fluorides found in waters east of the Appalachians.

Again it is emphasized that no causal connection has been established between the occurrence of fluorides in these waters and the mottled-enamel defect. However, McClure and Mitchell (*3*) report the profound influence of fluorine in the diet upon bone structure. This effect is either the deposition of an apparently abnormal constituent in the bones or the abnormal deposition of a non-calcium constituent as evidenced by an increase in the ash of the bones above normal. They also specifically state that fluorine in the diet at certain levels has a peculiar effect upon the development of teeth. Pending establishment of causal connection between fluorine at certain concentrations in water and the mottled-enamel defect, water chemists might well give attention to the problem of the control of fluoride concentration in drinking water. Two questions are raised by this discovery of unsuspected amounts of fluorine in drinking water: First, what physiological effects may be produced by these fluorides? Second, what can water chemistry contribute to the concentration control of fluorides?

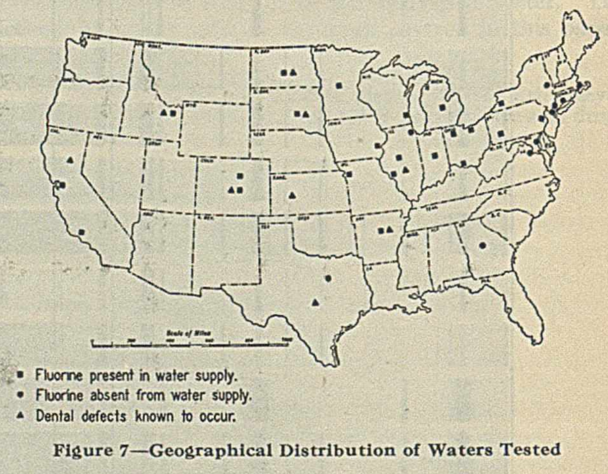

Figure 7—Geographical Distribution of Waters Tested

Acknowledgment

Acknowledgment is given to F. S. McKay of the Public Health Service for help in securing water samples from endemic areas.

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Corrosion of Metal Articles in Storage

Influence of Alkaline Surface Films[1]

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It is shown how the presence of small amounts of alkali deposited as an apparent uniform layer on metal articles serves to increase their freedom from tarnishing and rusting when stored in warehouses. Also, by choosing the most protective alkaline deposit, and adjusting and maintaining storage conditions in a state of constant control, it is possible to store articles for very many years without loss of luster. Costly storage loss is incurred by uncontrolled conditions seriously warrant investigation of the factors involved as described in this paper.

Speculatively, it is suggested that many cases occur where articles are being dipped in grease for storing, whereas investigation might prove that suitable alkaline treatment and control of warehousing would result in considerable saving of storage costs by utilizing a cheaper method.

SUCH mild steel articles as bolts, screws, hooks, and other repetition products of the hardware industry undergo varied and indefinite periods of storage in warehouses prior to dispatch to customers. Some articles are known to remain in stock for many years, while others may be only temporarily stored according to the market demand for such particular sizes or articles.

Following the final mechanical manufacturing operation, the articles are usually cleaned by washing, dried, and wrapped in cardboard and paper packages and transported to a warehouse for storing. Manufacturers generally provide a dry, heated warehouse to ensure that the articles retain their bright finish and luster, and are concerned with their liability to rust only from the commencement of manufacture until final dispatch from warehouse.

Being of readily corroded material, mild steel and wrought-iron articles are usually intended only for indoor or unexposed service, although even under these conditions tarnishing quickly occurs.

Under good warehousing conditions, articles are stored for many years without apparent tarnishing; on the other hand, cases arise when only 2 or 3 days' storage may be sufficient to reveal active corrosion taking place for which an immediate explanation is not readily obtainable. Occurrences of the latter involve frequent close inspection, rejection, recleaning, drying, and repacking, operations of considerable expense when considering the small price of the articles; yet it is essential that the articles present a bright lustrous finish, which is a factor seriously affecting salability.

Application of an antirust finish or film of grease is often economically impracticable on such small articles. Thus two problems arise—(1) to prepare the articles in such a way as to be least readily tarnished and (2) to provide storage conditions such as to give immunity from corrosion.

Omitting, for the present, consideration of applied grease films or other protective finishes generally known, it is essential that the steel articles present a smooth, dry, and lustrous surface. Having obtained this, the articles should be carefully packed in cardboard or paper cartons and deposited on shelves in the warehouse. Where control of the warehouse atmosphere is available, special ventilating apparatus, air filtration, and thermostatic regulation are in operation, since it is realized that pure clean dry and even warm air favors immunity from tarnishing. Close control of the wrappers and their testing for acidic and corrosive mineral constituents are also essential features of successful storage. After the final machining operation, a practice commonly followed is to immerse the articles in a hot solution of soda ash and soft soap in water, in order to remove acquired grease and dirt. This is followed by drying and finishing the articles by mixing with hot sawdust and revolving in steel barrels. The sawdust is then removed by sieving, and the steel articles are sorted by hand and placed in cartons for storage.

Upon one occasion, when a serious outbreak of rusting occurred, a batch was more thoroughly dried than usual by the same process. No improvement in corrosion resistance resulted, but on the contrary diminished. An even more thorough drying treatment again produced worse results, a phenomenon which convinced the writer that the general conception of drying (removal of moisture) as the fundamental basis of resistance was erroneous. Careful testing of lubricants, soda, soap, sawdust, water, wrappers, and atmosphere failed to produce evidence of corrosive agents likely to account for the trouble. This led to the beginning of the investigation of this problem. First of all, by laboratory duplication of the drying tests it was established that resistance to corrosion decreased with the intensity of drying. Upon consideration it appeared that during the washing operation in suds (soda-soap solution) the articles might become coated with the alkaline fluid, and that the effect of drying in sawdust might serve to remove the surplus solution and leave an adsorbed film of alkaline solution on the articles. This alkaline film would be expected to have mild protective properties against atmospheric corrosion. Disrupture or removal of this film would lead to early corrosion of the metal.

Nature of Film (Proof)

A length of bright drawn mild steel wire (carbon, 0.12 per cent) was turned up on a lath into a number of test pieces [2 inches by 2 inches (5.08 cm. by 5.08 cm.) diameter] using no cutting lubricant or fluid of any kind. After turning, the pieces were placed with aluminum forceps on a glass grid inside a desiccator containing phosphorus pentoxide. In all of the following tests, one test sample consisted of twelve individual test pieces or articles, and in every instance at least seven of the pieces behaved identically. In the case of samples taken from stock and from manufacturing operations, care was taken to select batches of one dozen made of the same material and produced at the same time under identical conditions. The manufactured articles themselves consisted of flat-head woodscrews, rivets, etc., of similar superficial area to the dry-turned test blanks. Reference to the respective samples used in these tests is as follows: (1) blanks, test pieces turned up dry as previously described; (2) treated blanks, test pieces as (1) but washed and dried as in the usual manufacturing processes; (3) machined, finished products taken direct from final machine operation without washing treatment, etc.; and (4) stock articles, finished products taken from the warehouse.

Samples of blanks, treated blanks, and stock were weighed and dried in an oven filled with nitrogen until they were of constant

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[1] Received February 26, 1931.

ultimate weight. The loss in weight of the treated blanks and stock was roughly one hundred times the loss sustained by the dry turned blanks.

Four rows of small test glasses of the same size were carefully cleaned and dried and an equal quantity of indicator solution put into each. The solution consisted of a 1 per cent solution of B. D. H. universal indicator in conductivity water. By means of a superimposed rack from which the test samples were suspended by silk threads, they were all simultaneously immersed in the indicator solution. The treated blanks and stock instantly changed the color of the solution to a violet color (pH 10.0, approximately), while the blanks only slowly changed the indicator solution toward alkalinity. This test was repeated with various sizes and shapes of stock samples with the same results.

Samples of blanks, treated blanks, and stock were placed in separate dried Pyrex flasks and a quantity of distilled water added to each. A few cubic centimeters of purest hydrochloric acid were added and the mixture allowed to stand for about half an hour. The solutions were then filtered and evaporated to dryness in platinum dishes, and tested chemically and spectroscopically. With both the treated blanks and stock samples, positive evidence of the presence of sodium compound was obtained.

Samples of blanks and treated blanks were exposed to indoor and outdoor atmospheres and daily observed for corrosion by visual inspection and weighings. In the exposure tests, shielded wooden cabinets were used to prevent direct or irregular currents of dust, rain, etc., impinging on the samples. The blanks began to tarnish and then rust almost immediately, while the treated blanks were only slowly affected but, when corrosion had set in, rusting progressed rapidly.

Samples of stock and treated blanks were placed in a desiccator containing phosphorus pentoxide for one day; a similar set of samples was dried in an oven containing nitrogen at 110° C.; and another similar set was taken when the previous samples were ready after drying. All these samples were submitted to the indoor and outdoor exposure tests, and those which had been subjected to drying processes gave earlier evidence of corrosion than the undried.

The foregoing tests appear to prove definitely the existence of an alkaline film as has been suggested, and the possession by the film of mild protective properties against corrosion.

Essentially the protective film consisted of an adsorbed layer of washings suds (soda-soap solution) which was no doubt somewhat concentrated upon the metal surface during the drying operation. During the exposure tests it was observed that tarnishing and rusting occurred evenly over a smooth surface, indicating somewhat uniform distribution of the alkaline layer. Being of small dimensions and weak properties, this film was readily influenced by external and adjacent conditions. First of all, different composition of soda-soap solutions would not be expected to yield films of similar protective nature. Again, the film, being of a soluble nature, would be very readily affected by atmospheric conditions, and adjacent materials, such as wrapping paper, might be expected to exert influence on the general stability and protective properties of the film.

Tests Showing Effect of Influencing Factors

COMPOSITION OF FILM—In these tests the sawdust was freshly obtained from yellow pine wood, and tested for freedom from acidic materials. The washing and drying tests were similar to the manufacturing operations used at the factory being investigated. After immersing the samples for five minutes in soda-soap solutions maintained at 90° C. (losses by evaporation were controlled by means of a condenser) and then shaking in proportional weights of sawdust for 10 minutes in revolving small iron drums, the samples were separated from the sawdust by sieving. Handling was by means of clean steel forceps, and the following materials were used:

Soda ash, tested at 58 per cent total alkali, traces only of chlorides, sulfates, etc., found.
Soft soap, pure commercial variety about 40 per cent total fatty acid, with 1.5 per cent free alkali.
Water: distilled.

Solutions were made covering the following ranges of composition:

(1) 0–10 per cent soda ash alone, as grams per 100 cc. water.
(2) 0–10 per cent soft soap alone, as grams per 100 cc. water.
(3) 0–10 per cent soda ash, to which 0–10 per cent soft soap was added, as grams per 100 cc. water.

Some of the solutions, particularly the more concentrated ones, were impractical, owing to separation, and only when the latter were clear solutions at operating temperature (90° C.) were they used; otherwise they were rejected.

Samples of blanks, machined, and stock, the last mentioned being recently finished products from a section of the factory in which no trouble was experienced, were treated with all the ranges of solutions. They were then dried and submitted to the exposure tests.

At the same time samples of good stock articles directly from a section of the factory in which no trouble was experienced were likewise submitted to the exposure tests with the previously mentioned test samples. Several of the individual good stock, blanks, and machined treated test pieces were sealed in test tubes containing phosphorus pentoxide, and these were used as standard brightness comparators—i. e., to note the tarnishing and rusting of the test pieces.

The exposure test comprised the following, using shielded cabinets in each case: laboratory atmosphere, indoor workshop atmosphere, and outside atmosphere. Using the standard brightness comparators, the relative rate and order of corrosion was followed by daily inspection and recording. As indicated previously, rusting proceeded at a rapid rate as soon as the appearance of brown rust was observed after the completion of the tarnishing stage. All three exposure tests produced practically the same relative order of corrosion of the test samples which had been treated with the ranges of solution previously mentioned.

It was concluded from the total results of these exposure tests that the following range of solution was the most effective under the circumstantial conditions of the tests:

Soda ash, 0.05–0.5 gram per 100 cc. water
Soft soap, 0.25–3.0 gram per 100 cc. water

The previous tests were then repeated with the same range of washing solutions and, by more carefully noting the relative order of corrosion, a solution composition was obtained which appeared to be the ideal and which is hereafter referred to as the standard-solution suds:

Soda ash, 0.2 gram per 100 cc. water
Soft soap, 1.5 grams per 100 cc. water

It is to be particularly noted that the results obtained apply only to the conditions and circumstances prevailing in the factory at the time this investigation was made, and no suggestion of general application is intended.

HARMFUL CONSTITUENTS AND VARIATION IN CONTACT MATERIALS—It is naturally to be anticipated that wrapping papers having acidic reaction or containing filling materials of corrosive nature, such as sulfites, chlorides, etc., would have adverse effects upon the wrapped articles. This factor had been realized some time before, and at the factory all types of wrappers were frequently tested, and were generally found to have a slight alkaline reaction (about pH 9). Cases of corrosive paper had been previously detected by chemical analysis, and the alkaline film was found to have no material protective action against such corrosive wrapping. The main factor associated with wrappers as well as with the surrounding atmosphere is that of humidity.

HUMIDITY AND DRYING ACTION—Samples of treated blanks (treated in the standard-solution suds) and of stock were submitted to the following atmospheric conditions for one week;

at the same time sheets of wrapping paper were also submitted to these conditions for the same length of time:

(1) Desiccator containing phosphorus pentoxide, at 60° F. (15.56° C.).

(2) Desiccator containing saturated solution of $CaCl_2.6H_2O$, at 60° F. (15.56° C.), relative humidity, 35 per cent.

(3) Warehouse, at 60° F. (15.56° C.), relative humidity, 60–70 per cent.

(4) Desiccator containing saturated solution $CaSO_4.5H_2O$, at 60° F. (15.56° C.), relative humidity, 99 per cent.

First of all it was observed that under conditions (1), (2), and (3) the samples were little, if any, tarnished by the week's treatment but, in the case of (4), tarnishing and rusting were visible. As in previous tests, standard brightness comparators were used in judging the degree of tarnishing. After the week's treatment the samples were taken out and submitted to exposure tests as before. The results showed the following order of resistance to corrosion, best to worst:

1—Samples exposed to treatment (3)
2—Samples exposed to treatment (2)
3—Samples exposed to treatment (4)
4—Samples exposed to treatment (1)

Samples of stock and treated blanks (using standard solution) were enclosed in the various treated wrappers and placed in the warehouse for one week, taken out and wrapper discarded, and the samples submitted to the usual exposure tests. The following order of resistance was obtained:

1—Samples wrapped in papers treated by (3)
2—Samples wrapped in papers treated by (2)
3—Samples wrapped in papers treated by (1)
4—Samples wrapped in papers treated by (4)

These tests appear to prove that a drying atmosphere has the effect of dehydrating and thereby disrupting the mild protective alkaline film. In a similar manner a wet atmosphere dilutes the film and renders the base metal readily accessible to atmospheric corrosion. These influences are exerted both directly and indirectly via the wrapping.

Atmospheric Impurities—In industrial localities the presence of sulfurous and other deleterious impurities of the atmosphere naturally affect successful storage of articles. In this particular warehouse a regulated system of ventilation existed with forced intake, air filtration, and humidifying control, by which it was possible to regulate the air so as to obtain and maintain it at about 60° F. (15.56° C.) and relative humidity of 60–70 per cent. Check tests were periodically taken against other impurities, but actually no remedying treatment was required in this instance although, elsewhere in the neighborhood of severe industrial fumes, further treatment would have been necessary.

Dust—The influence of dust from wrapping papers and other materials in the warehouse was shown to affect the corrosion of articles by the fact that shielded samples of various kinds corroded more readily than unshielded ones when submitted to warehouse conditions. In consideration of the results obtained it was decided to use wrapping paper of a strong and smooth variety which would not readily shed dust particles and which was not open pored. Likewise measures were taken to minimize the raising of dust of any description.

Moisture Content of Wrapping Papers—Samples of Kraft and Rope-Strip wrapping papers showed, on testing, a moisture content varying from 8.0–12 per cent as stored in the different paper storehouses. Upon exposing samples of these papers to the warehouse atmosphere, the papers singularly assumed a similar moisture content (8.9–9.1 per cent). Exposure to laboratory atmosphere likewise gave similar moisture content (10.8 to 11.5 per cent); while in a desiccator containing saturated zinc chloride solution (relative humidity, 10 per cent), a practically constant moisture content of 4.8 per cent was obtained. These tests, as well as those previously described, illustrate the important action that humidity can exert on wrapping papers and, in consequence, on the contained articles.

Shape of Articles—As previously stated, the blanks consisted of smoothly turned cylindrical pieces of steel, while the stock articles were wood screws, rivets, etc., having similar superficial area. In the exposure tests it was observed that the smooth surfaces—i. e., the heads and shanks of the finished products—suffered corrosion first, usually in a regular manner. Such places as depressions inside the threads were affected by corrosion last, apparently because of the presence of a larger amount of alkaline fluid; on the other hand, sharp corners and edges suffered early attack, owing to lack of protective film. It is also interesting to note that those portions of wrapped articles in direct contact with the wrapping paper were the parts first affected. This was particularly noted during the exposure tests in connection with humidity and dehydration.

An additional investigation carried out with the cutting fluid used in the machining operations of manufacture showed that articles initially in contact with dirty fluid were less resistant than articles produced with clean fluid, although given identical washing and drying treatment. This is no doubt due to the fact that contamination of the original metal surface with dirt is not wholly removed by washing.

Factors Governing Storage Problem

Upon consideration of the results of these investigations, it appears that storage of mild steel articles for a length of time requires coating the articles with a good protective film, and adjusting and maintaining conditions of handling and storage such that the film is apparently in a state of stability or undisturbed equilibrium.

Film—Upon immersing the articles in a nearly boiling solution of soda-soap suds, they acquired a certain amount of latent heat which was liberated when they were immediately put into the sawdust for drying. This liberation of latent heat resulted in a concentration of the washing solution on the metal surface, resulting in the alkaline film layer. In the particular experiment referred to the resisting power of sodium carbonate was enhanced by the addition of soap, which no doubt increased the stability of the film. Neither substance individually was as protective as when mixed, and from the experiments described, was derived a formula of maximum protection, consistent with the circumstances and conditions existing at the factory at the time of this investigation. Too concentrated solutions were not effective and were, in fact, the actual cause of trouble experienced at that time. In general, no doubt a definite alkalinity as pH is necessary, while physical characteristics of the film determine its stability.

Factors Affecting Stability of Film—In connection with both atmosphere and wrapping paper it has been indicated that drying or hydrating action seriously affects the duration of protection from corrosion. Dehydration by virtue of low humidity or relative unsaturation of the wrapping paper can result in actual dehydration and disruption of the protective film. On the other hand, under humid conditions, dilution of the film occurs with possible carriage of air, carbon dioxide, etc., toward the metal surface, thereby lessening the resistant power of the film. It appears that for longest protection from corrosion a state of physical and chemical equilibrium is necessary for the complete system:

$$\text{metal/film} \rightleftharpoons \text{wrapper} \rightleftharpoons \text{atmosphere}$$

and it is necessary to consider each of these factors in turn with respect to obtaining a state of final equilibrium. In the previous tests these factors were considered on rhe lines of investigation as described, and in consequence the following ideal conditions were resolved:

(1) Washing the articles in a solution of 0.2 gram soda ash and 1.5 grams soft soap per 100 cc. water.

(2) Maintaining warehouse at constant humidity and temperature—i. e., relative humidity, 65 per cent, temperature, 60° F. (15.56° C.).

(3) Preserving wrapping papers at same constant humidity and temperature as warehouse.

(4) Constant control of all materials and agents for possible impurities and variations likely to cause corrosion.

It should be noted that all conditions must be maintained strictly constant, otherwise the supposed equilibrium is disturbed.

Limitations

Naturally this form of protection is of a relatively small order and applies only to indoor storage conditions, particularly because of the solubility of the film. Also, the small magnitude of the film is well manifest when one considers that mere handling of the articles, especially by a person with perspiring hands, is quickly shown by the fact that corrosion sets in very early at the parts so handled.

Articles with very sharp edges and corners, such as deeply cut close-threaded bolts, etc., are not successfully protected in stock by the usual alkaline washing treatment and necessitate dipping in thin mineral oil, lanolin solution, or similar greasings. This appears to be associated with the fact that, as stated previously, sharp edges of metal are not coated with as efficient an adherent layer of alkali as the smoother surfaces.

Dependence of Reaction Velocity upon Surface and Agitation

II—Experimental Procedure in Study of Surface[1]

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The cube root law has been experimentally verified throughout a wide variety of conditions in the study of heterogeneous reaction kinetics in the solid-liquid dissolution system. Its experimental verification in the solid-gas system (naphthalene-air) has been made, and certain variables have been studied.

The study of a solid-liquid chemical system (alum-aqueous ammonia) has been described in which the effect of protective coatings upon the operation of the law was satisfactorily explained.

The work of other investigators upon certain autocatalytic reactions in solid-solid systems has been correlated to that contained in this paper.

THE experimental verification of the cube root law in a solid-liquid dissolution system has been accomplished under various types of agitation. Its special cases were investigated and shown to apply under many different experimental conditions. It was found that the cube root law was very general in its application, and a study of several other types of agitation systems was made—e. g., the solid-gas and solid-liquid chemical systems.

Verification of Cube Root Law

Direct Method—In most cases the change in weight of the solid was determined by removing it from the liquid and actually weighing it after each time interval. Considerable care was taken to maintain standard time intervals for its insertion and withdrawal, and these were kept negligible compared with the solution intervals. It was soon found that by the proper choice of materials, concentration, agitation, and amount of surface, the rate of solution could be varied over a wide range so that there was no necessity for working with a rate so fast that sensible errors would be introduced in the insertion and removal of the solid. When the solid was slightly volatile, as in the case of naphthalene, it was always weighed and handled in tightly stoppered weighing bottles.

Indirect Method—When the distribution of the dissolved solid was sufficiently uniform so that it was apparent that the loss in weight could be computed from the concentration change, the method of withdrawing and analyzing samples of the solution was employed. For the lower intensities of agitation this method is unsuitable, but it is sufficiently accurate for the higher intensities. For the verification of the law only the direct method was employed.

As both of these methods have long been used in studies of the rates of dissolution, their employment seemed to be justified. The direct method is obviously to be preferred whenever its use is possible, since the rate of distribution does not need to be considered. In all cases, unless otherwise stated, the liquid in contact with the surface of the particle was in motion. Complete stagnation was not desired, as this would be the condition for diffusion. Also, unless differently stated, the temperature used was 20° ± 0.2° C.

General Law, Equation 4—The general law may be illustrated by the following experiment, whose results may be found in Table I and Figure 1:

(a) *Conditions*—Naphthalene, alcohol (95 per cent), uniform free rotational agitation.

(b) *Method and Apparatus*—The container was a cylindrical weighing bottle, 4.1 cm. in diameter and 5.1 cm. high, with a capacity of 50 cc., stirred with a small L-shaped single paddle glass agitator of 150 r. p. m. The particle was a common ellipsoidally-shaped naphthalene mothball such as can be purchased at any drugstore. It had evidently been molded by tightly pressing the ground particles together while they were slightly warm. There were no airholes or irregularities in it at the start, nor did any appear during the run. It was well rinsed off with alcohol before using, in order to remove surface grains, etc. Its maximum length (L) was 21.5 mm., and its width (W) was 17.5 mm. Ratio $L:W = 1.23$. Weight (w_0) = 3.5324 grams. Area = 520 sq. mm. (approx.). Amount of alcohol used, 28.25 grams (35 cc. at 20° C.) which required a weight (w_s) of 1.8520 grams of naphthalene for saturation. The vessel was kept covered

Note—The solubility of naphthalene in 95 per cent alcohol was determined experimentally. The following data were obtained by use of the synthetic method: at 11.9° C., 20.1750 grams of alcohol dissolve 1.0 gram; at 14.8°

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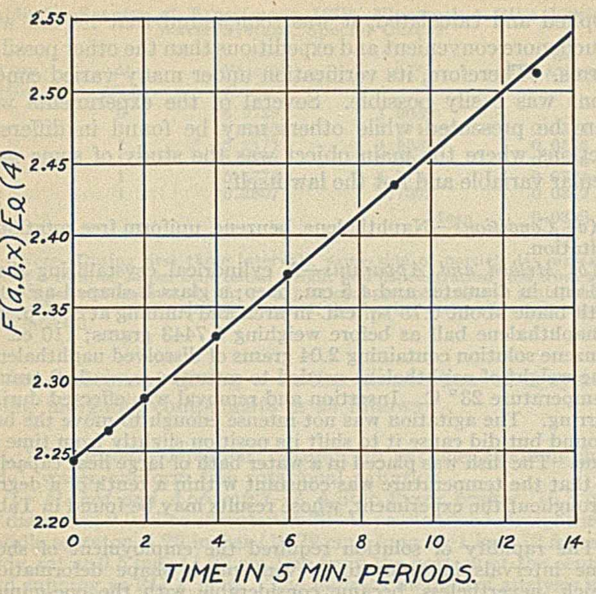

Figure 1—The General Law, Table I

C., 1.1 grams; and at 22.1° C., 1.4 grams of naphthalene. A curve plotted from these values gave a solubility of 6.56 grams of naphthalene per 100 grams of 95 per cent alcohol at 20° C. This region of the curve was also checked with a larger amount of alcohol and found to be correct.

during the run except at the times of insertion and withdrawal of the particle. Constant temperature was maintained by placing the vessel in a large-capacity water bath whose temperature did not vary appreciably. As the agitation was not intense enough to move the naphthalene ball, it was turned every 2 minutes by means of a very fine wire. In order for it to receive the same agitation during each period, it was always dropped in at the same spot. It was inserted and removed while stirring. After removal, it was rapidly dried between filter papers, gently blown with air for a moment, and then placed in a weighing bottle and weighed. These operations were all standardized so that they were uniformly executed.

Table I—Results of Experiment 111, Illustrating General Law

Time	Δt	Weight	$w^{1/3}$	Equation 8 $1/3$ K^{c}_{5}	Equation 6 $-2/3$ K^{c}_{5}	Equation 10 log K^{c}_{5}	Equation 4 $\tan^{-1}$ K^{c}_{5}
Min.	*Min.*	*Grams*					
0	0	3.5324	1.5229	.....	.....	.....	.....
5	5	3.4336	1.5086	0.0143[a]	0.0082[a]	0.0238[a]	0.01942[a]
10	5	3.3254	1.4926	0.0151	0.0088	0.0257	0.02124
20	10	3.1481	1.4656	0.0143	0.0086	0.0252	0.02125
30	10	2.9920	1.4410	0.0136	0.0084	0.0249	0.02139
45	15	2.8060	1.4104	0.0125	0.0079	0.0240	0.02110
65	20	2.6177	1.3782	0.0111	0.0073	0.0227	0.02051
			Mean	0.0133	0.0082	0.0245	0.02110
Av. deviation from mean, or av. D/M				9.1%	5.7%	3.7%	1.1%

[a] Omitted in calculation for mean.

Note—K^{c}_{5} is equal to the $(Ka^2)/V$ in the equation; for the significance of the *c* as a superscript see next experiment. Amount of naphthalene dissolved, 0.9147 gram, or about 26 per cent of its initial weight. Equation numbers (4, 6, 8, 10) refer to those of the corresponding equations in the theoretical part of this discussion (*5*).

The concentration of the dissolved naphthalene rose from a 0 to a 49 per cent saturated solution. This manner of describing the concentration will be found most suitable for comparative purposes in this kind of work (*8*). At the end, the naphthalene ball showed a slight change in shape, having then a length of 19 mm. and a width of 16 mm. Ratio $L:W = 1.19$. When compared with the ratio of 1.23 at the start, it shows a slight rounding which is reflected in the decreased value of the constant and is due to a decrease in the specific surface. Sharpening, on the other hand, involves an increase of the specific surface, and therefore increases the value of the constant. While the naphthalene balls used in this work could not be called strictly homogeneous in structure, they were always found to be without air bubbles, holes, or cracks of any kind, no matter how thin a section was prepared. It was not possible to correlate any irregularity of action with their structural composition. The particles of which they were composed were crystalline in character.

In the columns of constants which are calculated according to the equations designated, there is a comparison of the closeness with which each of the equations fits the experimental data. The first value in each case has been omitted from the mean on account of the common uncertainty regarding the first determination, due to possible initial surface irregularities which sometimes cannot be eliminated. If we assume that the magnitude of the average deviation from the mean is a measure of the relative closeness with which a given formula fits the observed values, the interesting effect of introducing the concentration into the formulas is easily noticeable. Equation 8, where the concentration is considered as constant, is, of course, out of the question. The data show clearly that the application of Equation 4 is justified although the logarithmic formula is also close. However, since the latter is based on the assumption of constant surface, this closeness must be incidental, as the next section will show.

No further attempt will be made to describe the agitation, first, on account of the difficulty of specifying it, and second, because it is felt that its uniformity is more important than its type. As will be seen later, the wide variety of types through which the law holds confirms this conclusion.

Finally, the laborious calculations involved in the use of Equation 4 acted as a deterrent in its general use in the study of other variables so that the more easily calculated special cases were chosen for the remainder of the work.

SPECIAL CASE 1, EQUATION 6, $W_0 = W_s$—This case may be illustrated by the following experiment, with results given in Table II and Figure 2.

(*a*) *Conditions*—Naphthalene, alcohol (95 per cent), uniform free rotational agitation.

(*b*) *Method and Apparatus*—A 250-cc. Pyrex beaker; a small glass agitator running at 518 r. p. m.; a naphthalene ball similar to that used in the last experiment, length 21.5 mm., width 17.5 mm., ratio $L:W = 1.23$. There was no motion of the ball due to the agitation, but it was periodically turned with a wire as in Experiment 111 and the same general precautions were observed. Insertion and removal were effected without stopping the stirrer. The weight of the naphthalene ball, $w_0 = w_s = 3.8752$ grams. The weight of alcohol taken was 59.00 grams, as this was the amount of alcohol just saturated by this weight of naphthalene at 20° C.

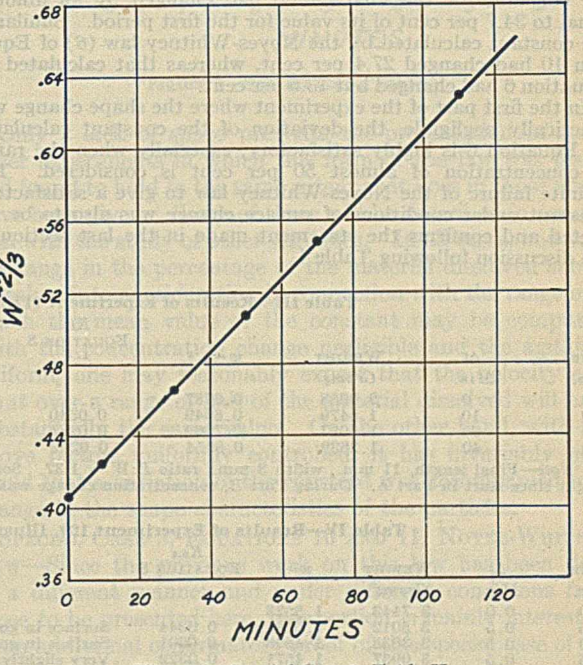

Figure 2—Special Case 1, Table II

In order to show the effect of a change in shape, the agitator in Experiment 112A was replaced by a larger one running at 290 r. p. m. This produced a more intensive agitation and caused the ball to roll around continually. In this case it was necessary to stop the agitator each time in order to remove the ball, but the time required for this operation was only 2 or 3 seconds and was negligible in comparison with the total length of the time interval. With these exceptions, everything else was the same as in the first part of the experiment. The results are given in Table III.

Table II—Results of Experiment 112A, Illustrating Special Case 1

TIME	Δt	WEIGHT	$w^{-2/3}$	K^p_{10} EQUATION 8 $1/3$	K^p_{10} EQUATION 10 N. W. L.	K^p_{10} EQUATION 6 $-2/3$
Min.	*Min.*	*Grams*				
0	0	3.8752	0.4053	....	.....	....
10	10	3.6041	0.4254	0.0375	0.00210	0.0201
30	20	3.1477	0.4656	0.0338	0.00196	0.0201
50	20	2.7691	0.5071	0.0306	0.00185	0.0207
70[a]	20	2.4628	0.5483	0.0269	0.00169	0.0206
110	40	2.0058	0.6287	0.0223	0.00148	0.0201
			Mean	0.0302	0.00181	0.0203
			Av. *D/M*	26%	10.3%	1.2%

[a] Ball at this point gave length of 18 mm. and width of 14.5 mm. Ratio $L:W = 1.24$. Shape practically same as at start. It had lost 36.5 per cent of its weight. At end of final time interval it had lost 48.5 per cent of initial weight and solution concentration was similarly 48.5 per cent saturated. At end, ball was quite smooth and showed no etching or corrosion except for one barely noticeable pit about 1 mm. in diameter and 0.5 mm. deep. Any change in shape from original was inappreciably slight.

Note—Values of constants are obtained by progressively calculating from one period to the other—e. g., $K^p_{10} = 0.5(w^{-2/3}_{30} - w^{-2/3}_{10})$, etc., and will be called the "progressive constants" (K^p), in contrast to the "cumulative constants" (K^c), which are obtained by calculating each period independently from zero time and which were used in the last experiment—e. g., $K^c_{10} = {}^1/_7(w^{-2/3}_{70} - w^{-2/3}_0)$. A mean of the K^c values tends to represent the experiment as a whole when compared to others, while K^p values show better how action progresses in each case in particular. Hereafter K^p values will be used without superscript unless otherwise designated.

The predominating change of shape was in the direction of rounding, especially on the sides where the band about the midpart of the ball disappeared completely. This was due to the rolling of the ball about its major axis and its considerable wobbling. The final body was tending toward a spindle-shaped figure. Because of these effects, the $L:W$ ratio does not indicate what happened in the main change of shape that occurred. This shows that the two types of shape change, rounding and sharpening, can occur simultaneously. The constants for the different equations are tabulated, and it is interesting to compare the relative percentages of change in their values caused by the change of shape in this part of the experiment. For Equation 8 the constant for the final period had changed by an amount equal to 34.7 per cent of its value for the first period. Similarly, the constant calculated by the Noyes-Whitney law (*6*) of Equation 10 had changed 27.4 per cent, whereas that calculated by Equation 6 had changed but 13.5 per cent.

In the first part of the experiment where the shape change was practically negligible, the deviation of the constant calculated by Equation 6 is highly satisfactory, especially when the range of concentration of almost 50 per cent is considered. The definite failure of the Noyes-Whitney law to give a satisfactory constant under conditions of surface change was also to be expected and confirms the statement made in the last section of the discussion following Table I.

Table III—Results of Experiment 112B, Illustrating Change of Shape in Special Case 1

TIME	Δt	WEIGHT	$w^{-2/3}$	K_{10} EQUATION 8 $1/3$	K_{10} EQUATION 10 N. W. L.	K_{10} EQUATION 6 $-2/3$	REMARKS
Min.	*Min.*	*Grams*					
0	0	2.0058	0.6287	....	.....	....	Still in good shape
10	10	1.8479	0.6649	0.0340	0.00237	0.0362	Band on side rounding off; no pitting
30	20	1.6027	0.7302	0.0284	0.00206	0.0326	Band practically gone but still smooth
70	40	1.2639	0.8554	0.0222	0.00172	0.0313	Same; elliptical in cross-section; not pitted

Note—Final length, 11 mm., width 8 mm.; ratio $L:W = 1.37$. Solution was now 67.5 per cent saturated, and particle had lost 67.5 per cent of initial weight since start in Part A. During Part B, concentration change was almost 20 per cent—i. e., from 48.5 to 67.5 per cent.

Table IV—Results of Experiment 109, Illustrating Naphthalene-Benzene System, Special Case 2

TIME	Δt	WEIGHT	$w^{1/3}$	$K_{0.5}$ EQUATION 8	REMARKS
Min.	*Min.*	*Grams*			
0.0	0.0	3.7443	1.5528	....	
0.5	0.5	3.5012	1.5184	0.0344	Surface in good condition
1.0	0.5	3.3038	1.4893	0.0291	Surface in good condition
1.5	0.5	3.0937	1.4571	0.0322	Very slightly pitted, all very small
2.0	0.5	2.8951	1.4251	0.0319	Several pits slightly deeper
2.5	0.5	2.7065	1.3936	0.0326	Slightly more pitted; some 0.5 mm. deep
3.5	1.0	2.3682	1.3329	0.0304	Still more corrosion and shape altering
4.5	1.0	2.0312	1.2664	0.0333	Indented badly; one end much pitted and shape changing fast, especially one end
(*a*)			Mean	0.0319	
			Av. *D/M*	4.0%	
5.5	1.0	1.7062	1.1949	0.0358	Pitting and shape considerably worse
6.5	1.0	1.4026	1.1193	0.0378	Estimate two-thirds of surface not pitted, but remainder very bad with shape changed markedly

Note—Initial concentration, 3.3 per cent saturated; at point *a*, 4.5 per cent saturated; final, 7.2 per cent saturated. Weight loss up to *a*, 45 per cent; total weight loss, 63 per cent.

Comparing the rate in the first part with the initial rate in the second part, the increased agitation in the second part is shown to have almost doubled the velocity of dissolution. This quick response to changes in agitation indicates the importance of keeping the agitation uniform during the run.

SPECIAL CASE 2, EQUATION 8, NO CONCENTRATION CHANGE—As this form of the general law is the most easily applied and calculated, it was soon found that its use was much more convenient and expeditious than the other possible forms. Therefore, its verification under many varied conditions was easily possible. Several of the experiments will here be presented while others may be found in different sections where the main object was the study of some particular variable and not the law itself.

(*a*) *Conditions*—Naphthalene, benzene, uniform free rotational agitation.

(*b*) *Method and Apparatus*—A cylindrical crystallizing dish, 7.6 cm. in diameter and 4.5 cm. deep; a glass L-shaped agitator with blade about 0.75 sq. cm. in area and running at 83 r. p. m.; a naphthalene ball as before weighing 3.7443 grams; 110 cc. of benzene solution containing 2.04 grams of dissolved naphthalene. The weight of naphthalene needed to saturate, $w_s = 61.0$ grams. Temperature 23° C. Insertion and removal was effected during stirring. The agitation was not intense enough to move the ball around but did cause it to shift its position slightly from time to time. The dish was placed in a water bath of large heat capacity so that the temperature was constant within a tenth of a degree throughout the experiment, whose results may be found in Table IV.

The rapidity of solution required the employment of short time intervals in order to prevent much shape deformation, which, nevertheless, became considerable with the one-minute periods in the latter parts of the experiment. In the case of very soluble solids, the difficulty of pitting and surface increase is always encountered, especially if the saturation concentration is low. The effect of this is easily seen in the constant after the point *a* was reached. The extent of pitting tends to increase rather than to decrease as the dissolution proceeds. This is particularly true if the condition of flow of the solvent around the solid tends to stagnancy and the solid is relatively quite soluble in the liquid. This is very probably the reason for carrying on the previous work on solution with either slightly soluble solids or, if the more soluble solids were used, highly concentrated solutions. This property must not be confused with the production of the so-called etch figures which are due to the anisotropic solubilities of the solid itself.

SYSTEMS USING INORGANIC COMPONENTS—An example of a system whose components are inorganic compounds will next be given with results shown in Table V and Figure 3.

(*a*) *Conditions*—Very irregular crystal particle of blue vitriol, water, uniform free rotational agitation.

(*b*) *Method and Apparatus*—A 100-cc. Pyrex beaker; the same agitator as in Experiment 109, but running at 152 r. p. m. The particle did not move. It was rinsed and dried before use and possessed no visible checks, cracks, or irregularities of composition. It was always placed in the same spot in the beaker for each interval, and insertion and removal were effected during stirring. A 70-cc. portion of water at 25° C. was used. The weight of $CuSO_4.5H_2O$ needed for saturation was 15.9 grams.

Table V—Results of Experiment 108B, Illustrating Blue Vitriol-Water System, Special Case 2

TIME	Δt	WEIGHT	$w^{1/3}$	K_1 EQUATION 8
Min.	*Min.*	*Grams*		
0	0	6.9229	1.9059	....
1	1	6.5540	1.8714	0.0345
2	1	6.2171	1.8388	0.0326
3	1	5.8893	1.8058	0.0330
4	1	5.5772	1.7734	0.0324
5	1	5.2607	1.7392	0.0342
			Mean	0.0333
			Av. *D/M*	2.4%

Note—During first three intervals, same side of particle lay upward. It lost a total of 24 per cent initial weight and concentration rose from zero to 10.4 per cent saturated. At end, particle appeared to have initial shape except that one tip was sharply serrated, this having occurred largely during final interval.

An experiment giving a further illustration of a system using inorganic components is as follows:

(*a*) *Conditions*—Irregular, natural salt particles (sodium chloride), water, uniform free rotational agitation.

(*b*) *Method and Apparatus*—A 4-liter Pyrex beaker, 15.5 cm. in diameter; 2.0 kilos of water at 20° C.; a standard straight iron paddle agitator, 4.25 inches (10.79 cm.) long by 1 inch (2.54 cm.) wide, set at 0.5 inch (1.27 cm.) up from the bottom at the center, and running at 241 r. p. m. The indirect method of analysis was used—i. e., samples of approximately 20 cc. of solution were taken from the top by dipping at a point halfway from the center to the wall of the beaker. The weight remaining undissolved was calculated from the percentage of solids obtained on evaporation of weighed amount of these samples. The salt used was a carefully sieved (twice by hand) 3–4 Tyler standard sieve cut of a natural mined rock salt. The weight taken was 40.0 grams. On the average this amount would contain 177 particles of an average weight of 0.2230 gram. Of this weight there was 0.479 gram of insoluble material for which a correction was made. The salt was not otherwise treated before use.

Table VI—Results of Experiment 53, Illustrating Rock Salt-Water System, Special Case 2

TIME	Δt	CONCENTRATION	WEIGHT DISSOLVED (20 × CONC.)	AMT. DISSOLVED	WEIGHT	$w^{1/3}$	K_{15} EQUATION 8
Sec.	*Sec.*	*Grams/100 Grams H₂O*	*Grams*	%	*Grams*		
0	0	0.000	0.00	0.0	39.521	3.4062	.....
15[a]	15	0.390	7.80	19.7	31.721	3.1655	0.2407
30	15	0.758	15.16	38.4	24.361	2.8989	0.2666
45	15	1.048	20.96	53.0	18.561	2.6477	0.2512
60	15	1.294	25.88	65.5	13.643	2.3895	0.2582
77	17	1.537	30.74	77.7	8.783	2.0632	0.2880
90	13	1.676	33.53	85.0	5.993	1.8168	0.2840
105	15	1.802	36.05	91.2	3.475	1.5146	0.3022
120	15	1.894	37.89	96.0	1.629	1.1766	0.3380
135[a]	15	1.955	39.11	99.0	0.411	0.7435	0.4331
		From 0 to 85% dissolved, mean (0 to 90 sec.)					0.2647
						Av. *D/M*	5.5%
		From 0 to 65% dissolved, mean (0 to 60 sec.)					0.2541
						Av. *D/M*	3.3%

[a] Values are in doubt, because of uncertainty about exact zero time of establishment of régime which was to predominate through larger part of dissolution, and because of small differences in analyses.

The agitation here was very vigorous with a vortex of approximately 3.75 inches (9.52 cm.) being obtained. The particles moved about very rapidly, circling around at a distance of 1 or 2 inches (2.54 or 5.08 cm.) from the center. After about 75 seconds they became so small that they began to travel near the outer edge of the beaker, and at 105 seconds a considerable number of them were above the agitator blade. This probably accounts for the faster rate and the higher value of the constant observed for this time. Such irregularities may be expected in the case of very high intensities of agitation, and especially with the use of the indirect method of analysis. For this reason the later values should not be taken too seriously. However, it is seen in Table VI that up to the point where more than 60 per cent of the solid is dissolved, the constant holds quite satisfactorily. It can also be added that this experiment is quite a severe test of the application of the law because of its freedom from the imposition of artificial conditions, since it represented the actual, ordinary operation of dissolving a solid in the common laboratory and plant manner.

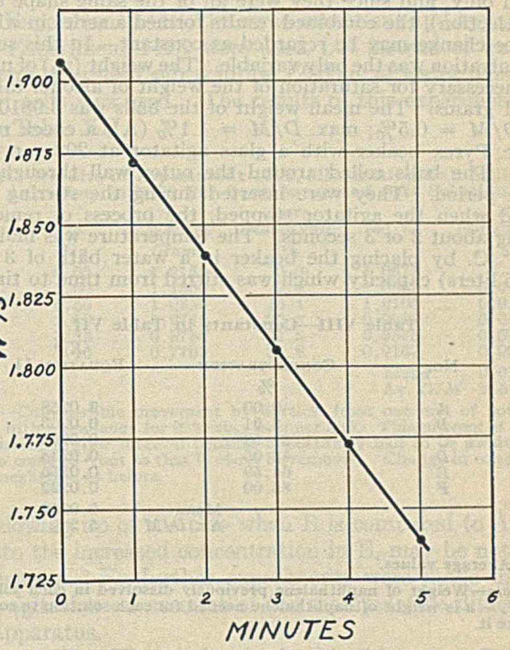

Figure 3—Special Case, Table V

Only a lack of space prevents the presentation of many other experiments in which this form of the law was tested and found to hold to the same extent as it does in those which have been given. Some of these will be described in connection with the study of other variables. In all cases, however, the range in the percentage of the material dissolved should be taken into consideration in connection with the range over which the mean value of the constant may be computed. With the concentration change negligible and the agitation uniform, one may reasonably expect that the velocity constant over a range of half of the material dissolved will have substantially the same value. On the other hand, with the above factors uniformly controlled, it has invariably been found that a variation of the constant was accompanied by a change in the shape characteristics of the particles.

SPECIAL CASE 3, EQUATIONS 10 AND 11, NOYES-WHITNEY LAW—Since the previous work on this law has been done in a different manner and under different conditions from those to be presented here, this portion is mainly interesting as an additional confirmatory proof of this special case of the more general law of Equation 4.

(*a*) *Conditions*—Naphthalene balls, alcohol (95 per cent), uniform free rotational agitation.

(*b*) *Method and Apparatus*—A number of naphthalene balls were prepared and weighed, and eight of them were selected

Table VII—Results of Experiment 115, Illustrating Naphthalene-Alcohol System, Special Case 3, N. W. L.

No.	CONCENTRATION	a	$\overset{n}{(w_s - a)}$	w_0	Δt	w	$w_0 - w$	$-\overset{n}{(w_0 - w)}$	K_3 EQUATION 11
	%	*Grams*		*Grams*	*Min.*	*Grams*			
A′	0.00	0.0000	5.2611	3.9868	5	3.7130	0.2738	4.9873	0.0242
A″	0.00	0.0000	5.2611	3.9343	5	3.6108	0.3235	4.9376	0.0275
B	8.61	0.4531	4.8080	4.0130	5	3.7301	0.2829	4.5251	0.0263
C	21.53	1.1328	4.1283	3.9617	7	3.6242	0.3375	3.7908	0.0264
D	43.05	2.2654	2.9957	3.9913	10	3.6799	0.3114	2.6843	0.0238
E	64.59	3.3984	1.8627	4.0024	15	3.7126	0.2898	1.5729	0.0245
E″	64.59	3.3984	1.8627	3.9869	5	3.8762	0.1107	1.7520	0.0266
F	85.00	4.4719	0.7892	3.9716	15	3.8595	0.1121	0.6771	0.0222

whose weights were very close to each other. Each one was allowed to dissolve for a short period of time in a solution of naphthalene in alcohol. Six different solutions were prepared for this purpose, each having a different concentration. Each of the solutions was made up from 80.2 grams of 95 per cent alcohol in which the calculated amount of naphthalene had been dissolved. The solutions chosen had the following concentrations in terms of per cent saturation: 0, 8.61, 21.53, 43.05, 64.59, 85.0. Each solution was treated with one naphthalene ball for one period only, and since they were all of the same shape and size (by selection), the combined results formed a series in which the surface change may be regarded as constant. In this series the concentration was the only variable. The weight (w_s) of naphthalene necessary for saturation of the weight of alcohol taken was 5.2611 grams. The mean weight of the balls was 3.9810 grams. Av. D/M = 0.5%; max. D/M = 1.1% (A″, a check run). A 250-cc. Pyrex beaker with a glass agitator at 292 r. p. m. was used. The balls rolled around the outer wall throughout the entire period. They were inserted during the stirring but removed when the agitator stopped, the process of removal requiring about 2 or 3 seconds. The temperature was maintained at 20° C. by placing the beaker in a water bath of 3 gallons (11.35 liters) capacity which was stirred from time to time.

Table VIII—Constants in Table VII

No.	Concentration		K_5[a] Equation 11
	%		
A	0.00		0.0258
B	8.61		0.0263
C	21.53		0.0264
D	43.05		0.0238
E	64.59		0.0256
F	85.00		0.0222
		Mean	0.0250
		Av. D/M	5.2%

[a] Average values.

Note—Weight of naphthalene previously dissolved in each solution, a; $n = w_s - a$ is weight of naphthalene needed for each solution to completely saturate it.

While it is realized that the assumption of constant surface conditions is not rigidly justified, it is felt that the approximate constancy obtained must be considered in connection with the very wide range of concentrations studied. The experiment as it was carried out also involved a comparison between different particles, which very likely accounts for some of the deviations obtained (*1, 2, 3, 4, 6*). Moreover, it might be well to add that the precision obtained throughout this entire work upon the surface effect compares excellently with that reported by other investigators who have worked in this field.

Table IX—Results of Experiment 125, Illustrating Impeded Rotational Agitation (*6*)

Time	Δ*t*	Weight	Amt. Dissolved	$w^{1/3}$	K_1 Equation 8	Remarks
Min.	*Min.*	*Grams*	%			
0	0	40.0000	0.0	3.4199	....	Several particles above water
1	1	31.0795	22.2	3.1440	0.2759	All now under water
2	1	22.9673	42.5	2.8425	0.3015	
3	1	16.2972	59.5	2.5353	0.3072	
4	1	11.0569	72.3	2.2278	0.3075	
5	1	6.9613	82.5	1.9094	0.3184	Many now with sharp edges
				Mean	0.3021	
				Av. D/M	3.5%	

Special Case 4, Shape Constant, Surface Variant, Rate per Unit Area—Merely in order to confirm the old and accepted principle that with other things equal the rate of dissolution is directly proportional to the area exposed to the solvent action, an experiment was run using two different known areas, and their respective losses in weight per unit area per minute were determined. The materials were naphthalene and alcohol, and the two surfaces were circular and plane. Further details will not be given here,[4] but the results from the two areas checked each other quite satisfactorily, showing that, other things being equal, the rate of dissolution is strictly proportional to the first power of the surface.

Thus, with the agitation uniform and the shape constant, the velocity of solution will vary directly as the surface changes, and this is one of the facts upon which the derivation of the general law has been based.

Other Types of Agitation

The intent of this section is to show that the operation of the law is not limited to any particular type of agitation, provided that it is uniformly periodic in its nature. Because of its simplicity and convenience, the law in the form of the special case 2, Equation 8, of no concentration change, will be used.

Impeded Rotational Type—One way in which this type of agitation may be obtained is to hold the solid in a screen or basket-like container which may be suspended or immersed in the liquid. In this case the flow of the fluid is impeded as it passes through the stationary mass. Another way is to place baffles in the container but still allow the solid to move freely. This will not be considered here but will be described later under the larger scale experiments. An experiment which will illustrate the operation of the law in this type of agitation is Experiment 125, described as follows and with results given in Table IX:

(*a*) *Conditions*—Irregular salt particles, water, impeded rotational agitation.

(*b*) *Method and Apparatus*—A 4-liter Pyrex beaker; a standard straight iron paddle agitator, 3.75 inches (9.52 cm.) long and 1 inch (2.54 cm.) wide, set at center and 0.5 inch (1.27 cm.) off the bottom, running at 82 r. p. m.; 4.0 kilos of water at 20° C.; 40.00 grams of irregular salt particles; a 2–3 mesh Tyler standard screen cut with an approximate average weight of 0.5 gram. They were held in a hemispherical screen, 2 inches (5.08 cm.) in diameter and of about 15 mesh, and lowered into the water at the top at exactly the same spot for each time interval, and were inserted and removed during stirring. On removal, the screen and its contents were instantly submerged in alcohol, and then washed, decanted, dried, and weighed.

Tumbler Type—Experiment 130A illustrates this type of agitation. Results are found in Table X.

(*a*) *Conditions*—Irregular salt particle, water.

(*b*) *Method and Apparatus*—An ordinary 8-inch (20.32-cm.) test tube was used as the container. A board was provided with two clamps into which the test tube could be quickly inserted and removed. This board was mounted on an axis so that when the test tube was in the clamps, the uniform rotation of the board which was geared to a small motor, turned the test tube end over end, so that its contents tumbled from one end to the other as the rotation proceeded. A 25-cc. portion of water at a temperature of 25° C. was pipetted into the test tube for each time interval. This amount occupied about 35 per cent of the available volume in the stoppered tube, so that during the rotation considerable turbulence was originated. The rotator was steady and ran at the rate of one turn every 11 seconds. The runs were made at room temperature, or 25° C.

The operation which was practiced until it was well standardized was as follows: With the water in the test tube which was in position in the clamps, the particle of salt was dropped in, the stopper inserted, and the rotator started. At exactly four rotations (44 seconds) the rotator was stopped, the tube removed, unstoppered, and its contents dumped on a screen from which the particle fell into a beaker of alcohol. From here it was washed by decantation in the alcohol, and dried and weighed in the usual manner. The operations involving the removal of

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[4] Details of this experiment may be found in the original dissertation by the junior author.

the particle took about 3 seconds, and this was regarded as part of the time interval. Only one particle was used, and it weighed 1.2943 grams.

Table X—Results of Experiments Illustrating Tumbler Type of Agitation (*6*)

TOTAL TURNS	ΔT TURNS	WEIGHT Grams	AMT. DISSOLVED %	$w^{1/3}$	K_{4T} EQUATION 8
		EXPERIMENT 130A[a]			
0	0	1.2943	0.0	1.0898	....
9	9	0.9017	32.4	0.9661	0.0550
13	4	0.7440	42.5	0.9061	0.0600
17	4	0.6103	52.5	0.8482	0.0579
21	4	0.4924	62.0	0.7897	0.0585
25	4	0.3895	69.5	0.7303	0.0594
29	4	0.3034	76.5	0.6719	0.0584
				Mean	0.0582
				Av. *D/M*	2.2%
		EXPERIMENT 130B[a,b]			
0	0	1.2687	0.0	1.0826	....
4	4	1.0714	15.6	1.0233	0.0593
8	4	0.9028	29.0	0.9665	0.0568
12	4	0.7539	40.5	0.9101	0.0564
16	4	0.6196	51.5	0.8525	0.0576
20	4	0.4991	60.6	0.7932	0.0593
24	4	0.3952	69.0	0.7339	0.0593
28	4	0.3080	76.0	0.6753	0.0586
				Mean	0.0582
				Av. *D/M*	1.8%
		EXPERIMENT 131A[c]			
0	0	5.0000	0.0	1.7100	....
4	4	3.2568	35.0	1.4822	0.2278
8	4	1.9402	61.5	1.2472	0.2350
				Mean	0.2314
				Av. *D/M*	1.5%
		EXPERIMENT 131B[d]			
0	0	5.0000	0.0	1.7100	....
4	4	3.7439	25.0	1.5527	0.1573
8	4	2.6825	46.4	1.3894	0.1633
12	4	1.8138	63.7	1.2195	0.1699
16	4	1.1498	77.0	1.0476	0.1719[e]
24	8	0.4271	91.0	0.7531	0.1472[f,g]
				Mean	0.1656
				Av. *D/M*	3.2%

[a] No particular change of shape.

[b] Conditions same as in 130A but used one particle whose shape differed a little from that used before.

[c] Conditions same as for other experiments but 35 cc. of water used each time and instead of one particle, 5 grams of a 4–6 mesh Tyler screen cut of salt that contained 62 particles used. Mechanical losses at end of second time interval caused experiment to be stopped.

[d] Same conditions and apparatus; 5 grams of a 3–4 mesh Tyler screen cut out of same salt containing 21 particles.

[e] Some crystals stuck to wall on last two turns.

[f] Estimated that three-fourths of particles stuck to walls on each turn. Considerable variation in size at end probably due to fact that many particles did not drop down from wall of tube when it turned. This did not happen in other experiments because particles did not get small enough. For this reason, last value is omitted from mean.

[g] Omitted in calculation of mean.

These four experiments were given because it was felt that if the law continued to hold under these conditions, it had survived a rather severe test, because of the more or less random nature of the type of agitation involved. The results, in spite of the operative difficulties encountered in the last one, are considered quite satisfactory.

BALL MILL TYPE—An example of this type is Experiment 144A, illustrated by Table XI.

(*a*) *Conditions*—Irregular salt particle, water.

(*b*) *Method and Apparatus*—An ordinary 5-pound (2.26-kg.), wide-mouthed chemical bottle was fastened to the rotator board used in the preceding experiments in such a way that it rotated horizontally about its central axis in the manner of a ball mill. Two hundred and fifty cubic centimeters of water were placed in the bottle for the entire experiment. This amount of liquid gave a depth of about 1 inch (2.54 cm.) at the deepest point, and its surface had a width of 4 inches (10.16 cm.) throughout the length of the bottle—i. e., about 6.5 inches (17.51 cm.). The bottle was rotated uniformly at 140 r. p. m., imparting a rockerlike motion to the salt particle. The action consisted in the particle periodically rising and sliding down the bottle wall. The bottle was tipped slightly toward the open mouth so that the particle tended to travel from one end to the other. It was inserted and removed by means of a pair of wide-faced tongs without stopping the agitation. After its removal it was immediately dropped into alcohol, and washed and dried in the usual manner. The temperature was maintained at 20° C. The particle weighed 1.0795 grams.

Table XI—Results of Experiment 144A, Illustrating Ball Mill Type of Agitation

TIME Min.	Δt Min.	WEIGHT Grams	AMT. DISSOLVED %	$w^{1/3}$	$K_{0.5}$ EQUATION 8
0.00	0.00	1.0795	0.0	1.0258	....
1.00	1.00	0.6945	35.0	0.8856	0.0701
1.50	0.50	0.5503	49.0	0.8195	0.0661
2.45	0.95[a]	0.3287	69.5	0.6901	0.0680
				Mean	0.0680
				Av. *D/M*	1.9%

[a] 57 seconds. General shape about same with some rounding. Concentration change negligible, 0.75 gram in 250 cc.

With Experiment 144B, the same conditions and apparatus as with Experiment 144A were used, but instead of water a 50 per cent saturated salt solution (250 cc. of water plus 44.9 grams of salt) was used. The results of this experiment are given in Table XII.

Table XII—Results of Experiment 144B, Illustrating Ball Mill Type of Agitation with 50 Per Cent Saturated Salt Solution

TIME Min.	Δt Min.	WEIGHT Grams	AMT. DISSOLVED %	$w^{1/3}$	K_1 EQUATION 8
0.00	0.00	1.2165	0.0	1.0675	....
1.00	1.00	1.1800	2.9	1.0567	0.0108
5.50	4.50	1.0319	15.1	1.0105	0.0103
7.50	2.00	0.9710	20.2	0.9902	0.0101
10.75	3.25	0.8780	31.8	0.9575	0.0101
14.91	4.16	0.7703	36.8	0.9167	0.0098
				Mean	0.0102
				Av. *D/M*	2.5%

Note—Considerable movement by particle from one end of bottle to the other with a tendency for it to stay in inner end. This prevented choice of any particular time interval because opportunity had to be awaited for particle to come to front so that it could be removed. Change in concentration was negligible as before.

The slowing up of the rate when B is compared to A, due largely to the increased concentration in B, may be noted in the constants. No further experiments were made in this type of agitation on account of the manipulative difficulties of the apparatus.

CONCLUSIONS—The results obtained in this group of experiments on other types of agitation show definitely that the application of the law to dissolution is independent of the type of motion producing the agitation.

Other Agitation Systems

SOLID-GAS SYSTEM—An experiment done with this system is Experiment 134, shown in Table XIII.

(*a*) *Conditions*—Irregular naphthalene particles; moist air at 65° C. dry bulb (D. B.), 49° C. wet bulb (W. B.), and 43 per cent relative humidity (R. H.); Carrier air-conditioning equipment.

(*b*) *Method and Apparatus*—The Carrier standard processing cabinet (2 × 2.5 × 4 feet) was used to obtain an automatically regulated supply of gas (air) having a constant temperature and composition. The circulation in this cabinet is stated to be about 400 cu. ft. of air per minute with an approximate linear velocity of 100 ft. per minute. Room conditions were 26° C. D. B., 19° C. W. B., and R. H., 50 per cent.[5]

After the cabinet had reached equilibrium under the conditions chosen for the experiment, the naphthalene particles were emptied from the weighing bottle on to a small tinned plate and quickly placed on the lower shelf of the cabinet. At the end of the period they were removed and emptied into the weighing bottle and weighed as rapidly as possible. They were then replaced in the cabinet for the next period. In the meantime, the small amount of naphthalene that had sublimed while the particles were in the weighing bottle was weighed, and the gross weight corrected for this amount (usually 1 to 3 mg.). As usual, all of these operations were well standardized by practice. It was found possible to control the humidity within a range of 2 to 3 per cent and the dry bulb temperature within 1° C. The naphthalene consisted of 32 irregular-shaped particles of fairly uniform size (unscreened) which had been well rinsed with alcohol and examined for possible fractures, cracks, and other irregularities. Their weight was 6.7468 grams.

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[5] The Bulkeley Chart published by the American Society of Heating and Ventilating Engineers was employed for the humidity data reported in these experiments.

Table XIII—Results of Experiment 134, Illustrating Solid-Gas System (*1*)

(65° C.; R. H., 43 per cent)

Time	Δt	W. B.	D. B.	Weight	Amt. Dissolved	$w^{1/3}$	K_{20} Equation 8
Min.	*Min.*	*° C.*	*° C.*	*Grams*	%		
0	0	51.0	65.0	6.7468	0.0	1.8895	....
20	20	49.0	65.0	5.3398	20.7	1.7478	0.1417
40	20	48.5	65.0	4.3291	35.8	1.6298	0.1180
60	20	49.0	65.0	3.3173	50.5	1.4914	0.1384
81	21	47.5	65.5	2.4621	63.5	1.3503	0.1344
						Mean	0.1331
						Av. D/M	5.6%

There was considerable variation in shape during the run.

Experiment 136A is another example of the solid-gas system (Table XIV).

(*a*) *Conditions*—Irregular naphthalene particles; moist air at 65° C. D. B., 49° C. W. B., and R. H. 55 per cent. Same equipment as before.

(*b*) *Method and Apparatus*—Same as for Experiment 134 except that the naphthalene used consisted of 210 irregular-shaped particles which had been well examined, washed with alcohol, and dried, after which they were carefully screened to give a 3–4 mesh Tyler screen cut. They weighed 19.8208 grams.

The operation was the same as before, the room conditions, 25° C. D. B., 19° C. W. B., and R. H., 55 per cent.

Table XIV—Results of Experiment 136A, Illustrating Solid-Gas System (2)

(65° C.; R. H., 55 per cent)

Time	Δt	Weight	Dissolved	$w^{1/3}$	K_{15} Equation 8
Min.	*Min.*	*Grams*	%		
0	0	19.8208	0.0	2.7063	.....
15	15	17.4833	11.8	2.5954	0.1109
30	15	15.3348	22.6	2.4844	0.1110
45	15	13.1588	33.7	2.3609	0.1235
60	15	11.4589	42.2	2.2545	0.1064
75	15	9.9778	50.0	2.1528	0.1017
105	30	6.9031	65.4	1.9041	0.1243
135	30	4.0829	79.6	1.5983	0.1529[a]
				Mean	0.1129
				Av. D/M	6.3%

[a] Omitted in calculation for mean.

The final particles showed a considerable variation from the original ones in shape. However, up to 50 per cent dissolved the constant shows that the action is normal. The mean value of the constant calculated up to the point of 50 per cent dissolved is 0.1107 with an av. $D/M = 4.8$ per cent, which is quite satisfactory for this kind of work.

SOLID-LIQUID CHEMICAL SYSTEMS—These experiments will show what happens when a particle dissolves in a liquid with which it reacts to form a precipitate which is deposited on the surface of the solid as a protective coating and which tends to prevent the further solution of the solid.

Table XV—Results of Experiment 161, Illustrating Alum-Ammonia System with No Protective Coat

Time	Δt	Weight	Amt. Dissolved	$w^{1/3}$	K_1 Equation 8
Min.	*Min.*	*Gram*	%		
0.00	0.00	0.5380	0.0	0.8133	....
2.00	2.00	0.4925	8.4	0.7897	0.0118
6.00	4.00	0.4142	23.0	0.7454	0.0111
10.16	4.16	0.3429	36.2	0.6999	0.0109
14.26	4.10	0.2773	48.3	0.6521	0.0116
17.26	3.00	0.2338	56.5	0.6161	0.0120
				Mean	0.0115
				Av. D/M	3.3%

Experiment 161 shows that the action is normal provided the agitation is intense enough to remove the coating as fast as it is formed. The results are presented in Table XV.

(*a*) *Conditions*—Irregular alum particle, aqueous ammonia, free rotational agitation.

(*b*) *Method and Apparatus*—A 4-liter Pyrex beaker; a standard straight iron paddle agitator 3 inches long (7.62 cm.) and 1 inch (2.54 cm.) wide, set at 0.5 inch (1.27 cm.) off the bottom at the center and running at 291 r. p. m.; 2000 cc. of water to which were added 50 cc. of concentrated ammonia (sp. gr. 0.90) giving a 0.63 per cent solution. The alum (potash) was an irregular particle weighing 0.5380 gram. It was dropped in with the agitator running but was removed with a pair of wide-faced tongs immediately after stopping the stirring. It moved quite rapidly in the solution and it was impossible to detect the presence of a coating upon it at any time. The hydroxide showed up in the form of small flakes in the solution. After removal, the particle was dropped into alcohol, washed, dried, and weighed. The temperature was 16.5° C. throughout the experiment.

Experiment 162 shows that if the agitation is not intense enough to remove the coating as fast as it is formed, the reaction is slowed down depending on the length of the time interval or the thickness of the protective coating. The results are given in Table XVI.

(*a*) *Conditions*—Same as in Experiment 161, but 5 per cent ammonia solution was used.

(*b*) *Method and Apparatus*—A glass crystallizing dish 2 inches (5.08 cm.) in diameter; a small glass agitator running at 150 r. p. m.; 43.5 cc. of water to which 10 cc. of concentrated ammonia were added to give an approximately 5 per cent solution. The experiment was run at room temperature, 21° C. The irregular particle of alum weighed 2.4607 grams. The particle was always placed in the same spot and lay on the same side. It was not moved by the agitation, and inserted and removed with the agitator stopped. Owing to the shallowness of the container, these operations required only 2 or 3 seconds so that their effect upon the total time period is negligible. After removal, the particle was thrown into alcohol and its coating was immediately washed off, after which it was dried and weighed.

Table XVI—Results of Experiment 162, Illustrating Alum-Ammonia System with Protective Coat

Δt	Weight	Amt. Dissolved	$w^{1/3}$	K_1 Equation 8
Min.	*Grams*	%		
0	2.4607	0.0	1.3500	....
4	2.2289	9.3	1.3062	0.0109[b]
2	2.0790	15.4	1.2763	0.0149[a]
4	1.8860	23.2	1.2355	0.0102[b,d]
4	1.7050	30.6	1.1946	0.0102[b]
2	1.5896	35.3	1.1671	0.0137[a,e]
2	1.4742	40.0	1.1381	0.0145[a]
4	1.3252	46.1	1.0984	0.0099[b]
8	1.1370	53.8	1.0437	0.0069[c,f]
2	1.0462	57.4	1.0151	0.0143[a]
4	0.9368	61.8	0.9784	0.0092[b,g]

[a] 2-minute period.

[b] 4-minute period.

[c] 8-minute period.

[d] Cracks appear in coating in same places each time and leave corresponding indentations on particle's surface.

[e] One-half minute on different side.

[f] Crack in coat became about 1 mm. wide by end of period.

[g] Particle slightly flatter on lower side, other sides and edges sharp and same as in original.

Throughout the entire run it was observed that on the leeward side of the particle, density waves or striations occurred, indicating that some kind of solution or liquid was coming through the coating into the main solution. This material did not form a precipitate with the ammonia, so it was probably the potassium sulfate solution formed from the decomposition of the alum and was passing out into the solution.

The dependence of the value of the constant upon the time interval substantiates the statements made before, as there are here three distinct values for the constant—viz., 0.0143, 0.0101, and 0.0069—showing that the reaction slows down as the coating gets thicker. The cracking of the coating at the same spots each time within a few seconds after insertion was evidently due to the pressure caused by the increasing precipitate forming below it. Their position probably depended upon the initial shape of the particle and the way the coating reacted to relieve the strain.

In the first experiment the constant did not depend on the length of the period. In the second experiment, it did. This is additional evidence that the thickness of the coating regulated the speed of the reaction during each time interval.

COMMENT AND CONCLUSIONS—Concerning the application of the law to other systems, enough has been presented to show that it probably is of very general application. However, one must be careful in the substitution of experimental values in the equations that the conditions under which the values were obtained were the same as those which are demanded by the equations. It is again recalled that this law expresses a rigid mathematical relation between the velocity of transformation and the surface and concentration factors only. All of the other numerous factors that affect this velocity are required by the equation to be held constant. Naturally, the relative importance of these factors varies greatly in passing from one system to another. For example, in the solid-liquid dissolution system which was used for the main study, the most disturbing factors were the shape and specific surface of the solid particle, whereas the disturbing influences of temperature and heat transfer were not so important. On the other hand, in the solid-gas system these latter factors became quite important when the size of the particle was increased. In the solid-solid system which was mentioned, such disturbing factors as relative hardness, cushioning, and directional abrasion appear. Likewise, in the solid-liquid chemical system which was studied, the agitation and the protective coating have great effects on the question of whether the law is applicable. In each case, it is a question whether the conditions demanded by the equation have been fulfilled. Each system, therefore, has, according to its nature, certain factors whose constancy can be obtained only with difficulty.

Then, if it is assumed that all of the other factors except concentration and surface can be held constant in any given agitation system, the kind of transformations may properly be considered. The law, especially Equation 8, should be operative in those transformations where the size of the particle, drop, or bubble decreases with the time as the reaction proceeds. This, of course, is on the assumption that the rate at which the transformation proceeds is proportional to the surface exposed.

Theoretically, the law should also be applicable in the other alternative (where the size increases with time), but the work has not progressed far enough to obtain any information on this point. In the first class, we ought to find such operations as the dissolution of solids, liquids, and gases, evaporation, sublimation, and abrasion. In the second class we might find such possible operations as agglomeration, condensation, and crystallization. In both cases the terms used are to be taken in their most general sense.

With respect to the application of the surface-film principle, it can be said that there is no disagreement between that viewpoint and the one that has been here formulated. Here, the force residing in the system due to its being at a distance from the final equilibrium is considered as the prime operating force, regardless of whether that equilibrium is momentarily and continually set up in a surface film, or whether it is regarded as eventually and completely set up throughout the entire volume.

After the completion of the experimental work that is here presented, an article was encountered in which the derivation and verification of Equation 8 was reported (7). This was in connection with a solid-solid system in the study of several autocatalytic reactions. The thermal decomposition of several compounds was studied, one, for example, being potassium permanganate. The hypothesis upon which the authors based the derivation of the equation was that the velocity of the reaction was directly proportional to the interfacial contact surface between the decomposition products and the undecomposed permanganate. From this they developed an expression which is identical with Equation 8. Their results supported this equation in a very satisfactory manner.

This independent and simultaneous corroboration of the specific application of the cube root law in a type of reactions of a nature so different from those studied in this research can only be considered as a strong confirmation of the more generalized viewpoint which has been elaborated in this dissertation.

Miscellaneous Disturbing Factors

Several experiments were made which showed clearly that a sharp and definite change of shape was associated with a correspondingly sharp and definite change in the value of the constant. Another experiment was made to discover as much as possible about the structural texture of the naphthalene balls used in these experiments. Using a very thin plate fashioned from one of these balls and subjecting it to the action of a solvent, it was observed that at no time during its solution was there any crumbling, hole formation, cracking, or irregularity of that nature, regardless of how thin the section became, and even at its thinnest it still presented the appearance of a delicate mosaic. Therefore, so far as the action of these balls toward dissolving in liquids is concerned, it would seem proper to consider them as isotropic bodies.

Because of lack of space, these experiments and certain others cannot be presented here, but can be found described in full, by reference to the dissertations from which this article has been abstracted.

Disappearance of Particles

If a large number of small particles are mixed with a smaller number of larger particles and the combination is subjected to the process of dissolution, the rate of the mixture will at first be very rapid until all of the small particles have disappeared. The rate will then decrease to that of the larger ones alone in that concentration of solution. Therefore, when comparative experiments are made, it is inadvisable to have such a variation in size or to run the experiment so far that there will be a material change in the number of the particles. With screened products of the character that have been used in this work, it is quite safe to make comparisons over a range of the first 50 per cent of the material dissolved, as the change in the number of particles can then be considered negligible.

Precision of Results

In the case of the ordinary dissolution of a solid, it has been seen that the values of the constants generally show an average D/M of 1 to 4 per cent. If, however, only the first half of the dissolution is considered, it will be found that in many cases the agreement is still better. In general, it is felt advisable to restrict the study to this range of the action due to the difficulties involved in changes of shape, especially in the case of a solid.

On the other hand, it is not believed that this decision in any sense acts to invalidate the application of the law for the remainder of the range of action. The work done in other systems indicates that a precision of practically the same magnitude is easily obtainable.

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Corrosion Rates of Steel and Composition of Corrosion Products Formed in Oxygenated Water as Affected by Velocity[1]

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Studies were made of the rates of corrosion of steel obtained in oxygenated water at various speeds of rotation. As the rotational velocities increased, the corrosion rate increased to a maximum, decreased to a very low value, and increased again to a somewhat higher value at very high velocities. The variations in corrosion rate are due to (1) differences in the type and uniformity of corrosion-product film formed, (2) changes in liquid-film thicknesses, and (3) erosion. At low velocities the corrosion product formed is a non-resistant granular magnetic oxide of iron and corrosion rates increase with increasing velocity because of a reduction in the thickness of the liquid film. At higher velocities, corrosion rates are low because of the formation of ferric hydroxide which is extremely resistant to the transfer of oxygen. At extremely high velocities, corrosion rates increase because of the nonuniformity of the ferric hydroxide film caused by mechanical removal of the corrosion product. A maximum corrosion rate is reached at some velocity because of the presence of two opposing tendencies—namely, (1) the accelerated transfer of oxygen due to a reduction in liquid-film thickness and (2) the increased rate of formation of ferric hydroxide resulting from the oxidation of ferrous ions.

As EARLY as 1910 Heyn and Bauer (*8*) observed that the velocity of the corroding medium had a marked effect upon the rate of corrosion of iron in oxygenated water. Friend (*6*) and Russell, Chappell, and White (*9*) obtained results which were very similar to those of Heyn and Bauer, but not identical. These investigators found that increasing the velocity increased the corrosion rate until a maximum rate was reached, and that further increase of velocity caused the rate to decrease to a very low value. Although the above investigations yielded analogous results, the absolute values did not check very closely. Speller and Kendall (*10*) under radically different conditions of experimentation found by the oxygen-drop method that the corrosion rate of steel pipe with water flowing through it increased with increasing velocity and approached an asymptotic value which varied depending upon the diameter of pipe being tested. In their investigation in acids Friend and Dennett (*7*) found that the corrosion rate of an iron disk rotated in dilute sulfuric acid (0.05 to 1 per cent) was directly proportional to the speed of rotation. This investigation differed from those reported by others (*6, 8, 9, 10*) in that no films of corrosion products developed, while in the other investigations cited the solution was essentially neutral and hence films or corrosion products could be formed.

A number of previous investigations (*1, 2, 3, 4*) have demonstrated not only the presence of oxide or hydrous oxide on metals, but also the effect of their presence on changing corrosion rates of metals. These papers do not, however, discuss the effect of external factors, such as distribution of ions and dissolved oxygen in the corroding medium and the effect of these factors upon the type of film formed. A recent paper (*5*) has indicated the importance of the turbulence of the oxygenated water upon the type of film formed in the corrosion of steel, and hence upon the corrosion rate. If the water was stirred rapidly, the film consisted of red gelatinous ferric hydroxide, whereas if the film was formed in an unstirred solution, the corrosion product was a loose granular precipitate of magnetic oxide of iron It was also found that the magnetic oxide, under the conditions of its formation, afforded little resistance to the diffusion of oxygen but that the ferric hydroxide did, thereby reducing the corrosion to a relatively low value.

Since in oxygenated acid solutions in which films of corrosion products do not form, the corrosion rate was found to be directly proportional to the velocity (*7*), it seems highly probable that the corrosion rate in oxygenated water of a metal covered with a corrosion-product film which offered little or no resistance to oxygen diffusion would increase with increasing velocity. On the other hand, since increasing the velocity of oxygenated water promotes the formation of ferric hydroxide rather than the magnetic oxide (the former being more resistant to oxygen diffusion than the latter), it would be expected that if the rate of oxygen diffusion could be held constant in any given type of apparatus, the corrosion rate in oxygenated water would decrease with increased velocity. These opposing tendencies may be diagrammatically represented by the broken lines in a sketch such as shown in Figure 1. On the basis of this reasoning it would therefore be expected that, upon increasing the velocity, the corrosion rate in oxygenated water should at first increase because of decreased water-film thickness and then decrease because of increased film resistance. The net effect would be expected to follow some curve such as is indicated by the solid line in the sketch.

In consideration of these hypotheses it was deemed advisable to determine the corrosion rates of steel in oxygenated water in an apparatus in which the velocity of metal relative to that of the water would be the only variable condition.

Experimental Procedure and Results

The experimental procedure used was essentially that described in a previous article in which turbulence could be considered as a function of speed of rotation alone. Rotating cylinders of low-carbon annealed steel were rendered oxide-free by treatment with 10 per cent hydrochloric acid. The adhering acid was removed by washing with a stream of oxygen-free water until the effluent was neutral. The specimen was then subjected to the action of oxygenated water and the corrosion measured by determining the decrease in oxygen concentration during the test. The only departure from the previous procedure was to equip the synchronous motor with sets of interchangeable gears. By this means the speed of rotation could be conveniently varied.

The results of the corrosion rate determinations at different speeds of revolution are represented graphically in Figure 2. The corrosion rates are plotted as cubic centimeters of

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[1] Received May 1, 1931.

oxygen (0° C., 760 mm. of mercury) consumed per minute per square decimeter of metal, corrected for differences in oxygen concentration. The correction was made by dividing by the arithmetic-average oxygen concentration (cubic centimeter per liter) existing in the corrosion cell during the oxygen-drop determination.

At the end of each determination, visual examinations of the films formed during the corrosion-rate determinations showed the conditions recorded in Table I. The effect upon the corrosion rate of the speed of rotation at which films were allowed to build up on the specimens is given in Table II.

Table I—Conditions of Films Formed on Iron at Different Speeds of Rotation

Run	Speed of Rotation	Appearance of Film
	R. p. m.	
1	6.34	Large areas of loose black granular film Small areas of loose red gelatinous film
2	57.0	Similar to run 1
3	85.5	Similar to runs 1 and 2, except for some gelatinous red film on black substance
4	114.0	Similar to run 3
5	171.0	Similar to runs 3 and 4, except for considerable amount of red gelatinous film
6	228.0	Uniform thin layer of red gelatinous film, metal surface visible through this layer
7	278.0	Similar to run 6
8	342.0	Similar to runs 6 and 7, except for striations in film in direction of rotation.

Table II—Effect of Liquid Films and Corrosion-Product Films on Corrosion Rate

Run	Point of Formation of Corrosion Product	Appearance of Films	Point of Determination of Corrosion Rate	Corrosion Rate[a]
	R. p. m.		*R. p. m.*	*Cc.*
1	0	Granular, black	0	0.0014
2	0	Granular, black	228	0.0098
3	228	Gelatinous, red	228	0.0010
4	278	Gelatinous, red	278	0.00065
5	278	Gelatinous, red	228	0.00065
6	342	Gelatinous, red[b]	342	0.0053
7	342	Gelatinous, red[b]	228	0.0053

[a] Oxygen consumed/sq. dm./minute/av. cc. oxygen/liter.

[b] At this speed of rotation there were striations on the film due to erosion.

Discussion of Results

An inspection of Table I shows that marked differences are to be noted in the character of the films formed upon corroding oxide-free steel surfaces in oxygenated water at different speeds of rotation. Figure 2 shows that corrosion rates also vary markedly, after the initial period, when the rotational velocity is changed. The variation of corrosion rate with speed of rotation is more strikingly brought out in Figure 3 in which the ordinates represent the corrosion rates at the end of 900 minutes (obtained from Figure 2), and the abscissas, the speeds of rotation.

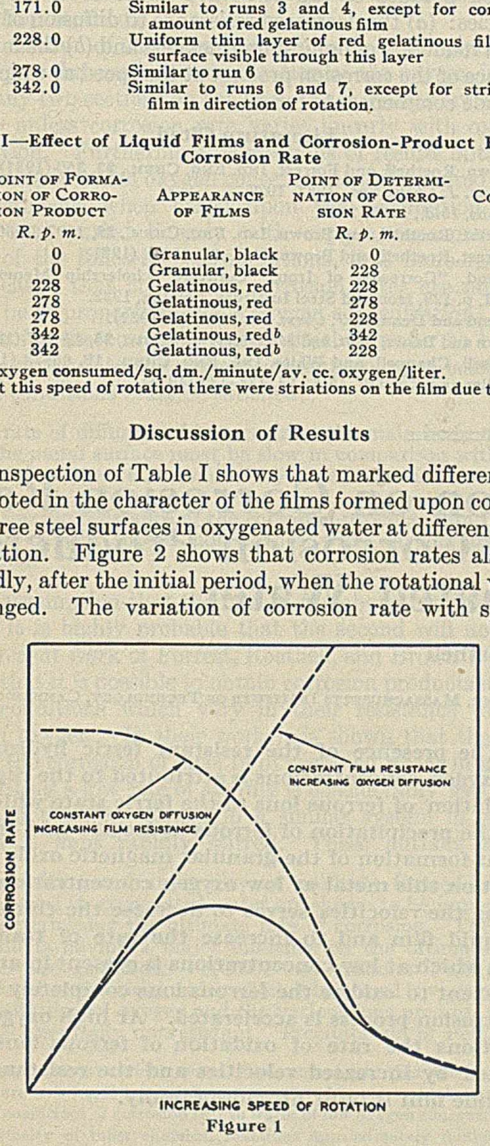

Figure 1

These phenomena may be explained by means of the data in Table II and the conclusions reached in a previous investigation (*5*) which attributed differences in corrosion rates to differences in the composition of the corrosion products. In the previous investigation it was shown that the presence of two products of corrosion had a major bearing upon the ultimate corrosion rates of steel in oxygenated water—namely, (1) a granular magnetic oxide of iron and (2) a gelatinous ferric hydroxide. The former afforded but little resistance to the passage of oxygen and various ions so that a high corrosion rate resulted; the latter, being of a gelatinous character, was found to be highly resistant and when present reduced the corrosion rate to a large degree. The factors determining which of these two types of films would be produced were found to be the solubilities of the ferrous and ferric hydroxides. The former required much higher hydroxyl-ion concentration for its precipitation than the latter at the same metallic-ion concentration and, under conditions of inadequate agitation, the concentration of hydroxyl ions in the liquid film became such that precipitation of ferrous hydroxide occurred. After the precipitation the ferrous hydroxide reacted with the ferric which was formed at a lower pH, and the loose granular magnetic oxide resulted. However, when the agitation of the liquid was violent, the hydroxyl-ion concentration in the liquid film was kept below the value necessary for the precipitation of ferrous hydroxide, and the concentration of oxygen in the regions where ferrous ions were formed was kept high so that the formation of ferric ions was accelerated and the precipitation of ferric hydroxide would occur without the formation of any of the ferrous hydroxide. In this manner a very protective film was formed.

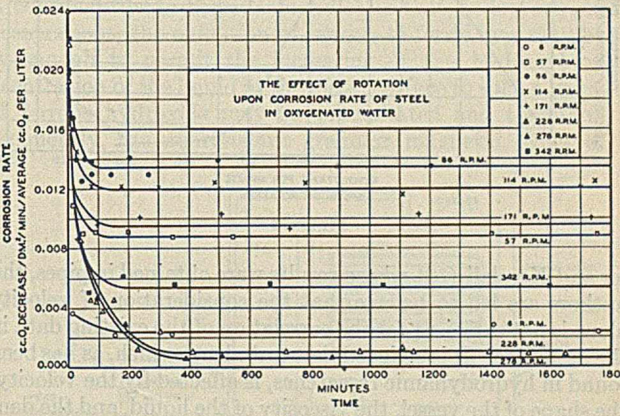

Figure 2

In runs 1 and 2 of Table II it is shown that films formed at low speeds of rotation are poorly protective and that the rate of corrosion depends primarily upon the rate at which oxygen can pass through the liquid film—i. e., upon the speed of rotation. From runs 3 to 7 of the same table it may be seen that the film formed at high speeds of rotation controls the corrosion rate despite the presence of a high oxygen concentration at the corrosion products—liquid-film interface. In consideration of the facts presented in the previous investigation (*5*) and in Table II, the effect of rotation upon the corrosion rates of steel in oxygenated water indicated in Figure 3 was to be expected. At low velocities the corrosion product consisted largely of the porous granular black magnetic oxide of iron. Increasing the velocity increased the rate of corrosion by decreasing the thickness of the water film in contact with the corrosion products and permitted a more rapid transfer of oxygen. At high velocities (above 228 r. p. m.) the corrosion product, consisting primarily of ferric hydroxide, was extremely protective and the corrosion rate was independent of the velocity until velocities were attained at which (as evidenced by the presence of striations in the film) erosion of the film began to take place. At intermediate velocities a balance was obtained between two tendencies: (1) the increased proportion of ferric hydroxide formed tending to reduce corrosion rates, and (2) the increased rate at which oxygen moved through the liquid film which tended to increase the transfer of oxygen to the metal surface.

From the results of this investigation, which are qualitatively in agreement with those of Heyn and Bauer (*8*), Friend (*6*), and Russell, Chappell, and White (*9*) and obtained in similar forms of apparatus, and in disagreement with those of Speller and Kendall (*10*) whose results were obtained in pipes, the authors are led to believe that the consideration of velocity alone is not sufficient for the correlation of the existing data in the literature. It is believed that turbulence which, as has been found in hydrodynamic researches, is affected by the velocity, the shape of the vessel, the viscosity of the liquid, and the density of the liquid, has a marked effect upon the types of corrosion product produced and hence upon the corrosion rate obtained under different conditions of investigation.

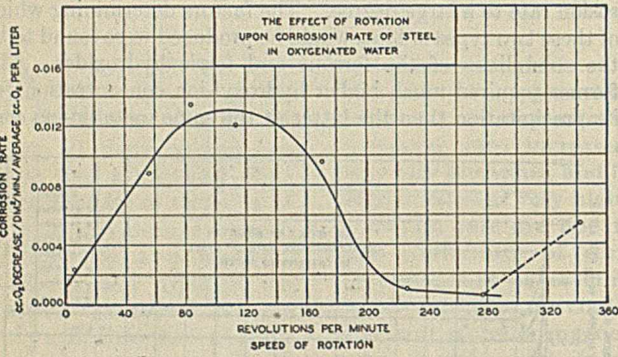

Figure 3

Conclusions

From the results of this investigation it may be concluded that:

(1) Variations in velocity during the corrosion of steel in oxygenated water alter the corrosion rate by influencing the thickness of the liquid film and the type of corrosion product formed.

(2) The corrosion product formed on steel at low rotational speeds is, for oxygen concentrations normally encountered, a granular nonresistant magnetic oxide of iron.

(3) The product formed at high speeds is a protective gelatinous ferric hydroxide.

(4) When the corrosion product is formed at low velocities, the corrosion rate is governed by the resistance offered by the liquid film to the transfer of oxygen, whereas, when formed at high speeds, the resistance of the corrosion product controls the rate of corrosion.

(5) A maximum rate of corrosion is obtained as velocity is increased because of the combined effect of two opposing tendencies: (*a*) the decreased resistance to diffusion of oxygen due to a reduction of liquid-film thickness and (*b*) the increased resistance of the corrosion product at the speed at which ferric hydroxide commences to form.

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Effect of Oxygen Concentration on Corrosion Rates of Steel and Composition of Corrosion Products Formed in Oxygenated Water[1]

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Short-time studies of the corrosion rates of steel in water containing varying amounts of dissolved oxygen (3 to 18 cc. per liter) show the rates to be approximately proportional to the oxygen concentration at concentrations below 5.5 cc. per liter. At higher concentrations, marked deviations from the linear relationship occur. The deviations become more pronounced as the oxygen concentrations increase, indicating that the resistance to the transfer of oxygen to the metal surface increases with increasing oxygen concentration because of changes in the nature of the corrosion products.

At low oxygen concentrations the corrosion product formed is composed primarily of a porous black magnetic oxide of iron, while at high concentrations the corrosion product is predominantly a red gelatinous ferric hydroxide. The presence of the resistant ferric hydroxide at high oxygen concentrations is attributed to the rapid rate of oxidation of ferrous ions to the ferric state which prevents the precipitation of ferrous hydroxide and the subsequent formation of the granular magnetic oxide of iron present on this metal at low oxygen concentrations. Increasing the velocities serves to decrease the thickness of the liquid film and to increase the rate of transfer of oxygen which at low concentrations is present in amounts insufficient to oxidize the ferrous ions completely so that the corrosion process is accelerated. At high oxygen concentrations the rate of oxidation of ferrous ions is accelerated by increased velocities and the resistant ferric hydroxide film is built up more rapidly.

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RAPID developments in recent years in the methods of corrosion testing in laboratories and on service installations have resulted in the need for accurate information regarding the effects of various factors which are likely to influence the validity of the tests. The theory of aqueous corrosion has been frequently stated and tested by various investigators, notably, Whitney (*18*), Walker (*14, 15*), McKay (*9, 10*), Evans (*2, 3, 4, 5, 6*), Wilson (*19*), Whitman (*16, 17*), Speller (*11*), and others. However, much contra-

[1] Received May 4, 1931.

dictory information still exists regarding the quantitative effects of the various factors which determine the ultimate corrosion rates.

In the aqueous corrosion of steel, the presence of oxygen was shown by some of the above investigators to be extremely important. The corrosion rate of steel in oxygen-free pure water at low temperatures was found to be negligibly small. In this laboratory, test pieces of steel exposed to boiling distilled water for a period of two weeks showed a negligible loss in weight due to corrosion. The presence of oxygen in pure water sufficed to cause corrosion to proceed at appreciable rates. In fact, Walker (*14*, *15*) and Speller (*13*) were led to believe from their investigations that the corrosion rate varied linearly with oxygen concentration. In the past this linear relationship has been used in corrosion testing as a basis for computing corrosion rates at different oxygen concentrations from known rates at other concentrations, and also has served as the basis for the interpretation of results obtained of the corrosion rates of steel pipes by means of the "oxygen-drop method."

The calculation of the rates of corrosion in water pipe lines is based upon the average concentration of the oxygen in the water at any two sections on the line. Such results are apt to be erratic unless corrosion rate varies linearly with oxygen concentration. Furthermore, corrections of results obtained from test data in which oxygen concentrations fluctuated have proved erroneous when based upon the assumption that corrosion rate varied linearly with oxygen concentration. On basis of the following considerations, it is more reasonable to believe that changes in corrosion rates are not expected to be in proportion to the oxygen concentration.

In order for the corrosion rate of steel in water to be directly proportional to the oxygen concentration, at least two important conditions must be satisfied:

1—The rate of diffusion of oxygen from the main body of the liquid to the metal surface must be slow in comparison with the rate at which oxygen is consumed by a reaction at the metal surface.

2—The specific resistance of the corrosion-products film to the diffusion of oxygen should not change with varying oxygen concentration.

On the assumption that the first of the above conditions is satisfied,[2] it is highly probable that the second will not be, since the recent work of Forrest, Roetheli, and Brown (*7*) has indicated that it is possible to obtain corrosion products under different conditions which vary in their resistance to the transfer of oxygen. In their work it is shown that the film formed in the corrosion of steel in oxygenated water in a system permitting a low rate of stirring is considerably less protective than the film formed in a similar system in which the liquid is kept rapidly stirred. These authors state:

> The composition and uniformity of products formed in the corrosion of steel in oxygenated water are shown to be important factors in determining the ultimate rate of corrosion. The corrosion products having a major influence on the ultimate corrosion rates are gelatinous $Fe(OH)_3$ and granular Fe_3O_4; the former under the conditions under which it is formed is very resistant to the diffusion of oxygen and the various ions present, while the latter is essentially nonresistant. Precipitation of $Fe(OH)_2$ on the metal surface at Fe^{++} concentrations encountered in neutral water is possible only at pH values higher than 8 (approximately) while $Fe(OH)_3$ may be precipitated at much lower pH values. However, the Fe^{++} ions initially formed must first be oxidized to Fe^{+++} by the oxygen present in the water. Once $Fe(OH)_2$ has been precipitated a reaction takes place between it and $Fe(OH)_3$ to form the black granular Fe_3O_4. Under conditions of agitation such that the pH of the liquid film adjacent to the metal is below the value necessary for precipitation of $Fe(OH)_2$ the red gelatinous $Fe(OH)_3$ will be formed which effectively reduces the corrosion rate to a very low value. When the pH in the liquid film is allowed to build up because of slow diffusion of OH^- ions from the liquid film to the main body of the liquid (due to poor agitation), $Fe(OH)_2$ will be precipitated and subsequently Fe_3O_4 will be formed. When the film is composed primarily of Fe_3O_4, the corrosion rate approaches that of a film free surface.

A consideration of these facts indicates that, at low oxygen concentrations, the oxidation of ferrous to ferric ions may be slow enough to permit the increasing of the hydroxyl-ion concentration of the liquid at the metal surface to such a value that ferrous hydroxide may be precipitated and therefore, subsequently, the nonresistant granular magnetic oxide of iron will be formed. In contrast to this, the oxidation of ferrous to ferric ions may occur rapidly enough at high oxygen concentrations to prevent the precipitation of the iron as ferrous hydroxide so that only ferric hydroxide will be formed. Therefore, at low oxygen concentrations the diffusion resistance of the corrosion film should be slight. As the oxygen concentration is increased, the film, owing to a more rapid formation of ferric hydroxide, should become increasingly protective. In other words, the corrosion rate should not increase linearly with oxygen concentration, but should show a decrease in the rate change as the oxygen concentration increases.

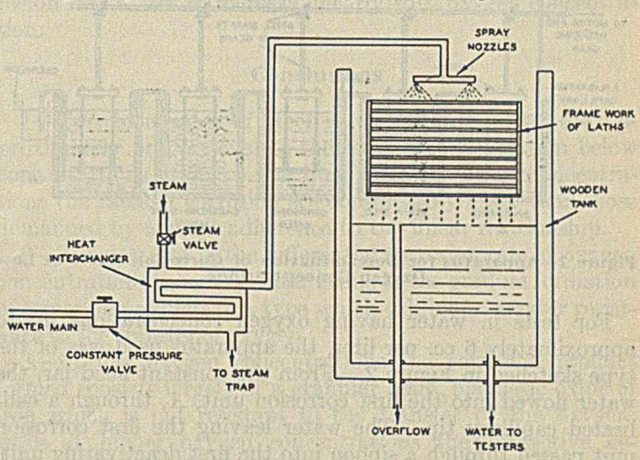

Figure 1—Apparatus for Saturating Water with Oxygen and Maintaining Constant Water Temperature

Experimental Method

The method employed in the investigation was designed to permit the gravimetric measurement of corrosion rates of steel in oxygenated water of different oxygen concentrations. The functions which the apparatus was required to perform necessitated the maintenance of (1) definite oxygen concentrations in the corroding water, (2) definite velocities of rotation of the metal in the liquid, (3) constant rate of flow of corroding water, (4) constant rate of flow of oxygen gas for oxygenation of the water, and (5) constant temperature.

The equipment necessary for satisfying the required conditions consisted of (1) a system for controlling the temperature and oxygen concentration of the feed water; (2) testing units in which the specimens were corroded under controlled conditions; (3) units for attaining the desired oxygen con-

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[2] Although the data which would prove completely that this assumption is valid are lacking, it is partially substantiated by data obtained on the temperature coefficient of corrosion rate in water of low oxygen concentration. Since the velocity of most chemical reactions approximately doubles for every 10° C. rise in temperature, ultimate corrosion rates should vary according to some power of the temperature if rate of oxygen consumption were governed by the reaction rate at the metal surface. However, Speller (*12*) has shown corrosion rate of steel in water of constant oxygen concentration (1.3 cc. per liter) to be linear function of temperature. Furthermore, fluidity (1/viscosity) of water (*8*) to the 0.8 power varies linearly with temperature, and since diffusion rate is a function of the 0.8 power of fluidity (*1*), it is apparent that at low oxygen concentrations diffusion rate of oxygen controls the corrosion reaction at the surface of the metal.

centrations in the various testing units; and (4), systems for the regulation of water and oxygen flow.

The system employed for controlling the temperature and oxygen content of the inflowing water is shown diagrammatically in Figure 1. The water from the supply main passed through a flow regulator to a steam heat interchanger in which the water was heated to the desired temperature. From the heater the water flowed to a saturator composed of a series of fine spray nozzles and a box-like system of laths. In the saturator, the concentration of air in the water was allowed to reach its equilibrium value for the particular temperature of the water. The water leaving the saturation unit was stored in a large wooden tank, and conveyed to the smaller constant head jars used in each testing unit.

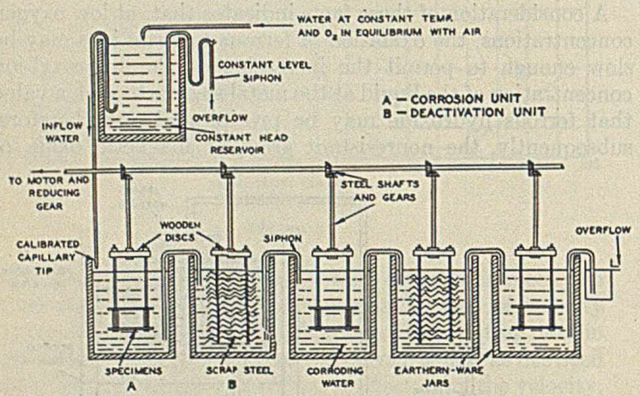

Figure 2—Apparatus for Determination of Corrosion Rates at Low Oxygen Concentrations

For tests in water having oxygen concentrations up to approximately 6 cc. per liter, the apparatus used was of the type sketched in Figure 2. From the constant head jar, the water flowed into the first corrosion unit, *A*, through a calibrated capillary tip. The water leaving the first corrosion unit passed through a siphon into the first deactivating unit, *B*, in which it was exposed to a large number of rotating steel sheets.[3] The oxygen concentration in this jar was reduced to a much lower value by the corrosion of the sheets. The effluent from this unit was fed to a second corrosion unit which contained test specimens. Three stages of this type were used in series, and the oxygen concentrations obtained in the three corrosion units were approximately 5.5,[4] 4.5, and 3 cc. per liter. The water from the last jar flowed through a vessel having an overflow at a definite level and maintained a constant level of liquid in all the jars.

In Figure 3 a sketch is shown of the apparatus used in the tests in which oxygen concentrations greater than 6 cc. per liter of the water were maintained. The feed water from the constant head jar passed through a capillary tip into the oxygenation jar, *A*, and was oxygenated by bubbling oxygen through at a constant rate. The oxygen concentration was varied as desired by changing the rate of flow of oxygen gas. The use of alundum crucibles in this operation permitted very rapid absorption of the gas.

The test jars were covered with steel plates and made gas-tight by means of rubber gaskets. The gas above the liquid in the oxygenation jar was carried over into the corroding unit from which it was allowed to escape under a slight positive pressure through a small exit. The water from the oxygenation unit was conveyed to the corroding unit and thence through a constant-level siphon to the drain.

In both types of testers the specimens were rotated by means of a system of shafts and gears operated from a reducing gear and motor. The speed of rotation was varied by changing the gear ratios. The velocity of the specimens through the liquid was determined by the difference between the speed of rotation of the disk and the rotation of the liquid in the same direction. The specimens were suspended in the corroding water by means of glass rods supported from wooden disks and were separated from each other by short pieces of glass tubing.

The specimens were cut from 26-gage sheet annealed steel of a carbon content approximating 0.1 per cent by weight. Before immersion, they were pickled in 10 per cent hydrochloric acid to remove the adhering mill scale, washed, scrubbed with steel wool, rinsed in reagent alcohol, dried, and weighed. After the test, the specimens were examined visually to note the type of corrosion products formed. The corrosion products were then removed by scrubbing with steel wool. The scrubbed specimens were subsequently washed, rinsed in alcohol, dried, and weighed. From the weights before and after the tests, the loss by corrosion was determined. Oxygen concentrations of the corroding water were determined by the Winkler method (*20*) twice daily to check the constancy of the oxygen concentration.

Results of Experiments

The results of the investigation are shown graphically in Figure 4. The curves show the variations in the corrosion rate of steel at four different velocities, in water containing different amounts of dissolved oxygen. The ordinates represent the average penetrations of four check specimens in centimeters per year, calculated from the losses in weight occurring during intervals varying from 5 to 7 days. The abscissas represent the concentrations of oxygen in the water, expressed as cubic centimeters of oxygen (at 0° C., 760 mm. of mercury) dissolved per liter of water.

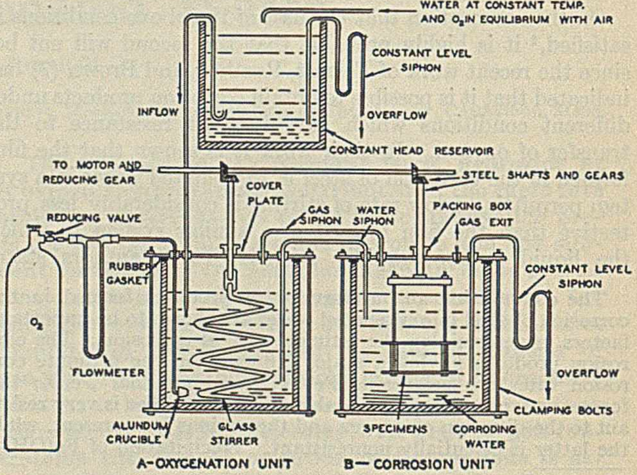

Figure 3—Apparatus for Determination of Corrosion Rates at High Oxygen Concentrations

In Table I are indicated the results of the visual examinations made of the products of corrosion obtained under the varying conditions of the experiments.

An inspection of the curves in Figure 4 shows that the corrosion rate of steel in oxygenated water is approximately proportional to oxygen concentration for oxygen concentrations up to about 6 cc. per liter. At higher concentrations of oxygen the corrosion rates are considerably lower than they

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[3] Another method of removing oxygen from the water was tried, whereby nitrogen gas was bubbled through the water. The apparatus was that described in Figure 2, nitrogen being used instead of oxygen. The values of corrosion rates did not vary more than 10 per cent from those determined as described above. These tests indicated that the method of removal of oxygen had practically no influence on the corrosion rate.

[4] This value is about 10 per cent below the value of oxygen at saturation (when in equilibrium with air) owing to the consumption of oxygen in the corrosion process.

Table I—Results of Examination of Corrosion Products

No.	Condition	Appearance of Product	Uniformity of Film	Tenacity of Film
1	Increasing oxygen from 3 to 6 cc. per liter at low velocity	Loose, granular black product, predominance of Fe_3O_4	Decreases slightly	Increases only slightly, easily removed
2	Increasing oxygen from 3 to 6 cc. per liter at high velocity	Loose, granular, mostly black, very little more $Fe(OH)_3$ than (1)	Decreases slightly	Increases slightly, adheres slightly more than (1)
3	Increasing oxygen above 6 cc. per liter at low velocity	Becoming more predominant in red $Fe(OH)_3$ than (2)	Increases slightly	Increases slightly, adheres better than (2)
4	Increasing oxygen above 6 cc. per liter at high velocity	Definite predominance of red $Fe(OH)_3$, small amount of black	Increases slightly	Increases very rapidly, difficult to remove with steel wool
5	Increasing velocity at oxygen concentration between 3 and 6 cc. per liter	Substantially the same as (1). Velocity seems to have no effect on products at low oxygen concentration	No appreciable change	Increases slightly
6	Increasing velocity at oxygen concentration above 6 cc. per liter	Predominance of $Fe(OH)_3$ increases slightly with velocity at high oxygen concentration	No change	Increases appreciably

would be if corrosion rate varied linearly with oxygen concentration. The deviation from the proportionality becomes more pronounced as the oxygen concentrations increase. Increasing velocity, in the range feasibly obtainable in the equipment used, is seen to increase the magnitude of the corrosion rate and also to make the deviations from the linear relationship more pronounced.

Table I indicates that the relative quantities of the black granular magnetic oxide of iron and gelatinous red ferric hydroxide in the corrosion products change for different oxygen concentrations, and that the physical properties such as tenacity (as measured by the ease of removal from the metal surface) also change considerably. The uniformity of the film remains substantially unaltered, with the exception that at low oxygen concentrations the film decreases slightly in uniformity, and at high oxygen concentrations the film increases slightly in uniformity, as the oxygen concentration increases.

An explanation of these phenomena presents itself as a result of a critical consideration of the work by Forrest and co-workers (7), who, as previously indicated, showed that corrosion rates in oxygenated water are markedly influenced by the proportions of black granular magnetic oxide of iron, and the red ferric hydroxide, present in the corrosion products film. Apparently the type of corrosion product is also markedly influenced by the relative rates of oxidation and direct precipitation (to form ferrous hydroxide) of freshly formed ferrous ions. The rate of oxidation will depend upon the rate of transfer of oxygen to the regions in which ferrous ions abound, and this, when the rate of diffusion controls, will in turn depend upon three factors, (1) oxygen concentrations in the main body of the liquid, (2) diffusion resistance of the liquid film, and (3) resistance of the corrosion-products film.

Since the factors affecting the liquid-film thickness (such as viscosity, density, and turbulence) are substantially constant for any definite velocity, the resistance of the liquid film may be considered constant for all concentrations of oxygen. However, increasing velocity for any definite concentration of oxygen diminishes the thickness of the liquid film and promotes more rapid diffusion of the oxygen to the ferrous ions, and, consequently, accelerates their oxidation. At very low oxygen concentrations the oxidation of ferrous ions to ferric ions probably remains incomplete even at higher velocities so that the effect of velocity will merely serve to increase the transfer of oxygen to the metal surface.

As the oxygen concentration increases at any definite velocity in the range studied, the change in the combined resistance of the liquid and the corrosion-products films, on the basis of the above, must be due to the changes in the resistance of the corrosion-products film. At low oxygen concentration (0 to 6 cc. per liter), because of incomplete oxidation of all the ferrous ions present, the corrosion film formed, composed largely of magnetic oxide of iron with small amounts of ferric hydroxide on the surface, is porous and may be considered to have a substantially constant low resistance over that range of oxygen concentration. Hence, with the total resistance of the liquid and corrosion-products film remaining substantially constant, corrosion rate should be very nearly proportional to oxygen concentration. On the other hand, at higher oxygen concentrations, the resistance of the corrosion-products film apparently increases steadily with oxygen concentration, because of the rapid formation of ferric hydroxide due to rapid oxidation of the ferrous ions and, hence, the sum of the resistance of the liquid and corrosion-products film ceases to remain constant. As a result, the corrosion rate ceases to increase linearly with oxygen concentration.

Conclusions

1—Corrosion rates of steel in oxygenated water are approximately proportional to the oxygen concentration below concentrations of 5.5 cc. per liter, while at higher concentrations the rates of corrosion are considerably lower than those demanded by a strict adherence to the linear relationship.

2—The decrease in the differential corrosion rate as oxygen concentrations become greater is due to the gradual formation of corrosion products to a type which exhibits a greater resistance to the transfer of oxygen.

3—At low oxygen concentrations the corrosion product formed consists largely of a granular black magnetic oxide of iron which is not resistant to the transfer of the oxygen, while at higher oxygen concentrations the protective gelatinous ferric hydroxide is formed.

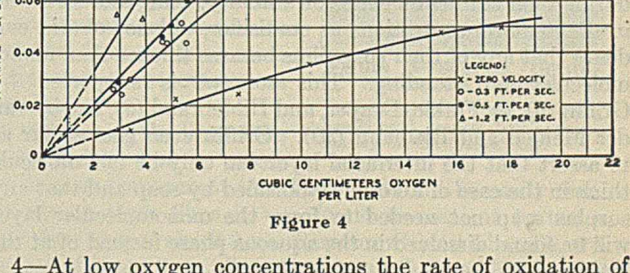

Figure 4

4—At low oxygen concentrations the rate of oxidation of ferrous ions to form ferric is slow enough to permit the precipitation of both the ferrous and ferric hydroxides with the subsequent formation of magnetic oxide. On the other hand at high oxygen concentrations the rate of oxidation of ferrous ions to ferric is high enough to prevent the accumulation of ferrous ions so that only the protective ferric hydroxide is precipitated.

5—At low oxygen concentrations the increased rate of oxidation due to increased velocities is insufficient to cause the formation of ferric ions from the ferrous ions, while at high oxygen concentrations the rate of formation of ferric ions is increased so that the differential change in corrosion rate becomes more pronounced as the velocity increases.

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Formation of Films at Liquid-Liquid Interfaces[1]

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Bancroft (*3*) has published a series of papers on "The Theory of Emulsification" in which he traces the development and deduces the underlying principles of the idea now commonly held that the effectiveness of emulsifying agents in stabilizing emulsions is due to the formation of a film of emulsifying agent as a separate phase at the liquid-liquid interface.

Since the publication of these papers by Bancroft, Langmuir (*17*) has suggested that the superficial layer of molecules at a liquid-gas or a liquid-liquid interface will have a definite orientation. Langmuir also points out that an oil containing polar groups will spread out on water until it forms a monomolecular layer and argues that this layer will be definitely oriented. Langmuir does not discuss the case of emulsifiers at a liquid-liquid interface in an emulsion.

Harkins (*11*), who had independently reached similar conclusions, extends the fundamental idea to emulsions by postulating that the film of emulsifying agent adsorbed at the interface is also definitely oriented. For example, when oil is emulsified in water by means of soap, the carboxyl group of the soap is supposed to extend toward the water and the alkyl radical of the fatty acid of the soap toward the oil. Harkins says, "Films of solutes positively absorbed at either liquid-vapor surfaces or liquid-liquid interfaces frequently become saturated." This concept seems to imply a monomolecular layer of emulsifying agent although Harkins does not state definitely that the interfacial film can never be greater than monomolecular. Harkins and Beeman (*10*), during their studies on emulsion stability, using sodium oleate in different concentrations as emulsifier, did not obtain evidence that any of their soap films became thicker than monomolecular on standing. This concept is supported by Griffin (*9*), by Finkle, Draper, and Hildebrand (*8*), and by van der Meulen and Riemann (*20*). Griffin even goes so far as to assert that the interfacial layer can only be one molecule thick in the case of kerosene emulsified by soap and that any surplus soap not needed to form the monomolecular layer will be found dissolved in the aqueous phase instead of at the interface.

Analytical evidence showing an impoverishment of the emulsifying agent in the outer or continuous phase as a result of the formation of an emulsion has been interpreted as showing the formation of an interfacial film by Storch (*26*) in the case of butter fat emulsified by casein in milk and cream, by Briggs (*4, 5*) in the case of benzene emulsified in water by soap, by Griffin (*9*) in the case of kerosene emulsified in water by soap, by Holmes and Cameron (*15*) in the case of glycerol emulsified in acetone by means of cellulose nitrate, and by Holmes and Williams (*16*) in the case of water emulsified in ether (and other organic liquids) by means of iodine.

Nugent (*21*) found that if caustic soda is added to a fresh emulsion of benzene with gelatin as emulsifier, the separation of benzene begins immediately, but if the emulsion is left undisturbed for some time before adding the caustic, the separation of the benzene is retarded. The duration of this inhibition period is found to depend upon the length of time which has elapsed between emulsification and addition of alkali. His interpretation is that the gelatin forms a protective film which increases in thickness with time. The older the emulsion, the thicker the layer and the longer the time required for the caustic to destroy the film and break the emulsion.

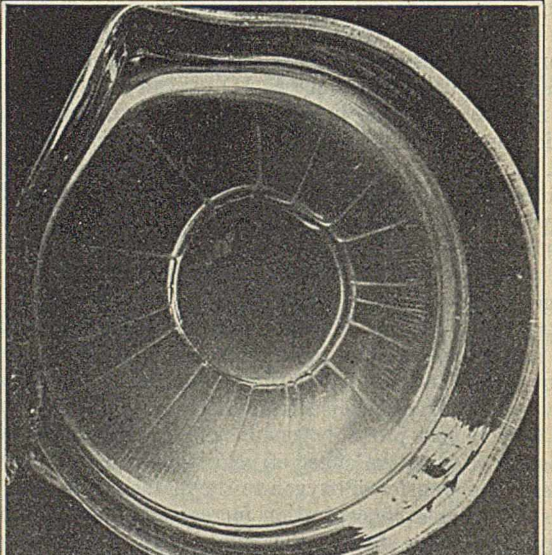

Figure 1—Irish Moss–Mineral Oil Interface

Concentration 0.8 per cent, age 12 days, temperature approximately 80° F. (26.67° C.)

Limburg (*19*) has carried out measurements on the cataphoretic velocity of oil particles emulsified by gelatin. He found that with low concentrations of gelatin the cataphoretic velocity depended on the concentration of the gela-

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[1] Received May 18, 1931.

tin, but that above a certain critical concentration of the gelatin the velocity became independent of the concentration. This is interpreted by Limburg as showing that, at the critical concentration or above, the oil particles are completely covered with a film of gelatin so that the oil-water interface has disappeared. Similar experiments have been conducted by Prieger (*22*) with milk-fat globules.

Wilson and Ries (*28*) have found that if drops of oil of different size are allowed to form at the ends of a capillary immersed in water containing an emulsifying agent, they remain for many hours without equalizing their shapes, which is interpreted as showing the presence of solid plastic films over the drops.

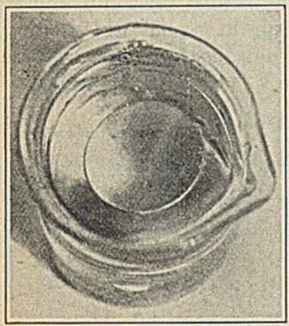

Figure 2—Saponin–Castor Oil Interface

Concentration 0.1 per cent, age 50 days, temperature approximately 70° F. (21.11° C.)

Wiegner (*27*) has observed that passing milk through a homogenizer caused an increase in viscosity which he interprets as due to passage of more casein into the film at the enlarged interface.

Lewis (*18*) has determined the drop number of mineral oil in a solution of bile salts as a function of the concentration of emulsifier. He prepared an emulsion and separated the disperse phase by centrifugal action. The drop number was determined in the clarified aqueous layer and found to have decreased. He argues that this proves that the emulsifier has been adsorbed in the interface and been removed with the disperse phase.

Many authors have stated that they have actually seen the film. Macroscopically the film has been seen around large drops of the internal phase with albumin as the emulsifying agent by Ascherson (*1*, *2*) and by Clark and Mann (*7*), with saponin by Ramsden (*23*), with casein by Robertson (*24*), with acacia and with gelatin by Briggs and Schmidt (*6*), and with cellulose nitrate by Holmes and Cameron (*15*). In none of these cases were the films photographed.

An especially interesting experiment has been carried out by Hauser (*14*) who made moving microphotographs of particles of rubber latex while he pierced a particle with a microscopic glass needle. The microphotographs reveal a liquid droplet emerging from the interior through the rupture and leaving behind a membrane which formed a skin around the particle.

Sheppard (*25*) has published microphotographs showing particles of lead salts gathered at the interface between nitrobenzene and sulfuric acid.

Hattori (*12*, *13*) has isolated the hull substance of milk-fat globules by treatment with solvents.

Although the methods of investigation referred to seem to establish the existence and importance of interfacial films of emulsifying agent, they are troublesome and not well adapted for a comparison of the properties of films of various emulsifying agents at water-oil interfaces. Nor are these older methods conveniently useful for determining the speed of formation of films at such interfaces or the factors influencing the properties or rate of formation of films. This information would be extremely valuable for the understanding of emulsification and in the development of practical methods of making emulsions.

Method of Preparing and Studying Films

In the course of studies to determine the most suitable emulsifying agents and the best method of preparation of stable and concentrated emulsions of mineral and of fatty oils in water for the manufacture of industrial products, an easy means of preparing and studying the films at the liquid-liquid interface was found. This consisted simply of placing about 30 cc. of a fresh aqueous solution of the emulsifying agent of known concentration in a small beaker and then gently adding with a pipet 10 cc. of the oil on top of the solution of emulsifying agent, taking care to avoid mixing. The beakers were then allowed to stand quietly for many days and examined at intervals. The emulsifier solutions studied were sodium oleate, 0.03, 0.06 per cent (Sterling, neutral, U. S. P.); sodium glycocholate, 0.03, 0.06 per cent (Eastman Kodak Company); triethanolamine, 0.03, 0.06 per cent (usual commercial quality); acacia, 0.5, 2.0 per cent; tragacanth, 0.5, 2.0 per cent; Irish moss, 0.4, 0.8 per cent; gelatin, 0.5, 0.3 per cent; and saponin, 0.1, 2.0 per cent. The oils used were olive oil, castor oil, cod-liver oil, and refined heavy mineral oil (stanolind). All of them were the best refined oils on the market. During these experiments no antiseptics were used for preserving the emulsifier solutions, in order to avoid complications due to the presence of extraneous materials and in order to test the emulsifiers in their natural conditions. Similar experiments with solutions containing antiseptics are in progress.

After standing for four weeks a film was formed in all of the cases tried except in that of mineral oil and an aqueous solution of triethanolamine. Since triethanolamine readily forms films and emulsions with the fatty oils but not with mineral oils it may be inferred that the effective agent is a salt of triethanolamine and a fatty acid. Some beakers were kept at room temperature, others at an elevated temperature, 38° C., and still others at about 8° C. With a few exceptions the films were kept under observation for four weeks only, as some solutions had begun to putrify by this time. With the single exception noted, it was apparent that a solid film had formed at the water-oil interfaces as shown by Table I. Microscopic inspection showed that the films are not of biological origin. In all except one of the cases examined up to the present time a film was formed at the interface, but the films were found to differ in appearance and in physical properties, depending both on the emulsifier used and on the oil. There was also a marked difference in the time required for the films to become visible as shown by Table II. In general, increasing the temperature and the concentrations seemed to cause the films to form more rapidly and to become more apparent.

Figure 3—Sodium Oleate-Mineral Oil Interface

Concentration 0.06 per cent, age 21 days, temperature approximately 85° F. (29.44° C.)

In some cases the films were readily visible, but in others they were so transparent that they could not be easily seen. In studying these films it was found convenient to use a simple wire ring of about 3 cm. diameter without a handle, or a wire loop of about 3 cm. diameter bent so that its plane was at right angles to a wire rod which served as a handle. In some cases when these loops were pushed against the films, the latter were not readily ruptured, but the entire film within the loop could be forced downward several millimeters into the water layer, and the film outside the loop was stretched and formed wrinkles which were easily visible. Figure 1 gives a photograph of such a case, made by pointing the camera downward. The lower aqueous layer contained 0.8 per cent of dissolved Irish moss and the upper layer mineral oil. After

Table I—General Properties of Films Formed at Room Temperature after 4 Weeks' Standing[a]

	Olive Oil	Castor Oil	Cod-Liver Oil	Mineral Oil
Sodium oleate	Opaque, granular, pulverulent, thick, weak	Transparent, very thin, weak	Opaque, granular whitish, pulverulent, thick	Translucent, thin, very weak
Sodium glycocholate	Translucent, almost transparent, thin, weak	Transparent, thin, weak	Opaque, granular, membranous, brittle, wrinkles	Thin, transparent
Triethanolamine	Transparent, weak, brittle	Transparent, weak, thin	Opaque, granular, weak, thick, brittle	No film
Saponin	Transparent, thin, weak, elastic	Transparent, thin, weak, plastic	Translucent, membranous elastic, can be folded	Thin, transparent
Irish moss	Opaque, strong, wrinkles	Transparent, very thin	Opaque, very thin, brittle, wrinkles	Translucent, membranous thick, strong
Acacia	Transparent, thin, elastic, wrinkles	Transparent, very thin	Opaque, membranous, strong, brittle, wrinkles	Transparent, thin, wrinkles
Tragacanth	Transparent, wrinkles, brittle	Transparent, thin	Opaque, membranous, elastic, folds	Transparent, thin, weak, wrinkles
Gelatin	Translucent, thin, wrinkles	Transparent, thin	Opaque, membranous, brittle, wrinkles, folds easily	Translucent, thin, weak, elastic

[a] Solutions contained no antiseptic.

Table II—Speed of Film Formation of Various Emulsifiers in Contact with Different Oils

(Observation time, 4 weeks)

	Olive Oil	Castor Oil	Cod-Liver Oil	Mineral Oil
Sodium oleate	Slow	Very slow	Very quick	Slow
Sodium glycocholate	Slow	Very slow	Very quick	Very slow
Triethanolamine	Very quick	Very slow	Very quick	No film after 4 weeks
Gelatin	Moderate	Slow	Quick	Very slow
Irish moss	Quick	Moderate	Quick	Very slow
Acacia	Quick	Slow	Quick	Quick
Saponin	Very quick	Very slow	Quick	Very slow
Tragacanth	Quick	Moderate	Quick	Very quick

NOMENCLATURE

Very quick, within 24 hours
Quick, 1 to 2 days
Moderate, 2 to 8 days
Slow, 8 to 15 days
Very slow, over 15 days

standing undisturbed at a temperature of about 38° C. for 12 days, a ring of platinum wire without a handle was dropped on the upper surface. It sank to the interface where it was caught by the interfacial film. The ring sank several millimeters below the original level of the interface, but it dragged the film with it and did not break through and sink to the bottom. The film outside the ring stretched and formed obvious wrinkles but did not break away from the sides of the beaker. The strength and elasticity of some of the films formed in this way, especially those made with Irish moss and mineral oil or olive oil, and acacia and cod-liver oil, are truly astonishing. In other cases the films were much weaker.

Figure 4—Films 28 Days Old; Surface Broken with Wire Loop on Twenty-third Day
A—Acacia 0.5 per cent, cod-liver oil. B—Acacia 2.0 per cent, cod-liver oil. C—Triethanolamine 0.03 per cent, cod-liver oil. D—Sodium oleate 0.06 per cent, cod-liver oil.

Figure 2 gives a photograph showing a saponin (concentration, 0.1 per cent)–castor oil interface which was 50 days old. The wire loop broke through and sank to the bottom of the beaker, leaving a wound which was visible for a long time and which is readily apparent in the photograph.

Sodium oleate with mineral oil gave a film which was much weaker. No wrinkles appeared when the film was pushed with the loop, and the film, although undoubtedly present, ruptured easily and left a wound which healed so quickly that a photograph, with sufficient contrast to justify an attempt to print it, could not be successfully obtained by pointing the camera from above. However, by pulling the film upward into the oil by means of a hook, it became clearly visible and several seconds elapsed before it went back to the interface. The film could be photographed as shown in Figure 3. The beaker in this photograph contained a 0.06 per cent sodium oleate solution on which mineral oil had stood for 21 days. The remarkable thing about these soap films is that, although they originally formed slowly, the films were promptly reformed after being ruptured.

Figure 4, A and B, shows films at a cod-liver oil–acacia, 0.5 and 2.0 per cent, interface. They were 28 days old. On the twenty-third day a wire loop was sent through the interface. The wound rehealed leaving protuberances which made the film easily visible. Figure 4, C and D, also shows the quite opaque films at cod-liver oil–triethanolamine, 0.03 per cent, and cod-liver oil–sodium oleate, 0.06 per cent, interfaces.

The influence of the oils on the properties of the films was more definite than that of the emulsifiers. Cod-liver oil formed an unmistakable film with all of the emulsifiers. Its speed of formation was also remarkable, as shown in Table II. With sodium oleate and triethanolamine the film was thick, granular, and opaque, but weak. With all of the other emulsifiers cod-liver oil gave tough opaque films. Some of them wrinkled when stretched with the wire loop. In some cases these films could be folded on themselves and then unfolded to their original condition. Olive oil comes next to cod-liver oil in the tendency to form films but these films were in general weaker and thinner and more transparent than the films given by cod-liver oil. Castor oil has a lesser tendency to form films. The films were transparent and weak and did not wrinkle in any case. Mineral oil has the least tendency to form films of any of the oils studied. However, films were seen with the higher concentration of the emulsifiers, except triethanolamine, during the four weeks they were observed. Thin films which were tough enough to give wrinkles were obtained with tragacanth and acacia.

At the interfaces where film formation took place there is no doubt that the film was polymolecular, as it was readily visible and coherent. It therefore seems probable that even in true emulsions the films formed may be thicker than monomolecular, provided the ratio of emulsifying agent to interfacial area is great enough.

The study of the films in this manner has helped considerably in the selection of the best emulsifier blends—that is, those which give both a quick and strong film formation for the industrial preparation of a stable emulsion. There are many other factors that must also be taken into consideration such as the protection from destruction by fermentation, putrefaction or mold growth, suitable viscosity, low interfacial tension, pH control, and degree of dispersion and means of attaining it. Quantitative measurements on the strength of the films are in progress.

Summary

A simple method of studying the formation and properties of films of emulsifiers at liquid-liquid interfaces has been developed and the properties and behavior of such films with eight different emulsifying agents and four different oils described. These observations have been helpful in the determination of suitable conditions for preparation of stable emulsions.

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Calculations on Water-Gas Equilibrium

Choice of Suitable Molecular-Heat Equations

Heat of Reaction and Free Energy as a Function of the Temperature[1]

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The thermal and equilibrium data for the water-gas reaction are assembled and discussed. $\Delta H_{298 \cdot 1}$ for the reaction $CO_2(g) + H_2(g) = CO(g) + H_2O(g)$ is calculated to be 9751 calories. This value is combined with molecular heat equations from several sources to yield expressions for ΔH as a function of the temperature. These equations, in turn, are used to show the order of agreement existing between molecular-heat equations of different sources. For this reaction specific heat equations of Lewis and Randall, of Eucken, and of Eastman give similar results. Partington and Shilling's equations do not agree with these results.

Expressions for the free-energy change, $\Delta F°$, and its temperature coefficient are derived, as well as for the corresponding reaction isochores. The equilibrium value of Neumann and Köhler at 1259.1° K. is used to determine the integration constants. It is shown that the molecular-heat equations of Lewis and Randall, of Eucken, and of Eastman, satisfactorily reproduce the experimental equilibrium constants in the water-gas reaction. It is also shown that Partington and Shilling's molecular-heat equations fail to reproduce these values. $\Delta F°_{298 \cdot 1}$ for the water-gas reaction is calculated. Numerical results ranging from 6828 to 6750 calories are obtained depending on the specific heats used. These values constitute the first step in a recalculation of the free energy of formation of carbon monoxide and dioxide.

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THE recent appearance of valuable new thermal and equilibrium data for the water-gas reaction makes it desirable to construct new expressions for the corresponding heat of reaction and free-energy change. These new data are of such a character that they fix within narrower limits the older directly determined equilibrium values, and permit of a more reliable extrapolation of the free energy to lower temperatures. Aside from its technical value, the water-gas equilibrium affords access to the free energy of formation of the oxides of carbon.

The early thermal data for the water-gas reaction are fully summarized by Haber (*16*). Apparently no direct experimental work has been done on this equilibrium above 1000° C. since that of Haber and Richardt (*19*) and that of Allner (*1*). The lower range, which at present is of greater industrial importance, has been rather extensively studied. The obscure Karlsruhe thesis of Engels (*10*) has been cited by Neumann and Köhler (*30*) with whose work Engels' values are in good agreement. Reinders (*38*) mentions an equally obscure paper of van Groningen (*15*) and while it has not been possible thus far to obtain van Groningen's actual figures, Reinders declares them to be in harmony with the work of Hahn (*20*), and of Haber (*16*). In 1924 Eastman and Evans (*7*) suggested that the equilibrium measurements of the carbon monoxide–carbon dioxide and water-hydrogen ratios over ferrous oxide and ferric oxide might be combined to yield true values for the water-gas equilibrium. The values so obtained were consistently about 40 per cent higher than previous direct determination would indicate. To clear up this matter, Neumann and Köhler (*30*) redetermined the values of the constant,

$$c_{CO} \times c_{H_2O}/c_{CO_2} \times c_{H}.$$

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[1] Received May 12, 1931.

They were able to check the previous direct determinations. Neumann and Köhler's equilibrium determinations are more consistent than those of the earlier workers, and the large number of individual observations made serves to further improve present knowledge of this reaction. Eastman (*5*) has recently published more data to support the high values obtained by the indirect method, particularly those from the oxidation-reduction equilibria in the presence of a tin–stannic oxide solid phase (*8*). Very convincing evidence in favor of the correctness of the direct equilibrium values is presented by Emmett and Shultz (*9*) who have obtained equilibrium constants by the indirect method, which are in good agreement with the work of Neumann and Köhler. They used a flow method and have shown that the anomalous results in the iron oxide systems obtained by Eastman and others (*7*, *41*, *42*, *43*) are traceable to the reactions

$$FeO + H_2 = Fe + H_2O$$
$$Fe_3O_4 + H_2 = 3FeO + H_2O$$

and that they are associated with the static method of attaining equilibrium first used by Deville (*3*). Results by this method, in fair agreement with those of Emmett and Shultz (*9*), have, however, been obtained by several experimenters (*2*, *3*, *37*).

Survey of Available Equilibrium Data

Figures 1 and 2 show graphically how the various determinations of the equilibrium constant of the water-gas reaction agree among themselves. The work of all the experimenters mentioned, except van Groningen, is shown in these diagrams. It will be noticed that Neumann and Köhler's, and Emmett and Shultz's points check very well, while Engels' values show fair agreement but are less consistent; also that Hahn's low-temperature points are all a trifle lower than those of the more recent work. The discrepancy between Haber's and Hahn's high-temperature results is plainly apparent in Figure 2 and is fully discussed elsewhere (*17*). Eastman's points are given for purposes of comparison.

Selection of Thermal Data

It is well known that the calculation of equilibrium in gaseous systems over wide ranges of temperature requires a knowledge of four factors: the molecular heats of the reactants and products, the heat of reaction, at least one known value of the equilibrium or equivalent free-energy data, and the deviations of the substances from the perfect gas. In the case of a reaction taking place at one atmosphere and elevated temperatures, it is generally agreed that the assumption of perfect gases introduces only errors that are negligibly small. This can safely be assumed to hold in the reaction

$$CO_2\,(g) + H_2\,(g) = CO\,(g) + H_2O\,(g)$$

Hence only the first three factors need be considered here.

In the water-gas reaction, the equilibrium and heat of reaction are known with considerable accuracy, and will be of service in selecting the most likely expressions for the molecular heats. Such a procedure has already been tried by Partington and Shilling (*35*, *36*) whose work, however, is marred by errors as will be shown further on.

A number of authors (*4*, *6*, *11*, *13*, *14*, *21*, *24*, *33*, *40*) have summarized the present experimental knowledge of the specific heats of gases in the form of analytical expressions for the most part empirical in nature. After careful comparison of a large number of these equations with the experimental specific heats, equations from four such compilations were selected for the present work. These molecular-heat equations are as follows:

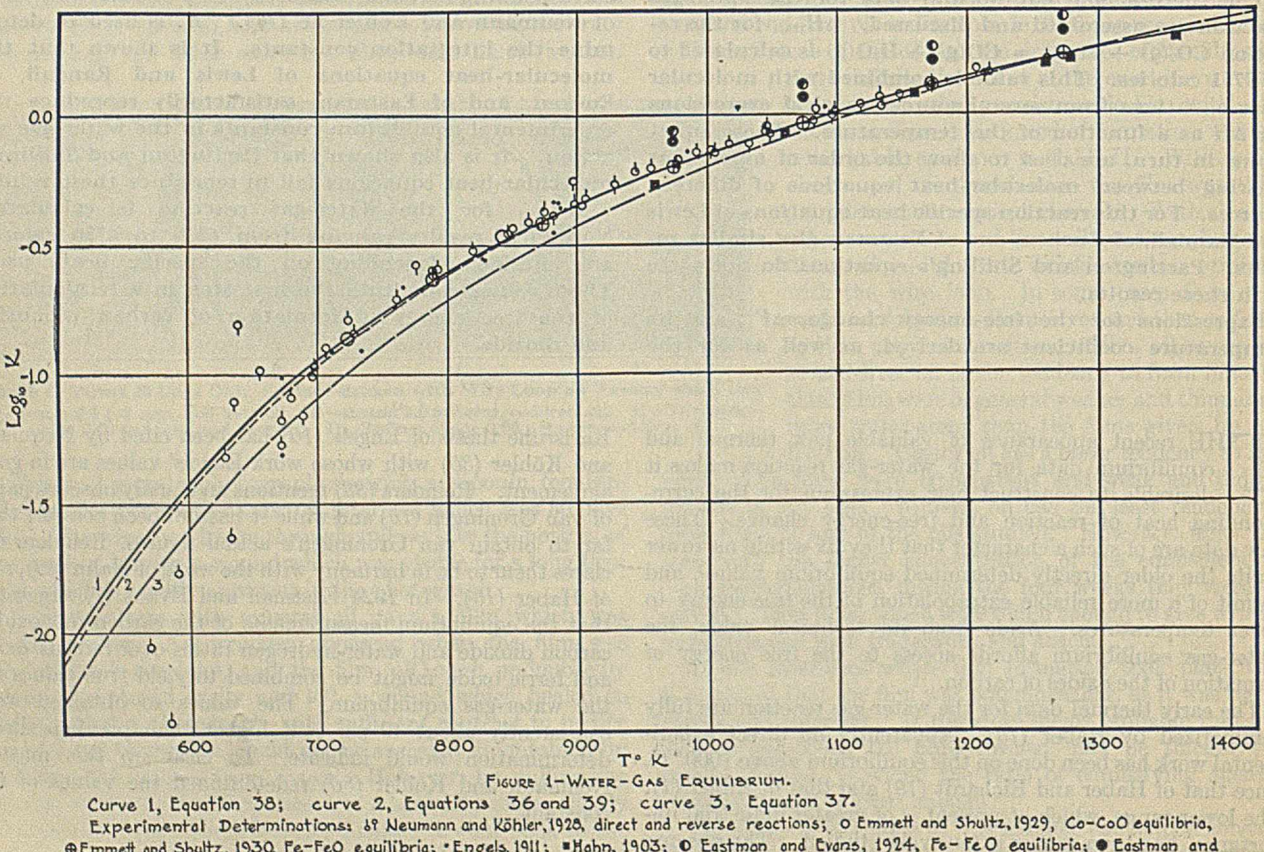

Figure 1—Water-Gas Equilibrium.

Curve 1, Equation 38; curve 2, Equations 36 and 39; curve 3, Equation 37.

Experimental Determinations: δ♀ Neumann and Köhler, 1928, direct and reverse reactions; o Emmett and Shultz, 1929, Co–CoO equilibria, ⊕ Emmett and Shultz, 1930, Fe–FeO equilibria; • Engels, 1911; ▪ Hahn, 1903; ◐ Eastman and Evans, 1924, Fe–FeO equilibria; ● Eastman and Evans, 1924, FeO–Fe_xO_4 equilibria, ▼ Eastman and Robinson, 1928, Sn–SnO_2 equilibria.

Lewis and Randall (*24*):

$$\text{CO: } C_p = 6.50 + 0.0010T \quad (1)$$

$$\text{H}_2\text{O: } C_p = 8.81 - 0.0019T + 0.00000222T^2 \quad (2)$$

$$\text{CO}_2\text{: } C_p = 7.0 + 0.0071T - 0.00000186T^2 \quad (3)$$

$$\text{H}_2\text{: } C_p = 6.50 + 0.0009T \quad (4)$$

Partington and Shilling (*34*):

$$\text{CO: } C_v = 4.924 + 0.00017T + 0.00000031T^2 \quad (5)$$

$$\text{H}_2\text{O: } C_v = 6.901 - 0.0019T + 0.00000234T^2 \quad (6)$$

$$\text{CO}_2\text{: } C_v = 5.547 + 0.0045T - 0.00000102T^2 \quad (7)$$

$$\text{H}_2\text{: } C_v = 4.659 + 0.0007T \quad (8)$$

Eucken (*12*)[2]:

$$\text{CO: } C_p = 6.96 + \psi\left(\frac{3090}{T}\right)\ (13) \quad (9)$$

$$\text{H}_2\text{O: } C_p = 7.95 + \psi\left(\frac{2300}{T}\right) + 2\psi\left(\frac{5800}{T}\right)\ (11) \quad (10)$$

$$\text{CO}_2\text{: } C_p = 6.96 + 2\psi\left(\frac{990}{T}\right) + \psi\left(\frac{1730}{T}\right) + \psi\left(\frac{3200}{T}\right)\ (13) \quad (11)$$

$$\text{H}_2\text{: } C_p = 6.96 + \psi\left(\frac{6100}{T}\right)\ (11) \quad (12)$$

Eastman:

$$\text{CO: } C_p = 6.76 + 0.000606T + 0.00000013T^2\ (4) \quad (13)$$

$$\text{H}_2\text{O: } C_p = 8.32 - 0.000653T + 0.00000270T^2 - 0.0000000006145T^3\ (6) \quad (14)$$

$$\text{CO}_2\text{: } C_p = 5.07 + 0.01630T - 0.00001290T^2 + 0.00000000391T^3\ (4) \quad (15)$$

$$\text{H}_2\text{: } C_p = 6.85 + 0.00028T + 0.00000022T^2\ (4) \quad (16)$$

Combining the molecular-heat equations for carbon monoxide and water, and subtracting those for carbon dioxide and hydrogen, the difference may be integrated with respect to the temperature according to the Kirchoff formula (*25*)[3]:

$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad (17)$$

or

$$\frac{d(\Delta E)}{dT} = \Delta C_v \quad (18)$$

ΔH and ΔE are the heats of reaction at constant pressure and constant volume, respectively, and are practically identical in the present case where the reaction takes place without change in the number of molecules.

In computing the heat absorbed in the water-gas reaction, the heats of combustion of hydrogen and carbon monoxide recently determined by Rossini (*39*) were used. These values are given directly for 25° C. and 1 atmosphere, and undoubtedly surpass all earlier work in precision. $\Delta H_{298.1}$ for the water-gas reaction is calculated as follows:

$$\text{H}_2\text{(g)} + {}^1/_2\text{O}_2\text{(g)} = \text{H}_2\text{O (l)}; \quad \Delta H_{298.1} = -68{,}313 \quad (19)$$

$$\text{CO}_2\text{(g)} = \text{CO (g)} + {}^1/_2\text{O}_2\text{(g)}; \quad \Delta H_{298.1} = 67{,}623 \quad (20)$$

Adding Equations 19 and 20 yields:

$$\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} = \text{H}_2\text{O (l)} + \text{CO (g)}; \quad \Delta H_{298.1} = -960 \quad (21)$$

The heat of vaporization of water at 298.1° K. and 1 atmosphere was calculated from the heat of vaporization at 373.1° K. (*22*) by means of the molecular heats of liquid (*23*) and gaseous water (*6*) (see Equation 14), and found to be 10,441 calories. The value is combined with that of Equation 21 to give Equation 23, the quantity sought:

$$\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} = \text{H}_2\text{O (l)} + \text{CO (g)}; \quad \Delta H_{298.1} = -960 \quad (21)$$

$$\text{H}_2\text{O (l)} = \text{H}_2\text{O (g)}; \quad \Delta H_{298.1} = 10{,}441 \quad (22)$$

$$\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} = \text{H}_2\text{O (g)} + \text{CO (g)}; \quad \Delta H_{298.1} = 9751^4 \quad (23)$$

The heat of reaction at 298.1° K., just computed, may then be substituted into the integrated forms of expressions, Equations 17 and 18, which, for convenience in treating the diverse types of specific heat equations, may be formulated as follows:

$$\Delta H = \Delta H_0 + \Delta C_{p0}\,T + \int_0^T \Delta C'_p dT \quad (24)$$

$$\text{and } \Delta E = \Delta E_0 + \Delta C_{v0}\,T + \int_0^T \Delta C'_v dT$$

where C_{p0} and C_{v0} represent the constant part of the specific heats, and C'_p and C'_v, the temperature coefficient. Equations 24 and 25 are then solved for ΔH_0 and ΔE_0. The completed expressions for the temperature variation of the heat of reaction are given below and the source of the molecular heats indicated:

Lewis and Randall:

$$\Delta H = 9570 + 1.81T - 0.00445T^2 + 0.00000136T^3 \quad (26)$$

Partington and Shilling:

$$\Delta E = 9512 + 1.619T - 0.00311T^2 + 0.00000122T^3 \quad (27)$$

Eucken:

$$\Delta H = 9612 + 0.99T + \int_0^T \left[\psi\left(\frac{3090}{T}\right) + \psi\left(\frac{2300}{T}\right) + 2\psi\left(\frac{5800}{T}\right) - 2\psi\left(\frac{990}{T}\right) - \psi\left(\frac{1730}{T}\right)\psi - \left(\frac{3200}{T}\right) - \psi\left(\frac{6100}{T}\right)\right] dT \quad (28)$$

Eastman:

$$\Delta H = 9420 + 3.16T - 0.008314T^2 + 0.00000517T^3 - 0.000000001131T^4 \quad (29)$$

Equations 26, 27, 28, and 29 have been solved for a number of temperatures to show the order of agreement that exists between the work of these authorities. The results are given in Table I and are plotted in Figure 3.

Table I—Heat of Reaction at Various Temperatures Using Molecular Heats from Several Sources

T ° K.	t ° C.	ΔH (ΔC_p Lewis and Randall)	ΔE (ΔC_v Partington and Shilling)	ΔH (ΔC_p Eucken)	ΔH (ΔC_p Eastman)
298.1	25.0	9751	9751	9751	9751
400	126.9	9669	9740	9618	9656
500	226.9	9532	9697	9415	9496
600	326.9	9348	9627	9174	9293
700	426.9	9122	9539	8911	9059
800	526.9	8866	9442	8648	8811
900	626.9	8585	9339	8376	8557
1000	726.9	8290	9241	8112	8305
1200	926.9	7684	9085	7602	7829
1400	1126.9	7114	9031	7126	7391
1600	1326.9	6645	9137	6620	6956
1800	1526.9	6342	9465	6251	6449

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[2] Eucken uses the Planck-Einstein function designated as ψ to express the temperature coefficients of the molecular heats of gases. Since the integration of this function is difficult, the tabulated integrals $\frac{1}{T}\int_0^T C'_T dT$ and $\int_0^T \frac{dT}{T^2}\int_0^T C'_T dT$ for different values of $\frac{\beta v}{T}$ have been given on pages 406–407. They are designated as Φ and Ψ, respectively.

[3] Lewis and Randall's system of notation will be used throughout except in the treatment of the Planck-Einstein function in which case Eucken, Jette, and LaMer (*12*) will be followed.

[4] Before the appearance of Rossini's work, the value $\Delta H_{298.1} = 9730$ was calculated from the older thermochemical data. The chief uncertainty lay in the heat of combustion of carbon monoxide determined by Thomsen [*Thermochem. Untersuchungen*, **2**, 288 (1886)], and Berthelot [*Ann. chim. phys.*, **20**, 255 (1880)]. These values, 67,960 and 68,300, respectively, were corrected for systematic errors as directed by Swietoslawski ("Ostwald-Druckers Handbuch der Allgemeinen Chemie," Vol. VII, p. 95, Akademische Verlagsgesellschaft, Leipzig, 1928) and converted to 15° calories by means of the factor 4.1819/4.185. The resulting values 67,638 and 67,567 were calculated to 298.1° K. by means of specific heats and the average, 67,610, combined with the heat of combustion of hydrogen [Roth, *Z. Elektrochem.*, **26**, 288 (1920)] and Lewis and Randall's value for the heat of vaporization of water at 298.1° K. ["Thermodynamics," p. 477, McGraw-Hill, 1923] to obtain the above heat of reaction. This value is inferior to the one used in the present paper, although probably better than those previously derived from uncorrected thermochemical data.

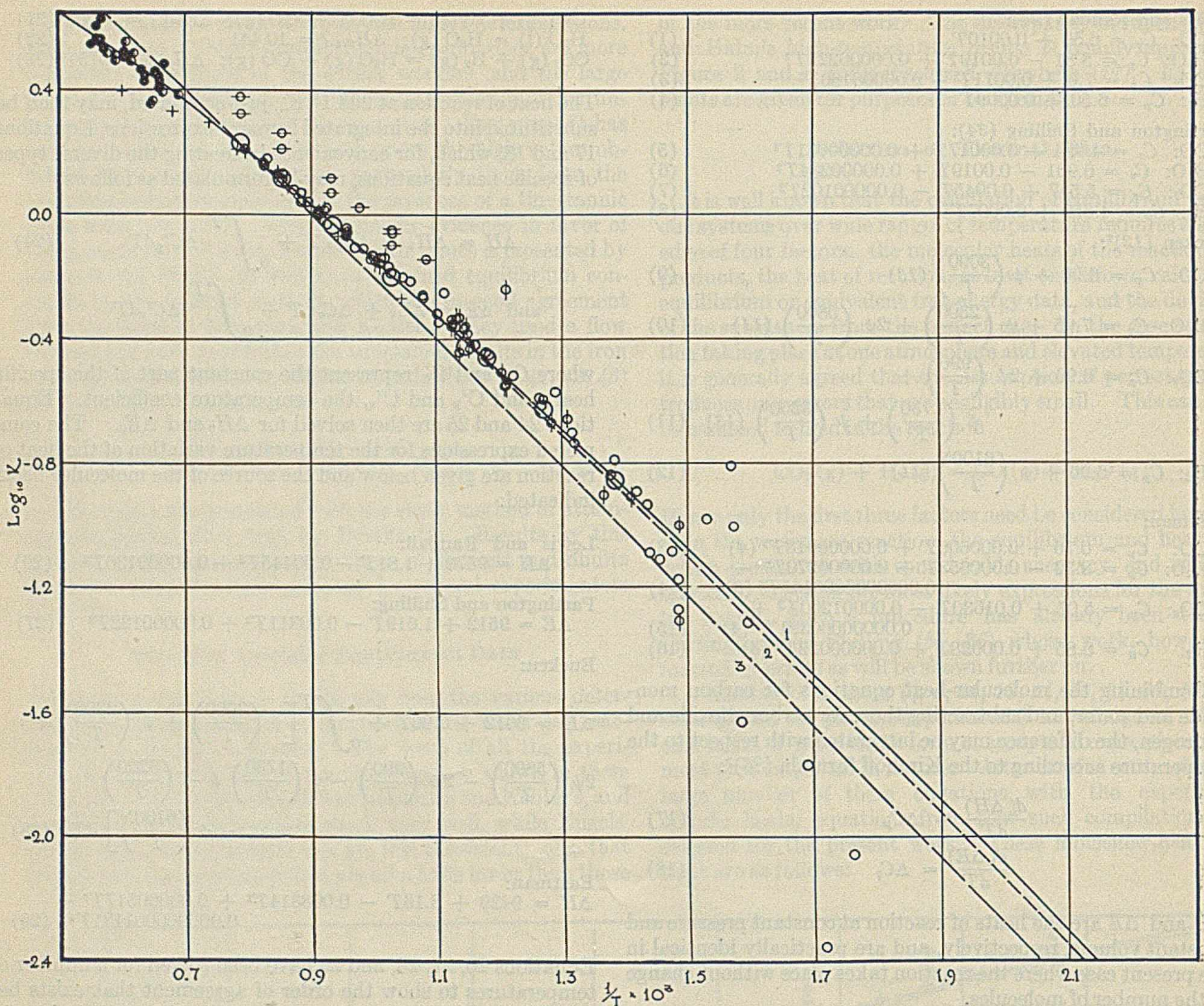

FIGURE 2 — WATER-GAS EQUILIBRIUM INCLUDING WORK AT FLAME TEMPERATURES.
Curve 1, Equation 38; curve 2, Equations 36 and 39; curve 3, Equation 37.
Experimental Determinations: O Emmett and Shultz, 1929-30; o Neumann and Köhler, 1928; ϕ Engels, 1911; + Hahn, 1903; ● Haber and Richardt, 1904, ◐ Allner, 1905; -θ- Eastman, 1924-28.

Inspection will show that the values of ΔH calculated from the molecular heats of Lewis and Randall, Eucken, and Eastman are fairly concordant, the greatest differences scarcely exceeding 300 calories. On the other hand, ΔE from Partington and Shilling's equations (in this case comparable with ΔH) shows temperature variation of entirely different character. The values differ from those of the first group by more than 1000 calories at temperatures below 1200° K.

This fact in itself is in no way prejudicial to the work of Partington and Shilling, but merely serves to expose a complete lack of agreement between these two groups of authorities. However, other evidence is available to show that Partington's specific heats are not in harmony with the known equilibrium in the water-gas reaction, while those of Lewis and Randall, Eucken, and Eastman will be shown to be in good agreement. A few years ago Partington and Shilling (*35*) published an article on the water-gas equilibrium with which their specific heats seemed to agree. Shortly afterward a small arithmetical error in this work was found by Travers and duly corrected by the authors (*36*) leaving the apparent agreement better than before. An unfortunate error in the conversion of their ΔC_v from the Centigrade to the Kelvin scale has been detected.[5] When the proper correction is made, the order of agreement between experiment and calculation is greatly impaired. The substitution of more recent ΔH and equilibrium values is not sufficient to remove the discrepancy, as an inspection of Table II and Figures 1 and 2 will show. Thus the only conclusion that can be drawn is that Partington and Shilling's specific heats are not able to correlate the other experimental data for the water-gas equilibrium.

Although the failure of specific heats to check with reliable thermal and equilibrium data leaves those specific heats open to question, complete agreement is no assurance that the C_p and C_v equations for the individual gases are correct, since compensating errors in the individual equations may cancel, leaving the summation sensibly correct. It is believed that this is the case with Lewis and Randall's C_p equations for carbon dioxide and water, which probably are not representative of the most recent experimental work, yet serve satisfactorily in calculating the present equilibrium. Eucken's molecular-heat formulas are more difficult to use than East-

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[5] The equation given in (*36*) reads: $\log K = -2125/T + 1.077 \log T - 0.0_3898\, T + 0.0_6133\, T^2 - 0.5425$. When the error noted here is corrected, the expression should read: $\log K = -2140/T + 0.815 \log T - 0.0_3680\, T + 0.0_6133\, T^2 + 0.0147$.

man's, although both seem to follow experiment closely. Eucken's equations are probably unique in that they possess some theoretical significance, since their temperature coefficients can be deduced from spectral measurements, although at present such interpretation of spectra presents many difficulties.

Temperature Coefficient of Free-Energy Change and Its Expression in Form of Reaction Isochore

When the heat of reaction has been expressed as a function of the temperature, it is a simple matter to derive an equation for the free-energy change at any temperature and to express this in terms of the fugacities (corrected partial pressures) of the molecular species present at equilibrium. Lewis and Randall (*26*) have outlined fully how this may be accomplished by means of the following relations:

$$\frac{d(\Delta F/T)}{dT} = -\frac{\Delta H}{T^2} \qquad (30)$$

and

$$\Delta F^\circ = -RT \ln K^6 \qquad (31)$$

Applying these principles to Equations 26, 27, 28, and 29 the following free-energy equations are obtained:

Lewis and Randall:

$$\Delta F^\circ = 9570 - 1.81T \ln T + 0.00445T^2 - 0.00000068T^3 + IT \qquad (32)$$

Partington and Shilling:

$$\Delta A^\circ = 9512 - 1.619T \ln T + 0.00311T^2 - 0.00000061T^3 + IT \qquad (33)$$

Eucken:

$$\Delta F^\circ = 9612 - 0.99\, T \ln T - T \int_0^T \frac{dT}{T^2} \int_0^T \left[\psi\left(\frac{3090}{T}\right) + \psi\left(\frac{2300}{T}\right) + 2\psi\left(\frac{5800}{T}\right) - 2\psi\left(\frac{990}{T}\right) - \psi\left(\frac{1730}{T}\right) - \psi\left(\frac{3200}{T}\right) - \psi\left(\frac{6100}{T}\right)\right] dT + IT \qquad (34)$$

Eastman:

$$\Delta F^\circ = 9420 - 3.16\, T \ln T + 0.008314T^2 - 0.000002585T^3 + 0.0000000003770T^4 + IT \qquad (35)$$

These in turn are converted to the form of the integrated van't Hoff isochore by means of Equation 31, where

$$RT \ln K = 4.5750T \log_{10} K$$

Lewis and Randall:

$$\log_{10} \frac{f_{CO} \times f_{H_2O}}{f_{CO_2} \times f_{H_2}} = \frac{-2091.8}{T} + 0.911 \log_{10} T - 0.000973T + 0.000000149T^2 + i \qquad (36)$$

Partington and Shilling:

$$\log_{10} \frac{f_{CO} \times f_{H_2O}}{f_{CO_2} \times f_{H_2}} = \frac{-2079.1}{T} + 0.8148 \log_{10} T - 0.0006798T + 0.0000001333T^2 + i \qquad (37)$$

Eucken:

$$\log_{10} \frac{f_{CO} \times f_{H_2O}}{f_{CO_2} \times f_{H_2}} = \frac{-2101.0}{T} + 0.4983 \log_{10} T + 0.2186 \int_0^T \frac{dT}{T^2} \int_0^T \left[\psi\left(\frac{3090}{T}\right) + \psi\left(\frac{2300}{T}\right) + 2\psi\left(\frac{5800}{T}\right) - 2\psi\left(\frac{990}{T}\right) - \psi\left(\frac{1730}{T}\right) - \psi\left(\frac{3200}{T}\right) - \psi\left(\frac{6100}{T}\right)\right] dT + i \qquad (38)$$

Eastman:

$$\log_{10} \frac{f_{CO} \times f_{H_2O}}{f_{CO_2} \times f_{H_2}} = \frac{-2059.0}{T} + 1.5904 \log_{10} T - 0.001817T + 0.0000005650T^2 - 0.00000000008240T^3 + i \qquad (39)$$

The integration constants, I and i, in the two previous sets of equations may be computed with considerable precision from the carefully determined equilibrium value of Neumann and Köhler (*31*) at 986° C., which is the mean of twenty individual observations. This result is as follows:

$$\frac{c_{CO} \times c_{H_2O}}{c_{CO_2} \times c_{H_2}} = \frac{f_{CO} \times f_{H_2O}}{f_{CO_2} \times f_{H_2}} = 1.611 \text{ at } 1259.1^\circ \text{ K.} \qquad (40)$$

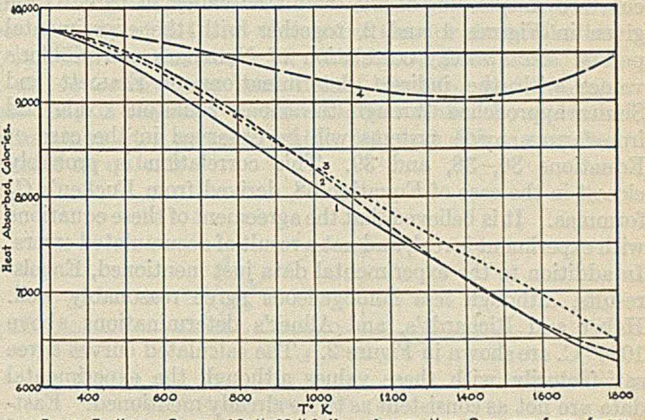

FIGURE 3 - HEAT OF REACTION $CO_2+H_2=CO+H_2O$. USING SPECIFIC HEAT DATA FROM SEVERAL SOURCES. Curve 1, Eucken; curve 2, Lewis and Randall; curve 3, Eastman; curve 4, Partington and Shilling.

The I values for each of the free-energy equations and the constant i for the corresponding van't Hoff equations are tabulated below, each opposite the number of its respective formula:

EQUATION	I	EQUATION	
32	−0.1514	36	0.0331
33	0.1048	37	−0.0229
34	−4.1106	38	0.8985
35	7.0057	39	−1.5313

Equations 36, 37, 38, and 39 were solved for a number of temperatures. For purposes of comparison the resulting equilibrium constants are given in Table II.

Table II—Equilibrium Isotherms for Water-Gas Reaction

T	t	$f_{CO} \times f_{H_2O}/f_{CO_2} \times f_{H_2}$			
° *K.*	° *C.*	(36)	(37)	(38)	(39)
298.1	25	9.85×10^{-6}	6.73×10^{-6}	1.12×10^{-5}	1.02×10^{-5}
400	126.9	6.44×10^{-4}	4.46×10^{-4}	7.29×10^{-4}	6.57×10^{-4}
450	176.9	2.48×10^{-3}	1.74×10^{-3}	2.78×10^{-3}	2.52×10^{-3}
500	226.9	7.23×10^{-3}	5.15×10^{-3}	8.00×10^{-3}	7.34×10^{-3}
550	276.9	1.72×10^{-2}	1.25×10^{-2}	1.89×10^{-2}	1.74×10^{-2}
600	326.9	3.53×10^{-2}	2.60×10^{-2}	3.81×10^{-2}	3.56×10^{-2}
650	376.9	6.43×10^{-2}	4.84×10^{-2}	6.85×10^{-2}	6.45×10^{-2}
700	426.9	1.07×10^{-1}	8.22×10^{-2}	1.12×10^{-1}	1.07×10^{-1}
750	476.9	1.65×10^{-1}	1.30×10^{-1}	1.73×10^{-1}	1.65×10^{-1}
800	526.9	2.40×10^{-1}	1.93×10^{-1}	2.49×10^{-1}	2.39×10^{-1}
850	576.9	3.32×10^{-1}	2.73×10^{-1}	3.45×10^{-1}	3.30×10^{-1}
900	626.9	4.42×10^{-1}	3.72×10^{-1}	4.50×10^{-1}	4.38×10^{-1}
950	676.9	5.68×10^{-1}	4.89×10^{-1}	5.72×10^{-1}	5.63×10^{-1}
1000	726.9	7.09×10^{-1}	6.25×10^{-1}	7.14×10^{-1}	7.02×10^{-1}
1050	776.9	8.63×10^{-1}	7.80×10^{-1}	8.60×10^{-1}	8.56×10^{-1}
1100	826.9	1.03	9.52×10^{-1}	1.03	1.02
1200	926.9	1.39	1.35	1.39	1.38
1400	1126.9	2.16	2.32	2.17	2.18
1600	1326.9	2.95	3.48	2.93	3.02
1800	1526.9	3.70	4.82	3.63	3.81

It will be recalled that the equilibrium constants given in Table II have been calculated using the heat of reaction from Rossini's heats of combustion of CO and H_2; the equilibrium data of Neumann and Köhler at 1259.1° K.; and the respective molecular heat equations of Lewis and Randall, Partington and Shilling, Eucken, and Eastman.

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[6] K may be assumed identical with K_p and K_c in the present case since, at 1 atmosphere and high temperatures, deviation from the perfect gas must be less than the experimental errors in determining the equilibrium. However, for extrapolation to lower temperatures, the calculated value K will be equal to the quotient of the fugacities rather than of the partial pressures.

Table III—Comparison of Constants, $f_{CO} \times f_{H_2O}/f_{CO_2} \times f_{H_2}$, from Several Sources

T	t	Haber	Lewis and Randall	Neumann and Köhler	Equation 36	Equation 38	Equation 39
°K.	°C.						
500	226.9	5.75×10^{-3}	5.20×10^{-3}	7.91×10^{-3}	7.23×10^{-3}	8.00×10^{-3}	7.34×10^{-3}
600	326.9	2.91×10^{-2}	2.77×10^{-2}	3.77×10^{-2}	3.53×10^{-2}	3.81×10^{-2}	3.56×10^{-2}
700	426.9	8.96×10^{-2}	8.91×10^{-2}	1.12×10^{-1}	1.07×10^{-1}	1.12×10^{-1}	1.07×10^{-1}
800	526.9	2.02×10^{-1}	2.10×10^{-1}	2.49×10^{-1}	2.40×10^{-1}	2.49×10^{-1}	2.39×10^{-1}
900	626.9	3.68×10^{-1}	4.01×10^{-1}	4.50×10^{-1}	4.42×10^{-1}	4.50×10^{-1}	4.38×10^{-1}
1000	726.9	6.76×10^{-1}	6.62×10^{-1}	7.25×10^{-1}	7.09×10^{-1}	7.14×10^{-1}	7.02×10^{-1}
1400	1126.9	2.12	2.18	2.23	2.16	2.17	2.18
1800	1526.9	3.69	3.88	3.65	3.70	3.63	3.81

It is readily apparent from Table II that the constants calculated from the equations of Lewis and Randall, Eucken, and Eastman are in good agreement. The values from Partington's specific heats, it will be noticed, differ from these. The curves corresponding to the calculated values in Table II are given in Figures 1 and 2, together with the experimental points. Noteworthy correlation of Neumann and Köhler's values with the indirect determinations of Emmett and Shultz approached through the cobalt–cobaltous oxide and iron–ferrous oxide systems will be observed in the case of Equations 36, 38, and 39. This correlation is probably closest in the case of Equation 38, derived from Eucken's C_p formulas. It is believed that the agreement of these equations with experiment is real, and not a result of accumulated errors. In addition to the experimental data just mentioned, Engels' results, although less homogeneous agree reasonably well. Haber and Richardt's, and Allner's determinations above 1000° C. are shown in Figure 2. The calculated curves agree satisfactorily with these values although the experimental data are not as consistent as those already mentioned. Eastman's determinations are shown in both of the diagrams and although thoroughly self-consistent, they differ from all the other data given.

In the author's opinion the analytical expressions for ΔH, ΔF, and the equilibrium constant K, based upon the specific-heat equations of Eucken and of Eastman, are the most reliable, since they reproduce experiment satisfactorily and at the same time are representative of present knowledge of specific heats. It is not possible to say with certainty which of these two series of formulas is the more reliable.

Survey of Earlier Equations for Water-Gas Equilibrium

There are a few earlier equations for the water-gas equilibrium which will be briefly discussed. Such expressions have been derived by Haber (*18*), Lewis and Randall (*27*), Neumann and Köhler (*32*), and Eastman (*5*). The first two have been derived from older data and hence cannot be expected to agree completely with the present calculations. Neumann and Köhler's equation is similar to Equation 38 and the agreement with experiment is good. For purposes of extrapolation to lower temperatures, this equation is probably less reliable, since some specific heats used differ from Eucken's latest values, and since the heat of reaction is not an independently determined quantity but has apparently been derived from their own equilibrium determinations. Eastman's equation has been derived from the abnormally high indirect-equilibrium experiments and for that reason is not in harmony with the present calculation. This equation will not be further considered. The equilibrium constants from the remaining three expressions are compared with those from Equations 36, 38, and 39 at several temperatures in Table III.

Standard Free-Energy Change in Water-Gas Reaction

There is frequent need for values of the free-energy change at 298.1° K., the standard reference temperature most used by Lewis and Randall (*29*), for the calculation of other reactions. Both these authorities (*28*) and Eastman (*5*) have calculated the free energy of the water-gas reaction as a means of approaching the corresponding free energy of formation of carbon monoxide and dioxide. These latter quantities are obtained by combining the free-energy data for the water-gas reaction with those for the reactions, C (β-graphite) + CO_2 (g) = 2CO (g), the well-known producer-gas reaction, and H_2 (g) + $^1/_2$ O_2 (g) = H_2O (g), the synthesis of water vapor, both of which may be computed with considerable accuracy.

The free-energy change accompanying the water-gas reaction at 298.1° K. and 1 atmosphere, as calculated from each of the Equations 32, 34, and 35 is as follows:

Equation	$\Delta F°_{298.1}$
32	6828
34	6750
35	6807

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Detergent Value of Sodium Metasilicate[1]

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Wetting, emulsification, deflocculation, and dissolving power are important considerations which affect the action of aqueous detergent solutions. Sodium metasilicate is more effective than NaOH, Na_2CO_3, or Na_3PO_4 in wetting glass. Sodium metasilicate is effective in displacing a petroleum oil from a glass surface over a wider range of concentration than the other alkalies here considered. Solutions of $Na_2SiO_3.5H_2O$ and $Na_3PO_4.12H_2O$ emulsify a light motor oil better than do those of Na_2CO_3 and NaOH. Qualitative tests show that solutions of $Na_2SiO_3.5H_2O$ have deflocculating power for bone black of at least the same order of magnitude as $Na_2O:3.25SiO_2$, $Na_3PO_4.12H_2O$, Na_2CO_3, and NaOH.

Sodium silicate yields solutions of higher pH than the other alkalies considered with the exception of NaOH. Sodium hydroxide is too caustic for many cleaning jobs. A larger proportion of the Na_2O in Na_2SiO_3 is available at an effective pH than in the other alkaline salts considered. Soap suds are associated with cleaning activity in soap solutions. A solution of 0.0088 per cent $NaC_{18}H_{35}O_2$ gives a more abundant suds at an optimum pH. Curves are given for the amount of foam formed at 60° C. over a range of pH and concentration for four alkalies. A solution of Na_2SiO_3 with $NaC_{18}H_{35}O_2$ gives more suds at all concentrations than NaOH, Na_3PO_4, and Na_2CO_3. Less soap is required to wash clothes when the suds are maintained at a relatively high pH, and dirt is removed at least as quickly.

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THE detergent action of aqueous solutions may be said to depend upon at least four principal factors: wetting power, emulsifying ability, deflocculating power, and dissolving power.

Quite obviously in any particular cleaning problem some of these factors are apt to be of greater importance than the others, but in most industrial cleaning all of them play some part.

In considering the value of a new detergent alkali, it seems wise to consider its behavior in respect to all of these factors. It is also important to know its action on the materials to be cleaned. Such an examination requires a comparison with other materials now in common use, as there seems to be at present no better method of evaluation.

Wetting

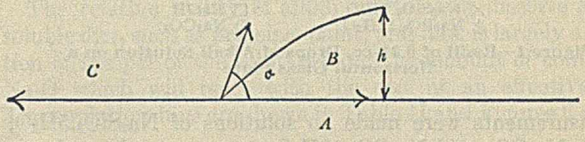
The first essential in a detergent solution is that it shall wet the surface to be cleaned. By so doing, it displaces therefrom the various forms of dirt clinging to it. For example, pure water does not wet the surface of glass sufficiently to remove a film of mineral oil. If a small amount of soap is dissolved in the water it may wet the surface of the glass, displacing the oil, and the surface is thereby cleaned.

It is also important that the solution wet the dirt particles themselves so that any agglomerates may be broken up and separated and thus be more easily held in suspension and washed away.

High wetting power is dependent upon a favorable balance of surface forces. These forces in turn are highly specific and vary with the solids and fluids concerned, the particular solution, its concentration and many other variables.

Many workers have measured the effect of various solutes upon the interfacial tension between water and another immiscible fluid. The assumptions have been that the solute which thus produced a lower interfacial tension increased the wetting power of the solution, and that the solute which produced a greater lowering than the other was the better detergent. Neither of these assumptions takes into consideration the effect of the solute upon the solution/interfacial tension. Although this situation has been recognized before, there has been no convenient method for determining the resultant of all the surface forces concerned.

The general case of wetting is expressed in the equation credited to Neuman by Rideal (*11*):



(1)

$$\sigma_{AC} = \sigma_{AB} + \sigma_{BC}\cos\alpha$$

where σ_{AC} = interfacial tension solid/air
σ_{AB} = interfacial tension liquid/solid
σ_{BC} = interfacial tension liquid/air
α = angle at which liquid meets solid.

This relation also holds for any two immiscible liquids at rest on a solid surface in contact with each other. It should be noted that this equation holds only in the special case where the drop is extremely thin.

In order to evaluate the horizontal resultant of the surface forces concerned, it is assumed that the drop considered has a finite thickness. Another quantity may then be added to the equation, thus:

$$\sigma_{AC} = \sigma_{AB} + \sigma_{BC}\cos\alpha - {}^1/_2\, gPh^2 \qquad (2)$$

where g = gravitational constant
P = density of liquid
h = greatest thickness of drop

If the drop is fairly thin and circular in form,

$$h = \frac{V}{\pi r^2} \qquad (3)$$

where V = volume of drop in cc.
r = radius of flattened drop

Then substituting (3) into (2),

$$(\sigma_{AB} + \sigma_{BC}\cos\alpha) - \sigma_{AC} = \frac{g\,P\,V^2}{2\pi^2r^4} \qquad (4)$$

By evaluating the right hand expression, the horizontal resultant of opposing surface forces can be obtained. Obviously the greater the value of r for drops of the same volume, the greater the wetting power of the solution. On this basis the relative wetting powers of aqueous solutions of the various common alkalies were determined.

A large sheet of plate glass was thoroughly cleaned by treatment with a strong solution of NaOH, rinsed, and then cleaned with a $Na_2Cr_2O_7.2H_2O$–H_2SO_4 mixture, thoroughly rinsed with distilled water, and dried at 110° C. for one hour. The plate was then laid over a sheet of millimeter cross-section paper and carefully leveled. The room was held at a temperature

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[1] Received March 27, 1931.

of 20° ± 1° C. The plate was allowed to come to this temperature and 0.31-cc. portions of the various alkali solutions carefully run onto the plate from a pipet.

The drops soon came to equilibrium and the radii in four directions were read off from the paper below. Usually five to eight drops of each solution were placed on the plate at one time, and all the values obtained on this group averaged for the final value. By doing this and by taking measurements on different days, it was felt that the results obtained were accurate to about 0.05 cm.

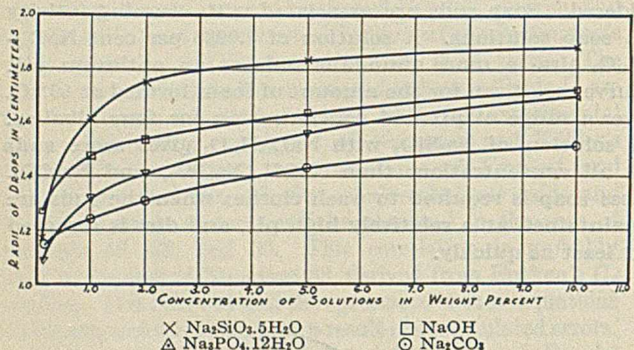

Figure 1—Radii of 0.31-cc. Drops of Alkali Solution on a Horizontal Glass Plate

Measurements were made on solutions of $Na_2SiO_3.5H_2O$, NaOH, Na_2CO_3, and $Na_3PO_4.12H_2O$ at concentrations of 1 to 10 per cent. The values for r obtained are plotted in Figure 1. The curve for $Na_2SiO_3.5H_2O$ is above those for the other alkalies at all concentrations, showing a much superior wetting power for this alkali.

Displacement of Oil from Surfaces

The relative ability of alkali solutions to displace oil from solid surfaces can be shown in the following way:

> A series of test tubes 10 mm. in diameter are carefully cleaned and dried. About 1 cc. warm petroleum oil is then placed in each tube while it is still hot and the tube rotated so as to distribute the oil evenly over the inside surface. The tube is immediately cooled and placed in the rack. A solution of a different alkali is then added to each tube, and the tubes allowed to stand undisturbed. The series may be observed after various lengths of time.

This method has been repeatedly applied to different oils. The results have been very consistent and are well represented in Figure 2. Here the effect of 0.1 to 5 per cent solutions of $Na_2SiO_3.5H_2O$, $Na_3PO_4.12H_2O$, NaOH, and Na_2CO_3 against a heavy automobile transmission oil are shown after standing for 6 days at 20° ± 2° C. In observing this photograph, care must be taken to distinguish between darkness due to oil adhering to the glass surface and darkness due to small amounts of oil emulsified spontaneously.

It is to be noted that two different factors seem to be at work in this case. One of these might be called emulsification and might explain the oil removed at lower concentrations. The other factor might be thought of as one of oil displacement from the glass surface due to a favorable balance of surface forces and might explain the removal of the oil by $Na_2SiO_3.5H_2O$ at the higher concentrations. This superiority of sodium metasilicate checks well with the curves of Figure 1.

In this connection it should be pointed out that, in industrial cleaning practice involving the use of an alkali in the absence of soap, it is customary to use from 2 to 5 per cent solutions. These high concentrations seem necessary in order to obtain a high bactericidal effect, to dissolve alkali-soluble dirt, and to offset the effect of dilution by rinse water.

The superiority of $Na_2SiO_3.5H_2O$ in wetting solid surfaces and in displacing oil from them has been well demonstrated in practice. Milk bottles washed with this alkali are characterized by a bright lustrous appearance and freedom from any greasy films. As a result the rinse water runs from them freely, leaving no hanging drops to deposit their load of solids upon drying. The importance of obtaining a perfectly clean surface on all objects intended to come in contact with food products cannot be overemphasized.

Silver (*13*) has found that this surface cleanliness may be more important to sterility than the use of extremely alkaline solutions and high temperatures. He removed a sample of wash water from a bottle-washing machine, which contained 4 per cent NaOH and had been maintained at 165° F., and obtained a heavy growth of several different organisms upon plating it out. The fact that many cities require high-alkali concentrations for washing dairy equipment and yet permit a film of spore-carrying grease on the washed surface is a matter of wonder.

Emulsification

Hillyer (*6*), Shorter and Ellingsworth (*12*), White and Marden (*18*), McBain (*9*), Stericker (*14*), Vincent (*17*), Vail (*15*), Donnan and Potts (*3*), Linder and Zickerman (*8*), and perhaps others have called attention to the parallelism between emulsifying power and detergent value of solutions. Stericker (*14*) has shown that petroleum oils can be emulsified by silicate solutions, although the emulsions are not as stable as those made with soap solutions. Vincent (*17*) does not consider silicate of soda to be an emulsifying agent.

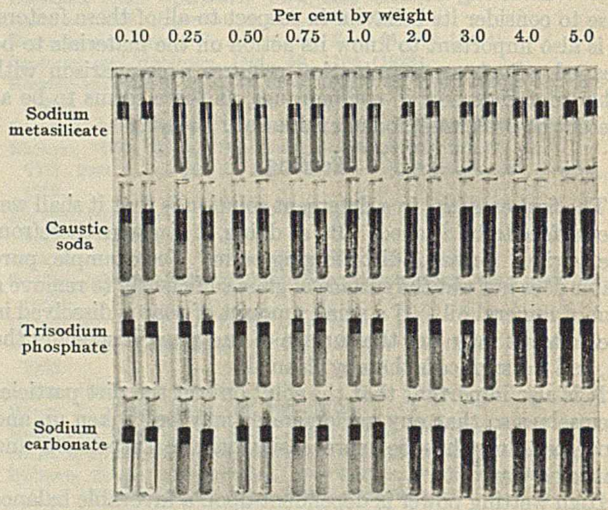

Figure 2—Relative Ability of Various Alkalies to Displace Oil from Glass Surface

The fact that the common alkalies are widely used in cleaning operations, where the presence of soap is not permitted, makes it important to know how they compare in respect to emulsifying power. Although the emulsions formed are not permanent in the sense that soap emulsions are, a comparison of their stability should help to evaluate them in this respect.

> Solutions were made up containing from 0.1 to 2 per cent of NaOH, $Na_2SiO_3.5H_2O$, $Na_3PO_4.12H_2O$, and Na_2CO_3. In each case 75 cc. of the solution was stirred with 75 cc. of a light motor oil for five minutes at 20° ± 3° C. in a motor-driven drink mixer. The mixture was then poured into a bottle and the depth of the oil emulsion and the aqueous layers measured after 24 hours. This was repeated five times, and the results averaged. The results as expressed in percentage of emulsion are given in Table I and also in Figure 3.

Table I—Volume of Oil Emulsion Formed by Aqueous Solutions of Alkalies

	%	%	%	%	%	%
Alkali concentration	0.1	0.15	0.25	0.54	1	2
	TOTAL VOLUME AS EMULSION					
$Na_2SiO_3.5H_2O$	81.5	79.1	74.2	55.4	24.8	2.8
NaOH	58.2	40.0	17.3	4.0	2.0	0.0
$Na_3PO_4.12H_2O$	78.8	77.5	73.0	64.5	47.8	3.2
Na_2CO_3	66.5	57.8	39.3	13.2	4.2	2.0

These results show that $Na_2SiO_3.5H_2O$ and $Na_3PO_4.12H_2O$ are much better emulsifying agents than the other alkalies considered. There seems to be a certain degree of parallelism between emulsifying power and wetting but not an exact parallelism, for if such were the case $Na_2SiO_3.5H_2O$ would be by far the best emulsifying agent.

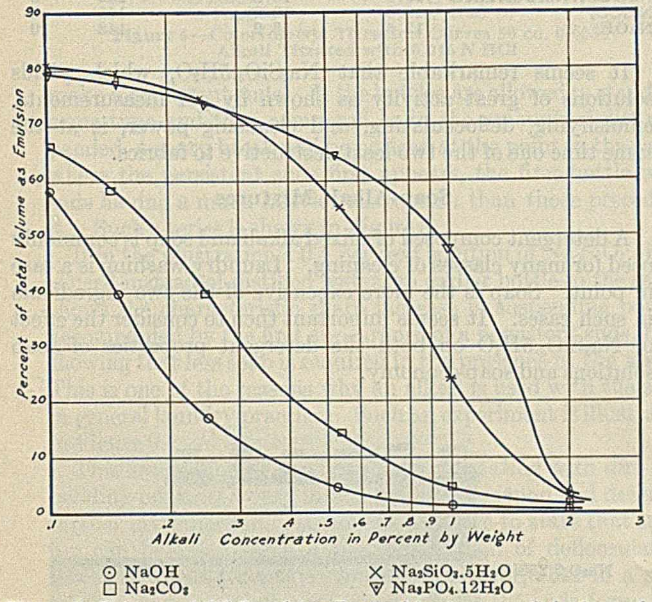

Figure 3—Volume of Oil Emulsion Formed by Aqueous Solutions of Alkalies

It is interesting to note that the relative stability of these emulsions as shown in the curves of Figure 3 is reflected by the tendency to form emulsions spontaneously as shown in Figure 2.

Deflocculation

Fall (*5*) has shown quite conclusively that silicate of soda, $Na_3PO_4.12H_2O$, NaOH, and Na_2CO_3 have strong dirt-suspending powers of their own in the total absence of soap. He worked at both 40° and 75° C. and showed that at a concentration of 0.025 per cent their relative dirt-suspending powers descend in the order given. He obtained values ranging from 445 cg. of MnO_2 per liter for Na_2O:$3.97SiO_2$ to 110 cg. for Na_2CO_3. A concentration of 0.15 per cent yielded the following values at 40° and 75° C., respectively: Na_2O:3.97 SiO_2, 396, 287; Na_3PO_4, 70, 274; NaOH, 17, 52; Na_2CO_3, .000, 12. Quite obviously the sodium silicate has the superior suspending power.

Fall (*5*) worked with three sodium silicates having SiO_2:Na_2O molecular ratios of 1.62, 2.82, and 3.97. He found them to have substantially the same suspending power at their optimum concentrations. At the time Fall did his work, the crystalline sodium metasilicate ($Na_2SiO_3.5H_2O$) was not available commercially, so no values were obtained for this salt.

In order to demonstrate qualitatively the comparative deflocculating power of $Na_2SiO_3.5H_2O$, two series of solutions were made up of the alkalies Na_2O:$3.25SiO_2$, $Na_2SiO_3.5H_2O$, $Na_3PO_4.12H_2O$, Na_2CO_3, and NaOH. The first series was made up to cover a range of concentration from 0.1 to 5 per cent. The second series was made up to cover a pH range of 9.2 to 13.2. One hundred cc. of each solution were placed in a glass bottle and 0.15 gram of bone black added. (The bone black was prepared by washing with alcohol, then ether, and evacuating at 100° C. for 6 days.) The bottles were then shaken and allowed to stand for 60 hours at room temperature, 20° ± 3° C. The appearance of the bottles at this time is shown in Figures 4 and 5.

It is evident from the illustrations that the dilute solutions are more effective in deflocculating the bone black than the concentrated ones. As the concentration or pH of each particular alkali is increased, a point is reached at which the deflocculating power of the alkali falls off very sharply. Much more work should be done before a satisfactory explanation of this phenomenon should be attempted, but it is interesting from a practical standpoint that only three of the alkalies considered showed an appreciable suspension at the concentration of 0.2 per cent. Of these three, $Na_2SiO_3.5H_2O$ was the only one which showed an appreciable suspension at a pH greater than 11. When considered in the light of the fact that alkali cleaning solutions are rarely used at a concentration less than 0.1 per cent, this is very interesting.

Dissolving Power

The relative ability of alkali solutions to dissolve alkali-soluble dirt, such as proteins, paint, and fats, is largely a question of the pH of the solutions and the amount of contained Na_2O which will react with the dirt at an effective pH. These relationships are shown in Table II and Figures 6 and 7.

Table II—Data for Colorimetric Titration Curves

[50 cc. 0.008 *N* alkali titrated with 0.016 *N* HCl]

0.016*N* HCl	NaOH	$Na_2SiO_3.5H_2O$	$Na_3PO_4.12H_2O$	Na_2CO_3
Cc.	*pH*	*pH*	*pH*	*pH*
0	11.6	11.4	11.3	10.9
1	11.5	11.3	11.1	10.8
2	11.5	11.3	11.1	10.7
3	11.4	11.2	11.1	10.6
4	11.4	11.2	11.0	10.4
5	11.4	11.1	10.9	10.2
6	11.4	11.1	10.7	10.0
7	11.3	11.1	8.7	9.7
8	11.3	11.0	8.0	9.5
9	11.3	11.9	7.5	9.1
10	11.2	10.8	7.2	8.8
11	11.2	10.6	7.0	8.1
12	11.2	10.3	6.8	7.1
13	11.2	10.0	6.6	6.8
14	11.2	9.7	6.3	6.7
15	11.1	9.6	6.0	6.6
16	11.1	9.5		6.3
17	11.1	9.4		6.0
18	11.0	9.3		5.7
19	10.9	9.1		
20	10.5	8.8		

It will be noted that at equivalent concentrations the $Na_2SiO_3.5H_2O$ solution has a pH between that of NaOH and Na_2CO_3. Also, a larger proportion of the Na_2O in the $Na_2SiO_3.5H_2O$ is available at a pH above 10 than in any other alkali except NaOH. For most practical cleaning operations, alkali, active below a pH of 10, is of little value. Although NaOH is thus shown to be a cheaper source of alkali than $Na_2SiO_3.5H_2O$, there are many cases where the more caustic alkali cannot be used.

Such a case is found in the cleaning of tin-plated dairy equipment and sardine cans after filling. In these cases the fats and other dirt can be removed successfully with $Na_2SiO_3.5H_2O$ without dissolving the tin. Sodium hydroxide at a concentration great enough to remove the dirt could not be used without severe danger of dissolving the tin. Vail (*16*) has shown that at a concentration of one per cent, $Na_2SiO_3.5H_2O$ attacks aluminum but very little, whereas solutions of NaOH, Na_2CO_3, and $Na_3PO_4.12H_2O$, containing the same amount of Na_2O, attack it vigorously. It is known that milk bottles and dishes which have been repeatedly washed with NaOH become etched as a result of a partial solution of the surface. Sodium metasilicate as applied to the washing of milk bottles has been found to be less severe in this respect.

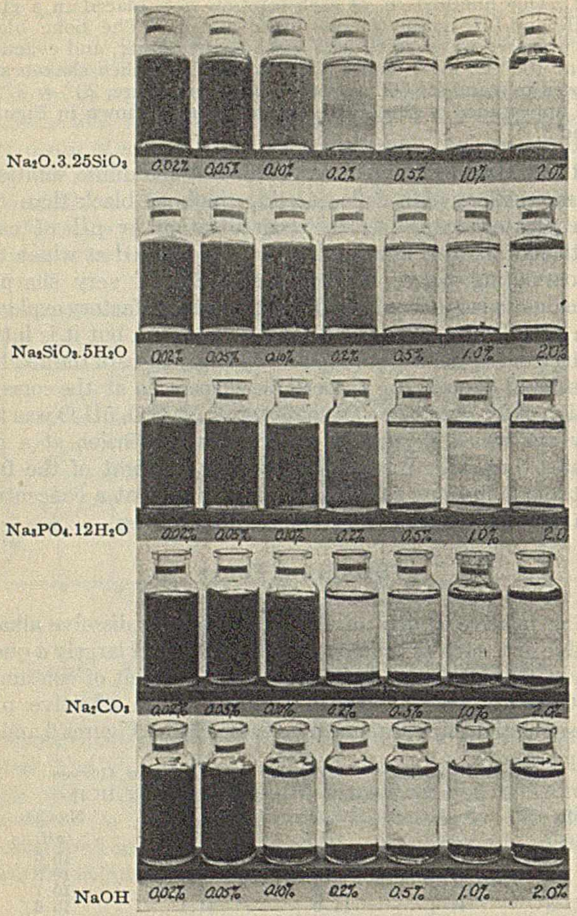

Figure 4—Effect of Varying Concentrations upon Deflocculating Power of Alkali Solutions

Effect of Alkali on Cotton Fabric

In laundry practice the cotton clothes remain immersed in the wash and rinse liquors for from 30 to 90 minutes, depending on the class of work. The temperature usually starts at about 80° F. (26.67° C.), rises to 160° F. (71.11° C.), and then drops again to 80° F. (26.67° C.). At the end of this operation the clothes are supposed to have been rinsed free of all alkali. In some cases there still remains a trace of alkali in the goods, however. When the goods pass through the ironer at about 130° C., the very dilute alkali solution remaining on the fibers becomes concentrated sufficiently to become destructive. Part of the destruction is the result of an oxidation of the cellulose, accelerated by the presence of the alkali. This oxycellulose quickly turns brown at the temperature of the ironer and this color becomes an easy means of checking incomplete rinsing.

Some laundries destroy the residual alkali in the clothes by the use of a sour. Such a practice is effective when properly used. There are certain classes of work that are seldom soured and many laundries do not sour at all. For these reasons it seems important to know how the different alkalies compare in their effect upon fabrics under the above described conditions.

An accelerated comparison of the common alkalies has been made as follows:

One per cent solutions of the chemicals were made up and strips of white cotton sheeting immersed in them for one hour. At the end of this time the strips were centrifuged separately. The strips were then wrapped around glass bottles and placed for one hour in a Freas oven at 110° C. The strips were then removed and compared as to depth of color. A value of 10 was assigned to the darkest strip, a value of 3 to a strip judged to have three-tenths as deep a color as the darkest one, and so on. The bursting strengths of the strips were also taken by use of the Mullen tester. The average of twenty breaks was taken on each strip.

The above tests were repeated five times and the averages of the results obtained are given in Table III.

Table III—Effect of Alkali on Cotton Fabrics

	0.1% Solutions	Amt. 0.2 *N* HCl to Neutralize 50 cc. 1% Alkali to Phenolphthalein	Bursting Strength	Depth of Color
	pH	*Cc.*		
$Na_2SiO_3.5H_2O$	11.6	21.5	157	3
$Na_3PO_4.12H_2O$	11.2	7.5	157	4
$Na_2B_4O_7.10H_2O$	9.0	10.5	154	3
$NaHCO_3$	9.0	....	153	6
$NaHCO_3.Na_2CO_3.2H_2O$	10.0	10.5	152	8
Na_2CO_3	10.8	19.2	145	8
NaOH	12.6	58.2	143	10

It seems remarkable that $Na_2SiO_3.5H_2O$, which yields solutions of great activity as shown by pH measurements, emulsifying, deflocculating, and cleansing power, is at the same time one of the two least destructive to fabrics.

Soap-Alkali Mixtures

A detergent composed of mixed alkali and soap is commonly used for many classes of cleaning. Laundry washing is a case in point. Soap is the more expensive of the two ingredients in such cases. It seems important then to consider the effect of $Na_2SiO_3.5H_2O$ on both the detergent properties of soap solutions and soap economy.

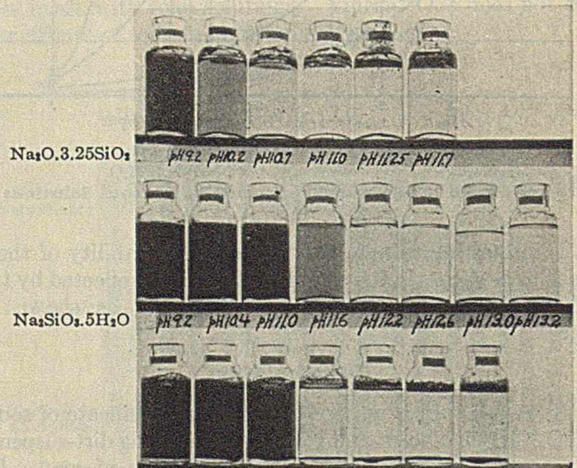

Figure 5—Effect of Varying pH upon the Deflocculating Power of Alkali Solutions

If to each of a series of ten 125-cc. bottles is added 0.07 gram of bone black prepared as described and 100 cc. of distilled water, followed with 10 drops of 10 A. P. H. A. soap solution in the second, 20 in the third, 30 in the fourth, etc., and the bottles then shaken, it will be observed that, after standing, a certain minimum quantity of soap is required to

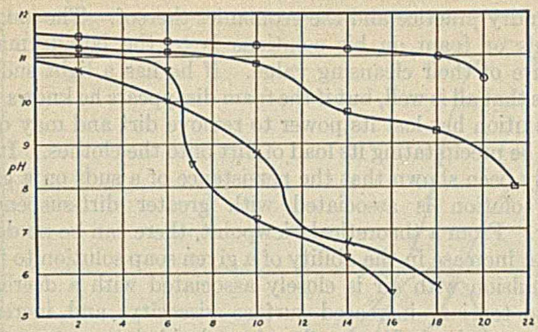

Figure 6—Colorimetric Titration Curves 50 cc. 0.008 *N* Alkali Titrated with 0.016 *N* HCl

make a persistent suds. If the bottles are allowed to stand for some time and then compared as to the amount of dirt suspended, a sharp break will be noticed at the point in the series where the persistent suds first appears, the first bottle with suds having a much heavier suspension than those preceding it. Such a series is shown in Figure 8.

If in the illustration a 0.4 per cent solution of $Na_2SiO_3.5H_2O$ is used instead of distilled water, an earlier bottle in the series shows the characteristic sharp increase in suspending power, accompanied by the first appearance of a persistent suds, thus showing that less soap is required in the presence of the alkali. This is one of the reasons why an alkali is used with the soap in general laundry practice. Such an experiment is illustrated in Figure 9.

This association of persistent-suds formation with dirt-suspending power is a very interesting phenomenon and deserves further investigation. It would be unwise to state that sudsing can be taken as a universal criterion of deflocculating power in all solutions. It appears, however, that in a soap solution the same influence which affects the suds formation has also an effect upon the suspending ability of the solution.

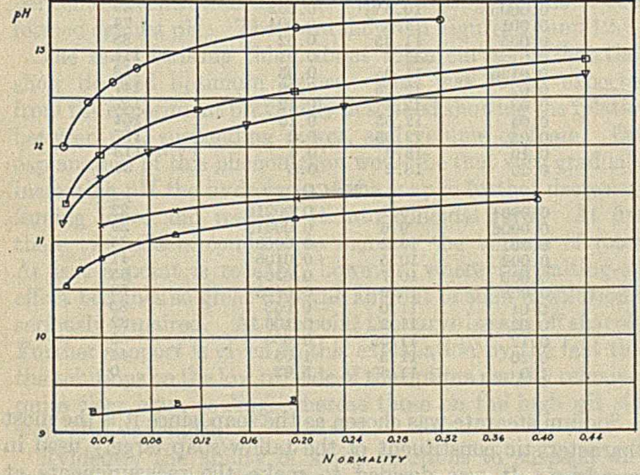

Figure 7—pH of Various Alkalies in Aqueous Solutions

Effect of pH upon Detergent Properties of Soap Solutions

McBain (*9*) has emphasized that in soap solutions the detergent properties are due to undecomposed soap. If this be true, part of the value of the alkali may be explained as being due to its effect in repressing hydrolysis of the soap. Since most soap solutions of laundry strength have a pH of about 10.5, an alkali would be most effective in this respect when so used as to give a pH greater than 10.5.

To illustrate this point, a series of eight solutions of Na_2SiO_3 were made covering a colorimetric pH range from 9.2 to 13.25. These were arranged in a row of 125-cc. glass bottles, and 0.12 gram of prepared bone black and 0.04 cc. of 10 A. P. H. A. soap solution equivalent to 0.0027 gram anhydrous castile soap added to each. The bottles were then shaken and allowed to stand. On observation, it was noticed that with increasing pH the volume of foam first increased and then decreased, showing an optimum at pH 12.2.

Figure 10 shows the appearance of the bottles immediately after shaking and again after standing 14 hours. This illustrates quite clearly that the dirt-suspending power of soap solutions is increased by raising the pH to a certain value. A pH in excess of this probably decreases the solubility of the soap as will be explained later. It also shows that the volume of foam produced is a good indicator of the dirt-suspending power of a given soap solution.

Almost every load of clothes that passes through a laundry contains a certain amount of acidic material. The pH of laundry-strength soap solutions is about 10.5. It seems evident then that even very weak acids, or other substances tending to decrease the hydroxyl-ion concentration, would be expected to decompose the soap with the production of acid soaps or even free fatty acid in extreme cases. That this very quickly decreases the detergent power of the solution is well known in laundry practice.

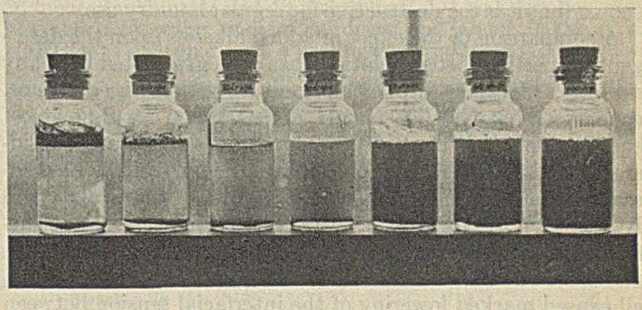

Figure 8—Effect of Varying Concentrations of Soap upon Foaming and Deflocculating Power of Solution

Hillyer (*6*) has measured the drop number of sodium oleate solutions containing an excess of free oleic acid ($C_{17}H_{33}$.-COOH) against kerosene and found that the surface tension of such solutions increases rapidly with excess of the fatty acid. His values are as follows:

Equivalents of $C_{17}H_{33}$.-COOH in excess	0	1/128	1/64	1/32	1/16	1/8	1/4	1/2	1
Drop number	274	273	270	240	216	164	117	84	58

From this it would seem that an alkali to be effective in protecting the soap from decomposition should have two qualifications: it should give a solution having a pH of at least 10.5 when used at a reasonable concentration; and it should have enough reserve alkali or be sufficiently buffered at this pH to maintain the prescribed hydroxyl-ion concentration after a considerable portion of it has been used up by neutralization. The characteristics of the more common alkalies are shown in Figures 6 and 7.

Figure 7 shows the pH values of solutions of NaOH, Na_3PO_4, Na_2CO_3, $Na_2B_4O_7$, and $NaBO_2$ at different volume normalities. The curve for Na_2SiO_3 was determined on the basis of weight normality but differs only slightly from the calculated volume normality curve. The curves show that only four alkalies give the desired pH value of 10.5 at sufficiently low concentrations to be used as soap builders.

Figure 6 shows the effect of partial neutralization upon the pH of 0.008 *N* solutions of NaOH, Na_2SiO_3, Na_3PO_4, and Na_2CO_3. Examination of these shows that the pH value of Na_2CO_3 and Na_3PO_4 falls below 10.5 when only a small portion of the total alkali has been neutralized. With Na_2SiO_3 a much larger quantity of acid is required to lower the pH below the effective value. In laundry practice the Na_2SiO_3 would be expected to hold the pH of the suds at the desired level with a smaller amount of the salt and under a wider range of operating conditions. Sodium hydroxide might be considered as still more valuable in this respect, but it has already been shown that it is too destructive for regular laundry use.

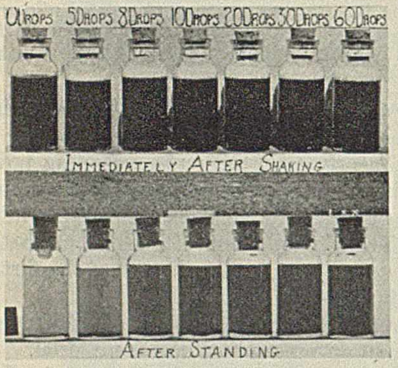

Figure 9—Effect of Sodium Metasilicate upon the Foaming and Deflocculating Power of Soap Solutions

Bottles contain 0.4 per cent Na_2SiO_3, washed bone black, and 10 A.P.H.A. soap, in drops.

A comparison of the effect of added alkalies upon the detergent properties of soap solutions has been attempted by many workers. Jackson (*7*), as the result of work with emulsions, concluded that Na_2CO_3, NaOH, NH_4OH, and $Na_2B_4O_7$ are of equal value when chemically equivalent weights are considered. This does not seem plausible in the light of the data already considered here. Bottazzi (*1*) found that NaOH and KOH, when added to their soaps, gradually decrease the surface tension to a minimum, after which it rises again. Ellidge and Isherwood (*4*) showed that NaOH, Na_2CO_3, and Na_3PO_4 all caused marked lowering of the interfacial tension between soap solutions and kerosene. Millard (*10*) measured the effect of NaOH, Na_2CO_3, and Na_3PO_4, and modified soda upon the interfacial tension between soap solutions and benzene at 40° C. over a limited range of concentrations. Chapin (*2*), from deflocculation work carried out at 30° C., claimed that the common alkalies increase the detergent value of soap solutions in the following order: $Na_2B_4O_7$, silicate of soda, Na_2CO_3, and NaOH. Vincent (*17*) found that NH_4OH, Na_3PO_4, and NaOH increased the emulsifying power of soap solutions.

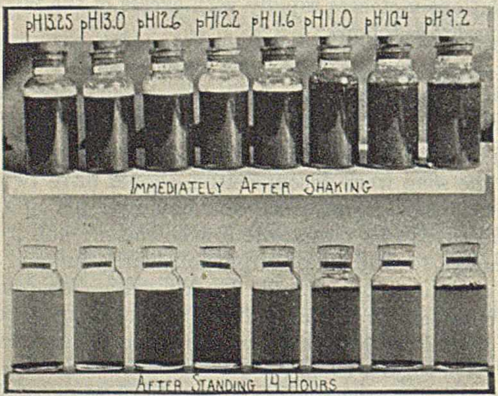

Figure 10—Effect of Varying pH upon Deflocculating Power of Soap Solutions toward Bone Black

Effect of pH on Soap Suds

It has seemed to the author that there was need of data on the subject that could be more readily interpreted into terms of laundry practice and the economics thereof. The amount of suds or foam on his solutions is to the laundryman a measure of their cleansing value. If he has a light suds he knows that all is well, but if the foam disappears he knows that the solution has lost its power to remove dirt and may quite likely be precipitating its load of dirt onto the clothes. It has already been shown that the persistence of a suds on a given soap solution is associated with greater dirt-suspending power. From a theoretical viewpoint, there can be no doubt that an increase in the ability of a given soap solution to form an emulsion with air is closely associated with a decreased surface tension, increased surface viscosity, and increased detergent value. It was therefore decided to measure the volume of suds formed by a given soap solution when built with different amounts of the common alkalies.

Table IV—Volume of Foam Formed at 60° C. on Solutions of Alkalies Containing 0.0088 Per Cent $NaC_{18}H_{35}O_2$

Normality	pH	Weight %	Volume of Foam Cc.
		$Na_2SiO_3.5H_2O$	
0.0002	8.9	0.0021	37
0.0004	9.2	0.00424	53
0.001	10.3	0.0107	65
0.002	10.85	0.016	84
0.004	11.0	0.0214	90
0.010	11.2	0.042	109
0.020	11.4	0.106	120
0.024	11.6	0.212	134
0.025	11.7	0.252	158
0.030	11.8	0.262	174
0.04	12.0	0.318	187
0.05	12.2	0.424	230
0.10	12.6	1.06	230
0.2	13.0	2.07	114
0.4	13.25	4.07	44
		$Na_3PO_4.12H_2O$	
0.0003	8.1	0.0038	22
0.0004	9.3	0.0057	28
0.0015	10.4	0.019	48
0.003	10.9	0.038	54
0.006	11.2	0.076	87
0.015	11.4	0.190	110
0.030	11.7	0.380	122
0.06	11.9	0.75	121
0.12	12.1	1.49	122
0.21	12.4	2.53	63
0.45	12.6	5.40	34
0.60	13.0	7.06	21
		NaOH	
0.0025	9.3	0.001	23
0.0005	10.6	0.002	49
0.001	11.0	0.004	74
0.005	11.35	0.02	88
0.01	11.7	0.04	114
0.0125	11.9	0.05	118
0.02	12.25	0.08	147
0.03	12.4	0.12	157
0.04	12.55	0.16	164
0.05	12.65	0.2	157
0.10	13.0	0.4	113
0.20	13.2	0.8	36
		Na_2CO_3	
0.0004	9.2	0.00212	22
0.0006	9.6	0.00318	29
0.001	10.2	0.0053	35
0.002	10.5	0.0106	41
0.005	10.7	0.0264	65
0.008	10.9	0.0423	73
0.01	11.0	0.053	85
0.02	11.2	0.106	82
0.12	11.35	0.636	65
0.20	11.5	1.06	44
1.0	11.6	5.02	0

Sodium stearate was chosen as the soap, since it is the most characteristic constituent of the tallow soap largely used in laundries. It was decided to make the measurements at 60° C., since this is representative of laundry conditions. The time of agitation was chosen arbitrarily at 30 minutes, as it was felt that this was sufficient time to establish equilibrium, and that a longer time would be of no advantage.

The agitating vessel was made by sealing a 320-ml. Kolle culture flask onto a graduated glass tube 25 mm. in diameter and 500 mm. long. This was suspended in a thermostat from a horizontal rocking shaft so that it extended 450 mm. below its axis. A suitable mechanical device was provided to rock the tube through an angle of 20° at a rate of 116 cycles per minute.

In operation, 50 cc. of the alkali solution, whose concentration was known and whose pH value has been measured colorimetrically, was pipetted into the flask. It was then agitated

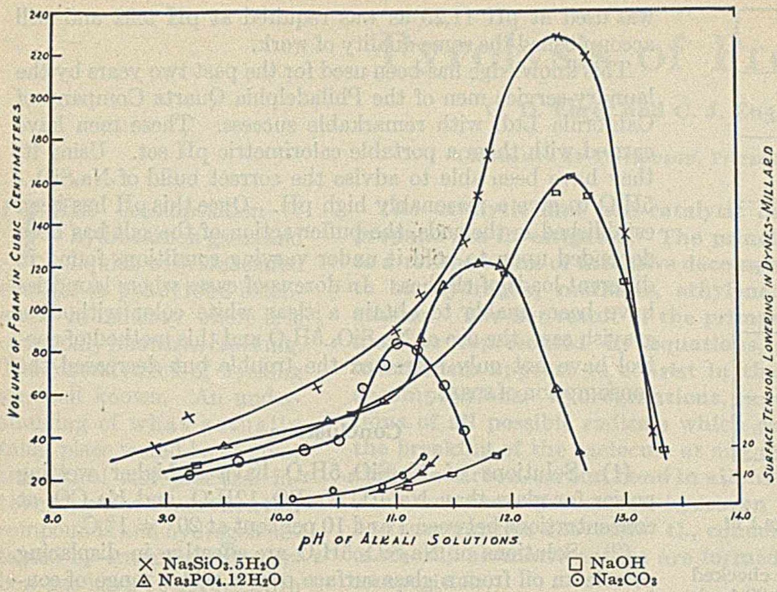

Figure 11—Volume of Foam Formed on Solutions of Alkalies Containing 0.0088 Per Cent $NaC_{18}H_{35}O_2$ at 60° C.

until it had come to the temperature of the bath. A concentrated solution of pure sodium stearate ($NaC_{18}H_{35}O_2$) was then added from a pipet graduated to deliver exactly 2.2 cc. of the solution. This gave a solution of exactly 0.0088 per cent $NaC_{18}H_{35}O_2$. A rubber stopper was placed in the flask and the agitation continued for 30 minutes. The flask was then removed from the bath, inverted, and the volume of suds read off. Results were usually obtained which checked within 5 ml. In establishing a point, at least five determinations were made with an alkali solution of the same strength, and the results averaged.

Solutions of $Na_2SiO_3.5H_2O$, NaOH, Na_2CO_3, and $Na_3PO_4.12H_2O$ were examined in this way over a range of pH from 9 to 13. The data are given in Table IV. From the data are drawn two series of curves, one plotting volume of suds against per cent concentration, and the other plotting volume of suds formed against pH. These are shown in Figures 11 and 12.

The most striking thing about these curves is that they show decided optimum values. This was to be expected from the experiment previously described showing the relation between pH, suspending power, and volume of foam. One explanation of this phenomenon would be that with gradually increasing pH the hydrolysis of the soap is further decreased, forcing more and more of it into colloidal form. At first these two effects combine to increase the volume of foam. At last a point is reached, however, where the salting-out effect becomes so great that the amount of soap in solution is seriously impaired. At this point the curve breaks off sharply. Further support is given to this explanation by the fact that the solutions on the low pH side of the optima usually remained quite clear upon cooling, whereas those on the high pH side were always clouded.

Evidently the ability of alkali solutions to suspend dirt, their effect on the surface tension of soap solutions, and their effect upon the foaming of soap solutions are all closely related. Fall (*5*) found that at their respective optimum concentrations for the suspension of MnO_2 at 75° C., silicate of soda, Na_3PO_4, NaOH, and Na_2CO_3 suspended 348, 291, 269, and 234 cg., respectively. The close check between this order and that of the foaming power as shown in the above curves is more than accident.

Millard (*10*) measured the decrease in the interfacial tension at 40° C. of soap solutions against benzene caused by addition of alkalies. The surface-tension lowering has been taken from his results and plotted against pH in Figure 11. Despite the fact that he used a different soap at a different concentration and worked at a temperature 20° lower, his results make an interesting comparison with the present work.

From a commercial point of view the above data are very valuable. First they show that, by the use of $Na_2SiO_3.5H_2O$ a more active detergent solution can be obtained with the same amount of soap. Second, they show that, by maintaining a reasonably high pH, a more active detergent solution can be obtained. In this connection it should be pointed out that a solution of $Na_2SiO_3.5H_2O$, once it has been brought to the correct pH, is more likely to maintain its pH level upon partial neutralization than any of the other salts here considered (see Figure 6).

pH and Soap Economy

This discussion naturally brings up the question of soap economy. It would seem that these factors which increase the detergent value of a soap solution would, when properly controlled, permit the use of a smaller amount of soap than that now used to accomplish the same results under less favorable conditions. To clear up this point, a series of practical laundry tests were run.

A wash wheel was used for this work having a wooden cylinder 36 inches in diameter and 48 inches long. It was supplied with hot and cold water of zero hardness and about 0.004 *N* in $NaHCO_3$ as delivered from a zeolite water softener. The wheel was also supplied with steam for heating the hot suds. The goods washed were soiled table napkins, as it was felt that they would be very uniform as to their condition of soil. Ninety pounds were carefully weighed out for each load. The washing formula used was as follows:

OPERATION	TEMPERATURE		WATER LEVEL	TIME
	° *F.*	(° *C.*)	*In.*	*Min.*
Low suds	75	(23.9)	3	5
Suds	90	(32.2)	3	5
Suds	110	(43.3)	3	5
Suds	140	(60.0)	3	5
Bleach suds	160	(71.1)	3	5
Rinse	135	(57.2)	10	5
Rinse	130	(54.4)	10	3
Rinse	110	(43.3)	10	3
Rinse	90	(32.2)	10	3

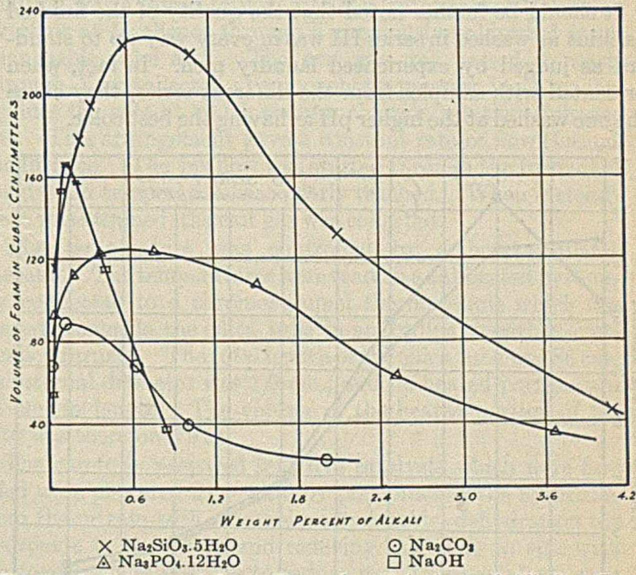

Figure 12—Volume of Foam Formed on Solutions of Alkalies Containing 0.0088 Per Cent $NaC_{18}H_{35}O_2$ at 60° C.

Three series of ten loads each were washed. Sodium metasilicate was used as the builder. The average pH levels of the discharged suds waters in the three different series as determined colorimetrically were held at 9.9, 10.8, and 11.3, respectively. A tallow soap containing 88 per cent fatty acid was used. Only enough soap was added to each suds operation to make a light running suds, as is the custom with laundry washmen. The

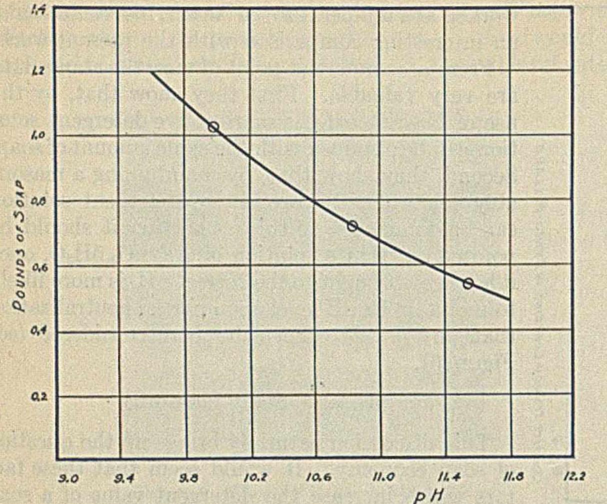

Figure 13—Soap Required to Wash 90 Pounds (40.8 kg.) of Clothes at Different pH

total amount of soap used on each series was carefully checked and found to be 10.4 pounds (5.18 kg.), 7.25 pounds (3.29 kg.), and 6.04 pounds (2.74 kg.), respectively, showing a steady decrease in soap consumption with increasing pH. This is illustrated in the curve of Figure 13.

pH and Rate of Dirt Removal

The amount of dirt removed was determined by centrifuging duplicate 100-cc. samples of the suds water as discharged after each suds operation. A centrifuge tube having a restricted and graduated portion at the bottom permitted the volume of dirt to be read off directly. The average values for each operation have been plotted for series I and III in Figure 14. The curve for series II takes a position intermediate between these two, but has been omitted from the figure for sake of simplicity. These curves show that a given amount of dirt can be removed with less soap when the pH is maintained at a higher level, and they give practical proof to substantiate the theoretical considerations and qualitative tests herein discussed.

It should be further noted that the quality of the finished napkins as washed in series III was in every way up to standard as judged by experienced laundry men. In fact, when presented with samples from the different series, they chose the one washed at the higher pH as having the best color.

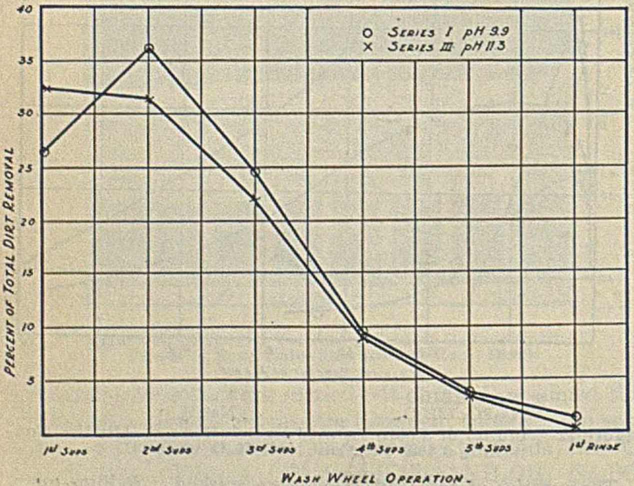

Figure 14—Total Dirt Removed in Each Wash Wheel Operation

The data obtained from the laundry test show that by proper control of the pH in washing solution the efficiency of the soap is sufficiently increased to permit the use of a much smaller amount. In this case only 60 per cent as much soap was used at pH 11.25 as was required at pH 9.92 and still accomplished the same quality of work.

This knowledge has been used for the past two years by the laundry-service men of the Philadelphia Quartz Company of California Ltd. with remarkable success. These men have carried with them a portable calorimetric pH set. Using it, they have been able to advise the correct build of $Na_2SiO_3.5H_2O$ to give a reasonably high pH. Once this pH has been established in the suds, the buffer action of the salt has been depended upon to hold it under varying conditions found in different loads of clothes. In dozens of cases where laundries have been unable to obtain a clear white color without a grayish cast, the use of $Na_2SiO_3.5H_2O$ and this method of control have not only corrected the trouble but decreased the consumption of soap.

Conclusions

(1) Solutions of $Na_2SiO_3.5H_2O$ have a higher wetting power for glass than NaOH, $Na_3PO_4.12H_2O$, and Na_2CO_3 at concentrations between 1 and 10 per cent at 20° ± 1° C.

(2) Solutions of $Na_2SiO_3.5H_2O$ are effective in displacing petroleum oil from a glass surface over a wider range of concentration than solutions of the other alkalies tried.

(3) Sodium metasilicate yields solutions of a higher pH than the other alkalies with the exception of NaOH.

(4) A larger portion of the Na_2O in $Na_2SiO_3.5H_2O$ is available at a pH effective in dissolving fats than in any other alkali salt considered.

(5) Qualitative tests show that $Na_2SiO_3.5H_2O$ has solid dirt-suspending powers comparable with those of the less alkaline silicates.

(6) Solutions of $Na_2SiO_3.5H_2O$ can be used for washing tin-plated equipment that would be attacked by the other alkalies.

(7) The character of the foam on a given soap solution is associated with its power to suspend solid dirt.

(8) Solutions of $Na_2SiO_3.5H_2O$ give a larger volume of foam with $NaC_{18}H_{35}O_2$ at 60° C. than the other alkalies tried. This is true of all concentrations except for a very small range where sodium hydroxide is superior.

(9) A smaller amount of soap is required to wash clothes when the pH is maintained above 10.5.

Acknowledgment

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Pyrolysis of Propane[1,2]

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The catalytic and non-catalytic decompositions of propane are investigated. The principal products, up to a temperature of intensive decomposition, are found to be hydrogen, methane, ethylene, propylene, and ethane. The net result of the primary decomposition may be represented by equations, but the actual mechanism appears to consist in the inter-reactions, decompositions, hydrogenations, and dehydrogenations of all possible radicals which can be formed by the breaking of the molecule at any point. The belief that the carbon-carbon bond in aliphatic hydrocarbons is weaker than the carbon-hydrogen bond is verified. At temperatures above 700° C., condensation products of an oily aromatic nature are formed by propane decomposition.

Catalysts containing nickel, cobalt, chromium, and iron cause increased yield of hydrogen from the decomposition.

A method is developed for analysis of cracked hydrocarbon gas by low-temperature fractionation supplemented by absorption and combustion methods.

THE decomposition of hydrocarbon gases and liquids with associated changes is practiced extensively in industry where it is commonly known as cracking. The general effects of cracking are well known. An understanding of what actually takes place would be of great theoretical and practical interest. The unsaturated compounds and hydrogen obtained by cracking hydrocarbon gas have considerable potential value, and are, in fact, already being used to some extent.

Many investigations of the pyrolysis of hydrocarbon gases have been made. The large amount of published information dealing with this subject is indicated by the lengthy historical résumé of Egloff, Schaad, and Lowry (*3*) which appeared recently.

Bone and Coward (*1*) suggested the formation of residues, such as $\vdots$CH, :CH_2, and .CH_3 by the decomposition of hydrocarbons.

Zanetti (*6*) decomposed a gas consisting of 97 per cent propane and 3 per cent butanes. Unsaturated and saturated gaseous hydrocarbons, aromatic hydrocarbons, and hydrogen were obtained. He also found that iron and nickel gauzes caused a rapid increase in the amount of hydrogen formed.

Pease (*5*) considered the two principal reactions in the decomposition of propane to be dehydrogenation and demethanation.

Hague and Wheeler (*4*) found that propane at rest began to decompose at 460° C. At higher temperatures the principal products of the decomposition were methane, hydrogen, ethylene, propylene, and ethane.

Davidson (*2*) investigated the effect of a large number of materials. Nickel, iron, and cobalt markedly decreased the percentages of unsaturates and increased the percentage of hydrogen at all temperatures (550° to 950° C.) at which investigations were made.

In all of the investigations mentioned above, there had to be made certain assumptions concerning the composition of the gas resulting from the decomposition. This was necessary because there is no accurate known method of selectively absorbing one of several unsaturated constituents, and not more than two saturated hydrocarbon constituents of a gas mixture can be determined by combustion and absorption methods. Only recently has apparatus been available for analysis by low-temperature fractionation. Analysis by this method, supplemented by absorption and combustion methods, make unnecessary any assumptions concerning the composition of the gas. This combination of methods was used in the analysis of the products of the decomposition of propane herein reported in cases in which it was desired to know rather accurately the composition of the exit gas for the purpose of studying the nature of the decomposition.

The purpose of the present work is to investigate the pyrolysis of propane by analysis of the products by an improved method, and to investigate the catalytic effect of several kinds and forms of catalysts.

Method of Decomposition

A 20-gallon (75.8-liter) cylinder of commercial liquefied propane under approximately 125 pounds (56.7 kg.) pressure was obtained from the Skelly Oil Company of Tulsa, Okla. The decomposition of this gas was 97.5 per cent propane, 1.7 per cent ethane, and 0.8 per cent butanes.

Figure 1 is a diagrammatic sketch of the apparatus used in the decomposition of the gas. The method of conducting an experiment depended somewhat upon whether or not the effect of a possible catalyst was being investigated. Gas was released from the cylinder into bottle *B*, from which it displaced sodium chloride solution. To pass gas through the drying apparatus into the silica reaction tube, saturated sodium chloride solution was allowed to flow into the water jacket *G* with an overflow at *H*, thence through a previously calibrated interchangeable tube at *I*. The exit gas was passed to waste through *X* or collected at atmospheric pressure in *D* by controlling the rate at which sodium chloride solution siphoned out. This arrangement gave a constant rate of flow through the furnace. The gas flow was started through the furnace as the desired temperature was nearly reached. When a steady state was attained, the exit gas was collected.

The temperature was controlled by a hand-regulated rheostat. The temperatures were read on a calibrated pyrometer connected to a chromel-alumel thermocouple which was placed alongside the silica tube in an ordinary carbon-combustion furnace. The total length of the silica tube was 86 cm., its internal diameter was 1.9 cm., and its heated portion was 28 cm. in length. The volume of the heated portion of the tube was therefore 79 cc.

The carefully prepared sensitive catalysts which were first tried were prepared in general by precipitating the hydroxide from the nitrate with ammonium hydroxide, dehydrating the hydroxide to the oxide, and reducing the oxide *in situ* with hydrogen, where possible to reduce it. These catalysts were held in place near the center of the heated vertical tube by a porcelain plate supported by a glass rod, when experimenting at lower temperatures, and an iron wire support was used at higher temperatures. These materials were found to have no catalytic effect. Nitrogen was passed through the tube to sweep out hydrogen. The hydrogen and nitrogen were allowed to pass into the air through *X*. Propane gas was passed

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[1] Received March 13, 1931. This paper is an abstract of a thesis presented by G. O. Ebrey in partial fulfilment of the requirements for the degree of doctor of philosophy in chemistry at the University of Pittsburgh.

[2] Contribution No. 206, Department of Chemistry, University of Pittsburgh.

into the heated tube for a definite period of time, and a sample was then collected for analysis. Blank runs were made under the same conditions.

In later experiments with more rigid catalysts, such as wire gauzes, a sample of gas was taken when a steady state had been reached, the exit-gas flow was diverted to waste, the stopper was quickly removed from the upper end of a heated silica tube, the catalyst dropped in, the stopper quickly replaced, one minute allowed to pass, and a sample collected in the usual way.

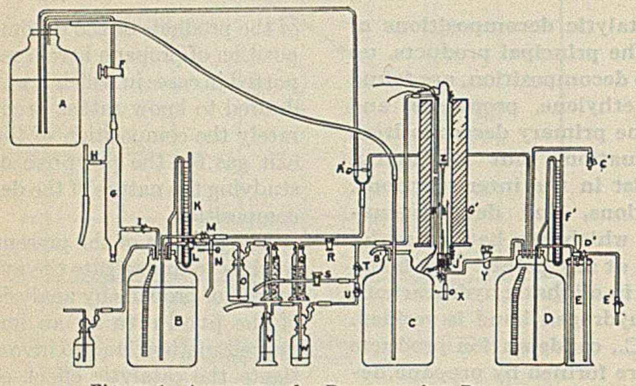

Figure 1—Apparatus for Decomposing Propane

Gas Analysis

In some cases the only analysis made of the gas was that of total unsaturates with bromine water, hydrogen with cupric oxide, and saturated hydrocarbons (where not more than two were present) by combustion. The limitations and inaccuracies of these methods for complex gas mixtures are well known. Complete analyses were made in some cases by low-temperature fractionation supplemented by absorption and combustion methods.

A diagram of the low-temperature fractionation apparatus is shown in Figure 2. For analysis by this method it was necessary to use a sample of about 20 liters. Liquid air was used as the cooling medium. It was possible to obtain good separation of all the components of the exit gas except propylene and propane. Three fractions were distilled by low-temperature fractionation. The first contained the hydrogen and methane, the second, ethylene and ethane, while the third fraction contained all higher hydrocarbons. Acetylene was not found. These simplified fractions were subjected to supplementary analysis by absorption and combustion.

Results of Decomposition and Analysis

A series of experiments was made in which the temperature was varied while the rate of flow of gas into the tube was maintained at 7.7 liters per hour. The total unsaturated and hydrogen content of the exit gas was determined. The percentage increase in volume on decomposition was calculated from the volumes of entering and exit gas. These results are shown in Table I.

Table I—Results of Variation of Temperature

Run	Temp.	Unsatd.	Hydrogen	Increase in Vol.
	° C.	%	%	%
1	600	4.2	2.5	17
2	650	12.0	5.9	30
3	660	25.0	10.7	...
4	700	26.0	10.7	45
5	760	33.2	15.6	81
6	800	29.0	22.1	105
7	830	22.0	26.5	130

It will be noted that the percentage of hydrogen steadily increases, while the unsaturates increase up to a temperature of about 770° C., then decrease.

The results of analysis by low-temperature fractionation were expressed by plotting the curve of the volume distilled as abscissas against the temperature of distillation as ordinates. The values in percentages of each component obtained by low-temperature fractionation supplemented by absorption and combustion are shown in Table II for a series of experiments.

Table II—Values of Components Obtained by Low-Temperature Fractionation

Run	Temp.	Amount in Exit Gas of: H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_3H_8 Decomposed
	° C.	%	%	%	%	%	%	%
8	660	11.0	20.1	15.0	4.7	10.7	40.7	43
9	760	16.8	35.5	27.1	8.5	6.6	7.3	87
10	830	26.5	38.4	20.0	12.8	0.0	0.0	100

The rate of gas flow into the reaction tube was 7.7 liters per hour in each of the three cases given in Table II.

Two decomposition experiments were made in which the temperature was constant at 830° C., while the rate of flow was changed. The composition of the exit gas is shown in Table III.

Table III—Results of Change in Rate of Flow

Run	Rate	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
	Liters/hour	%	%	%	%	%	%
10	7.7	26.5	38.4	20.0	12.8	0.0	0.0
11	17.7	20.1	34.7	29.8	13.6	1.1	0.0

In all runs at temperatures above 600° C., some carbon was deposited in the reaction tube. In all runs above 650° C. a tar fog was seen in the visible exit part of the tube and in the gas-exit line. In a few cases some of this fog was carried into the gas receiver by the gas stream. In such cases drops of oil collected on the surface of the water. The oil which condensed on the tube was of a black tarry nature with an aromatic odor. Not enough of the oil was formed for examination.

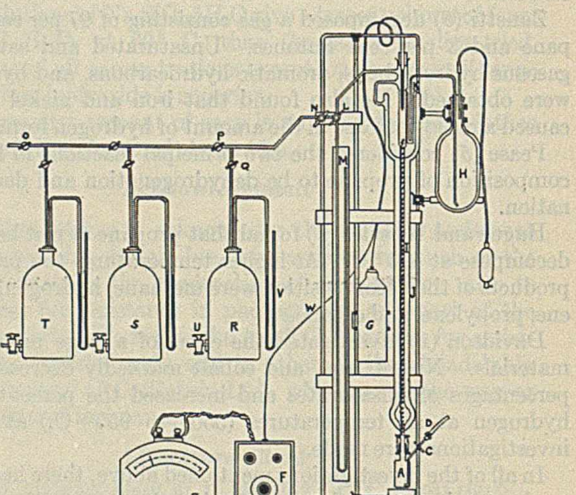

Figure 2—Low-Temperature Apparatus for Gas Fractionation

A—Condensing bottle
B—Electric heater
E—Millivoltmeter
F—Switch
G—Thermos bottle (hot junction of thermocouple)
I—Midgley wire spiral, coated with carborundum
J—Fractionating column (evacuated and silvered)
K—Copper container for liquid air
M, V—Mercury manometers
R, S, T—Calibrated aspirator bottles
W—Thermocouple

A series of experimental decompositions were made with carefully prepared granular catalysts of nickel, iron, chromium, copper, cobalt, aluminum, and magnesium. Runs were made with and without these catalysts under the same conditions of rate of flow and temperature (approximately 300° C.). So far as could be determined by analysis of the exit gas for hydrogen and unsaturates, these catalysts had no effect, although in some cases carbon was deposited on them. This seemed to indicate that catalytic effect (if present at all) was inhibited by carbon decomposition. The same iron catalyst had no appreciable effect at 760° C.

A series of runs was made with and without possible catalysts of a more stable and rigid nature. Data from this series are shown in Table IV.

Table IV—Effect of Catalysts

Run	Catalyst	Form of Catalyst	Preparation of Catalyst	Temp.	Composition of Exit Gas H_2	Composition of Exit Gas Unsatd.
				° C.	%	%
12	Iron	Gauze	Reduced with H_2	760	15.1	35.0
13	None	...	...	760	15.0	35.0
14	Iron	Gauze	None	830	18.5	30.7
15	Nickel	Gauze	None	830	25.0	21.0
16	None	...	...	830	26.5	22.0
17	Nickel	Gauze	Reduced with H_2	815	27.7	22.1
18	None	...	...	815	26.6	22.0
19	Carborundum	Granular	None	840	22.8	25.0
20	None	...	...	840	26.6	23.2
21	Calcium carbide	Granular	None	815	24.8	25.2
22	None	...	...	815	27.2	23.5
23	Activated alumina	Granular	Used as received	800	21.3	27.4
24	None	...	...	800	21.4	27.6
25	Monel metal	Gauze	None	830	32.2	16.5
26	None	...	...	830	26.7	20.4
27	Petroleum coke	Granular	Heated	800	22.2	28.5
28	None	...	...	800	24.8	26.2
29	Nickel	Gauze	None	800	36.1	15.4
30	None	...	...	690	34.8	22.0
31	Nichrome	Gauze	None	690	34.8	22.0
32	Monel metal	Gauze	None	830	55.8	3.6
33	Calcium-silicon alloy	Granular	None	700	20.3	31.8
34	Platinized pumice stone	...	Used as received	700	17.3	35.0
35	Palladized asbestos	...	Used as received	700	16.1	32.6
36	None	...	...	705	15.0	32.0
37	Reduced vanadium pentoxide	Granular	Reduced with H_2	705	14.3	34.6
38	Iron	Powder	...	760	17.3	17.2
39	Nickel	Powder	...	760	48.7	13.0
40	Steel	Gauze	...	800	43.0	11.0

From a comparison of the results at the same temperatures and rates of flow of Table IV, it is seen that catalysts composed of, or containing nickel, cobalt, chromium, and iron decidedly influence the decomposition products. The effect is principally that of increased production of hydrogen and methane. The rate of gas inflow was 7.7 liters per hour in each run of the above series.

In runs 25, 29, and 32 in which 150-mesh gauze was used, the gauze was found to be almost completely disintegrated after a few liters of gas had passed through it. The gauzes used in all other runs were 60 mesh. All gauzes were 6 by 3 inches (15.24 by 7.62 cm.). They were used in concentric roll form.

In one case it was found that by taking samples at 5-minute intervals, the composition of the exit gas varied during the time of catalytic effect. This situation was suspected but not shown to be true in all cases of catalytic effect.

After determination of unsaturates and hydrogen in the exit gas from runs 29, 32, and 39, the residual gas was found by combustion to consist mostly of methane.

Discussion of Results

Assuming that the two primary decomposition reactions may be represented by the equations,

$$C_3H_8 = CH_4 + C_2H_4 \quad (1)$$
$$C_3H_8 = C_3H_6 + H_2 \quad (2)$$

and considering the experimental decomposition at 760° C., the results of which are included in Table II, it will be seen that the volumes of methane and ethylene should be equal but are not. The same is true of propylene and hydrogen. Since ethane was found in the exit gas it may be that some of the ethylene produced in the primary decomposition has reacted with some of the hydrogen similarly produced to give ethane. Calculations made on this basis show very good agreement between the volumes of methane and ethylene resulting from primary decomposition by Equation 1. However, there is no definite proof that ethane was formed in this way. In fact, the hydrogenation of ethylene seems very unlikely under the conditions of this experiment. The ethane may be formed by the combination of methyl fragments resulting from the decomposition or by hydrogenation of the ethyl fragments resulting in the same way. After adding the amount of hydrogen which may have combined with ethylene to the amount found, there is still considerable lack of agreement between the amounts of propylene and hydrogen produced by primary reaction (2). Apparently some of the propylene has decomposed in secondary reactions.

Assuming that the methane found in the exit gas is a measure of the extent of Equation 1, the percentage of propane decomposing according to Equation 1 was calculated from the data: 7.2 liters of gas was passed into the reaction tube while the volume of the exit gas was 13.1 liters consisting of 35.5 per cent methane. According to this, 73 per cent of the propane decomposed as represented by Equation 1.

When the experimental decomposition at 660° C., results of which are shown in Table II, is considered in the same way as above, it is also impossible to show how the decomposition takes place. In this case 9 liters of propane were passed into the tube while the volume of the exit gas was 12.7 liters containing 20.1 per cent of methane. Calculation indicates that 66 per cent of the propane decomposed follows the course represented by Equation 1. Because of apparently intensive secondary reactions, it is not possible to treat the other decompositions as in the two cases already given.

In any experiment carried out here for which complete analysis of products was made, the proportion of product found could not be accounted for except by reaction or decomposition of radicals resulting from primary decomposition. The net result of the primary decomposition of propane can only be represented by equations showing the formation of compounds. The actual decomposition process of propane appears to consist of formation of fragments, such as methyl, ethyl, and propyl, which undergo changes, such as combination with other radicals, hydrogenation, or further decomposition. This same statement applies, of course, to other hydrocarbons, if true in the case of propane. The final resulting products apparently depended upon inter-reactions, decompositions, hydrogenations, and dehydrogenations of nascent radicals to a much greater extent than have been generally believed. Probably the best way to indicate the primary effect of the decomposition of a hydrocarbon is to represent it as decomposing to all possible radicals. Thus for propane,

$$C_3H_8 \longrightarrow CH_3 + C_2H_5$$
$$C_3H_8 \longrightarrow C_3H_7 + H$$

Acknowledgment

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Effect of Nitrogen on Steel[1]

A Practical Consideration as Applied to Commercial Open-Hearth Steel

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Numerous investigations made during the last fifty years have shown nitrogen to be the most detrimental of impurities found in iron and steel. It is present in all steel in various amounts and, because of this and the effect of various other elements and conditions on steel, the actual effect of the nitrogen on hot-rolled open-hearth steel has never been determined.

The effect of the nitrogen on steel has been magnified by nitrifying regular 8-ton ingots and comparing the physical properties of this steel to the regular product. Nitrogen has been found to have four times the effect of the same amount of phosphorus. An increase of 0.01 per cent in nitrogen content was sufficient to cause a marked difference in the physical properties of the steel. The coefficient of effect increased with the increase of carbon.

An equation has been derived whereby the effect of an increase of nitrogen on the elongation of the steel may be calculated quite accurately. Also the equation may be used to indicate the benefits to be derived by using a denitrifying agent.

The average amount of nitrogen found in open-hearth steel was 0.0045 per cent. Such an amount was not found to be seriously detrimental to the quality of steel.

With a better understanding of the many phenomena encountered in the manufacture of iron and steel, it will be possible to produce a sounder and more dependable steel quite economically. Although the problem of acquiring the necessary knowledge is difficult and complex, the accomplishment will be well worth the time and the work required.

One of the least understood of these phenomena is the effect of the ever-present nitrogen on the physical properties of hot-rolled commercial open-hearth steels. Numerous scientific investigations have been made during the last fifty years, and it is firmly established that nitrogen causes a hard and brittle steel of poor quality. However, metallurgists and commercial manufacturers of steel have never been convinced that these investigations have any practical value, and at present nitrogen is not considered when conclusions as to different properties of steel are drawn from its analysis.

That this may be a serious oversight is indicated by the fact that there have been numerous failures at this plant for which the authors have been unable to assign a reason. Microscopically and chemically the steel appears to be of a good quality, but the physical tests show it to be abnormally poor. These failures are similar in character to those caused by nitrogen, and it is believed that the effect of nitrogen on commercial steel is worth a detailed study and a practical consideration.

Historical Review

Historical perspective being invaluable to scientific progress, the first requisite preceding the start of work on any problem is a complete knowledge of previous work on the same subject. To give the reader a better understanding of the subject of nitrogen in steel, and to give the findings of this paper the proper importance, a review is given of all the published literature that may be obtained. In the following paragraphs is found a brief summary of the facts that are established and accepted as correct. At no time have so much contradictory evidence and claims by reputable chemists and metallurgists been found as are found in these discussions. This is owing, no doubt, to the difficulty in the actual determination of the nitrogen and to the difficulty in establishing the fact that the observed effect is in reality due to the nitrogen present. The nitrogen is always present in small quantities, and to determine its effect in the presence of so many potent factors is quite difficult. But by comparison of work and results obtained by fifty years of study and investigation, we are able to say definitely that certain effects are due to the presence of nitrogen in steel. And as the number of investigations has steadily increased during this time, it is evident that the results obtained are considered both valuable and important.

The earliest reference found to the effect of nitrogen on steel is a paper by Allen (*1*), written in 1880, wherein is described an analytical method for the determination of nitrogen in steel. This method is accepted today as the best for this analysis, although it has been modified numerous times (*22*). It is known that no combined nitrogen in ordinary steel escapes determination by this method (*33*). However, to get the total nitrogen present, a fusion in vacuum is employed, as this gives not only the nitrogen combined, but that in solid solution and that entrapped as a free gas (*21*).

All investigators agree that nitrogen is the most detrimental of all the impurities found in steel, and is present in some quantity in all steel. Tholander (*37*) in 1889 said, "Even the smallest amount of nitrogen absorbed by iron during fabrication has to be taken into consideration when conclusions on different properties of iron are drawn from its analysis." This expresses the opinion of the majority of the investigators who have studied the subject at any great length (*33*).

The source of nitrogen is, of course, the air, which is approximately 80 per cent nitrogen. Free nitrogen is absorbed by molten iron, and by solid iron at red heat under certain conditions, in amounts varying with the pressure of the nitrogen and the temperature of the iron. Sawyer (*33*) gives a formula by which the nitrogen to be expected in a cooled ingot of iron melted under an atmosphere of nitrogen may be calculated, and which is most generally accepted as correct.

$$\%\,\text{N} = K\sqrt{Pn}$$

where $\%\,\text{N}$ = per cent nitrogen in cooled ingot
K = constant having value of 0.02 for pure iron
Pn = pressure in atmosphere of nitrogen during melting and solidification

But the limiting amounts for pure iron, both solid and liquid, may increase when any of the elements silicon, manganese, aluminum, titanium, or vanadium are present in the iron (*2, 19, 23, 24, 26, 33, 39, 46, 47, 48*).

The nitrogen that can be introduced into iron is controlled by the temperature and the pressure. The chief factors

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[1] Received May 14, 1931.

affecting the nitrogen content of Bessemer steel are the temperature of the steel during the blow and the pressure of the blast. An increase of either increases the nitrogen content. In the Bessemer process, where the air is blown through the steel, and in the electric furnace with its reducing conditions, more nitrogen is absorbed than in the oxidizing open-hearth where the slag intervenes between the air and the metal (*33, 36, 47*).

Steel made by the Bessemer process or the electric furnace contains 0.010 to 0.024 per cent nitrogen; open-hearth steels only 0.003 to 0.008 per cent; and crucible steels least of all, 0.0005 to 0.002 per cent. Dudley found that steel rails containing 0.0147 to 0.0153 per cent nitrogen were likely to break in service, a fact which may explain the superiority of open-hearth steel for rails (*10, 33, 36*).

The nitride in steel is not unstable (*2*), and remelting or prolonged heating in vacuum near the melting point is necessary to remove it all (*31*). The amount of nitrogen remaining in highly nitrified steels after reheating is dependent on the reheating temperature, decreasing as it is raised. Pourcel (*28*) found that nitrogenized steel of high nitrogen content contained only about 0.015 per cent nitrogen after remelting. This is in agreement with Fry (*14*), who states that nitrogen may exist in solid solution in annealed low-carbon iron at room temperature only to the extent of 0.015 per cent.

Apparently deoxidation has practically no effect on the nitrogen content (*40*). Some investigators find that it lowers it slightly (*8*), others that it increases it slightly (*40*), and some find no change at all (*38*). Titanium and vanadium do not remove nitrogen from steel, but do combine with it as the respective nitride (*40*). As these nitrides are difficult to decompose, it is possible that they were not determined, or only partially determined, by the acid solution–distillation method then in use (*21*). This would explain the discrepancies of the various investigators. Some find that the addition of these metals actually increases the nitrogen content of the steel, and advise a shortening of the melting period of the titanium or vanadium steels (*40*). Chromium, manganese, ferrotitanium, ferro-aluminum, and ferrovanadium have a great affinity for nitrogen, whereas ferrochromium and ferromanganese absorb only small amounts, and ferrophosphorus and ferrotungsten none at all (*48*).

The effects of nitrogen are varied, and a number of them are quite definitely established. Nitrogen is known to make steel brittle, as small amounts are seen to have a marked effect on the ductility as measured by the elongation and reduction of area. It has been suggested that temper brittleness (*16*) and the blue-heat phenomenon (*9*) of steel may be due to nitrogen. Nitrogen is also believed to cause cold shortness in steel (*39*). Steel containing over 0.015 per cent nitrogen exhibits a great loss of ductility during the bending test (*33*).

Nitrogen is known to increase the hardness of the steel, a fact made use of extensively at present for case-hardening. Also, an increase of nitrogen increases the tensile strength of the steel, and raises the elastic limit (*2, 4, 8, 10, 15, 19, 33, 34, 35, 37, 39*).

Herwig (*19*) believes that blisters formed during the annealing of sheet iron are due to the presence of nitrogen, and also that nitrogen is the cause of numerous rail failures. He believes also, in contradiction to numerous other investigators, that hydrogen must always be present for the iron to combine with nitrogen, hydrogen being a catalytic agent.

The coefficient of effect of nitrogen on steel is not constant, but increases with the increase of the carbon and metalloids (*36*). It has been shown distinctly that phosphorus and nitrogen affect the mechanical properties of steel in the same way, but that the effect of nitrogen is the stronger. It is also shown that the segregation of the nitrogen and the phosphorus follow each other in nearly all cases (*36*).

The embrittling effect of nitrogen has been considered due to the tendency of the dissolved nitride to retain iron in the gamma state and the carbide in solution (*2*). Iron nitride is believed to prevent the coalescence of the iron molecules at the critical point, thus retarding the changes (*2*). Nitrogen can exist in solid solution up to approximately 0.03 per cent (*33*), and is often indistinguishable under the microscope until it exceeds 0.05 per cent (*5*). In carbon steel there may be no metallographic evidence of nitrogen even though 0.15 per cent is present (*29*). The iron nitride under the microscope may appear as pearlitic patches, as cementite, or as the characteristic nitride needle (*29, 45*).

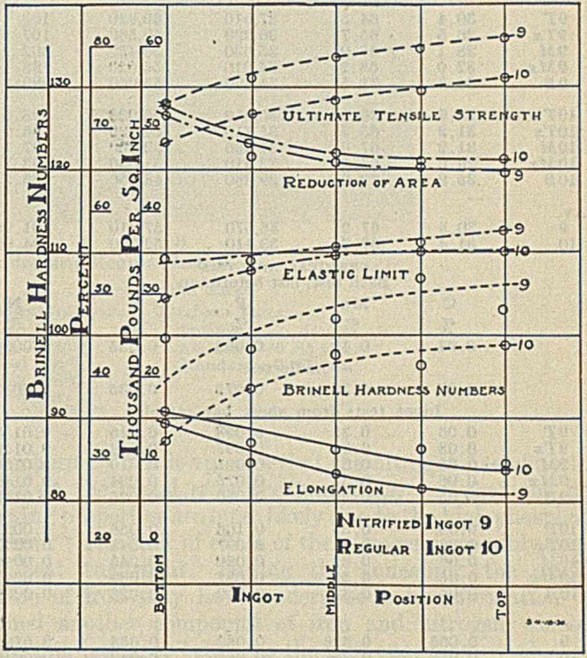


Figure 1—Comparison of Physical Properties of Samples of Soft Steel, Heat A

It appears certain that by heat-treating steel high in nitrogen a good quality steel can be produced (*19*). Arc-welded joints are frequently high in nitrogen and very brittle. By reheating the weld metal, using a modified treatment with the arc, a joint which is much refined in grain and superior in ductility is obtained (*33*). Also, by heat-treating a steel containing 0.10 per cent nitrogen, Hurum obtained a good quality of steel (*33*).

Lately there has been some discussion of a second form of nitrogen (*22*), different from nitride nitrogen, not determined by the Allen acid solution method. However, more work must be done to prove the fact (*44*).

A number of investigators (*28*) believe that the nitrogen present in commercial steel is not enough to warrant consideration (*17*). Very little work has been done on commercial hot-rolled steel, and most of the conclusions are based on data obtained from nitriding pure iron wire (*33*), or thin iron sheet, in an electric furnace with ammonia gas or pure nitrogen, under pressure (*14*). While there is a possibility that the experimental work done as described may be applicable to commercial steel, there is a probability that Tholander and Braune were correct, and that even small amounts of these substances have a marked effect on the quality of the steel in question.

Influence of High Nitrogen Content on Soft Steel and Steel Sheet for Galvanizing

Effect of Nitrogen on Soft Steel Sheet Bar—The actual effect of nitrogen in contributing to a poor quality of steel is so overshadowed by the various physical conditions and the chemical composition of the steel, that it is indiscernible as the effect attributable to this element if it is not exaggerated, with the other factors remaining the same. Accordingly, it was decided to nitrify one ingot from a heat of soft steel, thus intensifying the effect of nitrogen by comparison to another regular ingot, and enabling the observation of the behavior of the steel.

Table I—Physical Tests and Chemical Analysis of Test Pieces of Soft Steel Sheet Bar, Heat A

Sample	Elongation %	Red. of Area %	Elasitc Limit Lbs./sq. in.	U. T. S. Lbs./sq. in.	Brinell Number[a]
			PHYSICAL TESTS		
9*T*	30.4	64.5	37,610	60,920	103
9*Tx*	26.5	65.7	36,220	59,560	107
9*M*	28.1	65.9	35,630	58,480	102
9*Mx*	32.0	68.2	34,010	56,020	98.4
9*B*	34.3	71.5	34,390	53,060	99.5
10*T*	28.9	66.2	35,010	56,030	98.8
10*Tx*	31.2	65.9	35,110	54,120	96.2
10*M*	31.2	67.0	34,660	53,280	97.7
10*Mx*	29.6	66.5	32,910	51,930	93.7
10*B*	35.9	72.9	29,380	48,350	86.7
Av.					
9	30.3	67.2	35,570	57,610	101.98
10	31.4	67.7	33,410	52,740	94.62
			CHEMICAL ANALYSIS Bath test, last before tap		
	C %	Mn %	P %	S %	N %
	0.04	0.19	0.008	0.035	0.00341
			Ladle test		
	0.08	0.30	0.075	0.035	0.00372
			Ingot tests from sheet bar samples		
9*T*	0.06	0.33	0.098	0.045	0.01530
9*Tx*	0.08	0.33	0.097	0.046	0.01597
9*M*	0.08	0.33	0.091	0.040	0.01568
9*Mx*	0.06	0.32	0.075	0.034	0.01401
9*B*	0.05	0.32	0.050	0.025	0.01121
10*T*	0.08	0.33	0.106	0.056	0.00517
10*Tx*	0.06	0.34	0.097	0.048	0.00428
10*M*	0.06	0.32	0.090	0.045	0.00409
10*Mx*	0.05	0.32	0.081	0.039	0.00438
10*B*	0.04	0.32	0.049	0.023	0.00313
Av.					
9	0.066	0.326	0.082	0.038	0.01443
10	0.058	0.326	0.085	0.042	0.00421

[a] Brinell test for hardness was made on side of bar after outer scale had been removed by grinding.

After a search of literature, it was found that Herwig (*19*) had used calcium nitride to introduce nitrogen into an ingot, but as this had the added property of removing the phosphorus, this substance was considered undesirable. Therefore it was decided to use a cyanide, and potassium ferrocyanide was chosen as it was not a violent poison like the cyanide of sodium or potassium. Not knowing the efficiency of the reaction and wishing to introduce an appreciable amount, it was calculated that by adding 10.8 pounds (4.89 kg.) of the dry salt, and assuming 100 per cent efficiency, a nitrogen content of 0.03 per cent would be obtained. The ferrocyanide was dried at 212° F. (100° C.), and 10.8 pounds (4.89 kg.) taken to the open hearth.

Here ingots 9 and 10 were chosen from heat A as test ingots, and ingot 9 was nitrided by the addition of the potassium ferrocyanide during the pouring. The potassium ferrocyanide apparently decomposed and a white cloud of vapor, probably the volatilized potassium, was given off. The two ingots were allowed to "rim" similarly, and were marked so they could be identified during the rolling. No difference was noted during the rimming action between the treated ingot and the other ingots of the heat.

The two test ingots worked the same all through the rolling in so far as the metallurgist could observe. Ingot appearance and rolling were the same, and the surfaces of the sheet bars were not noticeably different.

The top crop of the nitrified ingot was sent to the laboratory to determine whether or not any nitrogen had been combined. This was sampled and analysis showed a nitrogen content of 0.0171 per cent. Although this was not as much as was expected, the sheet bar was sampled in five equal divisions to show the segregation in the ingot. These samples were called *T*, or top of the ingot; *Tx*, or between top and middle; *M*, or middle; *Mx*, or between middle and bottom; and *B*, or bottom.

At the laboratory, test pieces were cut from the sheet bar in the same relative positions and machined to standard sizes, the length between shoulders being 8 inches (20.3 cm.), the width 1.43 inches (4.6 cm.), and the thickness 0.340 inch (0.8 cm.). After the physical tests were made, the test pieces were drilled for chemical analysis. The results of these physical tests and the chemical analysis are given in Table I and also graphically represented in Figures 1 and 2.

To determine whether the ingots rimmed properly or whether the additions of the potassium ferrocyanide had had an effect on the action, the sheet bars from both ingots were sampled by sawing off pieces 2 inches (5.08 cm.) wide, and as long as half the width of the sheet bar. Then the sawed edges were ground smooth on the grinder, and the pieces deep-etched with 1:1 hydrochloric acid. This showed that the steel was nicely rimmed and had the usual structure in both ingots.

By nitriding this ingot it has been shown that even a small amount of nitrogen will have a great effect on the mechanical properties of soft steel. An increase of only 0.01 per cent of nitrogen has increased the tensile strength 5000 pounds per square inch, and lowered the ductility, as measured by the elongation, about 3 per cent. The nitrogen has also increased the resistance to deformation, as measured by the elastic limit, more than 2000 pounds per square inch. The Brinell hardness number also indicates that the nitrified steel is harder.

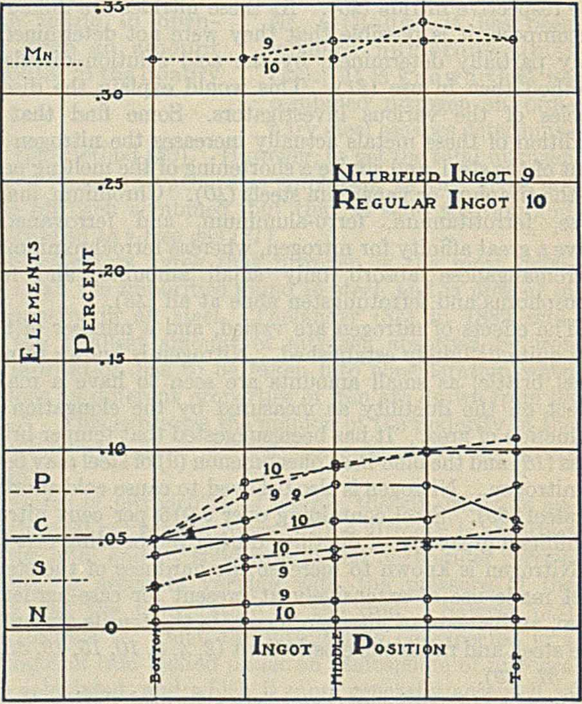


Figure 2—Segregation Shown by Chemical Analysis of Samples of Soft Steel, Heat A

This coefficient of effect on ductility, however, does not remain constant, but increases along with the increase of carbon. We know that phosphorus and nitrogen affect steel in the same way, and that the effect of the nitrogen is the stronger. It is possible that the injurious properties of nitrogen may be explained by its position in the same group

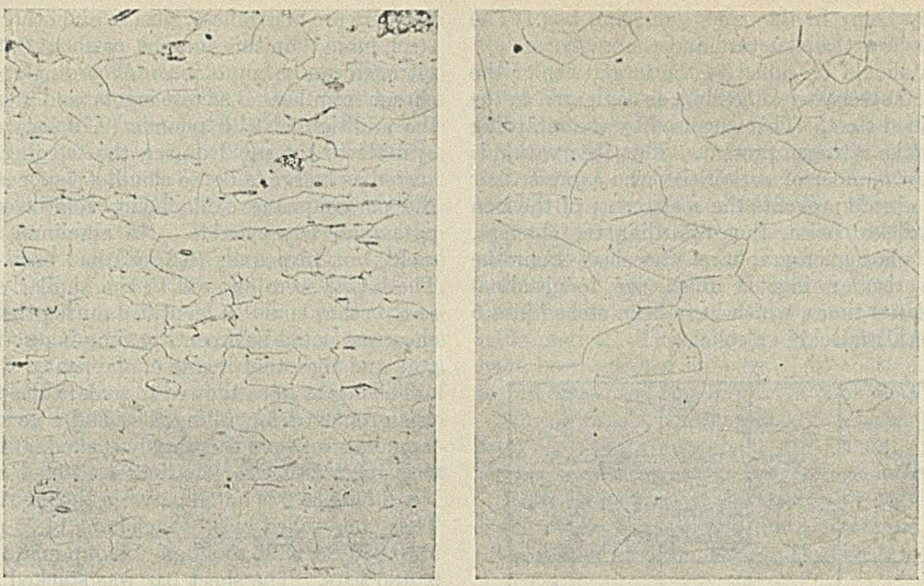

A B

Figure 3—Soft Sheet Bar from Nitrided and Regular Ingots

A—Nitrided Sheet
Chemical Analysis:
C—0.04%
Mn—0.33%
P—0.114%
S—0.055%
Si—trace
N—0.01634%
Erichsen Tests:
Thickness—0.96 mm.
Av. draw—9.05 mm.
Standard—9.90 mm.

B—Regular Sheet
Chemical Analysis:
C—0.02%
Mn—0.30%
P—0.056%
S—0.028%
Si—trace
N—0.00268%
Erichsen Tests:
Thickness—0.94 mm.
Av. draw—9.85 mm.
Standard—9.87 mm.

in the periodic arrangement of elements as bismuth, antimony, arsenic, and phosphorus. It is established that the more negative the element, the greater its injurious effect and, as nitrogen is more negative than phosphorus, it is more injurious.

The experimental results also show that what could be termed the critical amount of nitrogen has not been reached. The maximum of 0.016 per cent is not sufficient to cause a very brittle steel, even with 0.10 per cent phosphorus. However, the elongation of the steel is falling off at a rapid rate, and soon will reach a point where the steel is noticeably cold short.

EFFECT OF NITROGEN ON SHEET STEEL AND GALVANIZING—The sheet bar was meanwhile rolled into sheets, with no difference between the nitrified and the regular sheets being observed. These sheets were given the regular annealing treatment, and then galvanized.

From the nitrified ingot, 178 sheets were observed while being galvanized. One sheet had a large blister and three had small blisters (about 1/4 inch, or 0.8 cm., in diameter), and there were also three seamy sheets. The sheets had a nice spangle and a good surface.

From the regular comparison ingot, 155 sheets were observed while being galvanized. There were twenty blistered sheets. The sheets had many rolled-in scale marks and only a fair spangle.

Two sheets from each ingot in black, two sheets of each galvanized, and the galvanized sheet from the nitrified ingot that had the large blister, were sent to the laboratory for further tests. Each of these sheets was then sampled and the base metal given a complete chemical analysis. Also Erichsen tests and microscopical examination were made on each. The analysis of the samples and the results of the tests are shown in Table II.

An examination of the sheets after annealing and galvanizing shows the nitrogen content is scarcely, if any, affected by the heat treatment. The drawing properties of the sheet, as shown by the Erichsen test, are below standard in the case of the higher nitrogen when it is accompanied by a high phosphorus. But it appears that the nitrogen has almost no effect on the metal after the annealing, and that the poor drawing properties are most likely due to the high phosphorus content. This lack of effect of the nitrogen is possibly due to the heat treatment. During the annealing, the original nitride of iron may have undergone a transformation and formed another compound of iron and nitrogen which is neither so hard nor brittle as the first one.

The sheet from the nitrided steel was singularly free from blisters, had a good surface, and a good spangle after galvanizing. Some writers have attributed blistered sheet to nitrogen content, but from this evidence it appears that they were in error. Nitrogen up to 0.016 per cent has no deleterious effect on steel sheet or on the galvanizing of the sheet, so far as can be discovered.

Table II—Analysis and Erichsen Tests on Galvanized and Black Sheets, Heat A

DESCRIPTION	INGOT	CHEMICAL ANALYSIS					ERICHSEN TEST		
		C	Mn	P	S	N	Thickness	Av.	Std.
		%	%	%	%	%	Mm.		
Galvanized	10	0.03	0.29	0.053	0.026	0.00290	0.98	10.00	9.96
Galvanized	10	0.02	0.30	0.056	0.028	0.00268	0.94	9.85	9.87
Black	10	0.04	0.30	0.059	0.030	0.00267	0.94	10.06	9.87
Black	10	0.04	0.30	0.064	0.030	0.00327	0.93	10.45	9.83
Blistered	9	0.04	0.30	0.048	0.029	0.01230	0.98	9.39	9.96
Galvanized	9	0.04	0.33	0.109	0.053	0.01399	0.92	9.05	9.80
Galvanized	9	0.04	0.33	0.114	0.055	0.01634	0.96	9.07	9.90
Black	9	0.04	0.30	0.068	0.034	0.01292	0.92	10.02	9.80
Black	9	0.04	0.30	0.073	0.034	0.01270	0.86	9.98	9.65

METALLOGRAPHIC EXAMINATION—Two pieces of sheet bar, *9Tx* and *10Tx*, were cut, polished, and etched in a 5 per cent picric acid solution in alcohol for microscopic examination. A thorough examination under magnifications varying from 100 to 1500 times failed to reveal any characteristic that might suggest the presence of nitrogen. In both pieces there was observed a cementite divorce in about equal proportions. There were neither nitride needles nor characteristic nitride patches in evidence.

Two samples of steel sheet were used for metallographic examination, one from the nitrided steel, the other from the regular comparison steel. These had undergone the same treatment, actually being in the same annealing box. The photomicrographs show the structure and the analysis.

Special mention should be called to the larger size of the crystal in the regular steel after annealing, as compared to the crystal of the nitrided steel. This is caused by the retarding of their growth by the nitrogen present. This observation is in agreement with a number of authorities who express their opinions that iron nitride prevents the coalescence of the iron molecules at the critical point, thus retarding the changes.

Figure 3 shows photomicrographs of the sheet from the nitrided and the regular ingots. Both are longitudinal sections, magnified 100 times, which have been etched in a 5 per cent solution of nitric acid in alcohol.

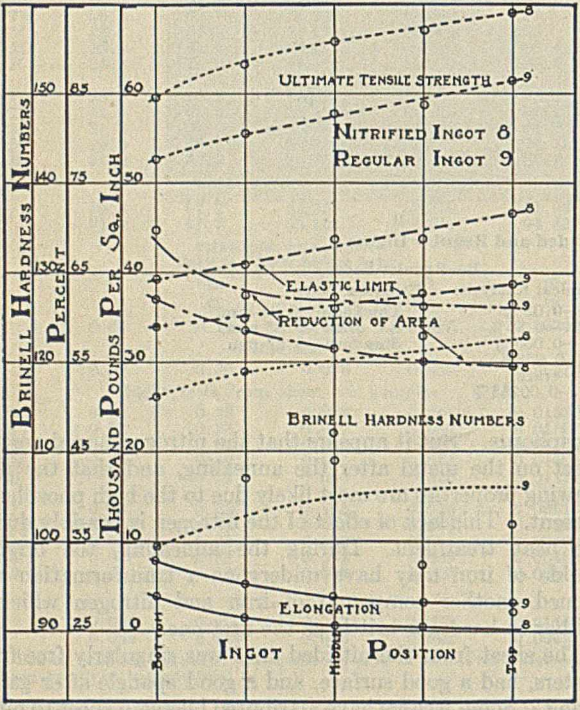


Figure 4—Comparison of Physical Properties of Samples of Soft Steel, Heat B

Photomicrograph A is of the nitrided sheet, and it is seen to be well annealed. The carbides are coagulated, and the grains are regular and well defined. There are very few inclusions evident. There is no evidence of the nitrogen, nor of nitride needles.

Photomicrograph B is of the regular sheet, and it is well annealed, with a slight tendency to over-anneal. The carbides are coagulated, and the grains are well defined and regular. There are no inclusions evident.

The surfaces of both sheets are good. The nitrided sheet is from a position near the top of the ingot, as indicated by the phosphorus and nitrogen content, while the regular sheet is from a position nearer the bottom of the ingot.

Verification of Influence of High Nitrogen Content on Soft Steel and Steel Sheet for Galvanizing

Effect of Nitrogen on Soft Steel Sheet Bar—In order to confirm the results just described as to the effect of nitrogen on soft steel and to add to this information, the previous work was repeated on another heat. As the combined nitrogen present in the other test ingot was only about 70 per cent of what may be obtained, it was decided to add twice the amount of potassium ferrocyanide that was added before. According to Sawyer (*33*) it is possible to have nitrogen in steel according to the equation

$$\%\text{N} = K\sqrt{Pn}$$

As there are manganese, silicon, and other elements present in steel, more than this amount, or about 0.020 to 0.024 per cent nitrogen can be combined. Accordingly, ingots 8 and 9 were chosen from heat B as test ingots, and ingot 8 was nitrided by the addition of 21.6 pounds (9.79 kg.) of potassium ferrocyanide to the mold during the teeming. The reaction occurred as before, a dense cloud of vapor coming off, probably the potassium as oxide being volatilized along with some potassium ferrocyanide. No aluminum was added to the mold, but 15 pounds (6.8 kg.) had been added to the ladle. The ingots were allowed to rim similarly, and were marked so that they could be identified during the rolling. No difference was noted between the rimming action of these two ingots and the other ingots of the heat.

The ingots were allowed to soak in the pits for 2 hours, and when removed for rolling they had a good even heat, a good temperature, were thoroughly soaked, and were clean, except that ingot 8 had a few light scattered scabs on the edges. No difference was noted between the ingots during the rolling. They were rolled into 12-inch bars, 14.75 pounds-foot weight, for 0.836–28 × 96 roofing. Ingot 8 made 176 bars, and ingot 9, 186 bars. The sheet bar was stacked hot and allowed to cool slowly. When the steel was cold, the bar from each ingot was sampled in such a way as to show the segregation.

At the laboratory, test pieces were cut from the sheet bar samples in the same relative positions. These were machined to standard sizes, the length between shoulders being 8 inches (20.32 cm.). After the physical tests had been made, the test pieces were drilled for chemical analysis. The results of these tests and the chemical analysis are given in Table III and also graphically interpreted in Figures 4 and 5.

Table III—Physical Tests and Chemical Analysis of Test Pieces of Soft Steel Sheet Bar, Heat B

Sample	Elongation	Red. of Area	Elastic Limit	U. T. S.	Brinell Number[a]
	%	%	*Lbs./sq. in.*	*Lbs./sq. in.*	
			PHYSICAL TESTS		
8*T*	27.3	54.8	46,770	69,110	121
8*Tx*	25.7	55.3	43,900	67,050	123
8*M*	25.7	56.4	43,780	65,950	112
8*Mx*	26.5	58.5	40,830	63,350	119
8*B*	28.9	61.9	39,170	59,570	116
9*T*	28.1	60.5	38,800	61,520	102
9*Tx*	28.1	60.1	37,670	58,770	97.3
9*M*	28.9	62.2	36,030	57,870	109
9*Mx*	30.4	62.5	34,870	55,410	107
9*B*	32.8	69.6	33,920	52,570	99.2
Av.					
8	26.82	57.37	42,890	65,006	118.2
9	29.66	62.98	36,258	57,228	102.9
			CHEMICAL ANALYSIS		
			Ladle test		
	C	Mn	P	S	N
	%	%	%	%	%
	0.12	0.48	0.084	0.038	0.00601
			Ingot tests from sheet bar samples		
8*T*	0.16	0.49	0.116	0.055	0.02183
8*Tx*	0.16	0.49	0.110	0.051	0.02160
8*M*	0.14	0.47	0.104	0.046	0.02086
8*Mx*	0.12	0.47	0.084	0.037	0.01995
8*B*	0.10	0.45	0.062	0.030	0.01617
9*T*	0.12	0.49	0.111	0.050	0.00683
9*Tx*	0.12	0.47	0.110	0.050	0.00683
9*M*	0.12	0.48	0.105	0.050	0.00579
9*Mx*	0.10	0.45	0.087	0.038	0.00533
9*B*	0.06	0.45	0.055	0.026	0.00462
Av.					
8	0.136	0.474	0.0952	0.0358	0.02008
9	0.104	0.468	0.0936	0.0428	0.00588

[a] Brinell test for hardness was made on side of bar after outer scale had been removed by grinding.

To determine whether the ingots rimmed properly or whether the addition of the potassium ferrocyanide had had an effect on the action, the sheet bars from both ingots were sampled by sawing off pieces 2 inches (5.08 cm.) wide, and as long as half the width of the sheet bar. The sawed edges were ground smooth on the grinder, and the pieces were deep-etched with hot 1:1 hydrochloric acid. An examination showed the steel, in both cases, to be well rimmed.

The photomicrographs of Figure 6 are given to show the grain structure and the condition of the carbides in the two plates used for comparison. In both the carbides are seen to be partially coagulated, with some evidence of cementite divorce. Both show the steel to be clean and of good quality.

In 8*Tx*, the section shown is near the center of the plate, where the segregation is greatest. The stringlike formation due to rolling is evident. In 9*Tx*, the photomicrograph was taken near the edge, and the denser skin of the metal is shown.

By nitrifying this ingot the evidence obtained in the previous test has been verified. A nitrogen content which is the maximum that can be held as combined nitrogen under a pressure of one atmosphere has been obtained. The effect of the nitrogen as shown by this test is the greatest that can occur in open-hearth steel of this analysis, under these conditions, and so may be considered to be the upper limit for practical purposes.

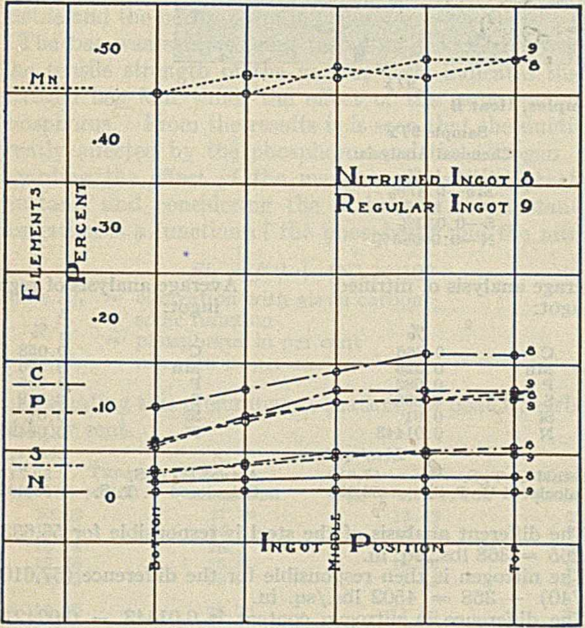


Figure 5—Segregation Shown by Chemical Analysis of Samples of Soft Steel, Heat B

The nitrided steel is harder, stronger, and more brittle than the regular steel. The nitrogen is higher in this test ingot than in the first one, and the phosphorus and carbon are higher in this heat than in the former one. In spite of all three of these being higher in this case, the steel is still workable. It appears certain, from these results, that soft steel made according to standard practice is not affected enough by this maximum nitrogen content to warrant further consideration, and as open-hearth steel of this analysis seldom has more than one-fifth of the amount the effect of the nitrogen will not be apparent.

Effect of Nitrogen on Sheet Steel for Galvanizing—(*a*) *Sheet mill rolling report.* At the sheet mill, the sheet bar was cut to length, heated to about 1400° F. (777.8° C.), and rolled into sheets. Three bars were rolled to pack and doubled. The nitrified sheet bar showed a large number of stringlike blisters on the breakdown pass, and also on the doubling and finishing passes. The regular ingot showed a few blisters. The sheets opened easily when matched and finished, and appeared rather seamy.

The blisters were not caused by excessive heating of the bars, as the bars were heated on the cool side. Except for the numerous blisters there was no marked difference between the two ingots.

(*b*) *Galvanizing report.* At the galvanizing department, the sheets were annealed, pickled, and given a commercial coating for roofing material.

On the nitrified sheet, the spangle was fair, but was not so bright as expected from this type of coating. The surface rolls were burned and cleaned with plenty of air, on full, but this did not brighten the sheets. The color was a dull gray smoky type, and looked much like that of tight coat. From 60 to 70 per cent of the sheets carried small blisters of the seamy type, which were undiscernible after the sheet had cooled, but were quite visible on the "wet" sheet. These blisters were of the same type as those observed in the sheet mill practice. These sheets were passed on roofing, but would have been rejected on extra tight coating. In general, they would have been classified as of poor quality.

On the regular sheet, a good bright spangle was obtained. Only five were blistered. In general, these sheets were average and satisfactory for roofing material.

Both ingots showed the steel to be quite seamy, the seams being of short length and quite numerous.

A summary of the data on the sheets shows the following:

INGOT	NITRIFIED	REGULAR
Bars cut	176	186
Pattern sheets made	348	359
Sheets rejected because of blisters	17	2
Total galvanized sheets weighed in	300	354
Quality	Poor	Average

(*c*) *Laboratory report.* Two sheets of each ingot in black and two sheets of each galvanized were sent to the laboratory for further tests. Each of these sheets was then sampled, and the steel analyzed. Also Erichsen tests were made on each, and two examined microscopically. The analysis and results of these tests are shown in Table IV.

Table IV—Analysis and Erichsen Tests on Galvanized and Black Sheets, Heat B

DESCRIPTION	INGOT	CHEMICAL ANALYSIS C	Mn	P	S	N	ERICHSEN TEST Thickness	Av.	Std.
		%	%	%	%	%	Mm.		
Galvanized	8	0.08	0.45	0.055	0.023	0.01587	0.56	8.46	8.78
Galvanized	8	0.12	0.50	0.094	0.041	0.01861	0.53	7.06	8.68
Galvanized	9	0.08	0.44	0.056	0.026	0.00374	0.52	8.48	8.65
Galvanized	9	0.12	0.46	0.090	0.038	0.00543	0.58	8.22	8.85
Black	8	0.12	0.48	0.089	0.041	0.01938	0.50	8.25	8.57
Black	8	0.16	0.51	0.105	0.047	0.02138	0.47	7.86	8.46
Black	9	0.11	0.47	0.087	0.037	0.00596	0.50	8.19	8.57
Black	9	0.12	0.49	0.105	0.044	0.00628	0.50	7.89	8.57

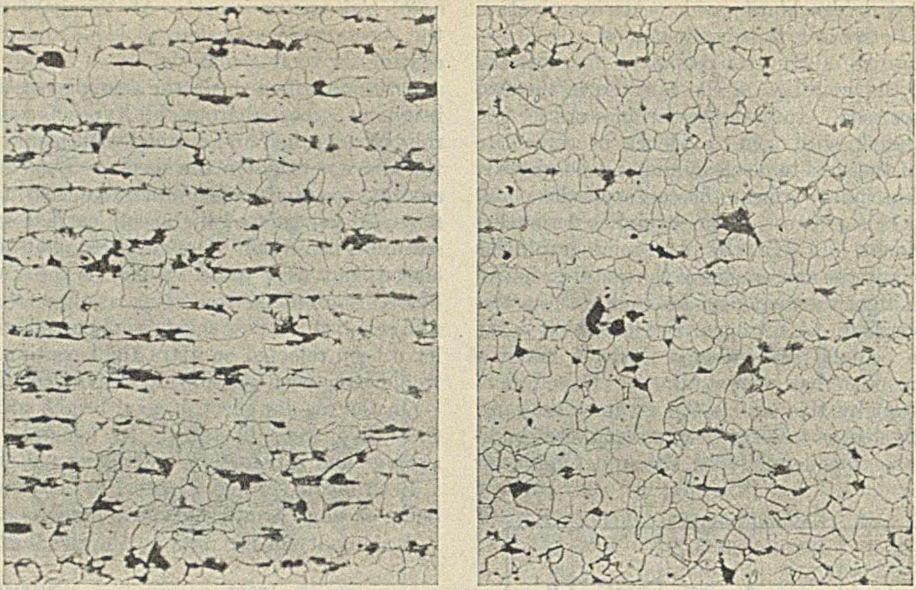
A micro-examination of these sheets showed that they were not well annealed, and there is also some evidence of a laminated condition. These facts, as well as a high phosphorus content in some cases, are the causes of the poor drawing quality of the sheet metal. The nitrogen content was unchanged by the annealing of the sheet, but has no apparent effect upon its ductility.

The steel sheet containing the higher nitrogen was covered with small blisters and showed a poor spangle after galvanizing. This is not in agreement with the previous test, but they are not comparable, as the latter ingot contained nearly 50 per cent more nitrogen. It is possible that this additional amount would cause these blisters.

From these two tests it appears that a nitrogen content greater than 0.016 per cent is a cause of blistered sheets. A low nitrogen, around 0.004 per cent, probably has no relationship to the blisters ordinarily observed. And so, in conclusion, nitrogen, in the amounts found in open-hearth steel, has no effect on steel sheet for galvanizing.

Figure 7 shows photomicrographs of the sheet from the nitrided and the regular ingots. Both are longitudinal sections, magnified 100 times, which have been etched in a 5 per cent solution of nitric acid in alcohol.

Photomicrograph A is of the nitrided sheet, and it is not well annealed. The grains are slightly elongated, irregular,



8*Tx* 9*Tx*

Figure 6—Sheet Bar Samples, Heat B

Sample 8*Tx*
Chemical Analysis:
C—0.16%
Mn—0.49%
P—0.110%
S—0.051%
N—0.02160%

Sample 9*Tx*
Chemical Analysis:
C—0.12%
Mn—0.47%
P—0.110%
S—0.050%
N—0.00683%

and not well defined. The inclusions are negligible. No evidence of the nitrogen is seen. Photomicrograph B is of the regular sheet, and it is under-annealed. The grains are poorly defined and elongated, and the carbides are in string-like formation. Although the inclusions are negligible, there is evidence of lamination.

The surfaces of both sheets are good. Both sheets come from positions near the center of the ingot.

Effect of Nitrogen on Ultimate Tensile Strength of Steel

It is easily seen from the tests made and the curves drawn that the tensile strength of soft steel increases greatly with a relatively small increase of nitrogen. It is also evident that the sampling of the steel in various parts of the ingots was such that the analysis and physical tests are comparative. However, small differences in analysis of the steel must be considered when the actual effect of the nitrogen is being determined. This is done by estimating, mathematically, the tensile strength of the steel according to its analysis, other than the nitrogen, and then correcting the gross increase of tensile strength to obtain the net increase due to the nitrogen.

A formula which has been quite successfully applied to hot-rolled, commercial open-hearth steel is one suggested by McWilliams and Barnes. It was originally suggested to be used on tests made with $^3/_4$ inch (1.79 cm.) round, but was applicable to other tests with the use of a constant to be added. In this work we are merely getting the difference between two similar steels, made and tested in the same way, and the constant need not be considered.

$$\text{U. T. S.} = 38{,}000 \text{ lbs.} + C[800 + 4(C - 20)] + Mn[100 + 2(C - 20)] + 1000\,P + 120\,Si$$

where U. T. S. = ultimate tensile strength
C = carbon in per cent × 100
Mn = manganese in per cent × 100
P = phosphorus in per cent × 100
Si = silicon in per cent × 100

Case I—Applying this formula to the first two ingots used for comparison:

Average analysis of nitrified ingot:

	%
C	0.066
Mn	0.326
P	0.082
S	0.038
Si	0.01
N	0.01443
	Lbs./sq. in.
Actual U. T. S.	57,610
Calculated U. T. S.	53,633

Average analysis of regular ingot:

	%
C	0.058
Mn	0.326
P	0.085
S	0.042
Si	0.01
N	0.00421
	Lbs./sq. in.
Actual U. T. S.	52,740
Calculated U. T. S.	53,265

The different analysis of the steel is responsible for 53,633 − 53,265 = 368 lbs./sq. in.

The nitrogen is then responsible for the difference (57,610 − 52,740) − 368 = 4502 lbs./sq. in.

The difference in nitrogen content is 0.01443 − 0.00421 = 0.01022 %.

0.01% nitrogen is equivalent to 4405 lbs./sq. in.

Case II—Applying this formula to the second two ingots used for comparison:

Average analysis of nitrified ingot:

	%
C	0.136
Mn	0.474
P	0.0952
S	0.0358
S	0.01
N	0.02008
	Lbs./sq. in.
Actual U. T. S.	65,006
Calculated U. T. S.	61,305

Average analysis of regular ingot:

	%
C	0.104
Mn	0.468
P	0.0936
S	0.0428
Si	0.01
N	0.00588
	Lbs./sq. in.
Actual U. T. S.	57,228
Calculated U. T. S.	59,182

The different analysis of the steel is responsible for 61,305 − 59,182 = 2123 lbs./sq. in.

The nitrogen is then responsible for the difference (65,006 − 57,228) − 2123 = 5655 lbs./sq. in.

The difference of nitrogen content is 0.02008 − 0.00588 = 0.01420 %.

0.01% nitrogen is equivalent to 3982 lbs./sq. in.

The nitrogen can be seen to cause an increase of 4000 pounds per square inch in the ultimate tensile strength for each increase of 0.01 per cent nitrogen. This is four times the effect of phosphorus and should be considered in the calculation of the tensile strength of steels. The formula would then be as follows:

$$\text{U. T. S.} = 38{,}000\ \text{lbs.} + C[800 + 4(C - 20)] + Mn[100 + 2(C - 20)] + 1000\,P + 120\,Si + 2000(2N - 1)$$

where N = nitrogen in per cent × 100

Effect of Nitrogen on Ductility of Steel

MATHEMATICAL DERIVATION OF RELATIONSHIP OF NITROGEN TO DUCTILITY OF STEELS OF VARIOUS CARBON CONTENTS—After the experimental work, the relationship between the nitrogen, carbon, phosphorus, and the elongation of steel must be determined, and this relationship expressed by means of a mathematical equation. When this is done, the behavior of other steels can be predicted accurately when the variables are changed. This will add appreciably to the knowledge of the chemical and physical relationship of steel.

The ingots were rolled at approximately 2030° to 2080° F. (1127.86° to 1155.64° C.), and the sheet bar coming from the rolls at a temperature slightly under 1500° F. (833.4° C.). The bar was stacked in piles, hot, and cooled slowly, possibly taking 2 to 4 hours to become black to the eye. This slow cooling allows a good grain growth, and the soft steel is ductile and the bar uniform in character.

The bar was sampled and tested as described previously. The tensile strength of the various tests indicates that the nitrogen has four times the effect of the same amount of phosphorus. From the results it is seen that the ductility is greatly affected by the phosphorus and the nitrogen. Disregarding the effect of the manganese, as it is practically constant, and considering the carbon to be constant, the elongation is a function of the phosphorus and the nitrogen.

$$El_c = f(P + 4N) \times 100$$

where El_c = elongation with given carbon
f = some function
P = phosphorus in per cent
N = nitrogen in per cent

Evaluating this preliminary equation, for heat B, carbon = 0.12 per cent.

	TREATED INGOT		REGULAR INGOT	
	(P + 4N) × 100	Elongation	(P + 4N) × 100	Elongation
	20.33	27.3[a]	13.63	28.1
	19.64	25.7	13.53	28.1
	18.74	25.7	12.67	28.9
	16.38	26.5	10.83	30.4
	12.82	28.9	7.35	32.8
Av.	16.90	26.70	11.60	29.66

[a] Not considered in average as obviously not representative.

$$\text{Slope} = \tan\theta = \frac{16.90 - 11.60}{29.66 - 26.70} = \frac{5.3}{2.96} = 1.7907$$

where θ = 60°49′

Evaluating this preliminary equation, for heat A, carbon = 0.06 per cent.

	TREATED INGOT		REGULAR INGOT	
	(P + 4N) × 100	Elongation	(P + 4N) × 100	Elongation
	16.09	26.5	12.67	28.9
	15.92	30.4[a]	11.41	31.2
	15.37	28.1	10.64	31.2
	13.10	32.0	9.85	29.6[a]
	9.48	34.3	6.15	35.9
Av.	13.51	30.22	10.22	31.80

[a] Not considered in average as obviously not representative.

$$\text{Slope} = \tan\theta = \frac{13.51 - 10.22}{31.80 - 30.22} = \frac{3.29}{1.58} = 2.0823$$

where θ = 64°21′

The curve was then accurately plotted from these points.

From Figure 8 and the calculations, it is seen that the angle varies as the carbon increases. Apparently 0.06 per cent causes a decrease of angle:

$$\theta\,0.06 - \theta\,0.12 = 64°21' - 60°49' = 3°32' = 3.5°$$

To determine the angle for any given carbon,

$$\theta = 64.35° - \left[3.5 \times \left(\frac{C - 0.06}{0.06}\right)\right]$$

where θ = angle
C = carbon in per cent

The slope may be evaluated thus:

$$\tan\theta = \frac{100\,(P_2 + 4N_2) - 100\,(P_1 + 4N_1)}{El_1 - El_2}$$

Substituting for Θ, we have the general equation

$$\tan 64.35° - \left[3.5° \times \left(\frac{C - 0.06}{0.06}\right)\right] = \frac{100\,(P_2 + 4N_2) - 100\,(P_1 + 4N_1)}{El_1 - El_2}$$

where C = carbon, in per cent, of steel
P_2 = phosphorus, in per cent, of steel in question
N_2 = nitrogen, in per cent, of steel in question
El_2 = elongation, in per cent, of steel in question
P_1 = phosphorus, in per cent, of steel of known quality
N_1 = nitrogen, in per cent, of steel of known quality
El_1 = elongation, in per cent, of steel of known quality

Sample Calculations

(1) Determination of nitrogen necessary to cause zero elongation.

QUESTION—How much nitrogen is required to destroy the elongation of a high-carbon splice bar?

GIVEN—C, 0.50%; Mn, 0.53%; P, 0.022%; S, 0.031%; N, 0.0046%; elongation, 20.0%. (Actual description of an average of 50 heats, May, 1922, to February, 1923. Nitrogen is an estimated average). Substituting in the general equation

$$\tan 64.35° - \left[3.5° \times \left(\frac{0.50 - 0.06}{0.06}\right)\right] = \frac{100(0.022 + 4N_2) - 100(0.022 + 4 \times 0.0046)}{20.0 - 0}$$

$$\tan\,(64.35° - 25.67°) = \frac{400(N_2 - 0.0046)}{20} = 20(N_2 - 0.0046)$$

$$\tan 38.68° = 20(N_2 - 0.0046)$$

$$N_2 = \frac{\tan 28.68°}{20} + 0.0046$$

$$= \frac{0.80067}{20} + 0.0046 = 0.04463\%$$

Therefore, 0.04463 per cent nitrogen is required to give a zero elongation with a 0.50 per cent carbon steel. This figure agrees with that shown by H. Braune (*4*). He states that 0.045 per cent nitrogen will destroy the elongation of 0.50 per cent carbon steel.

(2) Determination of the elongation decrease due to small increase of nitrogen.

QUESTION—How much decrease of elongation may be expected if the nitrogen in a rail steel increases from 0.0050 per cent to 0.0080 per cent?

GIVEN—C, 0.64%; Mn, 1.47%; P, 0.030%; S, 0.022%; Si, 0.141%; N, 0.0050%; elongation, 14.0%. Substituting in the general equation

$$\tan 64.35° - \left[3.5 \times \left(\frac{0.64 - 0.06}{0.06}\right)\right] = \frac{100(0.030 + 4 \times 0.008) - 100(0.030 + 4 \times 0.005)}{14.0 - El}$$

$$\tan 30°31' = \frac{3.2 - 2.0}{14.0 - El} = \frac{1.2}{14.0} - El$$

$$0.58944 = \frac{1.2}{14.0} - El$$

$$(14.0 - El) = \frac{1.2}{0.58944} = 2.036\%$$

Decrease in elongation will be 2.036 per cent.

This agrees with actual experimental work. Two similar steels, one with 0.00503 per cent and the other with 0.00805 per cent nitrogen were found to have elongations of 14.0 and 12.0 per cent, respectively.

This equation is applicable to carbon steels fabricated according to standard open-hearth and mill practice, and its application will show the effect of even small increases of nitrogen on the ductility.

To illustrate the extreme case, when the elongation becomes zero, a number of tests of known physical properties and chemical composition have been taken, and those of the same carbon content averaged. Using the formula suggested, the nitrogen necessary to destroy the ductility has been calculated, and the results given in Table V.

Table V—Nitrogen Necessary for Zero Elongation for Carbon Steel

No. of Tests	C	Mn	P	S	Si	N	Av. Elongation	N for Zero Elongation
	%	%	%	%	%	%	%	%
5	0.06	0.33	0.084	0.040	...	0.00421	31.80	0.1656
5	0.12	0.47	0.094	0.039	...	0.00588	29.66	0.1387
6	0.18	0.45	0.012	0.031	...	.....	28.10	0.1143
16	0.24	0.60	0.010	0.023	...	.....	27.60	0.0994
12	0.28	0.61	0.010	0.025	...	.....	26.41	0.0912
8	0.38	0.42	0.017	0.029	...	.....	27.30	0.0745
29	0.45	0.48	0.018	0.029	...	.....	24.80	0.0596
46	0.47	0.51	0.019	0.031	...	.....	22.30	0.0521
50	0.50	0.53	0.022	0.031	...	.....	20.00	0.0446
33	0.53	0.57	0.023	0.032	...	.....	18.70	0.0398
54	0.54	0.57	0.020	0.029	...	.....	17.60	0.0350
17	0.59	0.63	0.033	0.030	...	.....	15.10	0.0324
1	0.67	1.44	0.027	0.023	0.136	0.00503	14.00	0.0242
2	0.76	0.55	0.027	0.029	0.155	0.00534	13.00	0.01947
1	0.80	0.31	0.017	0.025	0.140	.....	8.60	0.01293
1	0.86	0.44	0.018	0.028	0.126	.....	7.30	0.01040

These results are shown graphically in Figure 9.

To illustrate its application to ordinary testing, seven standard-size tensile specimens, 2–0.505 inch, were taken from the "O" positions in the heads of different rails from the same heat. These were carefully tested and the pieces analyzed. The results of the physical tests and the calculated elongations are given in Table VI.

Table VI—Analysis and Calculated Elongations of Tensile Specimens

Rail Numbers	Chemical Analysis						Elongation	
	C	Mn	P	S	Si	N	Actual	Calcd.
	%	%	%	%	%	%	%	%
2A	0.64	1.49	0.028	0.022	0.166	0.00535	15.0	14.43
2A	0.65	1.49	0.028	0.022	0.162	0.00564	15.0	14.24
10A	0.65	1.48	0.031	0.022	0.152	0.00553	13.5	13.72
10B	0.65	1.46	0.030	0.023	0.134	0.00503	13.0	14.24
10C	0.65	1.46	0.030	0.022	0.152	0.00520	7.5	14.08
18A	0.64	1.48	0.029	0.022	0.158	0.00805	12.0	12.05
18B	0.64	1.47	0.030	0.022	0.141	0.00503	14.0	13.92

EXAMINATION OF METALLIC ARC WELDS IN SAMPLES SUBMITTED TO DETERMINE CAUSE OF PLATE FAILURE—To illustrate still another application of the equations, from them can be approximated the physical properties of electric-weld metal, and in so doing perhaps a failure of a given weld sample may be explained.

A certain company was experiencing trouble in arc-welding plates $^1/_2$ inch (1.27 cm.) thick or heavier, the welds themselves cracking or causing the plate to crack near the weld. At times the weld would crack and tear the plate. This difficulty was not encountered in lighter plate. A micro-examination indicated that it was not the fault of the plate, and so the failure must be caused by the weld metal itself.

A micro-examination of the weld metal showed only the characteristics of such metal. As usual, a number of oxides were evident, and the metal unsound in places because of that. But all the welds of this kind are "dirty" and possess the characteristics of cast metal. Moore (*25*), after a detailed study of welds, concluded that the low-endurance strength of deposited electrode metal could not be explained on the assumption of the inherently defective character of the weld metal. Also he found the fatigue resistance of welds to be distinctly lower than the metal itself.

In one case considered, we have a weld which held satisfactorily:

	Chemical Analysis					
	C	Mn	P	S	Si	N
	%	%	%	%	%	%
Plate	0.10	0.42	0.008	0.026	...	....
Weld metal	0.03	0.15	0.010	0.029	0.006	0.1433

In the second case, we have a weld which failed:

	Chemical Analysis					
	C	Mn	P	S	Si	N
	%	%	%	%	%	%
Plate	0.12	0.42	0.008	0.026	...	....
Weld metal	0.06	0.15	0.010	0.028	0.008	0.1379

	Average Brinell Hardness Number
Plate	107
Weld metal	156

Metal deposited by the electric arc is seen to contain a high nitrogen per cent (Figure 10). This is caused by a chemical combination of the nitrogen from the air and the iron at the extremely high temperature of the arc, and its possible ionizing powers. This nitrogen causes a hard and brittle steel. These properties may be predicted very closely through the application of two formulas derived and already described. Although they are not directly applicable to steel which has the characteristics of cast metal, as has this weld metal, they will have some value until a better means can be found for testing it.

The two formulas, for the necessary calculations, are as follows:

$$\text{U. T. S.} = 38{,}000 + \text{C}[800 + 4(\text{C} - 20)] + \text{Mn}[100 + 2(\text{C} - 20)] + 1000\ \text{P} + 120\ \text{Si} + 2000(2\text{N} - 1)$$

$$\text{Elongation} = El - \frac{100(\text{P}_2 + 4\text{N}_2) - 100(\text{P}_1 + 4\text{N}_1)}{\tan\left[64.350 - 3.5 \times \left(\frac{\text{C} - 0.06}{0.06}\right)\right]}$$

	U. T. S. *Lbs./sq. in.*	Elongation %
Case I:		
Weld metal	97,580[a]	0[a]
Plate	49,880	34.5
Case II:		
Weld metal	97,800[a]	0[a]
Plate	51,660	31.8

[a] According to formula, U. T. S. without nitrogen would be: case I, 42,260; case II, 44,740. Cast steel of this analysis has U. T. S. of 42,526 according to International Critical Tables, 1st ed., Vol. 2, p. 487, Table 2, Key No. 1. The tables also give an elongation of 24.5 per cent, a value used in calculation of elongation of weld metal.

With this understanding of the character of the weld metal, the failures and the satisfactory weld may be better considered.

First, the sound weld metal is very strong and hard in itself, but owing to its slag and oxide inclusions, is considerably weakened. Because of this, the mass of weld metal holding two plates together is greater than the space between the plates.

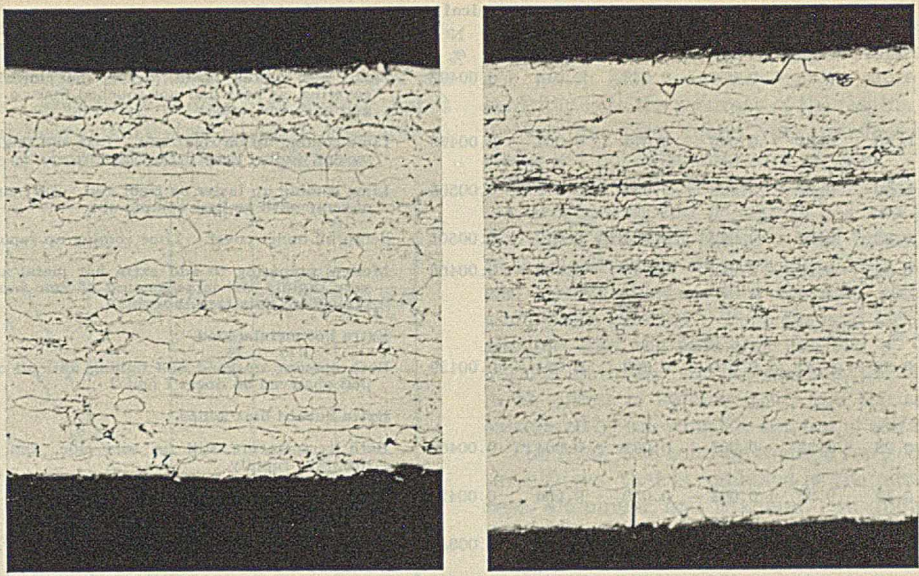
Second, owing to the difference of the expansion and contraction of the weld metal and the plate, strains are set up during the cooling that must be relieved by the elasticity of one of the two metals. The weld is not ductile, and if its strength, due to inclusions, or its mass, is not greater than the resistance of the plate to this deformation, the weld metal will fail. On the other hand, if the weld metal is sufficiently strong, the plate will relieve the strain.

Third, if the weld metal cracks and the plate is welded soundly, the superior strength of the weld is sufficient to cause the plate to tear at the point where the crack of the weld meets the plate.

Fourth, the lighter plate welded satisfactorily because the volume of weld metal was sufficient to overcome the resistance of the plate to deformation. If the cap weld on the heavier plate is increased proportionately to the increase of the plate's increase of resistance to deformation, the weld should be satisfactory.

Fifth, attempts are constantly being made to make the weld metal more sound and less brittle. New weld rods are made containing alloys, such as manganese, vanadium, and titanium, which combined more readily with oxygen and nitrogen than does the iron. Fluxing materials are being introduced to form slag that will remove these nitrides and oxides from the metal itself. When these rods are proved successful, the weld metal will be sound, and arc welding will become more successful.

Sixth, heat treatment is being tried on certain arc welds, as annealing of iron high in nitrogen will overcome much of its embrittling effect.



A B

Figure 7—Longitudinal Section of Sheet from Nitrided and Regular Ingots

A—Nitrided Sheet

Chemical Analysis:
C—0.12%
Mn—0.50%
P—0.094%
S—0.041%
Si—trace
N—0.01861%

Erichsen Tests:
Thickness—0.53 mm.
Av. draw—7.06 mm.
Standard—8.68 mm.

B—Regular Sheet

Chemical Analysis:
C—0.12%
Mn—0.46%
P—0.090%
S—0.038%
Si—trace
N—0.00543%

Erichsen Tests:
Thickness—0.58 mm.
Av. draw—8.22 mm.
Standard—8.85 mm.

The equations derived have many applications. They are naturally only a close approximation, as the cooling rate and physical soundness will affect the actual test themselves. For steel properly fabricated, however, they should be of considerable value.

Absorption of Nitrogen by Steel in Open-Hearth Furnace

To determine the behavior of nitrogen during the melting and purifying of the steel in an open-hearth furnace, bath tests were taken from the furnace and analyzed. A chronological record of this heat, heat C, was made, recording the additions to the bath and the reactions as observed. This record and the chemical analyses of the bath tests are given in Tables VII and VIII.

Table VII—Chronological Record of Heat C

Charge:	
Blooming mill scrap	44,600
Steel scrap	122,300
Hot metal	136,400
Ferromanganese (to bath)	3,900
Ferromanganese (to ladle)	2,000
Recarburization	27,900
50% ferrosilicon	1,100
Spiegeleisen	1,000
Extra burned lime	1,200
Total metallic charge	339,200
Time:	
Started to charge	6:15 A.M.
Finished charge	6:40 A.M.
First ladle hot metal	9:31 A.M.
Finished ladle hot metal	10:08 A.M.
Heat specifications:	
C	0.55/0.61
Mn	1.40/1.50
P	0.04
S	0.04
Si	0.15/0.25

Until 11:00 A. M. (see Table VIII) there was not enough molten metal to get a test, and it also would have been too cold to pour into a test mold.

Very little change is noted in the nitrogen content during the working of the heat. Although the nitrogen falls off to a minimum, it rises again upon the addition of the ferromanganese and the recarburizer, apparently owing, however, to the effect of the ferromanganese. The ferromanganese deoxidizes the steel, and through the removal of the oxygen causes the remaining gases to become more soluble. Apparently this action causes more nitrides to be formed, and the combined nitrogen is increased. This increase is approximately the same as the difference observed between the nitrogen content of the soft steel and the rail steel.

The action of the lime is probably the cause of the nitrogen decrease observed, if not directly, indirectly, as the basicity control. The addition of the burned lime apparently caused a decrease of the nitrogen.

Nitrogen as an acid element acts as expected. It is impossible to say from this heat what governs the action or equilibrium observed in the bath, but as the nitrogen in the various heats varies so little in the same grade of steel, there must be such a limiting factor in existence.

Representative Nitrogen Analyses of Various Types of Open-Hearth Steel

In order to determine what nitrogen could be expected in various types of steel, analyses were made on ladle tests of different heats with results as shown in Table IX.

The nitrogen found in the steels is very constant in amount, with a slightly greater amount occurring in the recarburized rail steel. This, however, is not always the case, as can be seen from the table.

Combined Nitrogen in Pig Iron

The grade of pig iron used in the manufacture of a given quality of steel must be carefully controlled. The "off-casts" caused by irregular blast-furnace operations have been found to cause the steel to be inferior. The grading of pig iron is in accordance to its chemical analysis, considering silicon, manganese, phosphorus, and sulfur, the silicon and the sulfur controlling the blast-furnace operation temperature. It is generally conceded that a high silicon, 2 per cent, and a low sulfur, 0.02 per cent, indicate a hot furnace, whereas a low silicon, 0.60 per cent, and a high sulfur, 0.06 per cent, indicate a cold furnace. The intermediate condition, silicon,

Table VIII—Chemical Analysis of Heat C

TEST	TIME	C	Mn	P	S	Si	N	NOTES
		%	%	%	%	%	%	
1	11:00 A. M.	1.51	0.20	0.072	0.039	0.014	0.00497	Scrap not melted down, mostly hot metal. Practically no slag covering, as heat had not touched lime to any appreciable extent, and bath was cold.
2	12:07 P. M.	0.80	0.28	0.046	0.042	0.004	0.00493	Lime coming up on right end. Left end, high pile of scrap piled up on end wall. Very little slag.
3	12:56 P. M.	0.50	0.27	0.028	0.038	0.010	0.00505	Lime coming up faster on right end. Left end still had exposed pile of scrap with no lime coming up.
4	1:37 P. M.	0.32	0.27	0.022	0.034	0.012	0.00505	Scrap all under cover. Lime coming up rapidly on right end.
5	2:07 P. M.	0.32	0.28	0.012	0.043	0.004	0.00462	Melters preparing to add extra hot metal as carbon was dropping very rapidly and large amount of lime was still down. Heat not pulling up lime fast enough.
	2:21 to 2:25 P. M.							Extra hot metal added.
6	2:40 P. M.	0.38	0.32	0.010	0.033	0.004	0.00429	Bath opening up good and pulling lime all over. Very heavy lime boil observed on doors 1 and 2.
	3:00 P. M.							Extra burned lime added.
7	3:11 P. M.	0.28	0.27	0.007	0.033	0.004	0.00400	Bath temperature still on cold side, and pulling lime. Carbon dropping rapidly.
8	3:34 P. M.	0.17	0.22	0.004	0.030	0.004	0.00423	Still pulling lime on doors 1 and 2, probably from sloppy bottom or old ridge.
9	4:05 P. M.	0.13	0.21	0.005	0.030	0.004	0.00356	Bath clear of lime, with slag slightly lumpy. Temperature a little low for high-manganese heat.
	4:11 P. M.							1000 lbs. spiegeleisen added.
10	4:27 P. M.	0.12	0.23	0.004	0.029	0.004	0.00377	Bath still dead. Temperature O. K.
11	4:40 P. M.	0.12	0.21	0.004	0.028	0.010	0.00340	Taken just before recarburizer was added.
	4:45 to 4:48 P. M.							27,900 lbs. recarburizer added. Bath foamed heavily with oil off.
	4:49 P. M.							3900 lbs. ferromanganese added.
12	4:57 P. M.	0.60	1.10	0.020	0.027	0.034	0.00800	Taken just before tap. Bath just beginning to open.
	5:06 P. M.							Tapped. 2000 lbs. ferromanganese and 1100 lbs. ferrosilicon, 50%, added to ladle.
	LADLE TESTS							
	(1)	0.62	1.44	0.021	0.027	0.160	0.00609	
	(2)	0.61	1.48	0.024	0.026	0.164	0.00583	

1.0 per cent, and sulfur, 0.03 per cent, is considered the most desirable. But there are many other factors besides the temperature of the furnace that may cause a variable analysis, the principal one being the slag, and these should be considered.

At times the pig iron does not make good steel even though the regular chemical analysis shows no change. This would indicate that some consideration is being overlooked, and for this reason the nitrogen content is being investigated.

Table IX—Analyses of Ladle Tests of Different Heats

TYPE OF STEEL	CHEMICAL ANALYSIS					
	C	Mn	P	S	Si	N
	%	%	%	%	%	%
Sheet steel	0.10	0.35	0.084	0.040	...	0.00354
Sheet steel	0.08	0.30	0.075	0.035	...	0.00372
Pure iron	0.05	0.10	0.008	0.035	...	0.00394
Rail steel	0.62	1.44	0.021	0.027	0.160	0.00609
Rail steel	0.82	0.78	0.032	0.030	0.176	0.00506
Rail steel	0.77	0.62	0.023	0.026	0.188	0.00507
Rail steel	0.74	0.79	0.022	0.028	0.182	0.00501
Rail steel	0.79	0.65	0.025	0.028	0.156	0.00415
Rail steel	0.58	1.48	0.026	0.030	0.158	0.00547
Rail steel	0.79	0.79	0.023	0.032	0.158	0.00422
Rail steel	0.75	0.84	0.024	0.029	0.180	0.00452
Rail steel	0.79	0.58	0.021	0.033	0.166	0.00422
Rail steel	0.71	0.63	0.019	0.029	0.176	0.00320
Rail steel	0.64	0.70	0.022	0.028	0.176	0.00405
Forging quality	0.43	0.50	0.021	0.027	0.166	0.00364
Bumper stock	0.91	0.30	0.011	0.024	0.200	0.00421
Bumper stock	0.93	0.37	0.016	0.027	0.182	0.00363
Bumper stock	0.93	0.35	0.012	0.024	0.216	0.00392
Spring steel	1.05	0.34	0.010	0.029	0.206	0.00392
Spring steel	0.94	0.25	0.012	0.028	0.220	0.00418

A Swedish metallurgist, Hjalmar Braune (*4*), found that the nitrogen content of pig iron was a better means of judging the operations of the blast furnace and the resulting quality of the iron than any other element of its analysis. Steel manufacturers using Swedish pig iron were unable to make fine steel using iron made in a blast furnace which was being driven with a high-temperature blast. This iron had the same chemical analysis, other than nitrogen, as the iron made in the same furnace but with a blast of lower temperature. Investigation showed that when the conditions favorable to the formation of alkali cyanides in the furnace were reached, the iron contained a high nitrogen percentage, 0.020 to 0.025 per cent. The pig iron high in nitrogen was shown to be the cause of brittle and poor quality steel, and therefore, the blast furnaces lowered the blast temperatures, and pig iron was produced that would make good steel. This pig iron was designated as "cold-blown" and sold at a premium to compensate for the extra costs of reduced production.

In the past, alkali cyanides have been found in our blast furnaces, showing that we have conditions similar to those described by Braune. His conclusions may be applicable to some phenomena observed here and, if so, may assist in their explanation.

Six samples of casts have been analyzed with the following results:

CHEMICAL ANALYSIS				
Si	S	P	Mn	N
%	%	%	%	%
1.90	0.023	0.230	2.04	0.0129
0.79	0.071	0.227	1.15	0.0054
0.58	0.056	0.227	1.40	0.0032
2.47	0.020	0.240	2.36	0.0111
1.18	0.025	0.245	2.03	0.0057
1.07	0.022	0.192	1.74	0.0074

Considering a high-silicon cast as a hotter one, the nitrogen content does increase with an increase of temperature. Although the silicon and the nitrogen vary similarly, it is believed that there is no direct connection between the two other than an indication of conditions suitable for the combination of the iron with the nitrogen.

Through the addition of hot metal as a recarburizer, iron nitride is introduced into the steel. If the cast is produced under normal operations, the pig iron will have a nitrogen content only slightly higher than the bath in the open hearth, and the increase of nitrogen will not be appreciable. However, if the hot metal is produced under abnormal conditions, the steel will not be so ductile, nor of the quality desired.

The elimination of the nitrogen during the working of the heat is not certain. Apparently it does vary slightly, but it seems possible that poor quality steel might be traceable to the original charge of abnormal hot metal or pig iron.

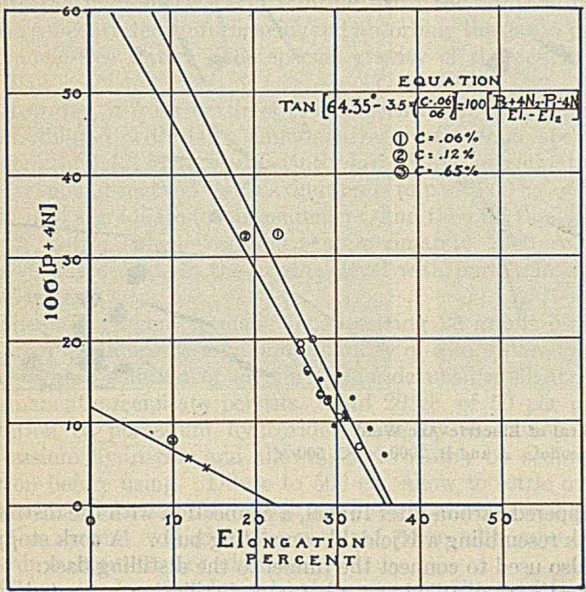


Figure 8—Effect of Nitrogen on Ductility of Steel

A study of the blast-furnace operations, considering the conditions necessary for the introduction of nitrogen into the iron, will doubtless explain some phenomena not now understood. The formation of cyanogen and the alkali cyanides probably governs the amount of nitrogen in the iron, and this formation appears to be controlled by the temperature and pressure of the blast, with a consideration of the moisture content of the air.

Nitrogen Content of Ferro-Alloys Used in Manufacture of Steel

Certain ferro-alloys are used in large quantities during the manufacture of carbon steel. As these are added to the metal in the furnace, or later to the ladle, it is important to know how much nitrogen is introduced through their use. Analyses of several of these were made with results shown in Table X.

Table X—Analysis of Ferro-Alloys

NAME	CHEMICAL ANALYSIS Mn	P	Si	N
	%	%	%	%
Ferro-phosphorus	...	18.23	...	0.0011
	...	19.76	...	0.0010
Ferromanganese	79.13	...	...	0.0288
	79.82	...	...	0.0208
Spiegeleisen	21.11	...	3.90	0.0066
	20.03	...	2.33	0.0059
Ferrosilicon	...	...	48.06	0.0054
	...	...	48.88	0.0061

This analysis would indicate that no appreciable amount of nitrogen is introduced through the use of these alloys.

Method for Determination of Combined Nitrogen in Iron and Steel

The method to be outlined and discussed in the following description is the one which has been used throughout this investigation, and found to be both practical and accurate. It is known as the iodide-iodate method, and is essentially the one approved and suggested by the Bureau of Standards (*22*), recommended by Fay (*12*), and first suggested by Petrén and Grabe (*27*) in 1907. Only one addition has been made, one which aids materially in the case of distillation and contributes to the accuracy of the results. This iodide-iodate method has been found very satisfactory for all ordinary steels, but not satisfactory for pig iron.

The theory of the method is most simple. Allen, in 1880 (*1*), proposed it, and though it has had numerous modifications, the principal theory is still intact. In brief, iron nitride dissolved in dilute hydrochloric acid gives ammonia and ferrous chloride, and the acid holds the ammonia as ammonium chloride. Then the acid ferrous solution is made alkaline, and the ammonia distilled off and determined by various methods. In this method, the ammonia is absorbed in an excess of sulfuric acid, and the amount of ammonia calculated by knowing the amount of sulfuric acid neutralized.

The Allen acid solution method for iron or steel determines the nitrogen that is combined as the nitrides of iron, manganese, aluminum, and titanium. In dilute hydrochloric acid, the iron nitride decomposes readily (*4*), the manganese nitride less readily (*18*) but quantitatively, and the aluminum and titanium is little, if at all, reacted with. However, the nitrogen of manganese (*18*), aluminum (*41*), and titanium nitrides (*32*) are converted to ammonia by the boiling alkaline solution during the distillation of the ammonia (*22*). Any nitrides of silicon are not affected by aqueous acids or alkalies (*43*), and a fusion with alkali is required to convert their nitrogen to ammonia (*22*). In ordinary open-hearth steel, the latter fact needs no consideration, as the silicon is quite low, and practically all the nitrogen is present as the nitride of iron.

APPARATUS—The apparatus described was constructed after the consideration of all possible details and the recommendations of the Bureau of Standards (*22*) and of Fay (*12*). By following the directions in detail, most of the errors due to the apparatus, usually encountered in the distillation of traces of ammonia, will be eliminated.

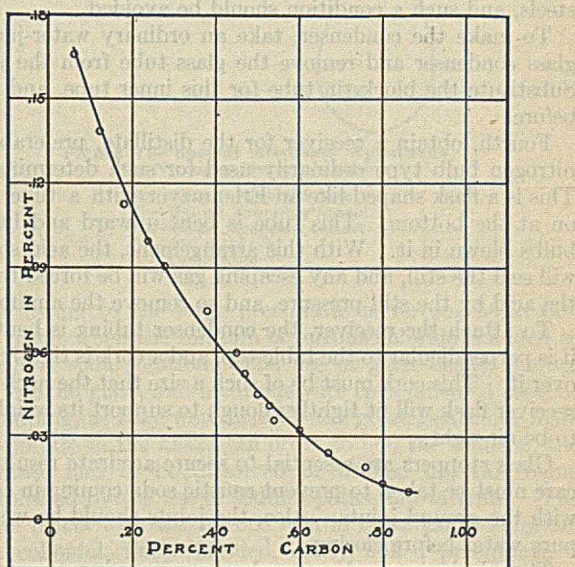
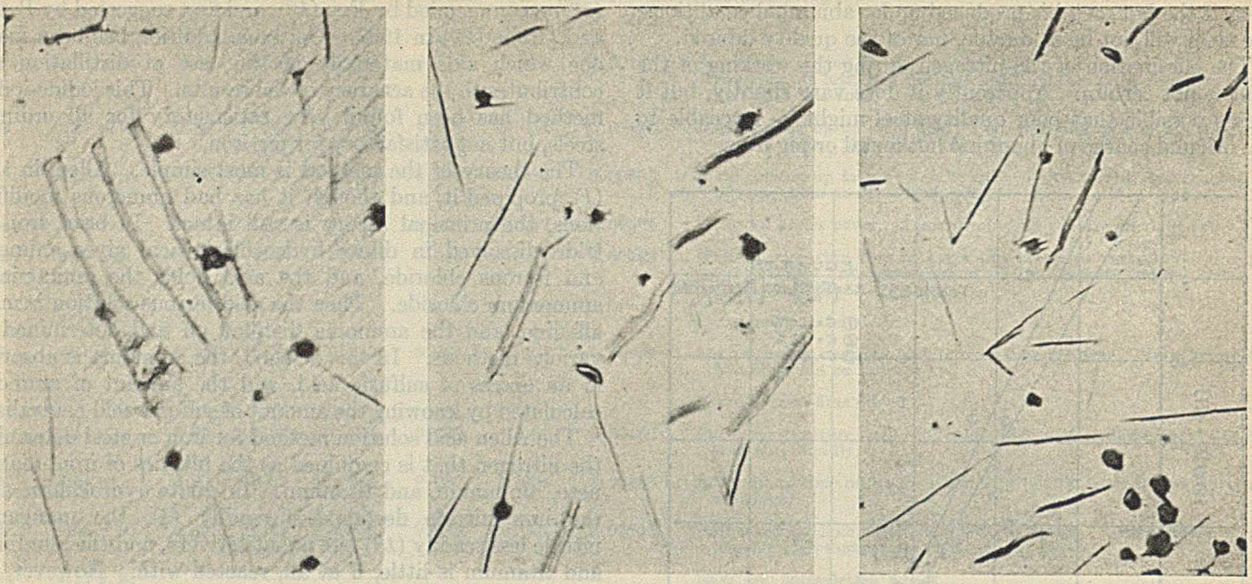


Figure 9—Nitrogen for Zero Elongation for Carbon Steel

First obtain a flask for dissolving the sample; a 250-cc. Pyrex glass Kjeldahl flask is most suitable. This should have a dropping funnel, condenser, and bubble tube connected to the flask by a ground-glass joint. The bubble tube will have a capacity of about 5 cc. of acid if properly constructed. Figure 11 illustrates the apparatus used in this laboratory.

Second, obtain a distilling flask; an 800-cc., Pyrex glass



A B C

Figure 10—Deposited Electrode Metal of Electric-Arc Weld

Samples etched in 5% nitric acid solution in alcohol. A and B, 2000 ×; C, 500 ×

Kjeldahl flask is preferable, connected as shown in the drawing. The tube from the dropping funnel must be as shown, as the acid solution should enter the flask below the level of the caustic soda. This will eliminate any error which might come from the acid spattering on the sides of the hot flask and then being volatilized as hydrochloric acid.

Third, obtain a length of block-tin tubing to use in the condenser. Glass tubing must not be used, as the ammoniacal condensate and the steam will leach a measurable amount of alkali from the glass. Of course, this alkali could be corrected for by running a blank, but the blank will be of the same order of magnitude as the amount of nitrogen found in most steels, and such a condition should be avoided.

To make the condenser, take an ordinary water-jacketed glass condenser and remove the glass tube from the jacket. Substitute the block-tin tube for this inner tube, and use as before.

Fourth, obtain a receiver for the distillate, preferably the nitrogen bulb type ordinarily used for such determinations. This is a flask shaped like an Erlenmeyer with a tube sealed on at the bottom. This tube is bent upward and has two bulbs blown in it. With this arrangement, the acid solution will seal the still, and any escaping gas will be forced through the acid by the still pressure, and so remove the ammonia.

To attach the receiver, the condenser tubing is bent until it is perpendicular to the table top, and a cork is tightly fitted over it. This cork must be of such a size that the neck of the receiver flask will fit tightly enough to support its weight and to be air-tight.

Glass stoppers are essential to secure accurate results, and care must be taken to prevent caustic soda coming in contact with the ground joints. Also, the joints should be wet with pure water before closing.

The block-tin condenser tube is quite advantageous and contributes much to the accuracy of the determinations.

All the analyses must be made in a room where the atmosphere is free from ammonia, as even a trace in the air will ruin the delicate determination.

Reagents—Pure ammonia-free water is the greatest requirement for this investigation. The apparatus used for the water still consists of a 2-liter Pyrex glass Florence flask and a condenser with a block-tin inner tube. The upper end of this tube is bent downward so as to form, with a cork-stoppered carbon-filter funnel, a connection with the distilling flask resembling a Kjeldahl connecting bulb. A cork stopper is also used to connect the funnel to the distilling flask.

Ordinary distilled water before redistillation is treated with a solution of alkaline potassium permanganate. This solution is made by dissolving 200 grams of potassium hydroxide and 8 grams of potassium permanganate in 1100 cc. of distilled water and then concentrating to 1000 cc. by boiling. This solution is used by adding to the distilled water to be purified in the ratio of 1 to 10.

The water containing the alkaline potassium permanganate solution is distilled until the distillate shows freedom from ammonia when tested with Nessler's reagent. Further distillation produces water which is collected for use in the determinations.

The sodium hydroxide used in the distillation of the ammonia must be prepared with special precautions. Regular c. p. grade sodium hydroxide is likely to contain nitrites and small amounts of nitrates, which may be reduced to ammonia by the ferrous hydroxide while the distillation is being made during the analysis. This difficulty is avoided by treating the caustic soda solution with a copper-zinc couple, which causes the nitrites to be reduced to ammonia. Then the solution is boiled in a distilling flask and the ammonia expelled. The small amounts of nitrates present do not interfere with the analysis, as they are not easily decomposed by ferrous iron so long as the concentration is low.

The copper-zinc couple used to destroy the nitrites, and to some extent the nitrates, is made by covering zinc finely with deposited copper. Pieces of mossy zinc are kept submerged 10 minutes in dilute copper sulfate solution, and then washed with distilled water. These pieces are saved, as only a few are used each time.

Four hundred grams of c. p. sodium hydroxide sticks are weighed into a liter Florence flask, and dissolved in 1 liter of distilled water. As soon as the solution cools to 50° C., a few pieces of the copper-zinc couple are placed in the alkaline solution and allowed to stand for 24 hours at 50° C. Hydrogen is seen to be given off around the pieces of zinc.

The nitrites are then reduced, and the sodium hydroxide solution decanted off into a distilling flask and boiled until the distillate tested with Nessler's solution shows that all ammonia has been expelled. The solution is then brought to the same molar concentration as the hydrochloric acid, of specific gravity 1.12. This is done by adding enough pure ammonia-free water to make the sodium hydroxide solution up to 1333 cc.

Pure hydrochloric acid always contains some traces of ammonia, and the acid used to dissolve the sample may have to be specially prepared. This is done by distilling the concentrated hydrochloric acid solution, with the addition of a little concentrated sulfuric acid, and absorbing the gas in pure ammonia-free water. The specific gravity of the acid is to be 1.12.

However, a fresh bottle of c. p. concentrated hydrochloric acid, diluted with pure ammonia-free water to a specific gravity of 1.12, gives a sufficiently low blank determination. A convenient method for this dilution is to pour 900 cc. of the acid into a graduate for measurement, and then fill the "five-pint" bottle, which contained approximately 2300 cc. of concentrated acid, to the original level with pure ammonia-free water.

Nessler's reagent is made by dissolving 25 grams of potassium iodide in the minimum quantity of cold water. Add a saturated solution of mercuric chloride until a slight but permanent precipitate persists. Add 20 cc. of 50 per cent solution of potassium hydroxide, made by dissolving the potassium hydroxide and allowing it to clarify by sedimentation before using. Dilute to 500 cc., allow to settle overnight, and decant. Fifty cubic centimeters of water and 2 cc. of the reagent will give the required color with ammonia within 5 minutes after addition.

The potassium iodide and iodate may be obtained in the regular c. p. grade and are free from the impurities which affect analysis. A 5 per cent solution of each is made by dissolving 5 grams of the salt in 95 cc. of water.

Sodium thiosulfate solution, 0.01 *N*, is made by dissolving 2.5 grams of crystallized sodium thiosulfate in pure water and diluting to 1 liter.

Sulfuric acid, 0.01 *N*, is made by adding 0.30 cc. of concentrated sulfuric acid to 1 liter of pure ammonia-free water. This is best standardized by means of barium chloride. A blank must, of course, be run and the correction applied during the calculation of the acidity from the weight of the ignited barium sulfate. Pure sodium carbonate may also be used for the standardization.

SAMPLING OF STEEL—The drilling of the metal for analysis must be done with great care, and even the finest dust produced must not be omitted. Nitrogen has the property of becoming segregated and is found in much greater quantities in the zone of liquation than in the outer zone. With this consideration, the drilling must be done in a manner that will give representative sampling.

In weighing the sample for analysis the same precautions must be taken. Proportional amounts of the powder, the fine pieces, and the larger drillings must be chosen for best results. To insure accurate analysis, it is best to make all determinations in duplicate.

SOLUTION OF STEEL—The drillings are placed on a clean paper and 5 grams of the steel weighed out. This is transferred to the bottom of the dissolving flask, and after moistening the ground-glass connection, the flask is connected to the other part of the apparatus. The bubble tube is sealed with approximately 5 cc. of hydrochloric acid, specific gravity 1.12. Through the dropping funnel, 40 cc. of the hydrochloric acid, specific gravity 1.12, are slowly introduced, and the flask is slightly heated. The steel dissolves rapidly and the evolved gases pass through the water-cooled condenser and out through the acid-sealed gas passage.

Vapors are condensed in the cool condenser and are returned to the flask. The acid-sealed gas passage washes the evolved gases, and any ammonia that might be carried off by the hydrogen and hydrocarbon gases is retained in the acid. Care must be taken to keep the temperature of the acid in the flask below the boiling point.

When the steel has been completely dissolved, the nitride nitrogen remains in the flask as ammonium chloride, with the exception of a very small amount found in the bubble tube. The contents of the latter are washed into the flask with several small portions of pure hydrochloric acid, specific gravity 1.12, and then the contents of the flask are washed with pure ammonia-free water into the dropping funnel of the distilling flask.

DISTILLATION OF SOLUTION CONTAINING AMMONIUM CHLORIDE—The distillation of the ammonia offers some difficulties. Violent boiling, detrimental shocks, and even explosions occur during the boiling of the alkaline solution. This is owing to the large precipitate of ferrous hydroxide which forms when the solution of ferrous chloride is added to the caustic soda solution. The use of glass beads, pumice stone, broken glass, and nichrome wire coils failed to prevent the bumping, as they were held by the great gelatinous mass of precipitate in the flask. In order to boil the solution, the precipitate had to be dissolved or broken up, this being accomplished by the use of sodium potassium tartrate. The tartrate reacts with the ferrous iron in the alkaline solution, and a colloidal, finely divided, easily boiled precipitate is formed. With this difficulty overcome, the following procedure is suggested:

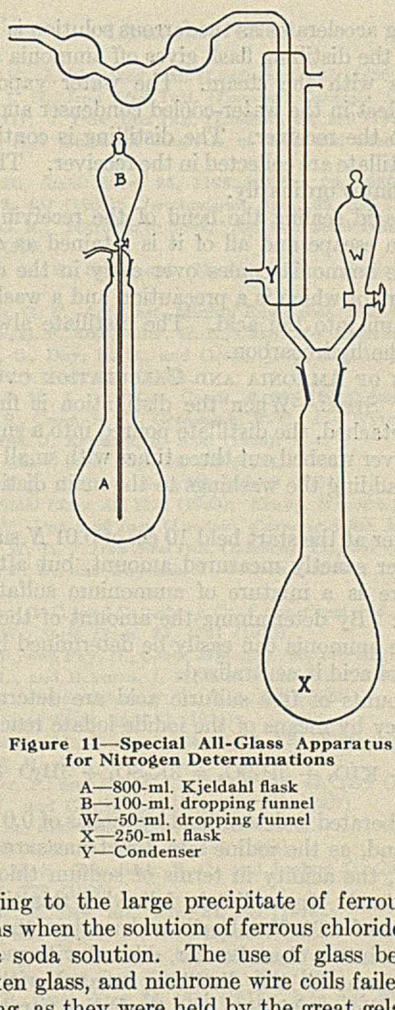


Figure 11—Special All-Glass Apparatus for Nitrogen Determinations

A—800-ml. Kjeldahl flask
B—100-ml. dropping funnel
W—50-ml. dropping funnel
X—250-ml. flask
Y—Condenser

> The distilling flask is cleaned with c. p. hydrochloric acid and rinsed with pure ammonia-free water. On the bottom are placed pieces of pumice stone which have been previously boiled with dilute hydrochloric acid and with alkaline ferrous hydroxide solution. Then 40 grams of sodium potassium tartrate crystals are placed in the flask, the sides washed down, and the ground-glass connection moistened with pure water. The flask is then connected to the rest of the apparatus.

Add 100 cc. of pure ammonia-free water through the dropping funnel. Then add at least 50 cc. of the sodium hydroxide solution and 10 cc. of potassium permanganate solution (8 grams of potassium permanganate and 200 grams of sodium hydroxide dissolved in 1000 cc. of pure water). Add 20 cc. more of the pure water, washing the dropping funnel clean. Boil the solution until the distillate is free of ammonia, as indicated by Nessler's reagent. This part of the determination is done while the steel is going into solution.

As soon as the distillate is free of ammonia, 10 cc. of 0.01 *N* sulfuric acid, or a larger exactly measured amount, is introduced into the receiver, which is then attached to the condenser tubing. The connection must be air-tight and the receiver must be kept in such a position that the bend is sealed with the acid.

The acid ferrous solution, which up to this time has been kept in the dropping funnel, is slowly run into the distilling flask. The caustic solution must be kept boiling steadily all the time while the ferrous solution is being added, and this is done by regulating the speed of the addition as well as the height of the gas flame.

The boiling accelerates as the ferrous solution is added, and the liquid in the distilling flask gives off ammonia and hydrocarbon gases with the steam. The water vapor and the ammonia collect in the water-cooled condenser and run down in drops into the receiver. The distilling is continued until 100 cc. of distillate are collected in the receiver. This requires about 30 minutes ordinarily.

With the acid sealing the bend of the receiving flask, no ammonia can escape and all of it is retained as ammonium sulfate. The ammonia comes over early in the distillation, the latter part of which is a precaution and a wash to get all the ammonium into the acid. The distillate always smells strongly of the hydrocarbon.

Titration of Ammonia and Calculation of Nitrogen Content of Steel—When the distillation is finished, the receiver is detached, the distillate poured into a small beaker, and the receiver washed out three times with small portions of pure water, adding the washings to the main distillate in the beaker.

The receiver at the start held 10 cc. of 0.01 *N* sulfuric acid, or some other exactly measured amount, but after the distillation there is a mixture of ammonium sulfate and free sulfuric acid. By determining the amount of the remaining free acid, the ammonia can easily be determined by knowing the amount of acid it neutralized.

Small amounts of free sulfuric acid are determined with great accuracy by means of the iodide-iodate reaction

$$5KI + KIO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3I_2$$

The iodine liberated is determined by means of 0.01 *N* sodium thiosulfate and, as the iodine is a direct measure of the free sulfuric acid, the acidity in terms of sodium thiosulfate has been determined. Immediately following this titration, the same amount of 0.01 *N* sulfuric acid used in the receiver is measured out into a clean beaker, diluted with pure water to the same volume as the distillate, treated with the same amounts of iodide and iodate, and the iodine titrated with the 0.01 *N* sodium thiosulfate. The difference between the two titrations represents the acid neutralized by the ammonia, and so gives the value of the equivalent nitrogen.

The titration is carried out as follows:

To the distillate in the beaker, add 4 cc. of the 5 per cent potassium iodide solution and 2 cc. of the potassium iodate solution, and stir with a stirring rod. Titrate the iodine liberated immediately with 0.01 *N* sodium thiosulfate, the end point being the disappearance of the last trace of yellow color. A beaker of water is necessary for comparison, and good daylight is required for best results. With practice, a variation of 0.10 cc. is easily discernible.

Immediately after this titration it is necessary to make the second one. For this purpose, 10 cc. of 0.01 *N* sulfuric acid, or exactly the same amount as originally used in the receiver, are measured from the buret into a clean beaker and diluted with pure water to the same volume as in the previous titration. The same amounts of iodide and iodate are again added, and the iodine set free is titrated as before. The amount of sodium thiosulfate is recorded and the difference between the two values represents the sulfuric acid equivalent to the ammonia absorbed. This acid neutralized is also a measure of the nitrogen in the steel.

Calculation—By the standardization of the 0.01 *N* sulfuric acid with barium sulfate, it was found to be 0.0103 *N*.

One cubic centimeter of 0.0103 *N* sulfuric acid is equivalent to (14/100 × 1000) × 1.03 = 0.000144 gram of nitrogen.

At the beginning, 10 cc. of the standard acid were added to the receiver. After the distillation, free sulfuric acid equivalent to 2.20 cc. of the 0.01 *N* sodium thiosulfate was found.

By the second titration, 10 cc. of the standard sulfuric acid were equivalent to 9.30 cc. of the 0.01 *N* sodium thiosulfate. Then

$$\begin{aligned} 1 \text{ cc. of } Na_2S_2O_3 &= \frac{10.00}{9.30} = 1.077 \text{ cc. } H_2SO_4 \\ 9.30 - 2.20 &= 7.10 \text{ cc. } Na_2S_2O_3 \\ 1.077 \times 7.10 &= 7.65 \text{ cc. } H_2SO_4 \text{ neutralized by } NH_3 \\ \text{As } 1 \text{ cc. } H_2SO_4 &= 0.000144 \text{ gram nitrogen} \end{aligned}$$

The nitrogen percentage in the steel is

$$\frac{7.65 \times 0.000144}{5} \times 100 = 0.02208\%$$

The method when carried through carefully and systematically as described, offers no difficulties. It is slow but accurate, and the average variation in duplicate determinations is 0.0003 per cent.

A blank determination on the acid, water, and reagents gives an average of 0.00038 per cent. This is so small that no correction need be made on the analyses, as the other factors give greater variation than this.

The Bureau of Standards has a sample of ingot iron, No. 55, with a nitrogen content of 0.0046 per cent. This was used regularly to check the reagents and the solutions. A few of these determinations are as follows:

Date	Nitrogen %
12-14-29	0.00439
12-20-29	0.00437
12-27-29	0.00463
1- 2-30	0.00442
1-10-30	0.00434
1-17-30	0.00470
2-12-30	0.00477
2-28-30	0.00460

These figures are all corrected for the blank of 0.00038 per cent.

The low percentage of hydrocarbons obtained from the steel has no effect on the iodine titration, although the distillate smells strongly of them. However, in pig iron, the great increase of hydrocarbons is found to cause high and erratic results using the iodide-iodate reaction and titration.

Method for Determination of Combined Nitrogen in Pig Iron

The method for the analysis of pig iron varies very little from that used for steel, as the main procedure and the apparatus are the same. The preparation of the sample and the final titration of the sulfuric acid are the only changes.

Sampling of Pig Iron—The representative sample of pig iron is pounded up in a mortar until it will pass through a 60-mesh screen. This fine division of the iron makes it easier to dissolve and gives a more homogeneous sample.

Solution of Pig Iron—Five grams of this powder are weighed out and transferred to the same flask used in the solution of the steel. The same procedure is followed as in the solution of the steel.

The flask must be agitated at intervals to aid the solution of the iron. The high carbon and silicon, with the gases evolved, cause a heavy foam which may support small particles and cause an incomplete reaction unless the samples are digested 3 to 4 hours with repeated agitation. This agitation breaks up the foam and allows an intimate intermixture of the iron with the acid. When the reaction is complete, the sample is washed with pure water into the dropping funnel of the distilling flask, and the distillation made in the same manner as with steel.

Titration of Ammonia and Calculation of Nitrogen Content—After the distillation, the excess acid is determined by titration with 0.01 *N* sodium hydroxide solution, using one drop of a 1 per cent aqueous solution of sodium alizarinsulfonate as the indicator. The end point is a complete disappearance of the yellow-green color, or the first indication of brown. Knowing the amount of acid neutralized by the ammonia, the nitrogen is calculated in the same manner as for steel.

This indicator may be used in place of the iodide-iodate reaction for the titration of the acid during the determination of nitrogen in steel. However, the authors find that a sharper and more definite end point is obtainable using the iodide-iodate reaction and, although the procedure is a little longer, the results are more consistent.

Conclusions

The following conclusions may be drawn from the work done and recorded in this paper.

(1) The addition of nitrogen to low-carbon steel increases the tensile strength, the elastic limit, and the Brinell hardness number, but lowers the reduction of area and the elongation. After annealing, the nitrogen had no effect on the drawing properties of the sheet made from this high-nitrogen steel.

(2) The high nitrogen content of the steel did not cause blistered sheets as had been thought heretofore.

(3) No nitrogen was lost through the annealing treatment of the sheets.

(4) No difference was discernible between the quality of the regular and the high-nitrogen sheet, in the black or galvanized. Therefore, no defects observed in ordinary practice can rightfully be attributed to the nitrogen content, as it has been shown that, even should the steel contain the maximum theoretical amount of 0.024 per cent, the quality is not affected.

(5) The nitrogen affects the physical properties of the steel in the same manner as phosphorus. However, its effect is four times that of the same amount of phosphorus.

(6) The coefficient of effect of the nitrogen on ductility increases with the carbon, and even the small amounts found in high-carbon steels made according to standard practice have a noticeable effect upon the ductility of the steel.

(7) Nitrogen and phosphorus segregate similarly, the segregation of nitrogen being the most marked. This combined segregation intensifies the effect of the small amount of nitrogen found in ordinary steels.

(8) Through the use of the formula derived in this paper, it is possible to predict the benefits which may be obtained by the elimination of nitrogen from the steel, and also the detrimental effects on ductility of small increases.

(9) The nitrogen content of the finished steel is fairly constant, as shown by the ladle tests. The minimum found was 0.0032 per cent, and the maximum, 0.0060 per cent, with an average of 0.0045 per cent. Low-carbon heats contain less nitrogen when finished than do high-carbon, recarburized, and deoxidized heats.

(10) Bath conditions in the furnace favoring a low-phosphorus steel will at the same time be found to cause a lower nitrogen content. During the working of the steel in the furnace, it has been found that the nitrogen decreases at the same time as the phosphorus.

(11) Ferro-alloys used as bath and ladle additions contain only small amounts of nitrogen, and need not be considered a source of nitrogen in steel.

(12) The nitrogen content of pig iron is more variable than that of steel, tests showing a range of 0.0032 to 0.0129 per cent. More nitrogen is introduced into pig iron if the blast furnace is operated at a high temperature. Under normal operation, the nitrogen content is approximately the same as that found in the open-hearth steel.

(13) For all the tests made in connection with these investigations, the iodide-iodate method, approved by the Bureau of Standards, and with one addition, has been found practical and satisfactory.

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Grading Aggregates

I—Mathematical Relations for Beds of Broken Solids of Maximum Density[1,2]

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Equations for the grading of broken solids are set up to give beds of maximum density. A consideration of the voids in a bed of the coarsest particles leads to two types of solution: the one for intermittent grading and the other for continuous grading. Theoretically, the first should give the best packing, provided suitable means of practical application are developed. An example is given of the method of calculating the sizes to be used for the intermittent grading. The second solution gives a system which has probable advantages of workability and its grading can be more or less closely approximated using commercial materials. The solution of the first equation is made and given graphically and the results so obtained have been used in plotting curves for the minimum possible voids on mixing 2, 3, or 4 sizes of materials. The method of solution of the equation for continuous grading is indicated. No single curve for continuous grading is sufficient for all systems. The type of curve for maximum packing is determined by (1) voids in a bed of normally packed, sized material, and (2) the ratio of the size limits of the system.

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The size composition of the system of aggregates which enter into the manufacture of mortar and concrete is a very important factor in determining the workability of the mix and the density of the product. A great deal has been done empirically to solve the problem of grading of aggregates, and the contributions of Feret (*4*), Fuller (*5*), Abrams (*1*), Graf (*7*), Talbot (*8*), and many others have been very helpful; but so far little success has been attained in the mathematical development of the laws of packing of beds of broken solids, which make up our mortar and concrete aggregates. In this article formulas are developed for two types of grading of aggregates. The first involves an intermittent grading, such as has been successfully worked out empirically by John J. Early of Washington, D. C., and the second is for the continuously graded materials most commonly used. The derivations have been made with the aid of certain assumptions and the proof of the equations must lie with experiment. This development has been carried out in close coöperation with Anderegg (*2*), whose data cover the experimental verification of these laws and their practical application. While the object in view during the course of this study was to set up equations which would be useful for mortar and concrete, it should be pointed out that the equations here set up might also be applicable to other systems when broken solids are involved. Among these might be asphaltic concrete, paint, putty, rubber, coal storage, fuel beds, catalytic masses, etc.

In a previous publication (*6*) the author has shown that in beds of broken solids containing two component sizes the composition of maximum density is one where the proportion of the larger size measured in absolute volume of particles is $1/(1 + V)$, where V is the fractional voids in a bed of sized material—that is, V is the volume of voids in a unit of total volume of bed. For practical purposes material may be considered "sized" if it passes one screen and stays on another which differs from it by the factor $\sqrt{2}$; for instance, through 3 mesh, on 4. This relation holds if the percentages of voids are the same for both component sizes.

Systems of More than Two-Component Sizes

The basic idea of the argument of the preceding paragraph is that if particles of infinitely small size are introduced into a bed of large pieces the small pieces will fill up the voids without changing the total volume. In practice it is found that introducing small pieces into the bed increases the total volume somewhat but the composition of maximum density is still given approximately by the proportion $1/(1 + V)$ until the sizes of the two components begin to approach each other. Extending the argument to systems of more than two-component sizes, assume that there are several sizes in the system and that each component size fills exactly the voids of the next preceding size, causing no increase in volume of the bed as a whole and leaving no excess material. This is a purely hypothetical case and is used only as a starting point. Such a system is roughly analogous to a telescope of many sections where each piece slides into the preceding one, or to the sets of hollow interfitting blocks of diminishing size which are used by children for building towers.

An equation will now be developed showing the relation between voids, size composition, and a number of component sizes for uniformly mixed beds of maximum possible density. Let Z be the proportion by absolute volume of the large size in a two-component bed of maximum density—that is, Z is the volume of large-sized material per unit volume of solid matter. Then

$$Z = \frac{1}{1 + V} \tag{1}$$

Equation 1 holds only for the case where the solid particles of the different sizes have the same shape so that the voids in the bed of the sized material are the same for each constituent size. The more complicated case of varying voids will be taken up later. In Equation 1, V is the fraction of voids in a bed of sized material, whereas Z is the actual absolute volume occupied by the larger particles in a two-component system of maximum density, when the actual absolute volume of both large and small particles is unity. Call the diameter of the large particles d_1. The amount of fine material of diameter d_2 which will exactly fill the interstices of d_1 is $1 - Z$, provided the small particles act as if they are infinitely small. Suppose that another set of infinitely small particles of diameter d_3 can be introduced into the voids of the second component. A better way may be to consider momentarily that each component is of finite size but that it has the packing properties of the infinitely small size.

If such an arrangement is assumed, the total absolute volume of each component size will be given by a series of terms of decreasing magnitude, the first term being Z and the second $1 - Z$, as mentioned before. The numerical ratio

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[2] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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between the second and first term is $(1 - Z)/Z$. This same factor persists throughout, for the same ratio of voids is left within each constituent size as it is added. Thus the series becomes a geometric progression and

Total absolute volume of solids =

$$\overset{d_1}{Z} + \overset{d_2}{(1 - Z)} + \overset{d_3}{(1 - Z)\left(\frac{1 - Z}{Z}\right)} + \overset{d_4}{\frac{(1 - Z)^2}{Z}\left(\frac{1 - Z}{Z}\right)}$$

Since, according to Equation 1, Z equals $1/(1 + V)$, the quantity $(1 - Z)/Z$, which is the ratio between terms, is equal to V. Therefore, the equation may be written

$$\text{Total absolute volume of solids} = \frac{\overset{d_1}{1} + \overset{d_2}{V} + \overset{d_3}{V^2} + \overset{d_4}{V^3} - - -}{1 + V} \qquad (2)$$

The number of terms in the numerator equals the number of component sizes in the system. This equation applies only when the voids in a bed of the sized material are the same for each component size. (The more general case will be discussed later.) Each term represents the absolute volume of the different component sizes in the mixture, the size being designated by the symbols d_1, d_2, etc., above each term. If all the solid pieces have the same density, $1/(1 + V)$ may be considered the actual absolute volume of all the solid pieces of the largest size, d_1, in a system of maximum density of two or more components. Then the absolute volume of the particles of the second size, d_2, will be $V/(1 + V)$, of the third size, d_3, $V^2/(1 + V)$, etc., as was explained by Equation 2.

Equation 2 is for the hypothetical case where each size acts as if it were infinitely small. However, it was found experimentally (*6*) that for two-component systems the equation was valid for systems where the ratio size (small to large) was as much as 0.2.

Relations between Layered and Uniformly Mixed Systems

If a system is made up of several different component sizes and if each size is placed on the bed as a separate layer, then the volume occupied by the entire bed will be

$$\frac{G_T}{G_a} S$$

where G_T = true specific gravity of particles in bed
G_a = apparent specific gravity of bed of sized material
S = sum of actual volumes of all particles of all constituent sizes, or summation of Equation 2 for as many terms or fractions of sized materials as are being considered

Now suppose that all the layers of the different sizes of materials are so well mixed that each size of particle is uniformly distributed throughout the bed. As separate layers of sized materials are mixed there will be a decrease in volume. If the particles of the first component, d_1, are quite large and all the other sizes, d_2, d_3, etc., are very small (ideally, infinitely small), the voids of the large pieces will be exactly filled and the final volume of the bed will be only that originally occupied by the largest size, or

$$\text{Volume} = \frac{G_T}{G_a} Z$$

where $Z = \dfrac{1}{1 + V}$ as defined by Equation 1.

In this case, then, the decrease of volume upon mixing of sizes is

$$\frac{G_T}{G_a}(S - Z)$$

This is the ideal case. For actual systems the volume decrease will be less than the above quantity, or

$$\text{Volume decrease} = y\,\frac{G_T}{G_a}(S - Z) \qquad (3)$$

where y is some factor ranging in value between 0 and 1.0. If the particles of the second component are infinitely small, y will be unity; if they are of the same size as the first component, y will be zero. (The value for intermediate size ratios will be discussed later.) The total volume of the mixed system, then, is

$$\text{Volume} = \frac{G_T}{G_a}[S - y(S - Z)] \qquad (4)$$

The weight of the entire mass of material is

$$W = G_T S \qquad (5)$$

The density of any system is

$$\text{Density} = \frac{\text{weight}}{\text{volume}} = \frac{G_T S}{\dfrac{G_T}{G_a}[S(1 - y) + yZ]} \qquad (6)$$

$$\text{Density} = \frac{G_a}{1 - \dfrac{y(S - Z)}{S}} \qquad (7)$$

Hypothesize a system of broken solids with a certain limiting ratio between the smallest and largest size. The question of size composition for the greatest possible density then becomes, how many intermediate sizes shall there be between the smallest and the largest in order to obtain the maximum density? As more component sizes are added to the system the total volume of material, S, increases but the value of the volume decrease factor, y, diminishes, so that there are two variable tendencies and the maximum density will be found by striking a balance between the two; the problem thus becomes one of maxima and minima, and the key to the solution is found in Equation 7. Inspection of Equation 7 shows that for density to be a maximum, the term $y(S - Z)/S$ must be a maximum, considering the changing of values of the two variables y and S as the number of constituent sizes is changed.

It is now necessary to introduce a new variable, n, which designates the number of component sizes added to the original single size of the system. It should be noted particularly that this value of n is one less than the total number of constituent sizes in the system. It is desired to determine when the quantity $y(S - Z)/S$ is a maximum. Therefore, it is necessary to differentiate this quantity with respect to n, set this derivative equal to zero, and solve this equation for n. Z is a constant for a given system. Therefore,

$$\frac{d\left[\dfrac{y(S - Z)}{S}\right]}{dn} = \frac{yd\left(\dfrac{S - Z}{S}\right)}{dn} + \left(\frac{S - Z}{S}\right)\frac{dy}{dn} \qquad (8)$$

Performing the indicated differentiation and setting the derivative equal to zero,

$$\frac{Z}{S(S - Z)}\frac{dS}{dn} = -\frac{dy}{ydn} \qquad (9)$$

In order to solve for the composition of maximum density, the quantities S and y must be determined. The value of S is equal to the right-hand member of Equation 2. This equation is a geometrical progression, the first term being Z and the ratio between terms $(1 - Z)/Z$. As was pointed out above, this ratio equals V. The sum of a geometrical progression is given by a formula of the general form:

$$S = \frac{A(1 - R^m)}{1 - R} \qquad (10)$$

where S = numerical value of sum of terms
A = first term of series
R = ratio between succeeding terms
m = number of terms

For convenience, the nomenclature involving Z will now be dropped and V will be used. The ratio in Equation 10 then is equal to V and $A = 1/(1 + V)$. The summation of the series of Equation 2 is

$$S = \frac{1 - V^{n+1}}{1 - V^2} \tag{11}$$

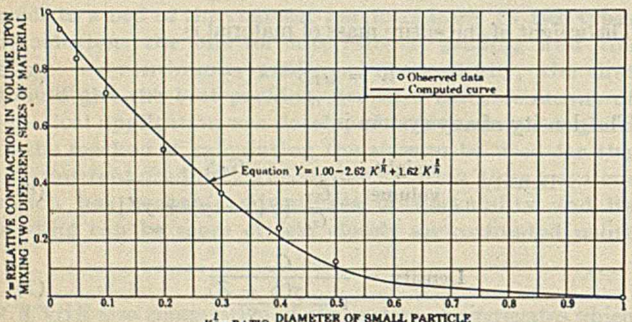


Figure 1—Relation between Size Ratio and Contraction in Volume upon Mixing for Two-Component Systems at Composition of Maximum Density

The exponent has been given as $n + 1$ to be consistent with the definition of n as given above—that is, n is the number of component sizes added to the largest size in the system and $n + 1$ is the total number of sizes present. The derivative of Equation 11 is

$$\frac{dS}{dn} = -\frac{V^{n+1}\ln V}{1 - V^2} \tag{12}$$

Evaluating y—The factor y, which appears in Equation 8, can be evaluated only experimentally; y is a number between zero and unity which represents the ratio of the decrease in total volume of the given materials, upon mixing, to the decrease if infinitely small particles were used. The larger the ratio of the small to the large particles the smaller y will become and, in the limit where the components become the same size, y will be equal to zero. It is understood that this discussion is limited to systems of maximum density. Therefore, y varies as some function of the ratio between the two sizes in a two-component system or as the ratio of consecutive sizes in a system of many components.

Designating the diameter of the smallest particle in a given system as d_{n+1}, that of the largest particle as d_1, and the ratio between the sizes of the smallest and largest particles as K, then by definition

$$K = \frac{d_{n+1}}{d_1} \tag{13}$$

Now the size composition for maximum density in a two-component system is dependent entirely upon the voids in sized beds of the two constituents. The percentage of voids in a bed of sized material, for a given amount of work of packing, is independent of the size of particle except for relatively small containers or for particles so small that the absorbed air film is significant. Therefore, the ratio between the successive sizes for maximum packing in one part of the system is the same as for any other part. In other words, for maximum packing in a system of many-component sizes, the ratio between the diameter of particles of successive sizes must be constant for the entire system. Therefore, in our ideal system

$$\frac{d_2}{d_1} = \frac{d_3}{d_2} = \frac{d_{n+1}}{d_n} \tag{14}$$

There are n size intervals and $n + 1$ is the total number of sizes. Therefore

$$\frac{d_2}{d_1} = \frac{d_3}{d_2} = \frac{d_{n+1}}{d_n} = K^{1/n} \tag{15}$$

K is defined by Equation 13 and $K^{1/n}$ becomes the ratio between adjacent sizes.

It is now necessary to evaluate the factor of volume decrease, y. From the former paper (*6*) on binary systems, data have been taken and a correlation made between the total volume decrease obtained by mixing two sizes of material and the size ratios. The equation of the relation is

$$y = 1.0 - 2.62K^{1/n} + 1.62K^{2/n} \tag{16}$$

where y = ratio of volume decrease upon mixing two sizes of material to what it would be if smaller size were infinitely small, same factor as y of Equation 7
$K^{1/n}$ = ratio between consecutive sizes

The computed curve and data points are shown in Figure 1. This relation apparently is independent of the voids in a bed of the sized material. Differentiating Equation 16,

$$\frac{dy}{dn} = \frac{2.62K^{1/n}\ln K}{n^2} - \frac{3.24K^{2/n}\ln K}{n^2} \tag{17}$$

The relation expressed by Equation 16 is purely empirical and was obtained from limited data. Further experimentation may show a more accurate relation. Substituting the values of Equations 1, 11, 12, 16, and 17 in Equation 9 and simplifying,

$$\frac{V^n \ln V\,(1 - V)}{(1 - V^{n+1})(1 - V^n)} = \frac{(2.62K^{1/n} - 3.24K^{2/n})\ln K}{(1.0 - 2.62K^{1/n} + 1.62K^{2/n})n^2} \tag{18}$$

where n = one less than total number of sizes for system of maximum density
K = ratio of smallest to largest size
V = fraction of voids in bed of sized material

As far as the author knows there are no means of solving the above equation directly, but it can be solved by a complicated trial-and-error method. The details of the work do not need to be gone into here for the solution has been made and the results plotted in Figure 2 as curves relating the size ratio of the limiting size K and the number of size components in the

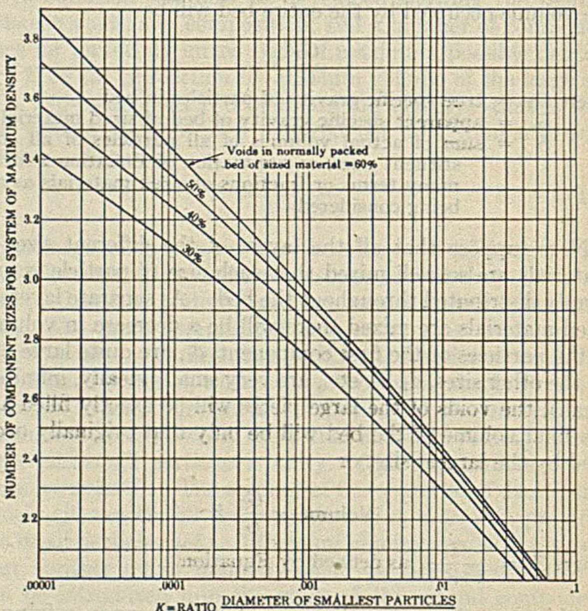
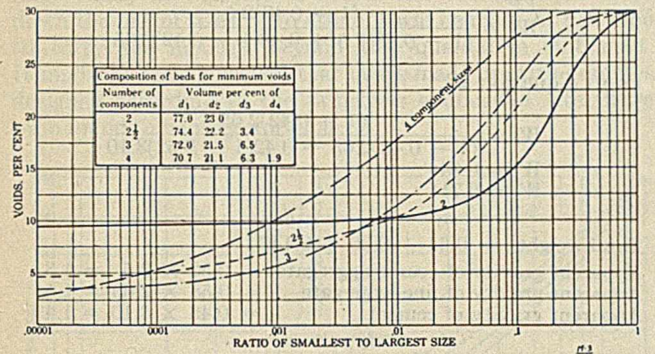


Figure 2—Relation between Size Ratio and Number of Component Sizes for Systems of Maximum Density

system for maximum density, for several values of V. It should be noted that the ordinate is not n but $n + 1$, for the first term of the series was dropped in our consideration of the maxima and the total number of sizes is therefore one more than the number of terms in the series considered.

It will be observed that the abscissas of Figure 2 are plotted on a logarithmic scale and that the size ratio decreases very rapidly. Thus for a system of maximum density to have three component sizes, the size ratio must be very small indeed.



Composition of beds for minimum voids

Number of components	Volume per cent of d_1	d_2	d_3	d_4
2	77.0	23.0		
2½	74.4	22.2	3.4	
3	72.0	21.5	6.5	
4	70.7	21.1	6.3	1.9

Figure 3—Computed Possible Minimum Voids in Beds of Two to Four Component Sizes if Initial Voids in Bed of Uniformly Sized Material Are 30 Per Cent

Concrete is usually a three-component mixture. If we assume that the average size of particles in a well-ground cement is 0.001 inch and that the voids in a sized bed of the coarse material are about 39 per cent, then from Figure 2 the size ratio for maximum density will be 0.00045. The size of the aggregate then should be

$$\frac{0.001}{0.00045} = 2.2 \text{ in.}$$

This figure is somewhat beyond the limits of most practice. It would seem then that concrete is not of maximum possible density but that the density may be increased by increasing the average size of the coarse aggregate as much as is commensurate with proper workability.

Significance of Fractional Values of the Number of Component Sizes

Assuming a concrete having cement particles of average size, 0.001 inch, and a coarse aggregate of average size, 1.0 inch, the size ratio is 0.001. If the average value of the voids in a sized bed of the coarse aggregate is 0.39, from Figure 2, the number of component sizes for maximum density is 2.85. This, of course, brings up the question of the significance of a fractional number of component sizes. If the ideal concrete is made up as a three-component system according to the preceding development, the proportions are given by the expression

$$\begin{array}{cccccc} & \text{Coarse aggregate} & & \text{Fine aggregate} & & \text{Cement} \\ & d_1 & & d_2 & & d_3 \\ \text{Total volume} = & \dfrac{1}{1+V} & + & \dfrac{V}{1+V} & + & \dfrac{V^2}{1+V} \end{array} \qquad (19)$$

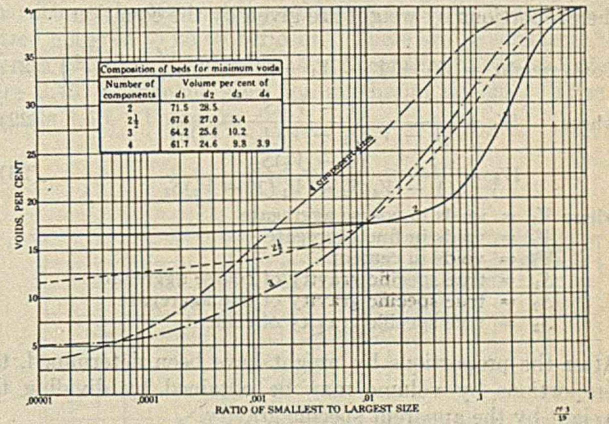
In the case under consideration the number of component sizes for maximum density is not even 3, but 2.85. The fractional size is best interpreted by saying that the quantity of the smallest size should be less than designated by Equation 19, and the logarithm of the size ratio of the last two terms should be larger than for an even number of component sizes. Calculation shows that using 0.85 of the third member produces only a slight change in the amount (from 9.7 to 8.6 per cent) and may well be neglected for most purposes. Again, application of the correction to the size of the intermediate material is made by using the equation

$$\log_{10}\frac{d_1}{d_2} = \frac{1}{0.85}\log\frac{d_2}{d_3}$$

changing the dimension of the fine aggregate from 0.032 to 0.024 inch. The former is the mesh dimension of the 20-mesh sieve while the latter is that of the 28-mesh sieve. According to this calculation, the mix by volume would be close to 65 parts coarse, 25 of fine aggregate, and 10 of cement. This means that every particle would have to go into the place where it belonged and because of the harshness of such a mix some special method of placing, such as effective vibration, would be required.

Computed Values of Voids at Compositions of Maximum Density

The preceding discussion has been limited to the determination of compositions of minimum voids and no mention was made of the actual values of voids in the bed of the mixed materials. With the aid of the preceding equations it is a simple matter to compute these voids for compositions of maximum density. This has been done for systems in which the voids of the sized material are 30, 40, 50, and 60 per cent for 2, 2.5, 3, and 4 component sizes. The curves are shown in Figures 3 to 6. The curve for 2.5 component sizes was computed by means of the principles cited in the preceding example. The curves of Figures 3 to 6 should be useful in predicting the actual density of beds of a given size composition when intermittent grading for maximum density is used.



Composition of beds for minimum voids

Number of components	Volume per cent of d_1	d_2	d_3	d_4
2	71.5	28.5		
2½	67.6	27.0	5.4	
3	64.2	25.6	10.2	
4	61.7	24.6	9.8	3.9

Figure 4—Computed Possible Minimum Voids in Beds of Two to Four Component Sizes if Initial Voids in Bed of Uniformly Sized Material Are 40 Per Cent

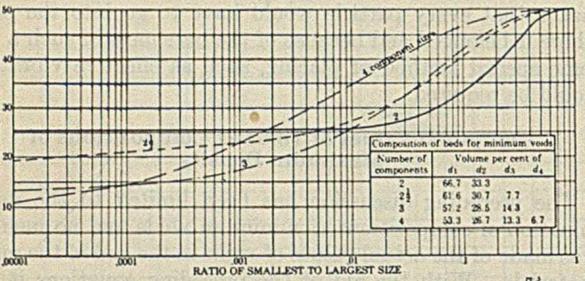
It may be assumed that the best combination of strength, durability, and economy can be secured with a concrete for which the aggregates are so chosen as to fill as much space as possible. For this purpose, according to the previous discussion, 3 component sizes would seem to offer the best practical solution. The cement may be regarded as one of these three sizes in view of the fact that the great bulk of the cement has no chance to hydrate before the concrete has been placed (*3*). Figure 2 shows that increasing the voids in a bed of the material increases the number of component sizes. Thus, for a system where the size ratio is 0.001 the number of component sizes for maximum density may be increased by increasing the voids in the coarse aggregate. This increase in voids may be accomplished by having the aggregate of more uniform size or less regular in shape. The conclusion is that to make a concrete of greatest possible density the coarse aggregate should be large, of uniform size, and of irregular shape.

If a system is such that 3 component sizes give maximum density, then the proper size of the fine aggregate is given by the equation

$$d_2 = \sqrt{d_1 d_3} \qquad (20)$$

where d_1 = average diameter of coarse aggregate
d_2 = average diameter of fine aggregate
d_3 = average diameter of cement

This equation should apply as a first approximation even if the number of component sizes for maximum density, as shown by Figure 2, is not exactly 3.0.



Number of components	Volume per cent of d_1	d_2	d_3	d_4
2	66.7	33.3		
2½	61.6	30.7	7.7	
3	57.2	28.5	14.3	
4	53.3	26.7	13.3	6.7

Composition of beds for minimum voids

Figure 5—Computed Possible Minimum Voids in Beds of Two to Four Component Sizes if Initial Voids in Bed of Uniformly Sized Material Are 50 Per Cent

Systems of Varying Voids and Densities

The systems considered so far have been for uniform voids and density of solids. Equation 2 gives the proportions of absolute volumes of particle for the different sizes of such a system. By referring to the development of the relations for two component systems of maximum density (*6*) it will be seen that for the general case of varying voids and densities the proportions by weight are given by the equation

$$\text{Total weight} = W_1 + 1 - W_1 + (1 - W_1)\left(\frac{1 - W_2}{W_2}\right) \qquad (21)$$

$$\text{where} \quad W_1 = \frac{(1 - V_1)S_1}{(1 - V_1)S_1 + V_1(1 - V_2)S_2} \qquad (22)$$

$$W_2 = \frac{(1 - V_2)S_2}{(1 - V_2)S_2 + V_2(1 - V_3)S_3} \qquad (23)$$

where V_1 = voids in coarse aggregate
V_2 = voids in fine aggregate
V_3 = voids in cement
S_1 = true specific gravity of coarse aggregate
S_2 = true specific gravity of fine aggregate
S_3 = true specific gravity of cement

After the proportions by weight have been determined, the proportions by volume may be obtained by dividing the weight by the apparent specific gravity.

$$\text{Apparent sp. gr.} = (1 - \text{voids})(\text{true sp. gr.})$$

The case of varying densities may also be handled by computing on a volume basis first, using Equation 19; relative weights being determined by multiplying volume proportions by specific gravity.

Determination of Mixture for Maximum Density

A concrete is made of limestone averaging 2 inches in diameter, voids 48 per cent, specific gravity 2.5; fine sand, voids 42 per cent, specific gravity 2.65; cement, average size 0.001 inch, voids 52 per cent, specific gravity 3.10. What should be the average size of the sand particles and what should be the size composition by volume to produce a concrete of maximum density? What percentage of voids will there be in the bed after mixing?

$$\text{Size ratio of system} = \frac{0.001}{2} = 0.0005$$

From Figure 2 it can be seen that for a system of maximum density there should be approximately 3 component sizes. Since the system is to have a symmetrical size distribution, the diameter of the sand particles should be the square root of the size ratio.

$$\text{Size of sand particles} = \sqrt{2 \times 0.001} = 0.045\text{-inch}$$
(approximately 14 mesh)

$$\text{Total weight of concrete} = \overset{d_1}{W_1} + \overset{d_2}{1 - W_1} + \overset{d_3}{(1 - W_1)\left(\frac{1 - W_2}{W_2}\right)} \qquad (24)$$

From Equation 22,

$$W_1 = \frac{(1 - 0.48)2.5}{(1 - 0.48)2.5 + 0.48(1 - 0.42)2.65}$$

From Equation 23,

$$W_2 = \frac{(1 - 0.42)2.65}{(1 - 0.42)2.65 + 0.42(1 - 0.52)3.10}$$

$$W_1 = 0.64$$
$$W_2 = 0.711$$

$$\text{Total weight} = \overset{d_1}{0.64} + \overset{d_2}{0.36} + \overset{d_3}{0.147}$$

Apparent gravity of coarse aggregate = 0.52 × 2.5 = 1.3
Apparent gravity of fine aggregate = 0.58 × 2.65 = 1.54
Apparent gravity of cement = 0.48 × 3.10 = 1.49

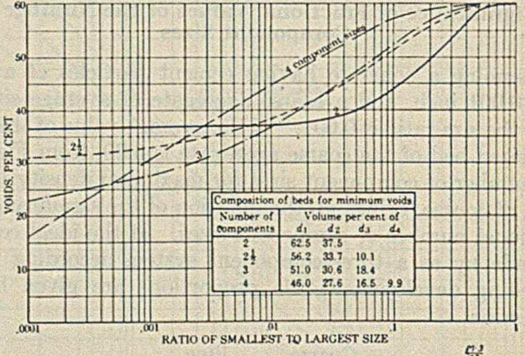
$$\text{Total volume} = \overset{d_1}{\frac{0.64}{1.3}} + \overset{d_2}{\frac{0.36}{1.54}} + \overset{d_3}{\frac{0.147}{1.49}}$$

$$= \overset{d_1}{0.493} + \overset{d_2}{0.234} + \overset{d_3}{0.0986} = 0.826$$

Proportion by volume = 59 per cent, 28.3 per cent, 12.0 per cent
Mixture for maximum density = 12 per cent cement by volume
= 28.3 per cent fine aggregate by volume
= 59.7 per cent coarse aggregate by volume

This is approximately a 1:2:5 mix.

The foregoing discussion was based on the assumption that the water of the concrete simply fills up the pores left in the mix by the various solid particles. The weighted average of the voids in beds of sized material in this system is 47 per cent. The voids in the mixed bed are found by interpolating between the curves for 3 components in Figures 4 and 5 (40 and 50 per cent voids). This gives a value of 13.8 per cent voids in the uniformly mixed beds. This space is largely taken up with hydrated cement and water at the time of placing. Also some air is probably mechanically included.



Number of components	Volume per cent of d_1	d_2	d_3	d_4
2	62.5	37.5		
2½	56.2	33.7	10.1	
3	51.0	30.6	18.4	
4	46.0	27.6	16.5	9.9

Composition of beds for minimum voids

Figure 6—Computed Possible Minimum Voids in Beds of Two to Four Component Sizes if Initial Voids in Bed of Uniformly Sized Material Are 60 Per Cent

Continuous Grading of Sizes

So far only those systems have been considered in which all of the constituents were carefully sized. This condition occurs only rarely in practice so it is necessary to consider the condition for maximum density when the bed of broken solids is not of uniform size but is continuously graded between definite limits. The question is: What form of the grading curve will produce a bed of maximum density? The relations obtained should be particularly applicable to the choice of aggregates for concrete and cement products. The question of the relationship between workability and grading is of great importance, and it is suggested that an analogy must exist between workability and ball-bearing friction, which decreases as the diameter of the ball approaches that of the shaft. That is, particles of the next size smaller than the largest may be expected to act as ball bearings, and so on down the line of sizes. No attempt will be made at this time to carry the analogy beyond this qualitative statement. It might be said, however, that mixes made up with gradings designed according to the principles enunciated later have been found to be very workable.

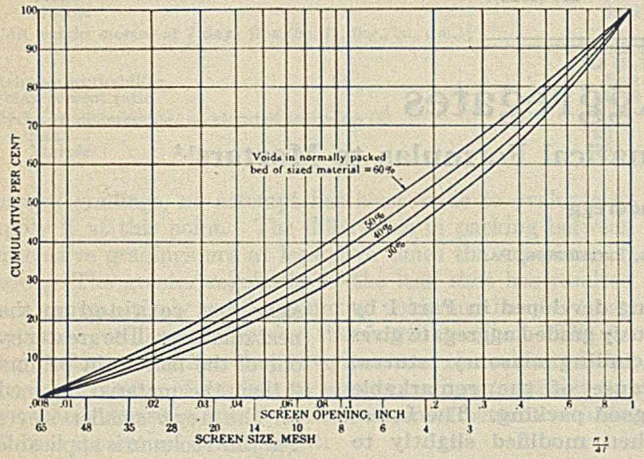


Figure 7—Computed Relation between Screen Size Plotted on Logarithmic Scale and Cumulative Per Cent for Beds of Maximum Density

Since a system which consists of only a few component sizes displays a maximum density for certain size compositions, it may be expected that the same qualitative rule will hold when the number of component sizes becomes very large and the grading becomes continuous. Presumably then, for each class of material there will be a certain constant ratio between the amounts of material of consecutive screen sizes which will give maximum packing for that system. Such a ratio will be designated by the symbol r. Arbitrarily, r is the ratio of the amount of material through and on two consecutive screens to the amount on the next smaller screen when the screen sizes vary by the factor $\sqrt{2}$. For example, the amount of material through 3 mesh and on 4 mesh shall be r times as much as that through 4 mesh on 6 mesh. It is understood that "amount" refers to absolute volume of particles. Measurement by weight is valid as long as true density is constant from size to size. It is recognized that the exact definition of r should be the ratio of the slopes of the curve at points differing by one screen size but the idea of the quantity through and on consecutive sieves is exact enough for the purpose and easier to understand and apply. Obviously in a continuously graded system

$$\frac{\text{Cumulative per cent}}{100} = \frac{S - S_s}{S_l - S_s}$$

subscript s refers to smallest size and subscript l to largest. Screen-size divisions are proportional to log d. Substituting log d for m in Equation 10 and using the appropriate subscripts and substitutions in the latter equation gives, on simplification,

$$\frac{\text{Cumulative per cent}}{100} = \frac{r^{\log d} - r^{\log d_s}}{r^{\log d_l} - r^{\log d_s}} \qquad (25)$$

where d_s = diameter of smallest particle
d_l = diameter of largest particle
r = ratio between consecutive sizes where "consecutive" sizes may be conveniently defined

In a previous section of this paper it was shown that for intermittent grading, for maximum density, the quantity of small particles divided by the quantity of large particles was equal to V, where V is the fractional voids in a bed of uniformly packed sized material. The definition of r given above reverses this ratio for convenience in plotting screen sizes, so as to give the curve for cumulative percentage of material passing the several sieves. Thus r is the quantity of large particles divided by the quantity of small particles. It is evident that if the quantities of large and small particles were comparable in both cases, r would be $1/V$. The quantities can be made comparable by a relatively simple device. $1/V$ stands for the ratio between sizes for maximum possible density in intermittent grading. In order to make the two systems similar it is necessary to set up the equation

$$r^{m/n} = \frac{1}{V}$$

Therefore

$$r = \frac{1}{V^{n/m}} \qquad (26)$$

where n = one less than number of component sizes for maximum density in intermittent grading (one less than ordinate of Figure 2)
m = number of screen-size intervals of ratio $\sqrt{2}$ included between size limits of system, or one less than number of screens used

For example, suppose the ratio of diameters of large to small particles to be 128 and the voids in a normally packed bed of sized material to be 40 per cent. There are 15 screens in the entire system and m equals 14. According to Figure 2 there are 2.45 component sizes for maximum density. Thus n equals 1.45. Therefore

$$r = \frac{1}{V^{1.45/14}} = \frac{1}{0.91} = 1.10$$

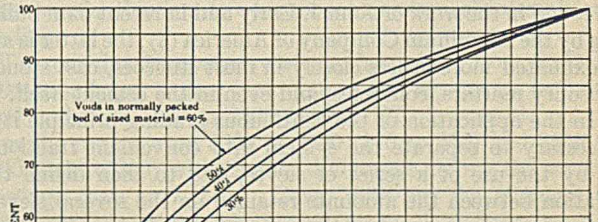


Figure 8—Computed Relation between Screen Size and Cumulative Per Cent for Maximum Density

This means that of each screen size there is 1.10 times as much material as of the next smaller screen size if the system is of maximum density. Since the size ratio (large to small) 128 is one which is convenient in grading aggregates, the values of r have been computed for this ratio and for normal voids of

30, 40, 50, and 60 per cent. The corresponding values of r are 1.12, 1.10, 1.075, and 1.058, respectively. It should be noted particularly that these values of r are only for ratios of amounts on screen sizes differing by the factor $\sqrt{2}$. For other factors m will be different and hence r will be different.

The computed grading curves for these systems are given in Figure 7 plotted on the convenient logarithmic scale and in Figure 8 on the more awkward linear scale. It will be noted that according to the theory advanced in the preceding discussion the type of grading curve for maximum density is determined by two factors: (1) the percentage of voids in a normally packed bed of sized material, which depends on the shape of the particles and (2) the limiting size ratio of the system. Thus, no single grading curve is sufficient for all types of material but each must be determined by Equations 25 and 26.

The author feels that this theory as developed should be useful in the correlation of experimental data and in prediction of the proper mixes for greatest density. Such experimental data are discussed in the accompanying paper by F. O. Anderegg.

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Grading Aggregates

II—The Application of Mathematical Formulas to Mortars[1,2]

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Of the two types of grading developed in Part I by Furnas (*6*), that for continuously graded aggregate gives best results in mortars, including masonry, stucco, and cast stone mixes, because of the remarkable workability combined with good packing. The intermittent or gap grading when modified slightly to improve workability and when carefully applied gives good results and is being successfully applied commercially in making certain concrete products.

ACCORDING to the Furnas development, the arrangement of the amounts of the successive sizes depends upon the voids in the bed of the coarsest size of aggregate present. A large number of voids means more fines to fill them. Two systems can be used to secure efficient packings, one having an intermittent or gap grading and the other a continuous grading. Examples of the former may be found in the work of John J. Early and in recent dam building by the Aluminum Company of America (*4*); the latter is approximated more or less closely in most stuccoes, cast stones, masonry mortars, concretes, and even in the cement itself.

In the application of the continuous grading principle it is necessary to separate the system into convenient fractions, as by the use of a series of sieves, and to then define the relation between the amounts retained on the several sieves. This relation is covered by the value r in the Furnas Equation 25 and may be defined for practical purposes as the ratio of the amount retained on any one sieve of a series to that retained on the next smaller. If the sieve dimensions had a constant ratio of ten, common logarithms could be conveniently used, but as most sieves have the ratio of two, or the square root of two, these values may be used as our logarithmic base. Table I gives a comparison of values for r for the several bases.

Table I—Comparative Values of r in Furnas Equation for Logarithmic Base, or Ratio of Sieve-Opening Dimension

10	2	1.414
1.0	1.000	1.000
1.5	1.130	1.063
2	1.232	1.110
3	1.392	1.180
5	1.624	1.274
10	2.000	1.414
30	2.785	1.669

This means that if the sieves of 200-, 100-, 50-, 30-, etc., mesh sizes are used, the ratio of material passing a certain sieve, but retained on the next smaller, will be greater by one of the factors in column 2 than the material retained on the next smaller sieve. The third column is applicable for the sieve series 200, 150, 100, 65, 50, etc., and has been used in these experiments.

Packing of Shot

A series of lead shot was obtained, including buck shot of numbers 000, 00, 0, 1, 2, 3, and 4 BB shot, drop shot of numbers 1 to 12, and shot dust. Several shot of the different sizes were measured accurately and were not found to vary greatly from true spheres. The ratio of largest to smallest diameter was slightly greater than 8. The Furnas Equation 25 was solved for the five intermediate gradings of Table III, and the amounts of the several sizes of shot were taken from the curves. While the grading of these shot was not quite continuous, the differences between sizes was small enough to give a close approach to continuity. A set of iron shot was obtained through the courtesy of the Pittsburgh Crushed Steel Company and treated in a similar manner. The ratio of largest to smallest was about 21. These shot were somewhat more irregular in shape than the lead shot. The results for dry rodding are given in Table II.

Table II—Packing of Lead and Iron Shot

Grading	Lead Shot		Iron Shot	
	Packing	Voids	Packing	Voids
r	%	%	%	%
1.063	58.7	31.3	..	..
1.110	70.2	29.8	63.6	36.4
1.180	70.7	29.3	64.5	35.5
1.274	71.2	28.8	63.8	36.2
1.414	70.6	29.4	63.5	36.5

These packings could be reproduced within ±0.1 per cent, using the same container and same method of tamping (twenty-five times on each third with a small pointed rod). Because of the small amount of shot available, the container was small (180 ml.), and as a result a small boundary error was introduced. As this must be nearly the same for the

[1] Received June 3, 1931.

[2] Contribution from the Portland Cement Fellowship, Mellon Institute of Industrial Research, Pittsburgh, Pa.

Table III—Aggregate Passing a 20-Mesh Sieve

Mix 1:2, both sand and crushed marble

	r, 1.00	r, 1.24	r, 1.41	r, 1.67	Intermittent	Standard Ottawa
Fineness modulus	0.98	1.34	1.70	2.01	2.15	3.0
Surface modulus	63.20	50.10	40.30	31.50	32.5	12.5
Unit weight dry rodded [lbs./cu. ft. (kg./cu. dm.)]						
Sand	114 (1.83)	116 (1.86)	111 (1.78)	113 (1.81)	119 (1.91)	103 (1.65)
Marble	110 (1.76)	113 (1.81)	110 (1.76)	112 (1.79)	116 (1.86)	
Cement						
Sand ratio for maximum dry packing	1:10	0:10	0:10	2:10	1:10	3:10
Water required for normal consistency, %						
Sand	15.4	14.5	14.5	14.3	14.6	12.8
Marble	16.2	15.5	15.4	15.4	15.4	
Compressive strength [lbs./sq. in. (kg./sq. cm.)]						
Sand 7 days	4780 (335)	5800 (406)	6200 (434)	5520 (387)	6350 (445)	3550 (249)
Marble 7 days	4360 (305)	4155 (291)	4100 (287)	3900 (343)	4850 (340)	
Absorption, 5 hours boiling, %						
Sand	7.1	7.1	6.1	6.7	7.1	7.8
Marble	10.5	7.7	6.7	11.1	7.9	7.8
Effect moisture change on weight, %						
Sand	2.0	1.7	2.5	2.4	1.7	2.7
Marble	4.2	4.0	3.1	3.3	2.5	
Effect moisture change on length, %						
Sand	0.10	0.08	0.083	0.083	0.070	0.070
Marble	0.09	0.11	0.12	0.083	0.077	
Unit weight mortar at 7 days [lbs./cu. ft. (kg./cu. dm.)]						
	142 (2.27)	143 (2.29)	144 (2.31)	145 (2.32)	147 (2.35)	149 (2.39)
	143 (2.29)	146 (2.34)	147 (2.35)	150 (2.40)	151 (2.42)	
Relative workability	Best	2nd	3rd	5th	4th	6th
Voids-cement ratio	1.42	1.28	1.25	1.29	1.20	1.07
Cycles to disintegrate, accelerated corrosion (*9*)						
Sand	20	19	13	16	13	
Marble	18	17	16	16	13	

several gradings, no attempt has been made to evaluate or apply it at this point. The differences in packing between successive gradings are at least five times the experimental error. The greater regularity of the lead shot has resulted in a comparatively small amount of voids and has led to an apparent void minimum for the fourth grading. The irregularities on the iron shot have increased the voids and also moved the type of grading to secure maximum packing toward an increase in fines (r is smaller), in agreement with the Furnas theoretical development.

Grading of Sand Alone

The first experiments were carried out before the equation for continuous grading was developed, the mixes being similar to those of Talbot and Richart (*9*). These included a straight line grading, for which their $n = 1.00$; a logarithmic grading corresponding roughly to their $n = 0.30$, except in the lower region; a grading intermediate between these two, $n = 0.60$; and a corresponding grading on the other side of the straight line, approximately, $n = 1.50$. The corresponding values for r in the Furnas Equation 25 are 1.0 for the logarithmic grading, 1.24 for the intermediate grading, 1.41 for the straight line, and 1.67 for the other. One mix with aggregate of intermittent grading was also made up, with 63 per cent passing a 20-mesh sieve but retained on a 24-, 24 per cent in the range between the 80- and 100-mesh sieve, fine round sand passing a 325-mesh sieve for the remainder. Both sand and crushed marble were used. In this series the upper limit was that just passing a 20-mesh sieve.

The cement for the first series was reground in a laboratory mill until 98 per cent passed a 200-mesh and 89 per cent a 325-mesh sieve, and until 61 per cent was below 30 microns, 50 per cent below 20, 37 per cent below 10, 26 per cent below 5, and 3 per cent below 2.5 microns. The determination was made partly by elutriation and partly by a projection method in which a magnification as high as 4600 diameters was obtained. A 1:2 mix was used, a ratio in which cement and sand are often applied in concrete. One-inch (2.5-cm.) cubes were molded mechanically (*3*), as were also bars of $^1/_2 \times {}^1/_2 \times 3$ inches ($1.27 \times 1.27 \times 7.62$ cm.), which contained small brass inserts in each end. These inserts contained a tiny hole for measuring change in length with an Ames dial sensitive to 0.0001 inch (2.5 microns) during a moisture-change cycle of 6 days at 75 per cent relative humidity and 24 hours' immersion in water, all at 70 ± 2° F. (21.11 ± 1.11° C.). These specimens were used for observing the effect of moisture change both on the weight and length. The consistency of the mortar was as close to that of a 1:3 standard Ottawa sand mix at normal consistency as could be judged by direct comparison, and the workability was estimated from the ease of placing in the molds.

The surface modulus was calculated according to the method of Talbot and Richart (*9*). After the dry rodded packing of the aggregate was determined, the cement was added by increments, and the packing was repeated. The ratio of cement to sand giving the best dry rodded packing is recorded in Table III. The addition of as little cement as 1:10 increased the amount of voids where most fines were present. Standard Ottawa sand has about 38 per cent voids dry rodded to which one-third its weight of cement could be fitted without excessive forcing apart of the sand grains. In other words, this is a two-component system of intermittent grading.

The one-day compressive strengths ranged from 2000 to 3500 pounds per square inch (140 to 245 kg. per sq. cm.) for sand and from 1500 to 2500 (105 to 175) for marble. At 3 days the ranges were 3000 to 3500 (210 to 385) and 3500 to 4000 (245 to 280) with smaller differences among the several gradings than at 7 days. These data are the averages of three or four specimens whose mean deviations usually ranged between 3 and 5 per cent. In this series the mix with $r = 1.23$ gave best general results. The intermittent grading also made a favorable showing. These two gradings are those corresponding to the Furnas equations.

The superior results obtained when using the sand with its very round grains, as compared with the more angular grained marble dust, is of interest. Angularity, a characteristic of calcite grains, has resulted in poorer packing, greater water requirement, lower compressive strengths, higher absorptions, and poorer workability.

The intermittent grading has differed from the mix containing standard Ottawa sand only by the substitution of some of the larger grains by smaller ones, resulting in some increase in water requirement, but also in a marked improvement in workability. Because of the great difference in physical nature between the standard Ottawa sand-cement mix and the commercial sand-cement mixes, it seems hardly fair to judge a cement from the first. This laboratory has found by experiment that certain commercial masonry cements actually gave poorer strengths with commercial sand and with ideally

Table IV—Effect of Humps in Grading Curve, Series 1[a]

(All mixes 1:3 by weight)

	Water Required		Compressive Strength at 7 Days		Compressive Strength at 28 Days		Absorption	
	N. C.	F. C.	N. C.	F. C.	N. C.	F. C.	N. C.	F. C.
	%	%	*Lbs./sq. in. (kg./cu. cm.)*	*Lbs./sq. in. (kg./sq. cm.)*	*Lbs./sq. in. (kg./sq. cm.)*	*Lbs./sq. in. (kg./sq. cm.)*	%	%
Standard graded	13.2	14.7	3623 (254)	3223 (226)	7310 (512)	6543 (453)	2.7	3.5
	13.2	15.0	3633 (255)	3275 (229)	7467 (524)	6442 (452)	2.8	3.6
Sized by sieves:			20 PARTS TO 80 PARTS STANDARD GRADED SAND					
8, 10	13.8	15.0	2620 (188)	2055 (144)	4828 (338)	4145 (290)	6.7	6.7
14, 20	13.7	15.0	2440 (171)	2540 (178)	4608 (323)	3948 (277)	6.4	6.7
28, 35	13.8	15.0	2445 (172)	1995 (140)	3583 (251)	3110 (218)	6.3	6.9
48, 65	13.8	15.0	2290 (160)	2260 (158)	3498 (245)	3155 (221)	6.2	6.5
100, 150	14.0	20.0	1810 (127)	1410 (99)	3288 (230)	2513 (176)	6.8	7.5
150, 200	14.4	17.4	1521 (107)	1050 (70)	2808 (197)	2250 (158)	7.5	7.7
200, 325	15.0	18.6	1591 (112)	1245 (87)	2432 (170)	2131 (149)	7.7	8.4
			10 PARTS TO 90 PARTS STANDARD GRADED SAND					
8, 10	12.6	14.4	3403 (239)	2870 (201)	6630 (465)	6200 (435)	5.5	5.9
10, 14	13.5	15.0	3200 (224)	2708 (190)	6555 (460)	6078 (426)	5.5	6.0
14, 20	13.5	14.9	3273 (229)	2788 (195)	6900 (483)	6123 (429)	5.2	5.7
20, 22	13.5	15.3	3290 (230)	2963 (207)	6985 (490)	5443 (381)	5.0	5.1
28, 35	13.5	15.0	3158 (221)	2893 (209)	6472 (453)	6047 (424)	5.6	6.2
35, 48	14.4	15.9	2937 (206)	2830 (198)	5907 (414)	5688 (399)	5.5	6.4
48, 65	14.4	15.9	2895 (203)	2497 (175)	5645 (395)	4793 (336)	...	6.5
65, 100	14.4	16.8	2697 (189)	2363 (165)	4830 (338)	4350 (305)	6.2	7.1
100, 150	15.3	16.8	2613 (183)	2325 (163)	4478 (314)	4083 (286)	5.9	6.3
150, 200	15.9	17.4	2570 (180)	2393 (167)	4507 (316)	4057 (284)	6.4	7.5
200, 325	16.5	19.5	2455 (172)	2293 (161)	4197 (294)	3853 (270)	6.9	7.5

[a] Normal and face-coat consistencies, combined storage, $r = 1.11$.

Table IV(*continued*)—Effect of Humps in Grading Curve, Series 2[b]

(All mixes 1 : 3 by weight)

5 PARTS TO 95 PARTS STANDARD GRADED SAND

Sized by Sieves	Water	Compressive Strength at 28 Days
	%	*Lbs./sq. in. (kg./sq. cm.)*
8, 10	15.0	6175 (432)
28, 35	15.0	5465 (383)
48, 65	15.0	4945 (346)
170, 200	15.4	4575 (321)
2.5 PARTS TO 97.5 PARTS STANDARD GRADED SAND		
8, 10	15.0	6075 (425)
28, 35	15.0	5473 (383)
48, 65	15.3	4678 (328)
170, 200	15.6	3870 (271)

MISCELLANEOUS AMOUNTS

Parts Sand	Sized by Sieves	Parts Standard Graded	Water	Compressive Strength at 28 Days
			%	*Lbs./sq. in. (kg./sq. cm.)*
25	35, 48	75	15.0	3010 (211)
50	35, 48	50	15.0	2813 (197)
75	35, 48	25	15.3	2985 (209)

Miscellaneous Sands

Standard Ottawa	15.0	2305 (162)
Ottawa run of mine	15.0	2820 (198)
River, St. Louis	15.9	2223 (156)
River, Memphis	16.5	1623 (114)
Lake, Chicago	18.0	1490 (104)
Standard graded, $r = 1.11$	15.0	6165 (432)
Standard graded, $r = 1.11$	15.0	6283 (440)
Standard graded, $r = 1.11$	15.0	5900 (413)
	Av.	6116 (428)

[b] Face-coat consistency, water storage.

graded sand than with standard Ottawa, while the reverse is true of most other cements.

The logarithmic grading has given specimens that showed the most resistance to crystal pressure in the modified sodium sulfate test (*3*).

These results with continuously graded sands confirm those obtained by Graf (*7*), who concluded that the best results for compressive and flexural strengths, shrinkage, abrasion resistance, and permeability were obtained with a grading of the sand approximating a curve lying between $r = 1.11$ and 1.18. The best resistance to chemical attack was exhibited by gradings in which r was closed to 1.00. None of the gradings used by Graf followed smooth curves and the harmful effect of humps in the grading curves, as will be shown below, probably affected the results obtained.

The void-cement ratios, calculated after the method of Talbot and Richart (*9*), are given in the table. On plotting, no correlation is apparent between these ratios and the compressive strengths.

Factors Affecting Compressive Strength

The factors that may be expected to affect the compressive strength are rather numerous. Among these, in the order of their importance, are (1) the amount of cement hydrated; (2) the water-cement or void-cement ratio; (3) the properties of the aggregate, including especially the surface condition which may determine the mechanical bond, and the specific adhesion of the cement itself; (4) workability of the mix, which is a factor in securing good packing and in lessening accidental errors; (5) structural features that are not properly understood, including the arrangement of particles in arches and the keying effect of large particles resisting the development of planes of weakness; (6) irregularities in grading which produce humps in the grading curve, resulting usually in poorer packing, higher water requirement, and probably the easier development of those planes along which shearing takes place preliminary to failure under crushing. In addition, accidental variations, such as uneven tamping, bridging, etc., introduce errors of varying magnitude. Many data have been obtained with other cements, both in 1:2 and 1:3 mixes, which substantiate those previously given. On leaving out the finer aggregate from the intermittent grading, results appreciably superior to those in Table III have been obtained.

Standard Graded Sand

Following the preliminary experiments previously described, the unit weight of a series of sands of smooth grading for the range, $r = 1.05$ to 1.20, was found constant within the experiment error and a sand grading was chosen intermediate in this region, with $r = 1.11$ running from 92 per cent passing an 8-mesh sieve down to 9 per cent through a 200- and 6 per cent passing a 325-mesh sieve. It was made up by combining, in suitable amounts, two grades of coarse sand-blast sand, standard Ottawa, run of mine Ottawa, a fine recovered sand, and crushed silica. The dry rodded weight of this composite sand was 122.5 pounds per cubic foot (1.96 kg. per cu. dm.). Some results obtained with it are given in Table IV. For some purposes the coarsest fraction might be left out, which would result in reducing the unit weight to 118 pounds (53.52 kg.).

Effect of Humps in Grading Curve

About thirty-five commercial sands have been tested by making sieve analyses and test specimens. It was observed that none of these came anywhere near the standard graded sand in high unit weight, in high strength, or in low absorption. The standard graded sand in high unit weight usually gave lower volume change. It compared favorably with most of the others in workability. When the amount of mixing water required was taken into consideration, it stood above all others.

The sieve analyses of the commercial sands showed various humps in the cumulative grading curves, suggesting that unevenness of grading might have a detrimental effect. The behavior of certain ready-mixed stuccoes, as described later, supported this idea very strongly.

To test this idea systematically, a series of mixes was made up, using 80, 90, 95, and 97.5 per cent of the standard graded sand as the base with 20, 10, 5, and 2.5 per cent of a sized sand. Thus different sized humps were introduced into the curve, being greater with the finer sizes than with the coarser. The results are given in Table IV, together with those of of several commercial sands. Specimens were made up at two different consistencies, the one normal (N. C.) closely similar to that obtained with standard Ottawa sand in making tensile briquets according to standard specifications, and the other made up to a consistency suitable for application as face-coat (F. C.) stucco, according to the judgment of a skilled mechanic. This probably represents the range of consistencies of mortars immediately after practical application, when due allowance is made for the moisture removed from most mortars by the absorbent materials (brick, stone, etc.), with which they are placed in contact.

Table V—Addition of Fine Limestone to Harsh-Working Sand

With Allegheny River Sand *Cement : Lime : Sand*	Compressive Strength, 28 Days' Water Storage *Lbs./sq. in. (kg./sq. cm.)*
1:1:4	870 (61)
1:1:4 + 0.5 limestone 1 sand	811, 866 (47, 60)
1:1:4 + 1 limestone 2 sand	688, 766 (48, 54)

The method of storage in Series 1 was 24 hours in the moist closet, 6 days in water, and 21 days in the air of the laboratory, which method is similar to the German combined storage and to the standard method of storage of stucco specimens in this country. In Series 2 the storage was in water only. The compressive results are each the average of three which were usually in close agreement. The absorption in the first series was determined by immersing the air-dried specimen, after weighing, in water for 24 hours. The two sets of specimens of standard graded sand were made at intervals of 2 months.

The cement used was a finely ground white one with which 5 per cent of hydrated lime was mixed before making up the specimens.

The presence of a hump in the grading curve due to the addition of 20 parts sized material added to 80 parts standard graded sand has reduced the compressive strength in percentages varying from 34 for coarse to 65 for fine added sizes. The 10 parts added have had less effect, about 8 per cent reduction being obtained with the coarsest and 36 per cent with the finest sized addition. Humps in the finest region produce most damage. While the addition of finely crushed solids, such as silica or limestone in reasonable amounts, should markedly improve the grading, some care should be taken to see that the fine material has a fairly even grading. Some of the people interested in cement products are beginning to appreciate this principle (*8*), but its application could be extended with profit.

Table VI—Commercial Ready-Mixed Stuccoes

Stucco	Passing 100 Mesh	Water	Compressive Strength, 28 Days	Absorption 28 Days	Unit Weight: As received	Unit Weight: At 28 days	Effect of Moisture Change: On length	Effect of Moisture Change: On weight
	%	%	*Lbs./sq. in. (kg./sq. cm.)*	%	*Lbs./cu. ft. (kg./cu. dm.)*	*Lbs./cu. ft. (kg./cu. dm.)*	%	%
1	38.5	20.3	3061 (214)	10.3	92 (1.47)	115 (1.84)	0.065	6.2
2	40.0	19.9	2523 (177)	9.6	89 (1.43)	113 (1.81)	0.071	8.6
3	30.6	23.5	1604 (112)	12.2	80 (1.28)	106 (1.70)	0.067	10.5
4	36.1	19.3	3570 (250)	5.4	107 (1.71)	127 (2.03)	0.049	6.7
5	35.6	22.5	2600 (182)	9.1	82 (1.31)	116 (1.86)	0.061	8.7
6	32.1	16.8	3559 (249)	6.2	111 (1.78)	120 (1.92)	0.047	8.4
7	39.0	18.7	1660 (116)	9.46	....	121 (1.94)	....	..
8	..	20.8	2586 (181)	7.88	....	123 (1.97)	....	..
9	27.0	22.5	1781 (125)	12.2	....	....	0.0787	9.2
10	37.0	15.5	2871 (201)	6.0	....	....	....	..

Masonry Mortars

Since most commercial sands are characterized by a hump in the 50- to 30-sieve range, the logical method of securing better results is to correct the grading. For this purpose the addition of a suitably crushed rock in amounts ranging from 5 to 20 per cent, depending upon the character of the sand, is most likely to give beneficial results. The rock must, of course, be of suitable soundness for use as an aggregate, and when crushed must be free from humps in the grading curve. A crushed limestone is available on the market at a reasonable price which can often be added to commercial sands with marked improvement.

It will sometimes be found profitable to add coarser aggregate because of the more efficient packing and the greater strength. A fine gravel may be available in certain places from which the desired sizes could be sieved. Again coarser gravel or rock might be cracked in a suitable mill.

Sieve analyses of sand obtained from the Allegheny River indicate a rather small amount passing the 50-mesh sieve. The sand works harsh in mortar requiring a large amount of cement and lime. For example, using equal volumes of cement and lime putty, all the sand that could be added on a large job to give the mason sufficient workability for his requirements was four volumes, a mix so rich that the occurrence of shrinkage crazes in the mortar is common.

Certain of the crushed commercial limestones made from clean stone were found to have a grading fairly suitable for supplying the lack in the sand. One volume was added, and then two more volumes of sand with the same workability as before. Judgment as to workability was made independently by three brick masons, all careful and observant mechanics. Actually for a number of experiments, a mix of equal volumes of cement, lime putty, and fine limestone with five volumes of local river sand gives fine results in Pittsburgh. In addition, the displacement of cement and lime by the cheaper limestone results in the actual saving of about 40 cents per thousand brick. This saving, however, is small compared to the saving possible in the greater amount of work accomplished with this more plastic mortar.

The specimens were 2-inch cubes molded in brass. Specimens made in contact with brick and stored partly in water and partly in air gave higher results. Here again evidence is presented of the applicability to practical problems of the principle of a smooth grading.

Ready-Mixed Stuccoes

In the application to stucco (also a mortar) the laws here examined indicate the importance of the fine aggregate in securing the desired workability, packing, and strength. Most stucco is made up in a mix of about 1:3, which means that an ideal grading calls for about 40 per cent passing a 100-mesh sieve, of which 25 per cent is cement and 15 per cent, or slightly more, is aggregate. The tentative specification of the American Concrete Institute (*1*) of a maximum of 35 per cent passing this sieve is unfair to a properly graded stucco. Of a large number of ready-mixed stuccoes examined in this laboratory, several having an amount of fine material in excess of this 35 per cent requirement have exhibited very desirable workability, strength, density, and durability under severe exposure.

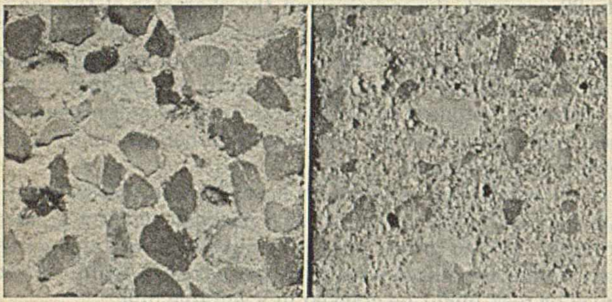
A B

Figure 1

A—Intermittent grading giving a terrazzo effect
B—Continuous grading with coarse aggregate less prominent

The intention of the committee to control the amounts of the various materials added as plasticizers is to be commended. It is suggested, however, that a much more effective method of making a specification would be in terms of the water needed to secure the consistency suitable for face-coat application. A stucco of suitable properties can be made requiring about 15 per cent of the weight of the dry materials, or a little less than 2 gallons per 100-pound sack of premixed stucco. A limit of 20 per cent is suggested, or $2^1/_2$ gallons. Some of the ready-mixed stuccoes now on the market require nearly 25 per cent and their actual crazing and poor weathering properties would appear to justify such a limitation, which, incidentally, is in line with much recent discussion on the water-cement ratio. Table VI contains some results on ready-mixed stuccoes tested according to the tentative specifications.

Two factors contribute to the workability in greatest amount. The amount of water in the system necessary to produce a working consistency is the more important factor and depends largely upon the amount of fine materials present. The grading of the aggregate comes next, and it has been found that the closer the approach to the ideal continuous grading for packing, the higher the workability and the higher the water-requirement ration for workability. In regard to grading of aggregate, those stuccoes whose r is closest to 1.1 have been found to give best results. Panels made from these stuccoes and exposed on the roof have weathered and crazed very little when the water required was low, but as that rose above 20 per cent, the effect was apt to be bad. Thus stuccoes 3 and 5 have developed serious cracks throughout and have weathered badly. Part of the trouble with these stuccoes as well as with stucco 9 can be directly connected with the hump found in their grading curves.

Aggregates for Cast Stone

The crushed marbles used in making cast stone at three commercial plants noted for quality products have been given a sieve analysis and in each case they were found to lie in grading close to the ideal curve which, for marble, is about $r = 1.1$ (1.2 with the sieve ratio of 2). One had a slight excess of material retained on the 8-mesh sieve which affected its workability adversely to a slight extent. The specimens made from these were very satisfactory as to strength, running close to 5500 after the baking (*2*). Qualitative experiments showed that addition of sized material to these marble gradings affected adversely the workability and water requirement.

Fuller Curve

The Fuller curve has been used in this country and abroad for grading of aggregates (*5*). When the sand part of the grading is plotted on a logarithmic scale or against the several sieve sizes, evenly spaced, the curve follows closely the one where $r = 1.11$ (for sieves of factor 2, $r = 1.2$ approximately). In other words, the Furnas equation for continuous grading gives the theoretical basis for the empirical findings of Fuller and Thompson, after more than twenty years of successful application of the latter.

Intermittent Grading

For a three-component system having 40 per cent voids, the Furnas Figure 2 indicates a ratio of small to large aggregate of 0.00042. Now with the aid of large elutriators it is possible to separate sufficient cement flour, ranging in dimension up to 10 microns, for experimental work. The large aggregate should then be in the neighborhood of 1 cm. (passing a $^1/_2$- but retained on a $^3/_8$-inch screen). Using Equation 14, $d_2/d_1 = d_3/d_2$, and setting $d_1 = 1$ cm. and $d_3 = 5 \times 10^{-4}$ cm., $d_2 = 0.022$ cm. which is intermediate between a 65- and 60-mesh sieve opening.

In experimenting with such a mix, an interesting complication was encountered. In determining the packing of the pebbles, a can was used with diameter and height both a little greater than 4 inches. The more regular pebbles were packed with dry rodding and were found to fill 0.636 of the space, leaving 36.4 per cent voids. The pebbles were counted, the number of pebbles in the top and bottom layers and in contact with the can observed, and the mean diameter of the pebbles calculated. The packing was obviously less efficient in the outside layer of the can. The packing inside the cylinder, circumscribed through the centers of the outside pebbles, was calculated to be 0.706, and that outside to be 0.472. This means that in making up specimens for compressive or flexural tests, a greater proportion of sand and cement would be required to fill the extra voids around the boundary than in mass concrete. The same thing holds in any concrete with a large surface, such as curbing or narrow curtain walls filled with much reënforcing. The ratio of surface to volume increases in proportion to the boundary correction and mixes designed for mass concrete may not always receive a fair test when 6 × 12 inch cylinders are used. A suitable correction is often made by the concreter, but it is sometimes disregarded.

Table VII—Boundary Correction[a]

	PEBBLES	
	More regular	Less regular
Weight of pebbles	1716 grams	1590 grams
Mean diameter of pebbles	1.19 cm.	1.13 cm.
No. in top layer	39	45
No. in bottom layer	58	68
No. in top layer touching circumference	14	17
No. in bottom layer touching circumference	18	19
No. in other layers touching circumference	212	188
No. in center	430	500
Volume, inside cylinder	716 ml.	728 ml.
Volume, outside inscribed cylinder	304 ml.	292 ml.
Packing in whole can	0.636 or 105 lbs./ft.^{3}	0.589 or 97 lbs./ft.^{3}
Packing of inner cylinder	0.706 or 117 lbs./ft.^{3}	0.651 or 108 lbs./ft.^{3}
Packing of outer ring	0.472 or 78 lbs./ft.^{3}	0.433 or 72 lbs./ft.^{3}
Voids in whole can	0.364	0.411
Voids in inside cylinder	0.294	0.349
Difference between last two	0.070	0.072
Increase required in mortar	24%	21%
Changing a 1:2:4 mix to	1:2:3.25 or to a	1:2:3.31 mix

[a] Ratio of diameter of container to that of pebbles, about 9. Container, 10.5 cm. diameter, 11.7 cm. height, 1020 ml. volume. Pebbles passing $^1/_2$-inch retained on $^3/_8$-inch screen. Sp. gr. 2.65.

For tests 2-inch cube molds and 2 × 2 × 6 inch bar molds were used and were first filled with the large aggregate. From the count of the pebbles on the inside and on the outside, the boundary correction was calculated and the extra space

Table VIII—Intermittent Grading

Standard cement, pebbles $^3/_8$ to $^1/_2$ in. (9 to 12 mm.)

MORE REGULAR PEBBLES				LESS REGULAR PEBBLES			
		28-DAY STRENGTH				28-DAY STRENGTH	
Mix	W/C^a	Modulus rupture Lbs./sq. in. (kg./sq. cm.)	Compression Lbs./sq. in. (kg./sq. cm.)	Mix	W/C^a	Modulus rupture Lbs./sq. in. (kg./sq. cm.)	Compression Lbs./sq. in. (kg./sq. cm.)
SAND, OTTAWA RUN OF MINE							
10:25:65	0.51	520 (36.4)	1513 (106)	10:25:52	0.59	459 (32.1)	3060 (214)
10:20:40	0.48	606 (42.4)	2013 (141)	10:20:40	0.50	630 (44.1)	2695 (189)
SAND, SIZED BY SIEVES 28 AND 52 MESH							
10:25:65	0.69	445 (31.2)	1991 (139)	10:23:52	0.56	570 (40.0)	2910 (204)
10:20:40	0.51	740 (51.8)	3515 (246)	10:20:40	0.51	656 (46.0)	2955 (207)
COARSE SAND, 8, 10 MESH AND CEMENT FLOUR							
				FINE SAND SIZED BY SIEVES			UNIT WEIGHT MORTAR Lbs./cu. ft. (kg./cu. dm.)
10:37:69	0.90	340 (23.8)	1357 (95)	170, 200			142 (2.04)
10:37:69	1.01	384 (26.9)	1368 (96)	150, 200			145 (2.08)
10:37:69	0.83	323 (22.6)	1235 (87)	150, 325			145 (2.08)
20:37:69	0.47	872 (61.1)	3207 (224)	170, 200			141 (2.03)

[a] To change the W/C ratio to gallons per sack of cement multiply by 11.27.

was filled with more of the mortar. Both the more regular and the less regular pebbles were used in two different mixes and with two different sands each, making a total of eight sets of bars and eight sets of cubes. These were mixed with water to a consistency closely approximating normal, and placed in the molds with a small tamper. Because of the harshness of the mix the work required to produce a water mark on the surface was much greater than for graded mortars.

The mixes were all harsh and very difficult to apply and, for successful working, some vibration system would be desirable. The segregating tendency is also troublesome. Since the graded sand gives better workability and is usually more readily obtainable than the sized sand, its use is preferred.

Although the specimens made of sand passing an 8-mesh sieve with a low cement content are quite heavy (a more efficient method of removing air bubbles should increase the weight appreciably), the strength is low because of the leanness of the mix (1:9). Doubling the amount of cement improves the workability, halves the water-cement ratio, and more than doubles the strength.

The character of this intermittent grading is illustrated in Figure 1, where the distinction from the continuously graded specimens is obvious. Terrazzo is a special type of gap graded mortar and a number of concrete products are being successfully manufactured similar to terrazzo. For practical application, special methods would be required and the remarkable work of John J. Early of Washington, D. C., in this type of grading shows that it is practicable.

Workability

Workability depends upon the water and the grading of the whole system, including the cementing material. Many organic substances improve the workability by imparting a lubrication which permits the ready packing of the mortar. But organic compounds, other than in very small amounts, are likely to be detrimental to the normal setting and hardening processes, and excess water is harmful.

In addition, the workability depends upon the presence of a sufficient number of ball bearings of suitable size distribution. The fact that the continuous grading most closely approaching the ideal developed in these articles has the best workability is probably more than a fortuitous coincidence. However, the relationship has not yet been worked out.

According to these ideas, admixtures serve a useful purpose in so far as they bring the grading of any part of the system closer to the ideal. When they go beyond this, however, producing humps in the grading curve so that more water is required, their effect may become harmful. Since commercial cements have different size distributions, admixtures will not behave consistently with different cements, which explains some of the apparent discrepancies found in the literature.

Summary

Since compactness is one of the many properties desired in cement products and concrete, means of securing it have been investigated by a joint theoretical and experimental study.

The first part of the theoretical treatment, described in Part I by Furnas (6), developed a system of intermittent grading of great compactness. When this is modified to include a graded rather than a sized fine aggregate and when a suitable method of application is used to overcome the harshness of the mix (already successfully done on a practical scale), it yields very fine results.

The second part of the theoretical study has produced an equation for a continuously graded system. Its application to mortars has given good results, including good workability, low water requirement, a remarkably high workability–water requirement ratio, and great compactness with high strength, low absorption, and fairly low shrinkage.

For mortars, very excellent results are obtained when the ratio of the fraction of aggregate retained on any one sieve to that on the next smaller, differing in mesh dimension by the square root of 2, is in the range 1.10 to 1.12 depending upon the voids in the coarse aggregate. If the dimension differs by a constant factor of 2, as in the set used for fineness modulus determination, the range of the ratios is about 1.20. This also applies for stucco, cast stone, and masonry mortar. The rational application of the continuous grading principle includes the grading of the cement and aggregate together. This has been done by having sufficient fine aggregate to carry the curve smoothly from the cement region into the sand region. Many cements have humps in their own grading curves which fault can be eliminated only by proper grinding.

The effects of deviations from the smooth curve of the formula caused by addition of sized aggregates have been studied. The introduction of a sized sand in various amounts up to 20 per cent of the total has resulted in strength diminutions as high as 65 per cent, the addition of the finer sizes causing the greater losses. Many of the other properties have also been adversely affected.

Experiments are described showing that voids as high as 53 per cent of the space next to the surface of a container are found, when filled with coarse aggregate, as compared with 35 or 40 per cent in the interior, requiring boundary corrections. This fact should be kept in mind when designing or testing a mix for any purpose.

The sand part of the Fuller grading curve is shown to closely approximate the ideal developed in this investigation.

Since most commercial sands contain more material in the 50- to 30-mesh range than is needed for high-grade work, it is suggested that the addition of sound, finely crushed rock of uniform grading for the lower part of the curve will frequently be economically justified. The upper part of the curve might often be improved by adding more coarse aggregate.

Admixtures are helpful in so far as they bring any part of the whole sand-cement system closer to the ideal.

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Vitamins in Canned Foods

XI—A Canned Food Diet[1]

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In a series of studies (2) pertaining to the vitamin content of canned foods, it has been found that each of the vitamins, A, B_1, B_2, and C, may be supplied in adequate amounts by various canned foods. This has been demonstrated in experiments in which a given canned food was required to be the sole source of one or another of the vitamins. The experimental period of these investigations has been the usual period prescribed for the various vitamin tests—that is, 60 days for vitamins A and B and 90 days for vitamin C. The experiments were directed primarily to the study of the stability of the vitamins to the canning process. Tests for vitamin D content have not been made because this vitamin has been shown to be stable to processes similar to those employed in canning, and because the vitamin D content of such foods as were tested is generally stated to be small.

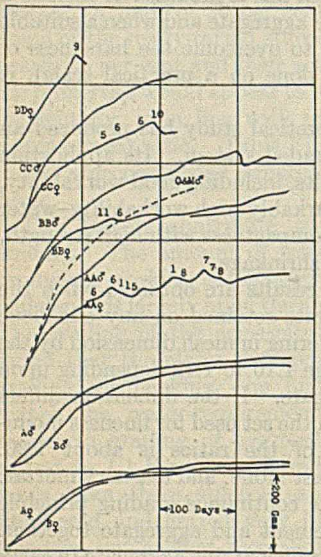

Chart 1—Average Growth Curves of Rats

It is generally accepted that nutritional deficiencies not in evidence in one generation may manifest themselves in subsequent generations. It was therefore deemed of interest to feed test animals on canned foods as the sole diet over a longer period than is covered by the classical vitamin test periods in order to determine the effect on offspring and longevity. The experiments instituted for this purpose and reported here to date are limited to white rats and guinea pigs. The plan of experimentation is to feed a variety of four or five canned foods chosen with a view to securing a balanced diet for a period of 5 days. These foods are not mixed, and the animals are allowed to eat according to their own choice. The animals receive no irradiation treatment, nor are they exposed to the direct rays of the sun. At the end of each five days, a change is made to form a new combination of canned foods. Thus far forty-nine canned foods have been fed in seventy-four combinations, the plan being to repeat the combinations after all of the common canned foods have been utilized. The purpose is not to study any particular food or group of foods, but rather to determine the nutritional adequacy of canned foods. The canned foods are purchased at grocery stores just as they would be purchased for home use. The foods used, therefore, represent those available to everyone.

Observations with Rats and Guinea Pigs

In beginning this experiment, three pairs of rats, 28 days old, were placed on the canned food diet. The weight of the females ranged from 53 to 55 grams and the males from 55 to 56 grams. Three pairs of guinea pigs were also placed on a similar diet. As these had to be purchased, their age is unknown, but the weight of the females varied from 330 to 395 grams and the males from 320 to 430 grams. Later a fourth pair of guinea pigs, 3 weeks old, was added, the female weighing 130 grams and the male, 135 grams. The experiment with rats has now been in progress for 15 months and the experiment with guinea pigs for 13 months.

As these animals give birth to young, a male and female from each pair are bred respectively with a female and male of another pair, and in this manner succeeding generations are obtained. A record of the number and size of litters is kept. After the required number for breeding purposes is selected, the extra young are discarded at weaning time, and data on growth and longevity are kept only on the animals necessary to continue the experiment with a constant number of pairs.

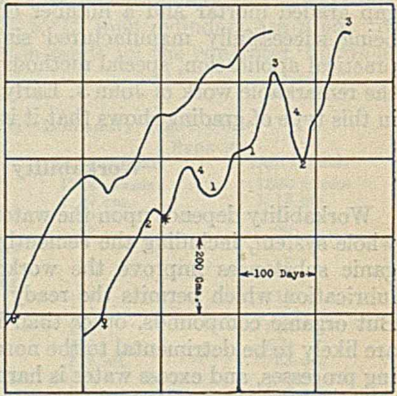

Chart 2—Average Growth Curves of Guinea Pigs

The rats have reached the fifth generation and the guinea pigs the third. Each generation is thriving apparently as well as these species of animals thrive under any conditions. Reproduction is as prolific as can be expected, the size of the litters is normal, lactation is adequate, and the young are making growths equal to that of the parents. The effect of longevity remains to be determined.

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[1] Received May 7, 1931. Presented before the Division of Biological Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

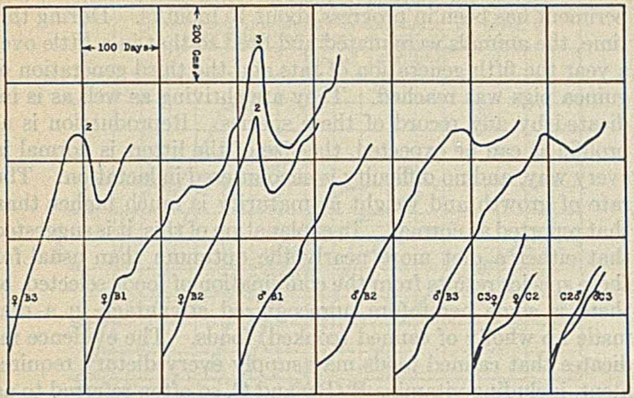

Chart 3—Individual Growth on Reproductive Curves of Second Generation of Guinea Pigs Fed on Canned Foods

By the end of one year, the female rats have attained weights varying from 305 to 330 grams; the male rats, 485 to 560 grams; the female guinea pigs, 785 to 1360 grams; and the male guinea pigs, 1025 to 1225 grams. The weight recorded as normal by Donaldson (*1*) for female rats at the end of one year is about 225 grams and for male rats about 300 grams. There is on record no standard weight for guinea pigs comparable to the standard on rats published by Donaldson. However, the rate of growth on guinea pigs on an exclusive canned food diet is as rapid as the authors have encountered under any conditions, and the weight reached after one year is considerably above what is ordinarily regarded as normal for guinea pigs.

The use of raw foods in the diet is frequently advocated so strongly as to give the impression that a certain amount of raw foods is a necessity. This advice is most commonly associated with discussions of vitamin C. The practice of cooking foods antedates history, and it is a practice with which civilization can ill afford to dispense. Furthermore, there is no record that the culinary art has had adverse consequences. The experiments here reported have gone far beyond the usual test for the vitamins, and thus far there is certainly no evidence that cooked foods, as represented by canned foods, are incapable of supplying all of the vitamins or other nutritional requirements in adequate quantities.

The rapid rate of growth and the maturity weight attained deserve further attention. Either these experimental animals have before them a more nearly optimum diet for growth and maturity weight than is usual, or there is some heretofore unrecognized advantage in the diet made up wholly of cooked foods as represented by canned foods. It is possible that thoroughly cooked foods are more easily digested and more highly assimilated, making possible a more efficient utilization. The desirability of thoroughly cooking foods for infants is well recognized. The medical profession has recently been emphatic in discussing the harm that may be done by too great a consumption of coarse roughage. As a matter of fact, there is a considerable feeling against the term roughage, as volume, bulk, or indigestible residue are more accurately descriptive of the dietary qualities in question. Cooking softens the texture of the fibrous material that constitutes the indigestible residue. In view of this, it is not unreasonable to assume that the two species of animals in these experiments may benefit by the softer texture of a cooked diet, although cooked foods are foreign to their natural mode of living.

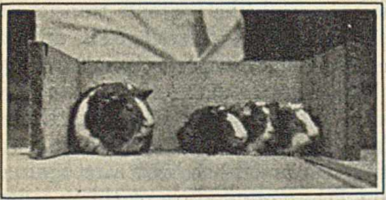

Figure 1—Mother and Litter of 22-Day-Old Guinea Pigs Reared Entirely on Canned Foods

In regard to an adequate supply of vitamins it should be noted that a number of the foods eaten only in the cooked form are the richest sources of certain of the vitamins, particularly vitamins A and C. As has already been brought out, vitamin A is unaffected by the canning processes, and although there may be some destruction of vitamin C, many of the succulent vegetables (particularly those of green color) that have vitamin C in very high concentration in the raw state are, after canning, still very potent sources of the antiscorbutic factor. As most of these are eaten only in cooked form, they represent a class of canned foods that are probably equal in vitamin content to any class of foods eaten raw. It may be added that a serving of a raw vegetable is generally much smaller than a serving of the same vegetable when cooked.

Figure 2—Third Generation of Guinea Pigs on Canned Food Diet
Left to right, 76 and 86 days old, respectively

Certain details of the reaction of these animals to a canned food diet are recorded in the accompanying charts. In Chart 1 the growth curves *A* and *B* are those published by Donaldson (*1*) as representing the normal for the rat.

The animals represented by *A* are said to have been fed on selected table scraps. Graphs *AA* are the average of three female and three male rats placed on a canned food diet when 28 days old. The numbers on the graphs representing the females are the number per litter of young. Superimposed on graph *AA* is another, *O* and *M*, representing the maximum rate of growth for male rats obtained by Osborne and Mendel (*3*). Graphs *BB* represent the average for three females and three males, and are the progeny of the animals represented by graphs *AA*. Graphs *CC* represent the average for two females and two males that are progeny of the animals represented by graphs *BB*. Graph *DD* represents the record of the one female of the fourth generation that has reached reproductive age. It is to be noted that the growth curves of Donaldson, even those for rats fed from selected table scraps, are materially lower than those for the animals fed on a canned food diet. It is to be noted also that succeeding generations of rats make as good growth as the first generation fed on canned foods.

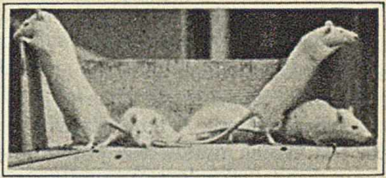

Figure 3—Rats 90 Days Old, Fed on Canned Foods from Time of Birth
Mother also reared on canned food

On Chart 2 is recorded the average growth curve of four male and of four to five female guinea pigs over the course of a year. These animals were placed on a canned food diet when their weight varied from 320 to 430 grams.

The numbers on the graph representing the females are the number of young per litter. One female died in parturition as indicated by an asterisk.

The graphs on Chart 3 represent the growth and reproductions of guinea pigs that have had only canned foods from time of birth, except for the milk of their mothers that subsisted on canned foods alone. They are the progeny of the animals represented by Chart 2. The *B* series represent the

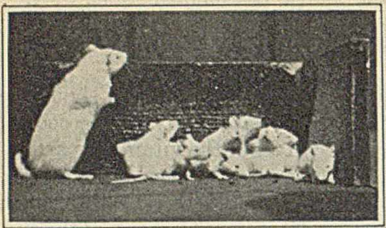

Figure 4—Mother and 28-Day-Old Litter, Representing Third and Fourth Generations of Rats Fed on Canned Foods Only

second and the *C* series the third generation on a canned food diet. The numbers on the graphs representing the females are the number per litter of young.

Figures 1 to 4 are photographs of typical animals on a diet made up exclusively of canned foods.

Summary

Three pairs of young guinea pigs, weighing from 320 to 430 grams, and one pair 3 weeks of age, and three pairs of young rats, 28 days of age, weighing from 53 to 56 grams, were placed on a diet consisting wholly of canned foods sterilized by heat. The plan is to feed such animals a similar diet over a number of generations. The foods are not irradiated nor do the animals receive irradiation nor direct rays of the sun. The experiment has been in progress about 15 months. During this time, the animals were mated and bred so that in a little over a year the fifth generation of rats and the third generation of guinea pigs was reached. They are thriving as well as is indicated by any record of these species. Reproduction is as prolific as can be expected, the size of the litters is normal in every way, and no difficulty is encountered in lactation. The rate of growth and weight at maturity is much higher than that reported as normal. In explanation of this, it is suggested that either a diet more nearly the optimum than usual for these species results from the combination of foods selected, or there is some heretofore unrecognized advantage in a diet made up wholly of canned (cooked) foods. The evidence indicates that canned foods may supply every dietary requirement, including vitamins B (B_1) and C, so often referred to as heat labile.

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Salmon Oil and Canned Salmon as Sources of Vitamins A and D[1]

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Bureau of Fisheries, Department of Commerce, and Bureau of Chemistry and Soils, Department of Agriculture, Washington, D. C.

Commercial salmon oil is an important source of vitamin D, but the commercial oil now produced is not representative in quality of the oil that can be produced from the standpoint of potency of vitamins A and D. The oil now produced is used largely for technical purposes, and the annual production is approximately 300,000 gallons. This quantity can be increased threefold by using products which are now discarded. The canned salmon consumed in this country carries a vast supply of vitamin D that has hitherto received little, if any, recognition.

The present annual production of salmon oil in this country is approximately 300,000 gallons (*11*). However, the quantity of oil that can be produced greatly exceeds this figure. There are about 500,000,000 pounds of salmon caught annually in the United States and Alaska of which 25 to 30 per cent becomes waste when the fish is canned. The waste will yield 15 to 20 gallons of oil per ton, which makes the potential production of salmon oil about 1,000,000 gallons annually.

In a study of the vitamin content of commercial fish oils, Nelson and Manning (*8*) found that a salmon oil was 50 per cent as potent in vitamin D as a medicinal cod-liver oil and that its vitamin A content was equal to the poorer grades of medicinal cod-liver oil. Other investigations have previously shown that oil from salmon contains vitamins A and D (*1*, *2*, *3*). Manning, Nelson, and Tolle (*6*) found that the vitamin D content of menhaden fish oil is influenced in part by the heat treatment to which the oil is subjected in the process of production. Because of the large potential production of salmon oil and the possibility of improving the quality of the oil by proper production methods, this product has been studied further. The studies herein reported were designed to obtain further information with respect to the vitamin content of oil prepared carefully from salmon offal, oil from canned salmon, and commercial salmon oils.

Sources of Materials

Samples of commercial oil were obtained from oils available on the market. Samples of oil were prepared from the canned offal of five species of salmon. The offal was obtained from fresh fish, placed in tin cans. The cans were evacuated and then heated in a retort for 5 hours at 212° F. (100° C.). When the cans arrived at the laboratory they were opened, the contents transferred to a hand press and the water and oil expressed. The oil was then separated from the water and suspended material, by centrifuging. Commercially canned salmon of five different species were obtained from packers. The oil was recovered in the same manner as from the salmon offal.

For a number of years cod-liver oil has been a recognized source of vitamins A and D. Examination of thirty-seven samples of medicinal cod-liver oil, for the Food and Drug Administration, United States Department of Agriculture,[2] has shown that only two of these oils varied more than 25 per cent in vitamin D potency from one of the samples chosen as a standard of reference. Some of these oils were found to be fully six times as potent as others in vitamin A. The cod-liver oil used for comparison in these studies was representative of the average medicinal cod-liver oil in vitamin D potency and considerably above the average in vitamin A potency.

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[1] Received June 1, 1931. Presented before the Division of Biological Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Nelson, E. M., unpublished data.

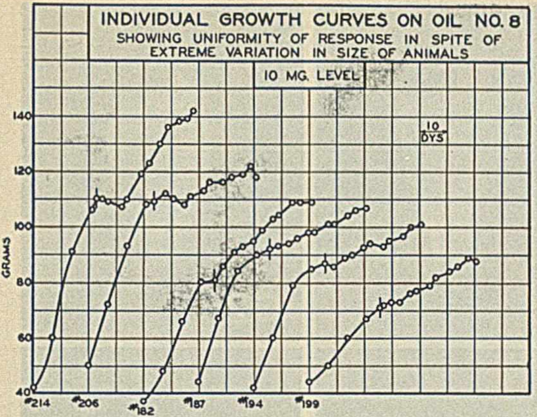

Chart 1

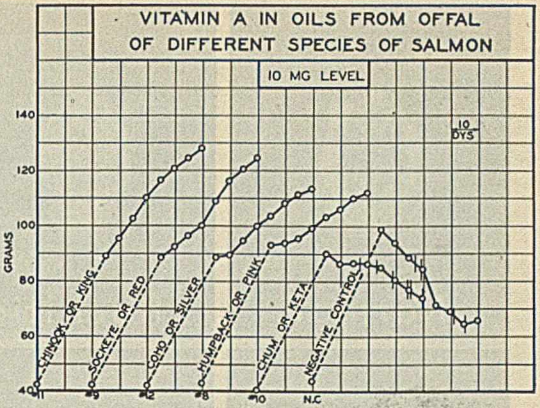

Chart 2

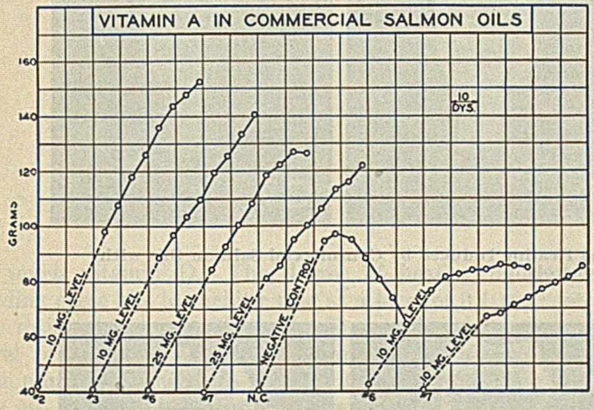

Chart 3

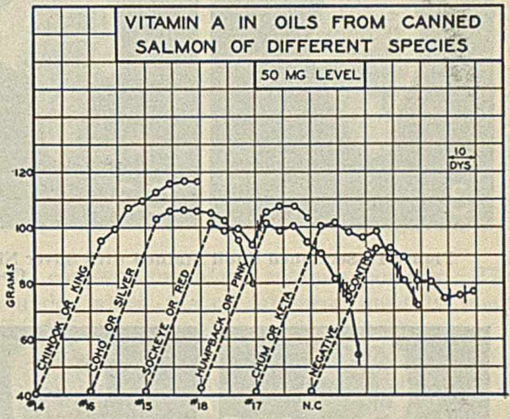

Chart 4

Biological Tests

Curative tests for vitamin A were conducted in the same manner as described by Nelson and Manning (*8*). Albino rats weighing approximately 40 to 45 grams were placed upon an A-deficient ration until stores of vitamin A had been depleted. When they showed distinct symptoms of ophthalmia, the curative tests were begun. This occurred in 21 to 26 days from the time of weaning. Their vitamin A storage had been controlled by the technic described by Nelson (*7*) which has proven more satisfactory to the authors than the common practice of keeping the stock ration low in vitamin A at all times when the young animals are to be used in vitamin A tests. The A-free ration had the following composition:

Alcohol extracted casein	18	Yeast	8
Salt Mixture IV (*9*)	4	Dextrinized corn starch	67
Agar	2	Peanut oil	1

One-sixteenth of the yeast used had been exposed to the rays of a quartz mercury-vapor lamp and it had been shown that this quantity of the irradiated product carried an adequate amount of vitamin D. The oils to be tested were diluted with peanut oil so that 0.1 cc. of the diluted oil carried the desired daily dose. This quantity of oil was measured into a glass dish with a pipet and placed before the animals.

Chart 1 shows the response of six rats from six different litters, all fed the same level of salmon oil. In this group there was the largest variation in weight at the time of weaning and also the greatest difference in gain in weight during the period of vitamin A depletion of any of the groups. The oil feeding was begun at the point indicated by a short vertical line intersecting the growth curve and consisted of 10 mg. per day of salmon oil No. 8, obtained from the offal of pink salmon. Most of the animals weighed 40 to 45 grams at the time of weaning. To maintain a uniform average starting weight in all the groups, the group which contained the animal having the maximum weight also contained the animal having the minimum weight at the time of weaning. Attention is called to the fact that all of the animals in this group were put upon the curative tests before their weights had become stationary. The average weights at the time of weaning and at the beginning of the curative period are indicated, and average weights at regular intervals during the 5-week test period are plotted. In the remaining charts the results have been summarized by plotting composite growth curves.

The curves shown in Chart 2 summarize the results of feeding 10 mg. daily of oil from the offal of salmon of different species as a source of vitamin A. Each curve is a composite representing the average performance of six rats, and the animals in each group are comparable as to parentage and sex. The portion of the curves indicated by a broken line indicates the average change in weight from the time of weaning until curative tests were begun. It is apparent that the oils vary widely in their vitamin A potency and there was a rather striking correlation between depth of color and vitamin potency. The oils which showed a distinct reddish cast, such as chinook and sockeye, contained much more vitamin A than chum, which had practically no red color and gave practically no response when fed at a 10-mg. level. The other oils, intermediate in color, were also intermediate in vitamin potency. Oil 10 was fed at a 50-mg. level in subsequent tests, at which level it produced fully as good growth as 10 mg. of oil 11. Each vertical line intersecting the last two curves indicates a point at which an animal died.

A number of preliminary tests were made on commercial salmon oils before the level was established at which the desired response could be obtained. The results obtained on oils 6 and 7 in these tests are shown in the two curves

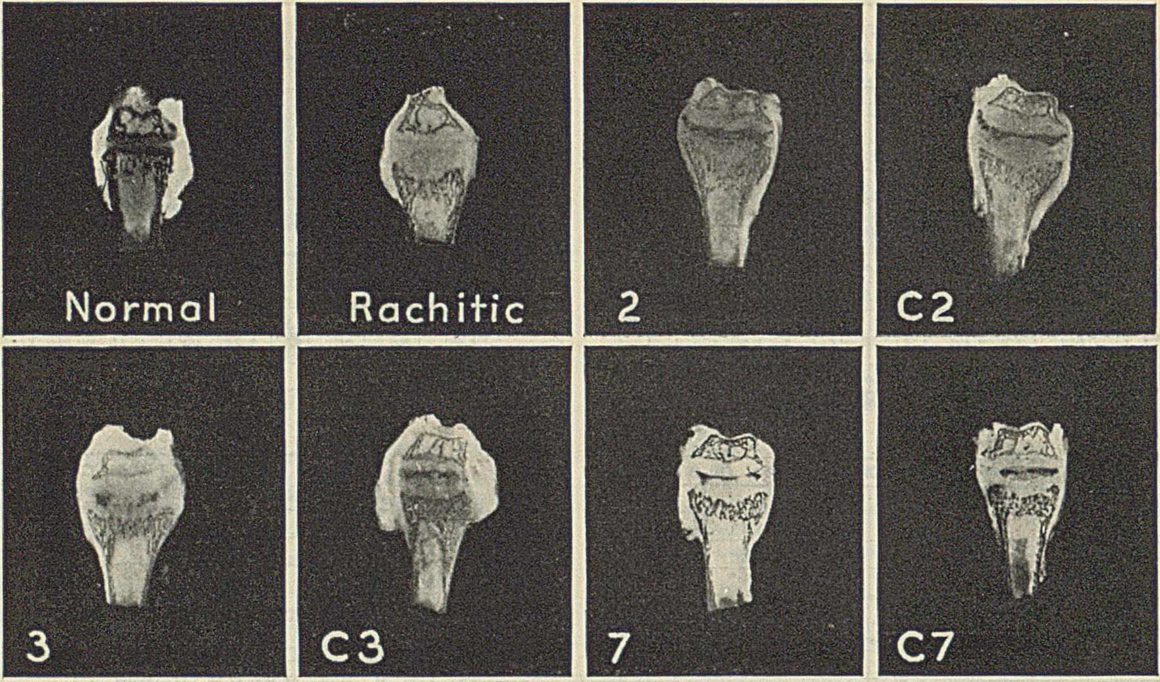

Figure 1—Sectioned Radii Stained with Silver Nitrate Showing Healing Induced by Commercial Salmon Oils with Cod-Liver Oil Controls

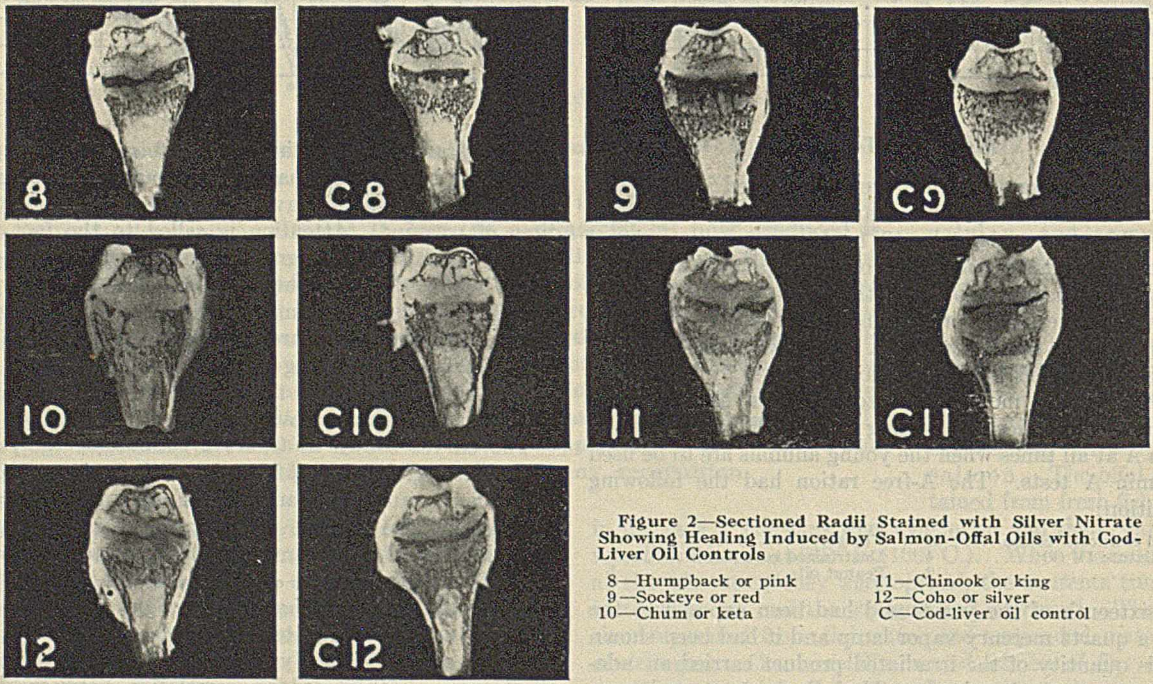

Figure 2—Sectioned Radii Stained with Silver Nitrate Showing Healing Induced by Salmon-Offal Oils with Cod-Liver Oil Controls

8—Humpback or pink
9—Sockeye or red
10—Chum or keta
11—Chinook or king
12—Coho or silver
C—Cod-liver oil control

at the extreme right of Chart 3. The remaining tests on commercial oils were carried out in one experiment on comparable animals. In vitamin A potency, these oils are all within the range of the oils prepared from canned offal. The significance of the broken portions of the curves is explained in the preceding paragraph.

The oils from commercially canned salmon of different species are not a particularly good source of vitamin A. These oils were first fed at a level of 10 mg. per day, but there was practically no response so that all of the oils were subsequently fed at a level of 50 mg. daily. The results obtained are shown in Chart 4.

Vitamin D tests were conducted in exactly the same manner as previously described (*8*). The results obtained by line tests are shown by photographic representations. The tests were made by using a litter of rats, feeding one-half of the litter 0.1 per cent of cod-liver oil during the curative period and the other half of the litter the desired level of the oil under examination. The bone of one animal, which was representative of the response obtained with salmon oil, was photographed. The results of the tests are given in Figures 1, 2, and 3.

As shown in Figure 1, of the three commercial salmon oils tested for vitamin D, two, 2 and 7, were found to have approximately the same vitamin D potency as a medicinal cod-liver oil, whereas the third contained about one-half

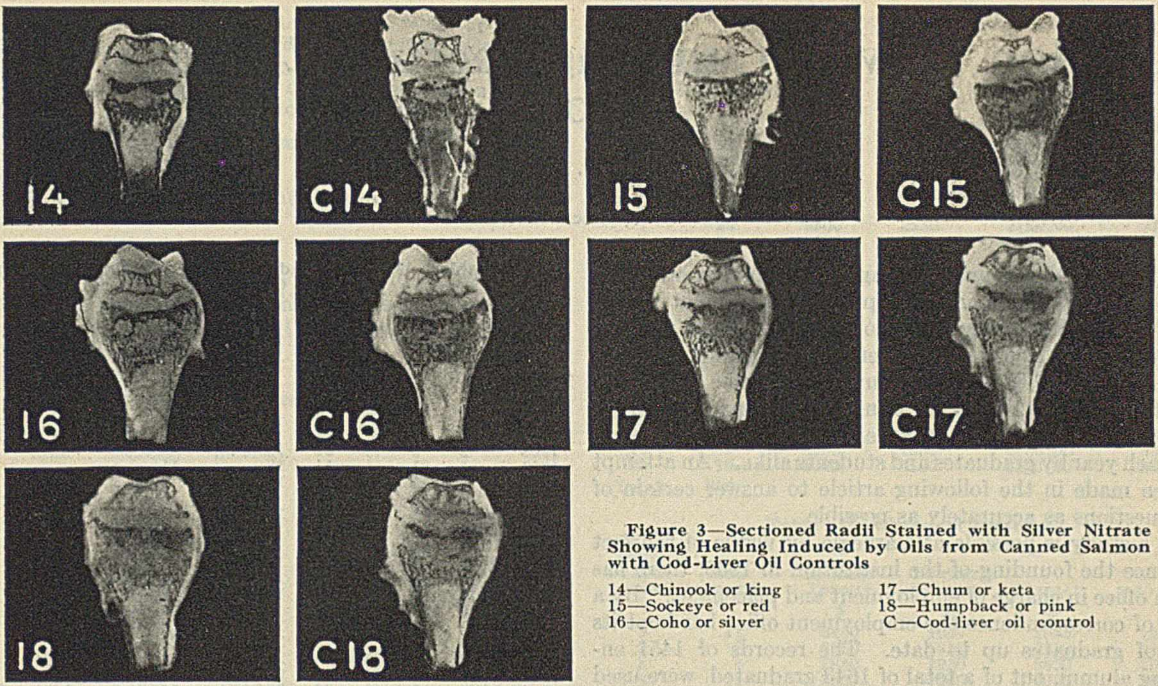

Figure 3—Sectioned Radii Stained with Silver Nitrate Showing Healing Induced by Oils from Canned Salmon with Cod-Liver Oil Controls

14—Chinook or king	17—Chum or keta
15—Sockeye or red	18—Humpback or pink
16—Coho or silver	C—Cod-liver oil control

as much vitamin D. The degree of healing induced by feeding these oils to rachitic rats at a level of 0.1 per cent of the ration, together with the healing produced by the same level of cod-liver oil, is shown in the photomicrographs. The number on the plate refers to the laboratory number of the oil. The prefixed letter, C, refers to the cod-liver oil control for that oil. Oil 3 was subsequently fed at higher levels, and it was found that 0.2 per cent of this oil in the ration induced the same degree of healing as 0.1 per cent of the cod-liver oil control. In the upper left hand corner of the figure are reproductions of bones similarly prepared and stained, one showing normal calcification and the other the degree of rickets produced in 30 days on the diet used.

As shown in Figure 2, oils from the offal of salmon of five different species were found to be excellent sources of vitamin D. Three of the oils, 8, 9, and 11, were fully twice as potent as a medicinal cod-liver oil; one oil, 10, about 50 per cent more potent; and another, 12, approximately equal to cod-liver oil in vitamin D. The photomicrographs show the healing induced by 0.05 per cent of salmon oil in the ration as compared to 0.1 per cent of cod-liver oil, using littermate animals.

As shown in Figure 3, oils obtained from commercially canned salmon are fully equal to a medicinal cod-liver oil in vitamin D potency. The oils were all fed at a level of 0.1 per cent in the ration together with littermate controls receiving the same level of cod-liver oil. Subsequent tests with lower levels of salmon oil showed that oils 15 and 18 were approximately twice as potent in vitamin D as the cod-liver oil.

Conclusions

The results obtained show that salmon oil can be produced which is equal to good grades of cod-liver oil in vitamin A content and approximately twice as potent as cod-liver oil in vitamin D. Commercial salmon oils now on the market show considerable variation in their nutritive value. This is due to a number of factors. Salmon oils have not been prepared particularly as a source of vitamins. The species of salmon used as a source of material will determine to a large extent the possible vitamin content of the oil. The heat treatment to which the oil is subjected must be controlled to conserve maximum vitamin potency. The conditions under which the oil is stored must be considered if the oil is to retain its maximum value in feeding.

The value of marine products in providing vitamin D in the diet of the American people is not generally recognized. Among the foods commonly eaten, eggs and dairy products alone are considered as carrying appreciable quantities of this vitamin. It has been shown that oysters and clams contain vitamin D[3] (*4, 5*), and canned fish must also be considered as a source of vitamin D. Statistics show that there are approximately 300,000,000 pounds of canned salmon produced annually in this country. This fish contains from 6 to 15 per cent of oil (*10*). From the data obtained on vitamin D content of the oil in canned salmon, it is quite apparent that there is more vitamin D in the canned salmon sold in this country than in the cod-liver oil used for both human and animal feeding.

Acknowledgment

The commercial oils were kindly furnished by four salmon-oil producers on the Pacific coast.

The samples of canned salmon were obtained through the kind coöperation of E. D. Clark, director of the Northwestern Branch of the National Canners Association, Seattle, Washington.

The canned offal was prepared by Harry R. Beard, director of Scientific Research, New England Fish Company, Vancouver, Canada.

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[3] Unpublished data. It has been shown that the ether-soluble material in oysters saponified with alcoholic potash carries appreciable quantities of vitamin D.

Relation between an Engineering Education and Income[1]

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How do the salaries of engineers compare with the salaries of men in other professions? What groups in the engineering profession receive the best salaries? How do the salaries of the engineering graduates of the Carnegie Institute of Technology compare with the salaries of graduates from other engineering institutions generally?

These questions and many others of a similar nature are asked each year by graduates and students alike. An attempt has been made in the following article to answer certain of these questions as accurately as possible.

Such a study is possible at Carnegie by virtue of the fact that, since the founding of the institution in 1905, there has been an office in charge of employment and placement. By a system of correspondence the employment office has kept its record of graduates up to date. The records of 1451 engineering alumni, out of a total of 1643 graduated, were used in this report. This includes all of the available records of Carnegie engineering alumni.

Some difficulty was experienced in obtaining figures that could be compared to the Carnegie statistics. Owing to reasons that will appear obvious later, it is necessary to interpret the results conservatively. It must be borne in mind that the cost of living varies greatly in different parts of the country. More than half of the Carnegie alumni are located in the Pittsburgh district where living costs and salaries are relatively high.

The first study attempts to compare the salaries received by Carnegie graduates during 1929 and 1930 with the results reported from a study made by the Society for the Promotion of Engineering Education of the salaries received by a group of engineers in various parts of the country. Table I shows the numbers and types of Carnegie engineering graduates by years as well as the number of alumni from each department. The bureau has been in touch with 88 per cent of these men during the past two years.

Table I—Numbers and Types of Carnegie Engineering Graduates

Year	Chemical	Civil	Commercial	Electrical	Mechanical	Mining	Metallurgical	Chemistry	Physics	Mathematics	Sanitary	Total
1908	2	8	..	21	16	..	8	..	..	.	.	55
1909	3	21	..	14	18	..	11	..	..	.	.	67
1910	5	5	..	3	12	3	2	..	..	.	.	30
1911	1	6	..	12	2	..	1	..	..	.	2	24
1912	6	15	..	9	17	2	7	..	..	.	.	56
1913	5	15	5	13	13	3	5	..	..	.	2	61
1914	6	10	11	11	12	2	5	..	..	.	.	57
1915	12	8	10	15	13	1	5	..	..	.	1	65
1916	12	13	11	15	11	..	2	..	..	.	.	64
1917	10	9	13	19	19	3	5	..	..	.	.	78
1918	3	10	4	11	9	..	4	..	..	.	1	42
1919	13	6	3	8	12	..	2	..	..	.	.	44
1920	18	13	18	13	24	3	14	3	2	.	.	108
1921	20	11	23	19	26	1	10	5	3	.	1	119
1922	16	15	22	19	26	12	10	..	3	.	.	123
1923	6	9	19	30	33	4	15	3	1	.	.	120
1924	7	9	19	23	24	4	8	1	2	.	.	97
1925	3	7	17	23	24	2	4	5	2	.	.	87
1926	9	19	22	22	9	1	3	3	6	.	.	94
1927	6	8	17	27	12	4	3	1	1	1	.	80
1928	7	16	12	21	15	..	4	1	2	2	.	80
1929	4	19	22	19	17	1	8	..	2	.	.	92
Total	174	252	248	367	364	46	136	22	24	3	7	1643

This information was secured by a card (see Figure 1) which was sent to all alumni. By use of a salary code (see Figure 2) the graduate was asked to give his approximate salary as well as the wage he would consider in changing his position. This last-named information is valuable to the bureau in its system of upgrading in alumni placements.

The tabulation of the approximate salaries, as reported by all engineering graduates, is shown in Table II.

For methods of comparison, it was necessary to determine the median wage. The following procedure was used:

The median term was located by dividing the number of terms plus one by two. Hence,

$$\frac{n+1}{2} = \frac{163+1}{2} = 82 \text{ (see total, first year, Table II)}$$

The median group is that group which contains the 82 term. By inspecting the cumulative entries, it is apparent that this is the D group, salary $1800–2100.

Table II—Salaries Reported by Engineering Graduates

Years since graduation...........	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Y Over $50,000	...	..	..	..	...	..	...	..	..	...	1	..	...	...	..	..	..	...	...	...	...	...
W 35,000–50,000	...	..	..	..	...	..	...	..	..	...	...	..	...	...	..	..	..	...	...	...	...	...
V 25,000–35,000	...	..	..	..	...	..	...	..	..	...	...	..	...	...	..	1	..	1	...	1	...	...
U 20,000–25,000	...	..	..	..	...	..	...	..	..	...	3	..	1	1	..	..	..	...	...	...	...	...
T 15,000–20,000	...	..	..	..	1	..	...	..	1	...	...	..	...	...	1	..	..	...	1	...	1	1
S 12,000–15,000	...	..	..	..	1	1	...	1	..	1	1	..	...	1	3	..	3	2	...	2	...	2
R 10,000–12,000	...	1	..	..	...	..	1	..	1	2	1	..	6	2	3	3	4	2	1	2	1	3
Q 9,000–10,000	...	..	..	..	...	..	1	..	2	...	...	..	4	...	1	1	..	1	...	...	1	...
P 8,000– 9,000	...	..	..	..	...	..	3	2	..	2	...	2	4	1	2	4	..	2	...	1	1	4
O 7,000– 8,000	...	..	..	..	1	..	...	1	3	4	2	..	3	1	4	4	..	1	1	3	...	1
N 6,000– 7,000	...	..	..	..	1	2	2	9	7	8	3	5	7	3	5	3	4	2	3	5	4	1
M 5,000– 6,000	...	1	..	1	6	7	7	4	5	14	6	4	15	10	5	5	8	3	3	5	...	4
L 4,500– 5,000	3	1	2	2	2	4	6	12	10	6	2	2	4	10	9	2	..	4	5	2	4	5
K 4,000– 4,500	2	2	..	3	8	7	11	15	11	13	6	6	8	4	3	2	3	4	...	2	1	2
J 3,600– 4,000	1	2	3	11	13	14	17	22	19	11	3	4	5	6	4	4	5	5	...	...	4	1
I 3,300– 3,600	5	3	5	10	7	12	17	8	8	6	6	6	5	2	2	3	2	1	2	...	1	2
H 3,000– 3,300	2	4	6	15	14	14	11	7	8	8	3	2	...	3	2	2	2	3	2	...	...	2
G 2,700– 3,000	5	18	19	17	13	16	10	7	2	4	3	2	3	1	1	1	2	1	...	...	1	...
F 2,400– 2,700	9	10	21	18	17	9	6	8	7	1	...	4	4	2	2	1	4	...	...	1	...	...
E 2,100– 2,400	21	25	17	13	14	2	5	..	1	2	3	..	1	1	1	..	..	...	...	...	...	...
D 1,800– 2,100	50	21	10	5	4	3	1	..	..	...	1	..	...	...	1	1	..	...	...	...	1	...
C 1,500– 1,800	40	8	4	2	2	..	...	3	..	...	...	..	...	...	..	..	..	1	...	...	...	...
B 1,200– 1,500	19	1	..	..	...	..	...	..	..	...	...	..	...	...	..	..	..	1	...	...	...	...
A 900– 1,200	6	..	..	..	...	..	...	..	..	...	...	..	...	...	..	..	..	...	...	...	...	...
Total	163	97	87	97	104	91	98	99	85	82	44	37	70	48	49	37	37	34	18	24	20	28
$\frac{n+1}{2}$ = median	82	49	44	49	52.5	46	49.5	50	43	41.5	22.5	19	35.5	24.5	25	19	19	17.5	9.5	12.5	10.5	14.5
First quartile	41	24.5	22	24.5	26.25	23	24.75	25	21.5	20.75	11.25	9.5	17.75	12.25	12.5	9.5	9.5	8.75	4.75	6.25	5.25	7.25
Third quartile	123	73.5	66	73.5	78.75	69	74.25	75	64.5	62.25	33.75	28.5	53.25	36.75	37.5	28.5	28.5	26.25	14.25	18.75	15.75	21.75

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[1] Received July 6, 1931.

[2] Secretary of the Bureau of Recommendations, Carnegie Institute of Technology.

The median value is approximated by interpolating within the median group on the assumption of an equal distribution within the class. Hence, following the procedure outlined:

82 − 65 (number of items below median group in A, B, & C group) = 17 (number of items required in the median group).

$\frac{17}{50} \times 300 = 102$ (distance of the median value from the lower limit of the group).

Therefore 1800 + 102 = 1902, the median wage for men out one year.

By this method a detailed study was made of the salaries received by the graduates from the various engineering departments and the results recorded in Tables III to IX.

Table III—Metallurgical Engineers

Years Since Graduation	Men Reporting	Highest Income	Lowest Income	Median	Average
		$	$	$	$
1	13	4750	1650	2175.00	2488.46
2	6	4750	1950	3150.00	3250.00
3	3	3450	2250	.....	2750.00
4	5	3800	2250	3733.33	3300.00
5	5	5500	2550	4000.00	3790.00
6	6	4250	1950	3075.00	3033.33
7	11	4750	2250	3450.00	3422.73
8	9	8500	3150	4000.00	4733.33
9	8	5500	2550	4125.00	3881.25
10	12	6500	2250	3450.00	3895.83
11	2	22500	3800	.....	13150.00
12	2	4250	2550	.....	3400.00
13	7	11000	3800	8000.00	7364.29
14	2	4750	4750	.....	4750.00
15	7	13500	2550	6500.00	6578.57
16	3	11000	3800	.....	6200.00
17	2	3800	3150	.....	3475.00
18	6	11000	3800	7500.00	6925.00
19	1	6500	..	.....	6500.00
20	3	13500	4750	.....	8583.33
21	4	17500	4750	.....	9312.50
22	6	17500	5500	12750.00	11000.00
Total	123				

Table IV—Commercial Engineers

Years since Graduation	Men Reporting	Highest Income	Lowest Income	Median	Average
		$	$	$	$
1	33	3450	1050	1827.27	1831.82
2	16	11000	1650	2350.00	3000.00
3	20	4750	1650	2625.00	2617.50
4	18	4750	1950	3037.50	3047.22
5	23	13500	1650	3600.00	3884.78
6	16	5500	2250	3250.00	3521.88
7	11	6500	2250	4125.00	3854.55
8	14	17500	2550	4187.50	5817.86
9	18	9500	2250	4625.00	4738.89
10	16	11000	3150	5125.00	5062.50
11	9	13500	3450	5500.00	6105.56
12	4	6500	5500	.....	6250.00
13	8	11000	4250	6250.00	6781.25
14	7	11000	2250	4750.00	5235.71
15	..	...	..	.....	.....
16	4	8500	2550	.....	6512.50
Total	217				

Table V—Mechanical Engineers

Years since Graduation	Men Reporting	Highest Income	Lowest Income	Median	Average
		$	$	$	$
1	22	3800	1350	1992.86	2102.27
2	20	3800	1350	2587.50	2552.50
3	14	3150	1950	2575.00	2528.57
4	20	5500	2250	2950.00	3102.50
5	24	17500	2250	3175.00	3804.17
6	21	5500	1950	3733.33	3750.00
7	21	11000	1950	3733.33	4350.00
8	25	13500	1650	4000.00	4384.00
9	21	17500	3150	4250.00	5297.62
10	20	13500	3150	4450.00	5340.00
11	8	6500	2850	5500.00	4900.00
12	13	6500	2550	3733.33	3884.61
13	20	11000	2550	5500.00	5772.50
14	8	5500	3150	4250.00	4275.00
15	17	17500	1950	7000.00	7517.65
16	8	11000	2850	6500.00	6668.75
17	12	13500	2550	4416.67	6475.00
18	7	13500	3150	6000.00	6214.29
19	5	17500	4750	5000.00	7450.00
20	10	30000	4250	6750.00	8950.00
21	5	11000	3800	5000.00	6570.00
22	8	11000	3150	4375.00	5393.75
Total	329				

Table VI—Electrical Engineers

Years since Graduation	Men Reporting	Highest Income	Lowest Income	Median	Average
		$	$	$	$
1	44	4750	1050	1922.73	2063.63
2	23	2850	1650	2228.56	2250.00
3	24	4750	1950	2550.00	2668.75
4	13	4750	2250	2900.00	3061.54
5	21	5500	1950	2880.00	2997.62
6	22	4750	2250	3175.00	3202.27
7	24	8500	2250	3720.00	3797.92
8	24	6500	2550	3720.00	3718.75
9	15	9500	2550	3933.33	4316.67
10	8	7500	3800	5750.00	5731.25
11	6	50000	1950	7500.00	13008.33
12	8	6500	2550	4375.00	4243.75
13	12	22500	3800	5125.00	6341.67
14	12	7500	3150	4916.67	4829.17
15	12	13500	3450	4916.67	5920.83
16	8	30000	3150	5625.00	8237.50
17	7	13500	2850	5666.67	6164.28
18	9	13500	1650	4666.67	5155.55
19	2	7500	3450	.....	5475.00
20	2	6500	5500	.....	6000.00
21	7	6500	1950	4750.00	4528.57
22	10	11000	3150	5500.00	6335.00
Total	313				

Table VII—Chemical Engineers

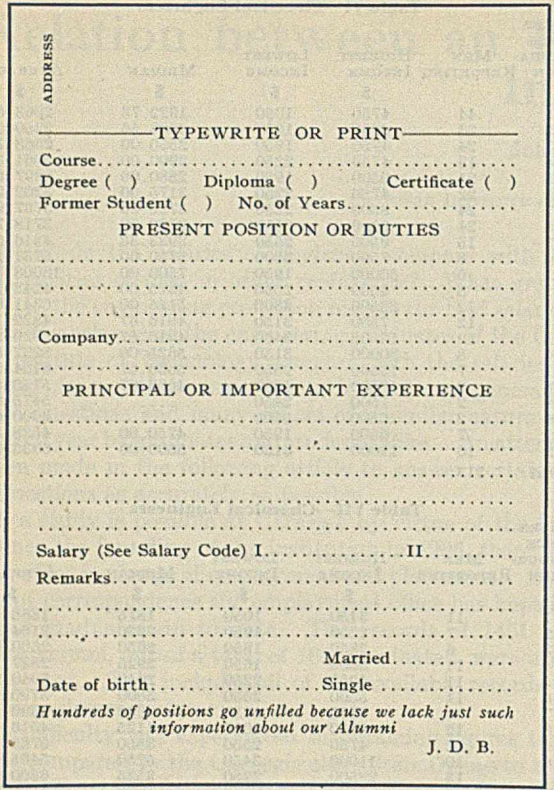
Years since Graduation	Men Reporting	Highest Income	Lowest Income	Median	Average
		$	$	$	$
1	11	3450	1050	1875	1868.18
2	7	2250	1950	2220	2164.28
3	6	2850	1950	2650	2600.00
4	11	3800	1650	2925	2827.27
5	11	4250	2250	2640	3040.91
6	11	5500	2550	3800	3790.91
7	11	5500	2250	3360	3390.91
8	12	6500	1650	4125	4016.67
9	12	4750	2550	3850	3766.67
10	10	11000	3450	5250	5465.00
11	13	22500	2250	3525	6300.00
12	5	5500	2850	4000	4100.00
13	8	9500	2550	6500	5700.00
14	4	13500	3800	..	7325.00
15	6	6500	2250	5250	4608.33
16	2	3450	3450	..	3450.00
17	4	13500	2550	..	6100.00
18	1	4250	..	..	4250.00
19	2	11000	6500	..	8750.00
20	3	8500	5500	..	7166.67
22	1	5500	..	..	5500.00
Total	151				

Table VIII—Civil Engineers

Years since Graduation	Men Reporting	Highest Income	Lowest Income	Median	Average
		$	$	$	$
1	31	3450	1350	1875	1950.00
2	17	3800	1950	2775	2694.12
3	11	3450	1950	2500	2495.45
4	19	3800	1950	2850	2757.89
5	8	6500	2250	2925	3293.75
6	9	13500	2550	3000	4877.78
7	12	6500	2850	4250	4308.33
8	11	6500	2550	4750	4522.73
9	6	4750	2550	3800	3558.33
10	11	8500	2550	4500	4468.18
11	5	5500	2850	4250	4130.00
12	5	8500	3150	4500	5570.00
13	11	11000	2550	3600	5154.55
14	15	22500	2550	5000	6316.67
15	7	9500	2550	3800	4428.57
16	11	8500	1950	4500	5354.54
17	10	11000	2550	5833	5590.00
18	8	9500	2850	5500	5450.00
19	9	30000	3150	5000	7416.67
20	4	11000	4250	..	6625.00
21	4	6500	2850	..	4350.00
22	3	8500	4750	..	6250.00
Total	227				

Table IX—Mining Engineers

Years since Graduation	Men Reporting	Highest Income	Lowest Income	Median	Average
		$	$	$	$
1	1	1950	..	.....	1950.00
2	1	1950	..	.....	1950.00
3	5	3800	2850	3150.00	3160.00
4	3	3450	1650	.....	2750.00
5	5	4750	2250	3300.00	3240.00
6	3	3150	2550	.....	2950.00
7	5	9500	3150	4000.00	5080.00
8	5	6500	3450	3866.67	4270.00
9	2	6500	3450	.....	4975.00
10	2	3800	2850	.....	3325.00
13	4	11000	2250	.....	5400.00
17	2	3800	3450	.....	3625.00
20	2	11000	6500	.....	8750.00
Total	40				



ADDRESS

TYPEWRITE OR PRINT

Course..

Degree ( ) Diploma ( ) Certificate ( )

Former Student ( ) No. of Years..................

PRESENT POSITION OR DUTIES

Company...

PRINCIPAL OR IMPORTANT EXPERIENCE

Salary (See Salary Code) I...............II..........

Remarks...

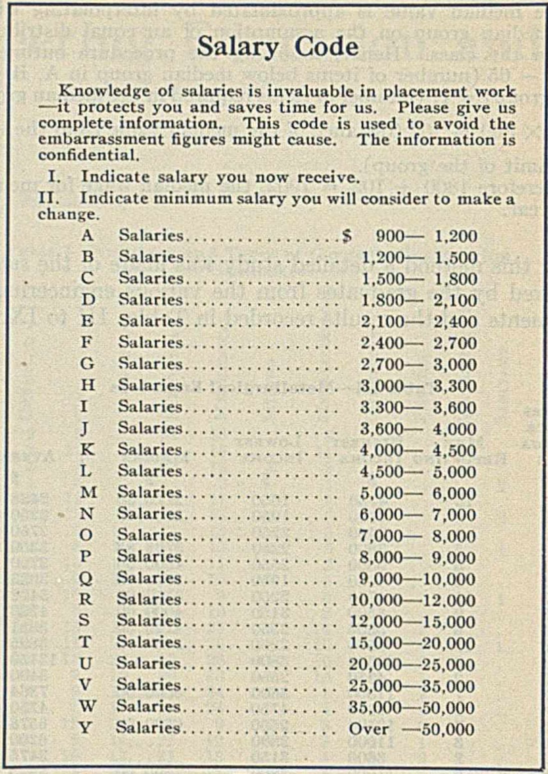
Married.............

Date of birth...................Single ....

Hundreds of positions go unfilled because we lack just such information about our Alumni

J. D. B.

Figure 1



Salary Code

Knowledge of salaries is invaluable in placement work—it protects you and saves time for us. Please give us complete information. This code is used to avoid the embarrassment figures might cause. The information is confidential.

I. Indicate salary you now receive.

II. Indicate minimum salary you will consider to make a change.

A	Salaries	$ 900— 1,200
B	Salaries	1,200— 1,500
C	Salaries	1,500— 1,800
D	Salaries	1,800— 2,100
E	Salaries	2,100— 2,400
F	Salaries	2,400— 2,700
G	Salaries	2,700— 3,000
H	Salaries	3,000— 3,300
I	Salaries	3,300— 3,600
J	Salaries	3,600— 4,000
K	Salaries	4,000— 4,500
L	Salaries	4,500— 5,000
M	Salaries	5,000— 6,000
N	Salaries	6,000— 7,000
O	Salaries	7,000— 8,000
P	Salaries	8,000— 9,000
Q	Salaries	9,000—10,000
R	Salaries	10,000—12,000
S	Salaries	12,000—15,000
T	Salaries	15,000—20,000
U	Salaries	20,000—25,000
V	Salaries	25,000—35,000
W	Salaries	35,000—50,000
Y	Salaries	Over —50,000

Figure 2

Inspection of these tables shows that the highest salaries were received by the graduates of the Metallurgical and Commercial Engineering Departments and the lowest by the Mining and Civil Departments.

The salary at the upper boundary of the minimum 25 per cent and the lower boundary of the maximum 25 per cent of all the Carnegie engineering graduates was calculated in the same manner as the median wage, from the first and third quartile figures. These data were derived so that a comparison with results of salary studies published by the Society for the Promotion of Engineering Education could be made. The results of this survey of all Carnegie engineering graduates are shown in Table X. These results are shown graphically in Figure 3.

Table X—Comparative Salaries of Carnegie Engineering Graduates

Years since Graduation	Men Reporting	Upper Boundary of Minimum 25%	Median	Lower Boundary of Maximum 25%	Average
		$	$	$	$
1	163	1620	1902	2214	2024.54
2	97	2021	2328	2842	2565.46
3	87	2241	2586	2921	2633.33
4	97	2475	2894	3405	2968.56
5	104	2510	3054	3838	3482.21
6	91	2869	3350	3971	3641.21
7	98	3075	3591	3329	3955.61
8	99	3300	3909	4708	4220.20
9	85	3431	3958	4925	4565.29
10	82	3588	4365	5804	4895.12
11	44	3363	4292	6250	7006.81
12	37	3375	4083	5625	4448.65
13	70	3980	5367	7417	6017.86
14	48	3817	4775	5775	5465.62
15	49	3950	5000	7623	6194.90
16	37	3750	5600	8125	6505.40
17	37	3525	5125	6625	5820.27
18	34	3740	4688	8125	6360.29
19	18	4575	5167	6750	6052.77
20	24	5250	6500	8750	7939.58
21	20	3825	4813	6938	5960.00
22	28	4525	5625	8938	7026.78

Total earnings of 1449 graduates, $5,711,500.
Average earnings of 1449 graduates, $3,942.

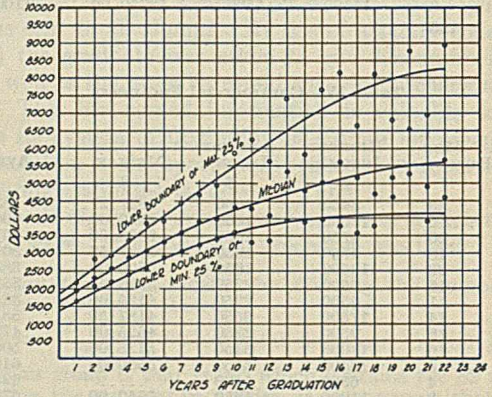


Figure 3—Range of Earnings of All Engineering Graduates, Carnegie Institute of Technology

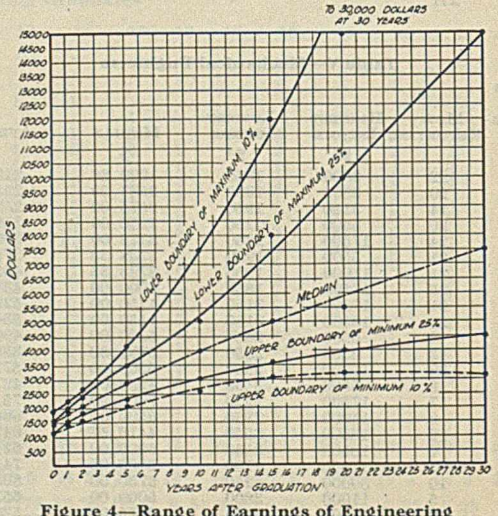


Figure 4—Range of Earnings of Engineering Graduates

The results of a similar study of 5123 engineering graduates as of June 1, 1924, made by the Society for the Promotion of Engineering Education (*2*) are shown in Figure 4.

It may be seen from a comparison of Figures 3 and 4 that the median yearly salary of Carnegie men for the first ten years out of school was higher than the median salary of other engineering graduates. After the ten-year period, the number of cases is so few that the results are not so reliable and have a greater deviation from the median curve line.

The average salaries received by Carnegie graduates in mechanical, electrical, and civil engineering are compared in Table XI with those of graduates of Land Grant Colleges and Universities in these same professions.

Table XI—Comparison of Salaries of Graduates of Carnegie and Land Grant Institutions

	Carnegie Institute of Technology		Land Grant Colleges and Universities	
Years since Graduation	Men reporting	Average salary	Men reporting	Average salary
		$		$
		MECHANICAL ENGINEERS		
1	22	2102	14	1893
2	20	2553	262	2293
5	24	3804	259	3186
10	20	5340	135	4581
15	17	7518	143	5606
20	10	8950	98	6306
		ELECTRICAL ENGINEERS		
1	44	2064	29	1810
2	23	2250	565	1989
5	21	2998	518	2889
10	8	5731	185	4231
15	12	5921	156	5357
20	2	6000	131	6452
		CIVIL ENGINEERS		
1	31	1950	28	1973
2	17	2694	459	2360
5	8	3294	362	3175
10	11	4468	207	4151
15	7	4429	246	5526
20	4	6625	148	6226

A comparison of the remuneration received by the members of the engineering profession with that received by the members of other professions was taken from a survey made by E. W. Lord (*1*) and is reprinted here by permission of the author in Table XII and Figure 5.

Table XII—Incomes of A. B. Graduates, Lawyers, and Physicians

Age	Men Reporting	Median Income	Highest Income
Years		$	$
		A. B. GRADUATES	
Under 25	62	1750	3600
25–29	74	2400	5200
30–34	102	3200	20000
35–39	111	4000	11000
40–44	83	5200	10000
45–49	61	5000	11738
50–54	34	5500	25000
55–59	19	5300	13800
60–64	7	6200	25000
65–69	2	(low) 3850	(high) 11000

		Median Income	Lowest Income	Highest Income
		$	$	$
		LAWYERS		
Under 25	12	2400	700	43000
25–29	17	2900	1150	25000
30–34	26	3900	950	15000
35–39	24	6000	1200	21000
40–44	17	8578	1350	30000
45–49	15	10600	2000	26000
50–54	11	11000	1800	43641
55–59	9	10000	3600	16500
60–64	8	9000	2200	14000
65–69	2	...	3500	16000
		PHYSICIANS		
Under 25	2	...	1750	1900
25–29	11	3200	2000	6000
30–34	11	4100	2000	8400
35–39	9	4800	2400	15000
40–44	7	4950	2000	10500
45–49	8	4700	2500	9000
50–54	6	6000	2400	16000
55–59	2	...	2500	13000
60–64	2	...	4500	9500

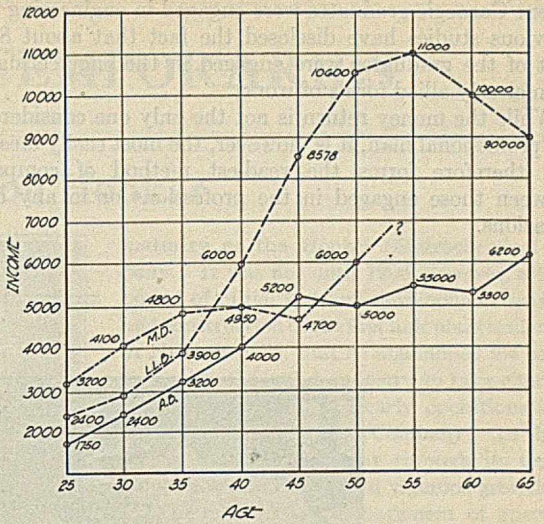


Figure 5—Median Income Curves of Lawyers, Doctors, and A.B. Graduates

In Figure 5 is shown the median income curve of lawyers and physicians, with that of A. B. graduates for comparison. In Figure 6 is the curve of the median wage received by Carnegie engineers at the same age on the graph shown in Figure 5. The age of graduation of Carnegie Engineers was assumed as 23. It may be seen therefore that the total income of Carnegie engineers over a twenty-year period compares favorably with the incomes of the members of other professions. It is generally conceded that the income of teachers and ministers is considerably lower than that of doctors and lawyers.

In view of the recent decline in wages and salaries, it may be supposed that the figures given in this study are relatively high. It may also be supposed, however, that this decline is taking place in all vocations to an equal extent.

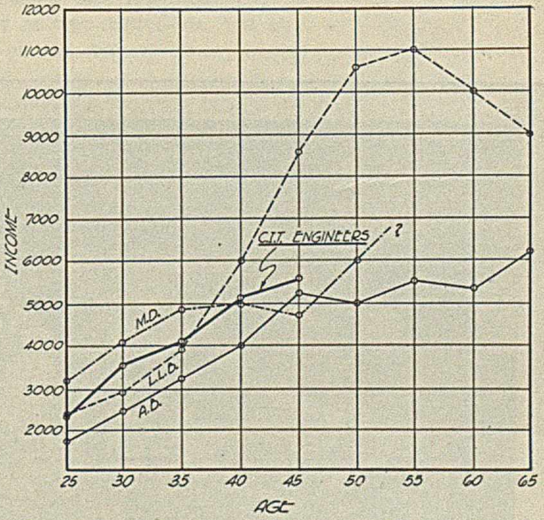


Figure 6—Comparison of Incomes of Graduates of Carnegie Institute of Technology with Those Shown on Figure 5

The relation between an engineering education and income has been forcibly demonstrated as far as the Carnegie Institute of Technology graduates are concerned by the fact that only 3 or 4 per cent of the alumni are unemployed at present (June, 1931). Estimates of the percentages of the total number of unemployed workers in the United States vary from 10 to 25 per cent.

In this study no attempt was made to ascertain to what extent Carnegie graduates were engaged in engineering work. Previous studies have disclosed the fact that about 80 per cent of the graduates were engaged in the engineering field or in closely allied forms of work.

While the money return is not the only one considered by the professional man, it is, however, the most easily measured and therefore forms the readiest method of comparison between those engaged in the professions or in any of the vocations.

Acknowledgment

Acknowledgment is made to Everett W. Lord for his permission in reprinting information contained in Tables XII, XIII, and XIV, and Figures 5 and 6.

Literature Cited

(1) Lord, E. W., "Relation of Education and Income," 1928.
(2) *Proc. Soc. Promotion Eng. Education*, **33**, 287 (1926).
(3) Survey Land Grant Colleges and Universities, *Bull.* **1**, Pt. V, No. 9, pp. 388–9 (1930).

THE ALCHEMICAL MAKING OF A MEDICINE IN THE SIXTEENTH CENTURY

This is a reproduction of a painting by Michael Z. Diemer in the Deutsches Museum, Munich.

L'ALCHIMIST

The original painting by David Teniers, the Younger, of this illustration is in the Royal Art Gallery in The Hague. It is reproduced here from an engraving by Perée, made from a drawing by Le Fort.

Illustrations reproduced through the courtesy of *The Percolator*, official organ of The Chemists' Club. New York.
[See IND. ENG. CHEM., **23**, 966 (1931).]

AMERICAN CONTEMPORARIES

Albert Huntington Hooker

A. H. Hooker

OLDEST of the five brothers now identified with the progressive and important Electrochemical Company which bears their name, "A. H." was born in Rochester, N. Y., November 26, 1865. His college education, chiefly at the University of Rochester, ran along somewhat unstereotyped lines. He took no regular course—his degree of M. S. was awarded *honoris causa* in 1920—but, partly through personal interest of some of his teachers (among them Professor Latimore and Henry Rachenbach), partly following his own bent, studied such chemical and technical subjects as his early realization that he did not desire to teach but to enter industry dictated. Two vacations spent working on bichromates at the Dighton Color Works, of which an uncle was the head, probably indicated some of these subjects; but the wide scientific curiosity which has always been one of his characteristics indicated more, and led him to take up such subjects as microscopy. "He was a bacteriologist when I first met him," his wife will tell you.

Such a course, however unconventional, at all events contained the essential elements of chemical engineering in a degree highly unusual at that date—or possibly even at this; and was an excellent preparation for the field which, for the next seventeen years, Hooker was to make his own. The field was that of paints, pigments, and allied products, which at that time had hardly started to emerge from the cookbook stage. It was the day of recipes, of secret formulas; men knew what they would get (sometimes and with luck) if this and that were so proportioned; but did not know why, and few troubled to inquire. "A. H." was one of that small band of pioneers, which included Max Toch, G. W. Thompson, and one or two others, who, at the turn of the century, were slowly bringing order out of chaos by the application of systematic observation and experiment.

After one or two years of experience as chemist with the Dighton Color Works, he took charge of the color department of Cary-Ogden Company, at Chicago, where he had the prompt and unpleasant experience of having a foreman and crew walk out, leaving him to make up orders with no formulas or records. He did it; he was twenty-five at the time. A similar demand for resourcefulness was met in his next venture—this time in window shade manufacture with the Opaque Shade Cloth Company. Left with an inoperable plant which had to be changed, bullied, or cajoled into shape, he and an associate buckled to and put matters to rights within three months. In 1894 he began his longest connection in the paint industry as chief chemist with Heath and Milligan in Chicago. Of his many contributions to paint technology during this period, mention of one must suffice—the discovery that the livering qualities of zinc oxide and leaded zinc were due to adsorbed sulfur dioxide in the pigments—a conclusion which resulted in radical alterations in bag-house practice.

It was an uncle whose influence started Hooker in paint chemistry; and it was a brother who deflected him to electrochemistry. About 1903 Elon Hooker had become interested in the Townsend cell, and "A. H." took a hand, along with a brilliant group of associates—Townsend, Baekeland, Sperry, and others, in the incubation of the infant that was to grow up to a flourishing maturity as the Hooker Electrochemical Company. It was not until 1906, however, after the period of initial test and development was over and construction of the first unit plant undertaken at Niagara Falls, that he abandoned his connection with the paint industry to take charge, as works manager, of the early operations of the Hooker Electrochemical Company. In this capacity he saw the infant through its teething troubles and its early and vigorous growth. In 1911 he relinquished management of operations to other hands, and since that time has devoted himself as technical director to the many problems of research, development, and service that have arisen in the growth to its present considerable stature of the company with which, for the last quarter of a century, his family name and his activities have been so intimately connected.

His technical history through that time has been that of the company; and since this has been set forth in the August, 1930, issue of INDUSTRIAL AND ENGINEERING CHEMISTRY and, in addition, is so widely known, no detailed reference need be made here.

In such connection a man's characteristics and achievements are known only to himself—and his associates. But when the latter tell you, as they will, of the remarkable breadth of his knowledge of technological processes, of his phenomenal memory, or of his ability to pull out the one significant fact from one technical connection and relate it to the equally significant fact in a profoundly different connection, of the value of his judgment based on ripe experience, you have no difficulty in correlating that picture with the many occasions on which you remember "A. H.," in personal conversation or in discussions at meetings, producing, like a rabbit from a conjurer's sleeve (though with a modest and entire absence of the conjurer's exhibitionism), highly significant and individual "slants" on an astonishing variety of technical topics. It is true these same associates will playfully ascribe to him a certain contempt of the commoner aspects of routine, and a tendency to regard his pockets as filing cabinets; but memories of the appearance from these capacious pockets of sheets inscribed with the most elaborate sort of curve families, revealing in a concentrated form Heaven—and "A. H."—only knew how much correlated technical data (and this twenty-five years ago when such things were as rare as they are common now), show his contempt for unessentials to be merely the obverse of an unusual devotion to systematic essentials. What we do not have to learn from his associates are his sociable personality, his geniality, and his kindliness; I am certain that no one who ever asked "A. H." a reasonable favor was refused.

Personally, "A. H." is so well known to and so well liked and respected by so many readers of INDUSTRIAL AND ENGINEERING CHEMISTRY that many words on his personality would be a superfluous impertinence. His modesty, however, tends to hide some of the facts of a very full and well-rounded life. Those who have known him as a keen pool shark, a respectable golfer, or a poker player (in which capacity, I am told, desire doth somewhat outrun performance) may not know of him as a crack shot, expert fisherman, and sportsman of the type whom, even today, it would not be safe to dare, on a bet, to jump in a swimming pool, clothes on, and swim to the end without rising for breath. Nor is it easy to probe the extent of his general interests and hobbies, which are and have been as wide and varied as his technical interests. But a caller at his home at Lewiston, below the Niagara escarpment and looking down at a spot on the river where commenced an old carry, may find himself regaled with a feast of historical and topographical lore on such topics as the history of the early French and English settlements and what constituted a desirable site for Indian villages; or to be shown furniture carpentered by "A. H." from historic timbers salvaged from the demolition of some ancient and noted building in the village, or a handful of arrowheads that might rouse even Whitney's envy.

Always an active member of technical societies, he has served on the boards of the Electrochemical Society and the American Institute of Chemical Engineers. In 1922, the legislature of the State of New York passed a law requiring a state license as a condition for the practice of professional engineering. There was much uneasiness at the time in respect of the motive, wisdom, and probable results of this requirement, and had the law been administered either on a political basis or in an inadequate manner, events might have justified this uneasiness. Fortunately, its administration was placed in the hands of an extremely competent board; and the licensing of engineers in New York State has been an entire success and was rapidly accepted as being as desirable as licensing in medical and legal practice. A. H. Hooker was appointed to the original board as representing, geographically, western New York, and, technically, chemical engineering; has served continuously on the board since—a record he shares with one other member—and is now chairman. His heavy share in the board's work has constituted an important service to the public, and a still more important one to his fellow engineers.

F. A. Lidbury

NOTES AND CORRESPONDENCE

Burning Characteristics of Smokeless Powder

Editor of Industrial and Engineering Chemistry:

In the article by A. M. Ball [Ind. Eng. Chem., **23**, 498–501 (1931)], a time-saving method of calculating explosion temperatures is presented, together with an interesting series of temperature calculations made by this method. It is admitted by the author that the chief value of such calculations is in giving useful relative results rather than reliable absolute values. In other words, the results are as good as the heat data from which they are calculated.

Even aside from this consideration, however, the reliability of the temperature values themselves can be enhanced by correction of an error which, though not great, should be pointed out in the interests of mathematical accuracy and clear reasoning.

Using the notation of the article referred to, if the sum of Q_3 and Q_4 is to be equated to Q, the heat liberated on complete oxidation of the powder in an oxygen-bomb calorimeter, then obviously Q_4 must equal the heat liberated on condensation of the water present in the "frozen" equilibrium mixture, plus the heat of oxidation of the hydrogen (to liquid water) and carbon monoxide. It may be noted in passing that the heat effect at room temperature due to any shifting of the water-gas equilibrium is nil:

$$\mathrm{CO + H_2O\ (liq.)} \xrightarrow{298^\circ\ \mathrm{K.}} \mathrm{CO_2 + H_2} \doteq 0\ \text{cal. (constant volume)}$$

The author's Equation 7 reads:

$$Q - Q_3 = Q_4 = 97[(\mathrm{CO_2}') - (\mathrm{CO_2})] + 57.5[(\mathrm{H_2O}') - (\mathrm{H_2O})] \\ + 29[(\mathrm{CO}') - (\mathrm{CO})] + 18.9(\mathrm{CH_4}') + 10.5(\mathrm{H_2O}')$$

The primed quantities are those found after completion of the combustion process and the unprimed refer to the concentrations which satisfy the water-gas equilibrium at the explosion temperature.

It is evident that where the combustion is completed in excess of oxygen,

$$(\mathrm{CO}') = 0$$
$$(\mathrm{H_2}') = 0$$
$$(\mathrm{CH_4}') = 0$$
$$(\mathrm{CO}) + (\mathrm{CO_2}) = (\mathrm{CO_2}') = \text{atoms C in 1 gram powder}$$
$$(\mathrm{H_2O}) + (\mathrm{H_2}) = (\mathrm{H_2O}') + {}^1/_2(\mathrm{HNO_3}') = {}^1/_2 \text{ atom H in 1 gram powder}$$

Equation 7 becomes, then,

$$Q - Q_3 = Q_4 = 97(\mathrm{CO}) + 57.5[(\mathrm{H_2}) - {}^1/_2(\mathrm{HNO_3}')] - 29(\mathrm{CO}) \\ + 10.5[(\mathrm{H_2O}) + (\mathrm{H_2}) - {}^1/_2(\mathrm{HNO_3}')] + 40.2(\mathrm{HNO_3}') \\ = 68(\mathrm{CO}) + 68[(\mathrm{H_2}) - {}^1/_2(\mathrm{HNO_3}')] + 10.5(\mathrm{H_2O}) + 40.2(\mathrm{HNO_3}') \qquad (7a)$$

This differs from the author's Equation *7a* by the inclusion of the term 10.5(H_2O). His values of Q_3 are thus too high. In the typical calculation given,

$$10.5(\mathrm{H_2O}) = 0.112 \text{ cal.}$$
$$\text{and} \quad Q_3 = \Sigma \int C_v dt = 1.129 - 0.112 = 1.017 \text{ cal.}$$

The temperature result calculated from this is about 200 degrees lower than that from the uncorrected value of Q_3.

If all the nitrogen be converted to nitric acid on combustion of the powder in the oxygen-bomb calorimeter, then of course

$${}^1/_2(\mathrm{HNO_3}') = (\mathrm{N_2}) = {}^1/_2 \text{ atom (N) in powder}$$

and Equation *7a* may be expressed differently. However, no evidence is given for this complete conversion.

It may be noted that Equation *7a* may be expressed in the following manner also:

$$Q - Q_3 = 68[(\mathrm{CO}) + (\mathrm{H_2})] + 10.5(\mathrm{H_2O}) + 6.2(\mathrm{HNO_3}') \qquad (7b)$$

This is only another way of expressing the zero heat effect at room temperature of the water-gas reaction. It indicates that when the powder is exploded in a closed container, the heat liberated falls short of that liberated on combustion of the powder in excess of oxygen. The difference depends largely on the sum of the carbon monoxide and hydrogen concentrations. This sum is independent of the water-gas equilibrium and can be calculated very simply from the ultimate composition of the powder, for, since

$$(\mathrm{CO}) + (\mathrm{CO_2}) = (\mathrm{C})$$
$$(\mathrm{H_2O}) + (\mathrm{H_2}) = {}^1/_2(\mathrm{H}$$
$$(\mathrm{CO}) + 2(\mathrm{CO_2}) + (\mathrm{H_2O}) = (\mathrm{O})$$
$$\text{Then} \quad (\mathrm{C}) + (\mathrm{CO_2}) + (\mathrm{H_2O}) = (\mathrm{O})$$
$$\text{and} \quad (\mathrm{H_2}) + (\mathrm{CO}) = 2(\mathrm{C}) + {}^1/_2(\mathrm{H}) - (\mathrm{O})$$

C. G. Dunkle

Box 271
Wharton, N. J.
July 17, 1931

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Editor of Industrial and Engineering Chemistry:

The writer wishes to thank Mr. Dunkle for pointing out the error in Equation *7a* and in the burning-temperature values calculated from it. As Mr. Dunkle calculates the correction, it amounts to about 200 degrees in the typical calculation. Since the amount of water formed in the combustion of all the powders considered varies only within quite narrow limits, a deduction of 200 degrees from each of the calculated temperatures should put them within the limit of error set in the original article. The relative values of the burning temperatures of the various powders are therefore unaffected by this correction. The compositions of the gases are changed only very slightly with this change of temperature.

The simplification in the labor of numerical calculation afforded by Mr. Dunkle's Equation *7b* will be appreciated by anyone who has to calculate a number of burning temperatures.

A. M. Ball

Hercules Experimental Station
Wilmington, Del.
July 28, 1931

BOOK REVIEWS

Algebraic Charts. By Edgar Dehn. 6 charts. Nomographic Press, 509 Fifth Ave., New York, N. Y., 1930. Price, bound, \$1.50; paper, \$1.00.

Nomography, as its name implies, is the art of drafting laws. The laws of that branch of logic to which the ancients gave the name of algebra are well established. By means of these laws, algebraic problems can be solved more or less readily by elementary analytical methods. Elementary methods are found wanting, though, when a problem finds symbolism in the form of simultaneous quadratics involving two unknowns. A way out is through the nomographic process, by graphic algebra.

This art of picturing symbolic logic can be extended indefinitely, including equations of any degree whatsoever, with as many variables as you please. These pictures demonstrate that algebraic expressions group themselves in definite family relationships, and thus we have families of so-called curves representing those of the ilk straight line, circular, parabolic, hyperbolic, exponential, and logarithmic, as well as numerous cadets or offshoots. It is not a new art. The French and Germans have always delighted in it. Newton was aware of it, and in his time one Thomas Baker published a treatise, entitled "The Geometrical Key, or the Gate of Equations Unlocked."

But if not new, neither is it exact. The results obtained, even under the most favorable circumstances, are only approximate. This approximation to actual values becomes vocal when one subjects to the graphic art individual problems in linears, quadratics, cubics, and quartics. When on a chart of normal dimensions is crowded a large algebraic family of varying coefficients, as is done here, and one has to cut and try, like a mathematical seamstress on a chart that resembles a woman's dress pattern, the process becomes confusing and tiresome. It were less laborious, we think, to brush up on the higher algebra and then solve our problems in cubics and quartics by the old-fashioned analytical methods. . . And typographically the book is marred and the reader bothered by finding the charts and directions for using them otherwise than on facing pages.—George A. Wardlaw

The Soil and the Microbe. An Introduction to the Study of the Microscopic Population of the Soil and Its Role in Soil Processes and Plant Growth. By S. A. Waksman and R. L. Starkey. 260 pages, 85 figures, and 56 tables. John Wiley and Sons, Inc., New York, 1931. Price, \$3.50.

This text is well written in a clear, lucid, and interesting style. The material is organized in a logical manner and is nicely illustrated with a series of aptly chosen figures. Most of the illustrations have been taken from original publications rather than from other tests. A small selected list of references at the end of each chapter is, for the most part, general treatises rather than original publications of research. Unfortunately, adequate references are not given to many of the figures and tables which are copied from original research publications.

The subject matter deals largely with the chemical transformations of the organic and inorganic materials in the soil as these transformations are brought about by microörganisms. The necessary background of the soil constitution and conditions, as well as a general discussion of microbic life, is included in the first chapters of the book. The microbiology of the soil is not treated in as great detail, however, as might be implied from the title. Methods of culturing and adequate descriptions of the cultural, morphological, and physiological characteristics of even the more important soil microörganisms have been omitted in many instances.

For the most part the authors have treated of material with which they are thoroughly familiar from an experimental standpoint. The result in most sections is an authentic presentation which is often lacking in texts. A few exceptions to this general statement are found, however—e. g., in the section on the nodule bacteria of the leguminous plants, certain ideas which are not strictly accurate have been copied from the older papers.

This text should prove useful to the advanced student and research worker in soils as well as to those interested in the more general phases of plant growth or microbiological transformations.—I. L. Baldwin

An Introduction to Biochemistry. By Roger J. Williams. xiv + 501 pp. Illustrated. D. Van Nostrand Co., Inc., New York, 1931. Price, \$4.00.

The author notes that "perhaps the most pressing need for a broader treatment of biochemistry comes from those students whose training is to be primarily in the field of chemistry. . . . Specialization has become so narrow that one may take a doctorate degree in organic chemistry and yet be ignorant of the most rudimentary facts relating to the chemistry of organisms. . . . There is an emphatic need in a well-rounded chemical curriculum for at least one course dealing with 'the chemistry of organisms.'" It was to supply a text for such a course that the present volume was written.

The author presupposes that the student will have already had an adequate course in organic chemistry and notes that a foundation course in general biology would be extremely desirable.

Following an orientation chapter where the eighteen major phyla of living organisms are listed and briefly discussed and where the relationships of biochemistry to biology and to chemistry are considered, the book is divided into six sections: I, The Composition of Organisms; II, The Nutritional Requirements of Organisms; III, Mechanisms Used by Organisms in General for Promoting and Regulating Chemical Changes; IV, The Metabolism of Single Cells; V, Metabolism in Green Seed Plants; and VI, Metabolism in Mammals.

The first section contains eight chapters dealing with cell structure, inorganic constituents, carbohydrates (34 pages), fats and related compounds (15 pages), proteins (26 pages), colloidal systems (28 pages), miscellaneous organic constituents (23 pages), and the essential characteristics of living matter (5 pages).

The second section contains four chapters dealing, respectively, with the nutritional requirements of bacteria and fungi, green plants, the lower animals, and the mammals. The third section contains only two chapters, dealing with permeability and enzyme action. The fourth section likewise contains two chapters in which the metabolism of bacteria and yeasts, protozoa, fertilized egg cells, and isolated tissue cells are discussed. The fifth section, containing three chapters, covers the metabolism of seeds, leaves, and the movement of materials, and general metabolism and excretion in green plants.

The last section of eight chapters, dealing with mammals, considers temperature regulation, metabolic rate, digestion and absorption, intermediate carbohydrate metabolism, intermediate fat and lipoid metabolism, intermediate protein metabolism, metabolism of miscellaneous food constituents and excretion. The book closes with 57 "suggested laboratory experiments" (33 pages) and a 22-page subject index.

There is no question in the mind of the reviewer that there is a real need in the curriculum of a chemist for a course in biochemistry and that this book would serve admirably as a text, providing that the students have an adequate background of organic chemistry, and that the instructor has an adequate background of biological knowledge and a true interest in biological phenomena. The task of a university offering such a course will not be to find interested students but rather to find instructors who are competent to teach chemistry with the proper biological viewpoint. The author's training in both chemistry and in biology has enabled him to write an excellent text.

There is so much to commend that the reviewer prefers to pass over most minor points where he would differ with the author. In discussing the structure of the carbohydrate, Williams has preferred the pentaphane oxide ring of Hudson for glucose, for the glucose residue in sucrose and lactose, and for one of the glucose residues of maltose in place of the hexaphane ring of Hayworth. In a discussion of the pectins no mention is made of the presence of uronic acids which Ehrlich and others have shown to be a major constituent; instead, the statement is made, "good evidence has been presented that in pectins, like in gum arabic, the carbohydrate residues are attached to an acid of unknown constitution." The symbol $\mu\mu$ is used for millimicron in place of the more correct mμ. The reviewer questions the author's argument (pages 117–19) in regard to the purity of "isoelectric" proteins. The author states that "gelatin of itself has weak acid properties and if a pure gelatin solution were electrolyzed the gelatin would migrate to the positive pole. It is necessary to add a small amount of acid to the pure gelatin solution to bring it to its isoelectric point. Gelatin which is brought to its electrokinetic isoelectric point is not the purest gelatin."

The isoelectric point is defined as that point where the ionization of an ampholyte as a base equals its ionization as an acid; accordingly, pure (uncombined) gelatin can exist only at that point on the pH scale. The reviewer is unable to follow the author's reasoning to the contrary.

In the chapter on the proteins it would seem that the few lines devoted to merely mentioning the fact that Fischer, Van Slyke, Kossel, and Dakin have devised methods of protein analysis might well be replaced with adequate references to sources where the student could find directions for carrying out these indispensable technics.

In many places the author seems over-cautious. The phrases, "is said to be," "is thought to be," "reaction is said to take place," etc., occur over and over again, and undoubtedly overemphasize the gaps in biochemical knowledge. In some instances the statements are justified, in others adequate evidence for or against the statement is in the existing literature.

By and large, however, the faults are minor, the merits are many. The book is heartily recommended for its intended purpose, and the reviewer would go further and say that in his belief a medical curriculum could well include a broad course of biochemistry modeled along the outline suggested by this text.—Ross Aiken Gortner

Dielectric Constant and Molecular Structure. By Charles Phelps Smyth. American Chemical Society Monograph No. 55. 224 pages. The Chemical Catalog Company, Inc., New York, 1931. Price, $4.00.

The purpose and scope of this work are well stated by the author in his preface: "The attempt has been made to correlate and organize a body of facts and to use them in a critical examination of the theories and hypotheses in terms of which they are interpreted. . . . It is also hoped that the summary of the literature and the brief account of the methods of investigation may be of service to those who have not had opportunity to follow the growing literature of the subject." As one who has himself contributed a great deal in the development of the particular field of physical chemistry, Doctor Smyth was eminently fitted to undertake this task and the result is a very readable and comprehensive review of present knowledge on the relation between dielectric constants and molecular structures.

The volume thus forms an excellent supplement to the classic work of Debye on "Polar Molecules." Chapter I presents the mathematical theory in a simple form and introduces the various fundamental concepts, such as electric moment, electronic and atomic polarization, and orientation polarization. The various methods for the determination of dielectric constant are discussed in chapter III, while chapters IV, V, and VI deal with the interpretation of data on electric moments from the point of view of structure of molecules and radicals, with special attention to cycle compounds. Electronic theories of valence are reviewed in chapter VII, with the conclusion that "there is, as a rule, little connection between the electric moment of a molecule and its reactivity, but, on the other hand, the assumption of polarities arising from the different electronegativities of radicals appears to be useful in explaining and predicting chemical behavior." Chapter VIII deals with electronic and atomic polarization as derived from investigations on refraction (Fajans), while the last chapter is entitled "Molecular Association." Finally, two appendices give tables of electric moments which should be of great utility to chemists.

In the reviewer's opinion, the volume, summarizing as it does a large number of investigations in a comparatively new field, presents a distinct contribution to the literature on the subject and is well worth the consideration of chemists as well as physicists.—Saul Dushman

A History of Chemistry. By F. J. Moore. Revised by William T. Hall. 2nd edition. 324 pages. McGraw-Hill Book Co., Inc., New York, 1931. Price, $3.00.

The first edition of this work has been in demand for over a decade, and the second, which has been revised in the light of recently discovered facts, will be even more welcome. The plan, as in the earlier volume, is to present the history of the origin and development of the more fundamental ideas of the science, interweaving the story with the personalities of the men whose efforts have contributed to that development. Even though this is a history of chemistry, some readers will be inclined to regret that a somewhat different plan was not followed in the work. If the work involved in some of the discoveries of considerable importance did not contribute a new fundamental idea, these discoveries are dismissed lightly. Further, a certain limitation arises when, as in the present instance, only the contributions of the chemists no longer living are taken into consideration. In the present edition there is an added chapter devoted to Americans who did much to develop chemistry in this country but, with a few exceptions where the work is mentioned in the main body of the text, this treatment is set apart and consists of a group of brief biographies, rather than of weaving into the general historical account a more complete discussion of the possible influence of their work upon the trend of chemistry in general. This results in chemistry in the United States enjoying but 16 pages in the entire work.

The book contains a number of portraits of men whose names are internationally famous and an occasional illustration of either historic value or direct bearing upon the point under discussion. While the volume is obviously written for those who are mature students of chemistry, as was its predecessor, it nevertheless will be found interesting to the general reader, particularly if, as a result of reading the more popular discussions, he has become interested in the origin, the philosophical basis, and the critical periods in the development of those fundamental ideas of chemistry so faithfully recorded in this volume.

Textbook of Pharmacy. By I. V. Stanley Stanilaus. 736 pages. D. Van Nostrand Company, Inc., New York, 1931. Price, $7.00.

This is not only a treatise on pharmacy but also something of a discourse on pharmacology, hydrogen-ion concentration, therapeutic classification of drugs, etc.

It is not, in the reviewer's judgment, essentially a textbook on pharmacy from a teacher's standpoint, because it overlaps other branches taught by others than a professor of pharmacy. It is, however, a concise and excellent book for students to review preparatory to examination, as it is concise and the tables given are excellent. It is worthy of a place in any pharmaceutical library.—S. L. Hilton

Soil Management. By Firman E. Bear. 2nd edition, 2nd printing corrected. 412 pages, illustrated. John Wiley & Sons, Inc., 1931. Price, $3.50.

The first edition of this book was published in 1923. The revised edition contains 246 more pages, 25 more illustrations, and 98 more references than the original edition. The number of chapters and their titles and sub-headings remain practically the same, although each chapter has new material added. The chapter on fertilizers has been expanded to nearly twice the space occupied in the first edition. The author states that the purpose of the book is primarily that of acquainting the student with the applications of those scientific facts and principles of use in planning constructive systems of soil management and increasing the productive capacities of soils. This thought seems to have been well carried out in the subjects discussed. The student as well as the practical farmer will find the book a valuable source of useful and practical information.—J. S. McHargue

MARKET REPORT—AUGUST, 1931

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, AUGUST 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.12
Adipic	lb.	.72
Linoleic	lb.	.16
Ammonium linoleate, drums	lb.	.15
Amyl furoate, 1-lb. tins	lb.	5.00
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	1.00
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.06
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.24
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.50
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.30
Ethyl acetoacetate, 50-gal. drums	lb.	.65
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys	lb.	.75
Dichloride, 50-gal. drums	lb.	.05
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.24
Monoethyl ether, drums, wks.	lb.	.17
Monoethyl ether acetate, drums, wks.	lb.	.19½
Monomethyl ether, drums	lb.	.21
Oxide, cyl.	lb.	2.00
Furfuramide (tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 100-lb. drums	lb.	.50
Furoic acid (tech.), 100-lb. drums	lb.	.50
Glyceryl phthallate	lb.	.26
Glycol stearate	lb.	.18
Isopropyl ether, drums	lb.	.10
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.15
Methyl acetate, drums	gal.	1.20
Cellosolve, *see* Ethylene glycol monomethyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Paraldehyde, 110–55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl.	lb.	.20
Propyl furoate, 1-lb. tins	lb.	2.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.09
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.40
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., powd., bbls.	lb.	.24
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks.	lb.	.10
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.60
56%, c/l., bbls.	100 lbs.	4.85
Glacial, c/l., bbls.	100 lbs.	9.23
Glacial, U. S. P., c/l., carboys	100 lbs.	9.73
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, bbls.	lb.	.06⅛
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.14½
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.35
Cresylic, pale, drums	gal.	.58
Formic, 90%, cbys., N. Y.	lb.	.10¼
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.85
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11
Mixed, tanks, wks.	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.50
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.13½
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.31½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.55
Amyl, from pentane, tanks	lb.	.203
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.15½
Cologne spirit, bbls.	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums	gal.	.27
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	1.00
Isopropyl, ref., drums	gal.	.60
Propyl, ref., drums	gal.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.73
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30
Chrome, casks, wks.	100 lbs.	5.00
Potash, lump, bbls., wks.	100 lbs.	3.35
Soda, bbls., wks.	100 lbs.	3.45
Aluminum, metal, N. Y.	ton	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.,	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.20
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.25
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks	lb.	.05625
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.35
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.25
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.22
Persulfate, cases	lb.	.26
Phosphate, dibasic, tech., bbls.	lb.	.10¾
Sulfate, bulk, wks.	100 lbs.	1.60
Amyl acetate, tech., from pentane, tanks	lb.	.173
Aniline oil, drums	lb.	.14½
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.50
Antimony, metal	lb.	.06⅝
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.08½
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Argols, red powder, bbls.	lb.	.07
Arsenic, metal, kegs.	lb.	.30
Red, kegs, cases	lb.	.09⅜
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	56.50
Chloride, bbls., wks.	lb.	.03¾
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05¼
Nitrate, casks	lb.	.07¼
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzidine base, bbls.	lb.	.65
Benzol, tanks, wks.	gal.	.18
Benzoyl chloride, cbys.	lb.	1.00
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, 5-liter bot.	lb.	1.20
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.22
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.50
Bismuth, nitrate, 25-lb. jars	lb.	1.25
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.50
Blanc fixe, dry, bbls.	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.02½
Bordeaux mixture, bbls.	lb.	.11½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butylacetate, drums, c/l.	lb.	.17
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.55
Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.00
Arsenate, bbls.	lb.	.06
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	22.75

Cyanide, 100-lb. drums	lb.	.30
Nitrate, bbls	ton	40.00
Phosphate, monobas., bbls	lb.	.08
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., cases	lb.	.55
Carbazole, bbls	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.05
Carbon black, cases	lb.	.06
Carbon dioxide, liq., cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls	lb.	.06½
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq., c/l., cyl	lb.	.04
Chlorine, tanks	100 lbs.	1.75
Chlorobenzene, mono-, drums	lb.	.10
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks	gal.	.10
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	1.35
Cod-liver oil, bbls	bbl.	30.00
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec	100 lbs.	7.50
Copper carbonate, bbls., 52/54%	lb.	.16½
Chloride, bbls	lb.	.22
Cyanide, drums	lb.	.41
Oxide, red, bbls	lb.	.15½
Sulfate, c/l., bbls	100 lbs.	3.60
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.22¾
Cyanamide, bulk, N. Y.	Nitrogen unit	1.10
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.24½
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.30
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.13
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.29
Diphenylamine, bbls	lb.	.37
Diphenylguanidine, bbls	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.80
Ether, U. S. P., drums	lb.	.09
Ethyl acetate, tanks, c/l	lb.	.075
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums.	lb.	.88
Ethylene dichloride	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks	lb.	.25
Feldspar, bulk	ton	6.50
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, C. P., drums	lb.	.11½
G salt, bbls	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls	lb.	.12
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	160.00
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	4.40
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls	lb.	.10
Oxide, litharge, bbls	lb.	.08¾
Peroxide, drums	lb.	.20
Red, bbls	lb.	.103
Sulfate, bbls	lb.	.06¾
White, basic carb., bbls	lb.	.07¼
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, crude	ton	32.00
Calcined, 500-lb. bbls., wks	ton	40.00
Magnesium, metal sticks, wks.	lb.	.48
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 50 lbs.	lb.	1.75
Mercury, flasks, 76 lbs	flask	82.00
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.80
Meta-toluylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, wks.	gal.	.37½
Tanks, wks	gal.	.35½
Methyl acetone, drums	gal.	.50
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	3.00
Naphtha, solvent, tanks	gal.	.25
Naphthalene, flake, bbls	lb.	.03¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.10½
Double, bbls	lb.	.10½
Niter cake, bulk	ton	12.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1.	lb.	.11
China wood, bbls	lb.	.06⅞
Coconut, Ceylon, tanks	lb.	.03½
Cod, N. F., tanks	gal.	.39
Corn, crude, tanks, mills	lb.	.03½
Cottonseed, crude, tanks	lb.	.06⅛
Lard, edible, bbls	lb.	.12½
Linseed, bbls	lb.	.085
Menhaden, crude, tanks	gal.	.21
Neat's-foot, pure, bbls	lb.	.10¼
Oleo, No. 1, bbls	lb.	.07¼
Olive oil, denat., bbls	gal.	.82
Foots, bbls	lb.	.06½
Palm, Lagos, casks	lb.	.05
Peanut, crude, bbls	lb.	.07
Perilla, bbls	lb.	.09
Rapeseed, bbls., English	gal.	.45
Red, bbls	lb.	.08⅜
Soy bean, crude, bbls	lb.	.071
Sperm, 38°, bbls	gal.	.84
Whale, bbls., natural, winter	gal.	.69
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums.	lb.	.28
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls	lb.	.27
Palladium, metal	oz.	19.00
Para-aminophenol, kegs	lb.	.84
Para-dichlorobenzene	lb.	.15½
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitroaniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls	lb.	.29
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.42
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.80
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	lb.	.42
Phosphorus trichloride, cyl	lb.	.35
Phthalic anhydride, bbls	lb.	.15
Platinum, metal	oz.	38.00
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.09
Binoxalate, bbls	lb.	.14
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks.	lb.	.05
Chlorate, kegs	lb.	.08
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.11
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.38
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	1.50
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P.	lb.	.18
R salt, bbls	lb.	.42
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	15.00
Saltpeter, gran., bbls	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.22⅜
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.15
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.50
Sodium acetate, bbls	lb.	.05½
Benzoate, bbls	lb.	.42
Bicarbonate, bbls	100 lbs.	2.00
Bichromate, casks	lb.	.07
Bisulfite, bbls	lb.	.04
Bromide, bbls., U. S. P.	lb.	.34
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.16½
Fluoride, bbls	lb.	.07½
Metallic, drums, 12¼-lb. bricks	lb.	.19
Naphthionate, bbls	lb.	.52
Nitrate, crude, bags, N. Y.	100 lbs.	2.05
Nitrite, bbls	lb.	.07¼
Perborate, bbls	lb.	.18
Peroxide, cases	lb.	.21
Phosphate, trisodium	100 lbs.	3.20
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs,	.75
Silicofluoride, bbls	lb.	.04½
Stannate, drums	lb.	.19½
Sulfate, anhyd., bbls	lb.	.02
Sulfide, cryst., bbls	lb.	.02½
Solid, 60 %	lb.	.03½
Sulfocyanide, bbls	lb.	.28
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.81
Strontium carbonate, tech., bbls	lb.	.07¼
Nitrate, bbls	lb.	.09
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.26½
Tin	lb.	.26
Tin tetrachloride, anhydrous, drums, bbls	lb.	.1785
Oxide, bbls	lb.	.25
Titanium dioxide, bbls., wks	lb.	.21
Toluene, tanks	gal.	.27
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls	lb.	.60
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.11
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks	gal.	.24
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	3.80
Zinc ammonium chloride, bbls	lb.	.05½
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls	lb.	.06½
Stearate, bbls	lb.	.20
Zinc dust, bbls., c/l.	lb.	.06

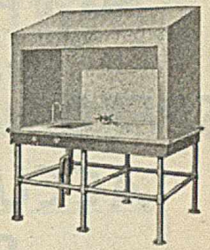
Kewaunee

Laboratory Furniture

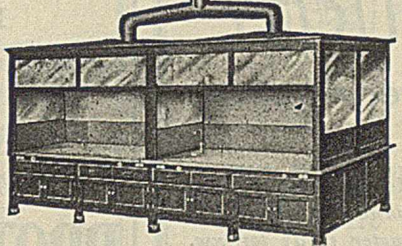
Saves Time - - Saves Space
Saves Money

Wall Form Chemistry Table No. D-741

Chemical Table
No. H-1533



Open Front Fume
Hood No. D-960



Industrial Fume Hood No. H-1546

Industrial
Laboratory
Table No. H-1527

Every modern convenience is obtainable in Kewaunee Laboratory Furniture. The entire line has been built to permit greatest possible efficiency and to conserve valuable time. Everything is at the chemist's fingertips. Water, gas, vacuum, air, sinks, drawers, cupboards—all are handy and arranged to save steps and unnecessary effort.

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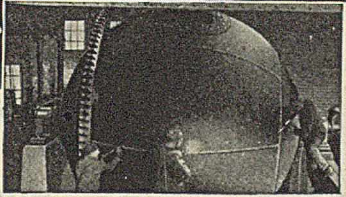
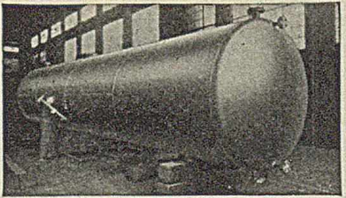
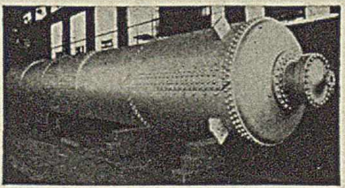
SAFE BIGGSWELD DUCTILE UNIFORM STRONGER THAN THE PLATE ITSELF



Biggs Welded Rotary Digester



High Pressure Welded Receiver



Riveted-and-welded Scrubber Tank

BIGGS builds and erects welded or riveted autoclaves, tanks, vats, stills, dryers, and high pressure vessels of practically every description for the process industries, made of steel plate, Enduro KA 2-S, and similar alloys, including monel and rubber lined retorts.

Write for our pictorial bulletin, "Unusual Steel Plate Construction"

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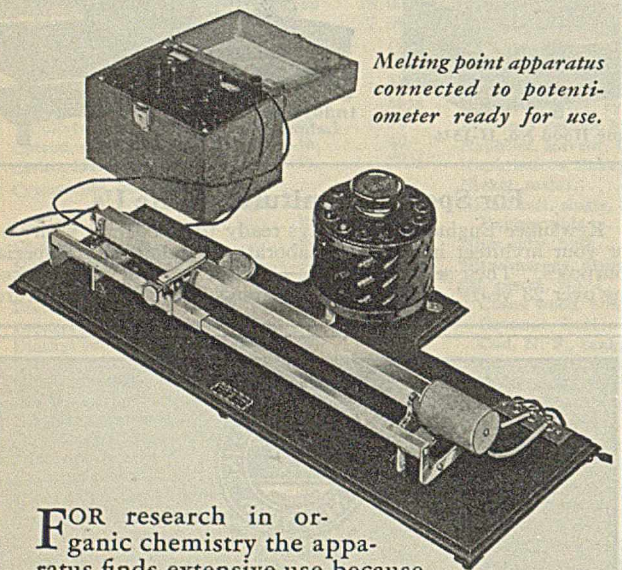
THE NEW
DENNIS
MELTING POINT
APPARATUS
assures
SPEED
ACCURACY and
SIMPLICITY
For Melting Point Determinations



Melting point apparatus connected to potentiometer ready for use.

FOR research in organic chemistry the apparatus finds extensive use because of the unusual speed and accuracy it provides in making melting point determinations. Even those materials which dissociate or sublime when heated can be tested with ease by this method.

In industrial control problems for controlling the melting point of materials the determinations are made easier with this apparatus.

By its use melting points can be determined with a high degree of accuracy and with a minimum of time and effort. All errors due to thermometer lag or due to moving the thermometer are eliminated. Its operation is so simple and direct that unskilled operators can make accurate determinations. Melting point determinations from 25°C. to 300°C. can be covered. Operates on a 110 Volt circuit.

For further information write for Bulletin E11.

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Machines Run 3 to 5 Times Longer Without Repairs

The purchase of a compressor, vacuum pump, Diesel engine or blower means a big investment. Is it worth trying to save the small cost of an air filter and let the dust and grit in unfiltered air wear and score the cylinders, pistons, bearings and valves and thereby cause excessive repairs?

Machines will operate 3 to 5 times longer before overhauling is necessary when equipped with a Protectomotor, because it removes 999 of every 1000 particles of dust and grit from the air.

Furthermore the Protectomotor Air Filter cuts carbon deposits 60 to 70%, saves oil and compressed air, and muffles suction noises of compressors and exhaust noises of vacuum pumps.

It operates from six months to a year without cleaning, and can be cleaned with compressed air without removing the filtering unit.

Protectomotor Pipe Line Filter

delivers dry, clean air, free from dust, water, oil, rust and scale, for compressed air tools, paint spraying, hoists, cleaning operations, agitating liquids, etc.

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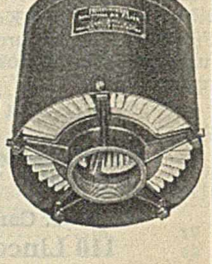
99 9/10 Per Cent
EFFICIENT
AIR FILTERS



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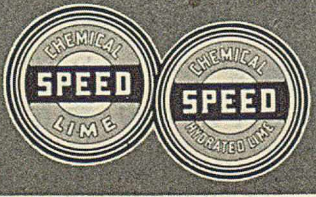
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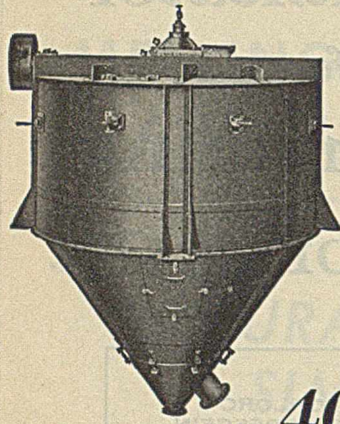
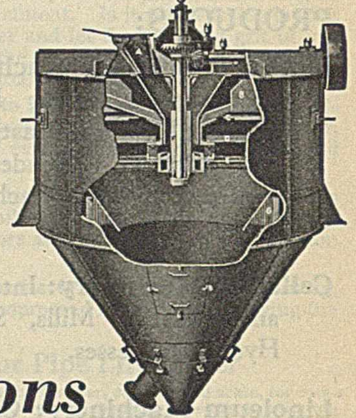
LIME
CHEMICAL
SPEED
HYDRATED LIME





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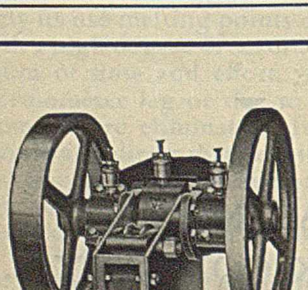

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For Hard or Soft Material

STEEL CONSTRUCTION—all essential parts, including frame plates, of steel. Bearings are split bushings, easily adjusted for wear and readily replaceable.

The Vibratory Jaw moves forward and downward, assuring positive feed and discharge.

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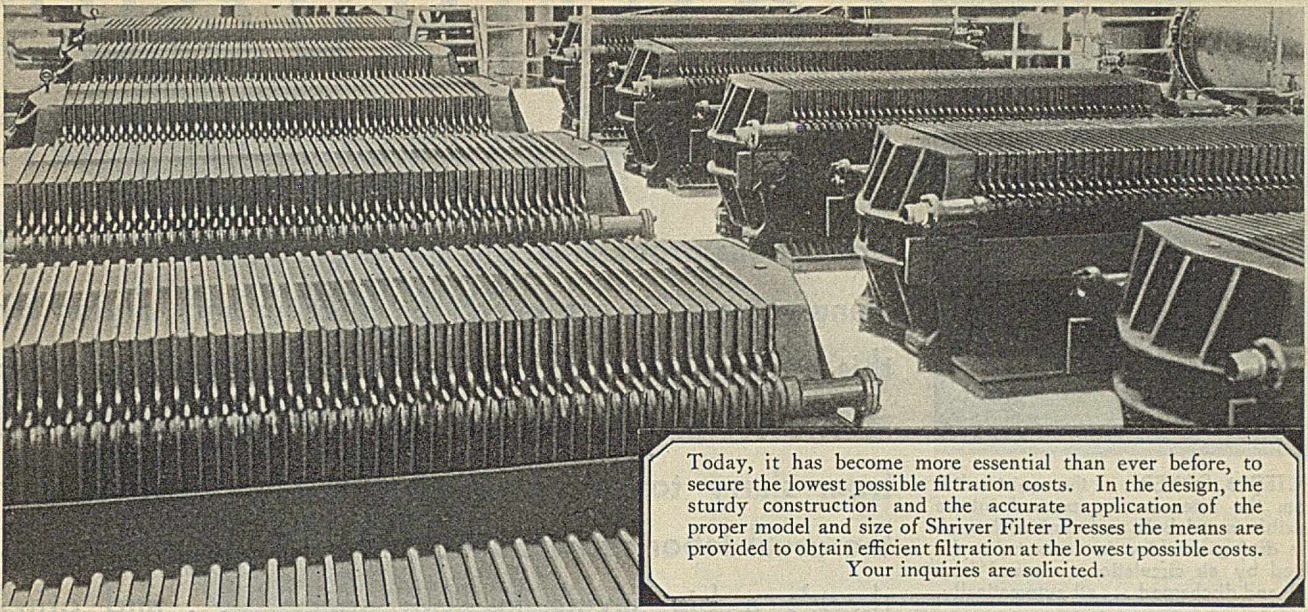

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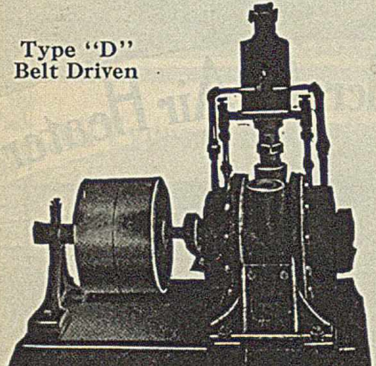

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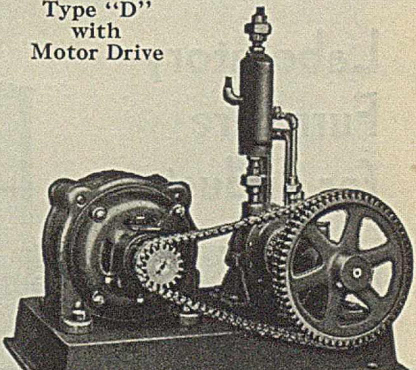

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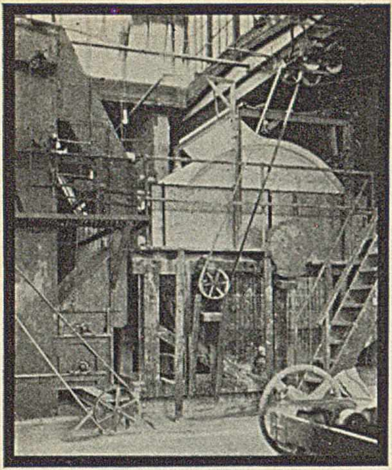

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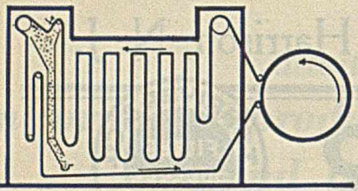

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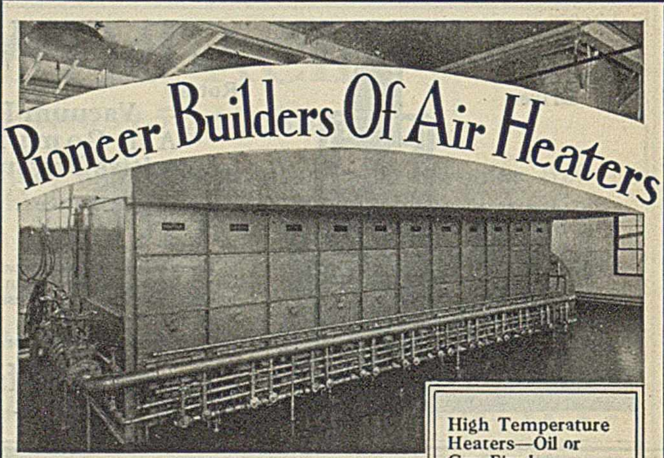

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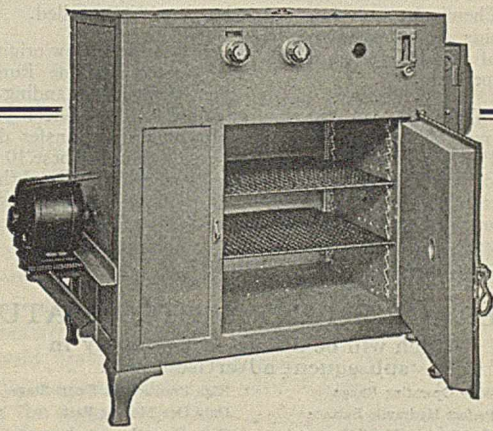
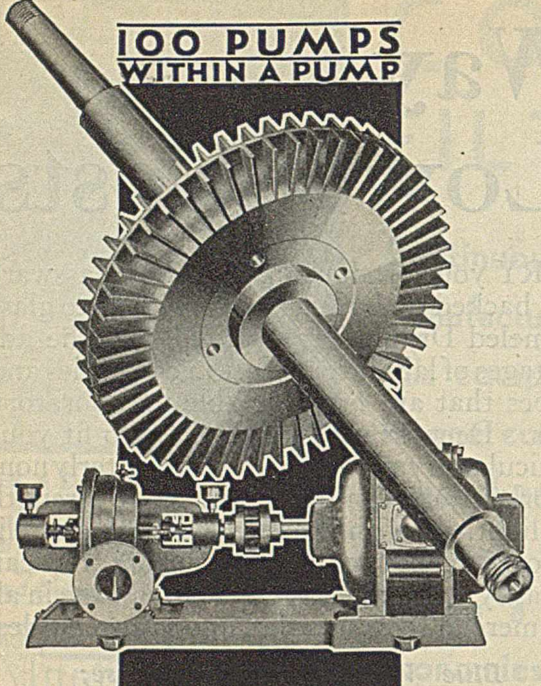


HEAT TRANSFER in Laboratory Ovens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