The GENIUS *of*
INDUSTRIAL RESEARCH

by

D. H. KILLEFFER

O, what a world of profit and delight,
Of power, of honour, of omnipotence,
Is promis'd to the studious artisan!
—Christopher Marlowe.

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For Peekah

with deep respect

and sincere affection.

Preface

During the summer of 1944, certain bodily infirmities and the heroic efforts of a number of singularly expert medical specialists to overcome them left me temporarily flat. Lifting my hand was in my weakened state a major exertion and twiddling my thumbs a major sport seeming to justify attention from the Olympic Games Committee. So it was that I read everything within my reach whose physical weight was not too great. At one time during this period, my good friend, Donald B. Keyes, sent me—out of the goodness of his heart—a manuscript of what had started out to become a book on methods of industrial research. He asked me what I thought of it. I read the material and became enthusiastic about it. The ideas expressed seemed to me sound and useful. Even in my debilitated state, I could see important possibilities in it in providing guidance to young research workers and others ambitious to undertake research.

In the course of time, the medical skill and the loving kindness lavished upon me had their effect and I was moved to do something about the manuscript. My resolution was strengthened by finding that most references bearing on the subjects of research itself or the psychological aspects of original thinking were either out of print or difficult to obtain. So it was that I imposed some of my thinking in the Keyes' manuscript and sent it to Don for his rebuttal. His reaction was to confer on me entire responsibility for our joint offspring.

This is the result. The discerning will easily recognize the Keyes philosophy and experiences at intervals throughout the book. For these have been gladly adopted and only because they have been much changed in the retelling have specific acknowledgements been omitted.

The cavalier treatment thus given a good friend and expected collaborator makes it only proper to note here several places in the literature where the ideas of Dr. Keyes are expressed as he would have them and not in Killefferan translation. His "Methods of Research" is found in *Industrial & Engineering Chemistry*, 15, 82 (1923); "Appraisal of Chemical Invention" in the same journal, 15, 972;

"How New Chemical Products are Invented" appeared in *Journal of Chemical Education,* 6, 2178 (1929); and a similar paper in *Scientific Monthly*, 26, 217 (1928). There are, of course, many others, but these will suggest the Keyes view on some subjects treated at length in this volume.

This treatment of modern industrial research and its methods is intended primarily to guide the ambitious young researcher, whatever may be his field, to a better understanding and a surer mastery of his craft. The material presented comes predominantly from the field of industrial chemistry for in no other is research so important, so well developed and so fruitful. For this, no apology is offered physicists, biologists, sociologists, psychologists and others interested in research. While they might prefer illustrative examples chosen from their own respective fields, they will be able to find much of value in what follows. So too, others of diverse backgrounds and interests may be led to understand and appreciate research methods—possibly even to use them—by reading here the fascinating accounts of how many important modern developments were achieved. These accounts are quoted directly from original presentations by those responsible, a method adopted to give the reader a clear insight into the reasoning behind these researches. The point of view throughout is that of the individual researcher and not that of management or direction.

In fulfilling its purpose, this discussion cuts across many accustomed boundaries and often departs from orthodoxy. Its attempt to convey psychological ideas to the inadept, for instance, may mildly shock professional psychologists, to whom it is obviously not directed. Because research has been practiced from the earliest times, one can hardly be expected at this late date to contribute anything new to the subject. Ancient astronomers, the Ptolemaic geometers, and the Greek philosophers of two or three millenia ago employed methods not essentially different from those which today form the basis of what we fondly imagine to be the ultra-modern and novel art of research. These methods have been discovered over and over again in the intervening stretches of time, and so the present author relies upon ample precedent for his "discovery of the obvious" as it appears hereafter.

Great sections of the text have been lifted bodily from the published papers of our most capable and eminent industrial researchers.

Among them, the honorable company of Perkin Medalists stand out. Quotations have been included from such of these as seemed germane to this subject matter. No apology is offered that the whole company of these eminent gentlemen is not represented; obviously not all of their addresses were designed for this purpose. Nor is apology offered for including expressions from others less eminent which also shed important light on the way research operates.

Finally, it is a privilege to acknowledge my deep indebtedness to the many authors, editors and publishers who have given permission to reprint much of the material of this volume. My sources are acknowledged in detail in the authors' index. My special thanks are due: to Walter J. Murphy, editor of *Industrial & Engineering Chemistry*, in which the Perkin Medal addresses with few exceptions have appeared; and to F. J. Van Antwerpen, editor of *Chemical Engineering Progress*, and Henry J. Masson, Assistant Dean in charge of the Graduate Division, New York University, College of Engineering, who have read this book in manuscript form and who have offered many valuable suggestions for its improvement.

D. H. K.

Crestwood, N. Y.
September, 1947

Contents

Chapter 1

Industrial Research is Methodical

"A good deal of the necessary work of the world has to be done by men who . . . have to achieve skill instead of receiving it at birth."
—Graham Wallas

"Gone are the days of Priestley and Faraday, who with little or no assistance could carry out highly significant experiments. Almost all of our major chemical problems now require the coordinated efforts of research teams, in which each individual forges an important link."
—Sir Ivan Morris Heilbron

Research often appears to be the work of genius. Indeed, results achieved by modern research workers and organizations strongly suggest by their revolutionary character that only genius could have attained them. Genius, that is, in the sense of inspiration but not work. This aspect of modern science has received special emphasis from the growing number of prolific writers who specialize in dramatizing science for the layman. Advertising, too, has shown no noticeable modesty in dealing with the accomplishments of advertisers' research staffs (to the great embarrassment of the researchers).

The picture thus presented of the orderly processes of research is badly warped and focusses an exaggerated light on earnest workers in the field. Not that results attained are not fully worthy, but rather that the omission of the successive steps by which an end is reached gives the result an undue aura of the miraculous.

A significant consequence of this spot lighting process is the strange picture it gives of both science and research. The impression conveyed to the lay public is of a series of marvelous effects without evident causes. They resemble nothing so much as the tricks of a magician who achieves success only through his ability to hide causes from his audience while showing them clearly the effects he desires.

Fulsome publicity for scientific findings dragged ruthlessly from their context has fostered broadly an essentially similar impression of research. A deplorable consequence grows out of that when scientists themselves join with their lay brethren in amazement and admiration that such a marvel should have been done by one of their own kind. Quite unconsciously scientists are thus led to join as sincere evangelists in the mythology of genius.

As true, and sometimes fanatical, believers in this distinctly human cult, scientists are likely to persuade themselves that research workers are and will always be born geniuses, and hence that there is no need to analyze their calling and methods to devise a course for training young men and women to follow them. In the face of such a belief, the scientific method of developing knowledge step by patient step loses caste before the far more romantic and laborless leaping about by giant strides to achieve an endless succession of miracles. It is all quite nice and unquestionably romantic and soul-satisfying for those already engaged in research.

But it just is not true, for the vital reason that both the premise and the reasoning from it are false. In creating a great hue and cry about science and research to gain support for worthy enterprises, scientists have unwittingly deluded themselves about the things they should know best: themselves and their own calling.

Ralph H. Ojemann in *Science* pointed out this aspect of publicity for science which has become basically a ballyhoo for results entirely removed from connection with any causes. Says he,

> "An appreciation of the nature of research involves a conception of the general method by which scientific results are obtained, the nature of these results, and what is needed to establish dependable findings. One may know what has been discovered without knowing much about how the knowledge was obtained.
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> "When we analyze the various dissemination activities of present-day science, they seem concerned mainly with informing their audiences of scientific findings. Textbooks used in schools, newspaper and magazine articles, and motion picture and radio reports center their emphasis on what is known.
>
> "Three ideas seem to be characteristically absent. The first of these is the nature of the method by which the findings have been derived. There is little or almost no discussion of the peculiar charac-

teristics of the scientific method or of the cost in human hopes and disappointments, as well as in money and other resources, by which these findings were developed. Consider, for example, the typical high school textbook in science. There may be short descriptions of the men who made scientific contributions and there may be names and dates; but there is little which helps the student to develop an appreciation of what it means to control the significant variables, the price that must be paid to apply this method, the difference between a good experiment and a poor one, or some of the difficulty man has experienced when he has tried to interpret and use the findings from studies in which the significant variables were not controlled. What is true of the typical high school textbook in science also tends to be true of other dissemination materials. As a result, we would expect that the vast majority of our population has grown up without even an elementary understanding of what the method really is and how long it takes to establish knowledge with a high degree of dependability.

"The second omission that appears from our analysis of current dissemination activities is that of the probability character, and especially the limits, of knowledge. Scientific knowledge as every investigator knows, exists in all degrees of refinement ranging from relationships that have been established with a high degree of probability (or a low probable error in the basic measurements) through less well-established generalizations to untested hypotheses. The degree of refinement determines the extent to which we can predict the probable result when knowledge is used in planning how to control the environment and ourselves. It determines the extent to which we can plan a course of action which will have the result we desire. For example, in the present state of knowledge there appears to be some relationship in young children between diet and tooth decay. It also appears that factors other than diet are involved in the production of caries. But what these factors are is not definitely known. An important one may be fluorine. The details of the relationships are, however, not clear. If the parent wishes to produce good teeth in his child he cannot logically expect that careful control of diet will certainly assure that the child will have perfect teeth when he takes him for his first visit to the dentist. Neither can the dentist assume that, because the child has many imperfections or cavities, the parent has neglected dietary principles. The parent may have been neglectful, but before one can infer this from the condition of the child's teeth the probable errors of the data expressing the relation of frequency and extent of caries to the food eaten must be reduced considerably.

"Finally, as every scientist knows, as long as scientific activity continues there is constant change in our knowledge. Hypotheses are subjected to test and changed into generalizations of known probability. More precise measuring instruments may be developed or more complete control of conditions may be achieved, with the result that generalizations having a relatively large probable error are replaced with generalizations having a small probable error, and so on."

This step-by-step confirmation of an original theory or hypothesis is the basic concept of the scientific method. It must recognize varying degrees of accuracy and of confirmation of any concept, and it cannot overlook the progressive narrowing of the application of an hypothesis or theory to increase its probability and its reality. If one ignores or neglects these basic concepts of the scientific method, then the methods of research become unfathomable. In the light of them, it is possible to discern significant patterns in most researches.

The great mass of what we shall presently define as pure science research is by its very nature outside of the range of most rules, and hence perhaps within the realm of genius. But industrial research can be reduced to certain clear patterns that have proved usable in many fields. This is fortunate, for industry requires that research be promoted and fostered so that industry may provide its fruits abundantly. This can be accomplished only by analyzing the tried and proved methods and procedures of research, as we propose to do in these pages, and applying them. It is quite beyond expectation that an analysis of this kind can materially affect pure research or those who pursue it; but should it prove possible to aid prospective industrial researchers in knowledge of their calling, our purpose will have been well served.

Actually, the pattern of successful industrial research as practiced in leading laboratories has assumed quite definite form. While no one can deny that genius is extremely valuable to a research worker, yet most modern developments are achieved with far less of this invaluable attribute than is commonly supposed. Imagination is essential and an ability to see beyond mere surface indications is unquestionably necessary to success in research. But given these qualities, an intelligent person properly trained is likely to be more productive in industrial research than a "genius" with the eccentricities likely to accompany this characteristic.

Basically research is a habit of thought and one that can be developed in the normally intelligent person quite as readily as a physical habit. Failure to cultivate research habits is responsible for many disappointments among hopeful young research workers.

The scarcity of brilliant investigators grows out of ignoring this fact, and particularly from its corollary, that methods of research and development as practiced in our industries are not taught in our colleges and universities. The average graduate or post graduate going into research has to learn, if he ever does, by hard experience the simple principles of his art.

Some able investigators even maintain that no such principles exist, that every operator has his own methods, his own peculiar ways of thinking, and his own schemes of solving problems. They will say, for example, that they themselves have no idea how to solve a future problem. When the problem is presented, they rely on hunches. If the hunches are correct, they are successful, and a few successes build a reputation as an expert.

Even the research "genius" often "just had an idea that so and so might work." He seldom knows where the idea originated. Apparently his subconscious mind is far more efficient than his conscious one. Somewhere in the back of his head certain brain cells reduce chaos to order and he is unconsciously guided toward the right solution. No wonder such men are considered geniuses; they can't even explain themselves how they did it.

Fortunately for others unendowed with a sixth sense to guide their hunches, these flashes of genius prove to be nothing more than a thorough knowledge of the subject combined with the application of certain common-sense principles. The mental processes necessary for successful industrial research are based on sound logic, and are by no means the aimless actions of a brilliant mind.

Research can be considered a game governed by certain rules. A close examination of these rules and the application of the general principles derived from them are sure to improve one's chances.

One would not attempt to play contract bridge, for example, without first learning the fundamental rules and the methods of bidding and playing. Anyone so unwise as to try to compete with a professional bridge player without this knowledge would find himself in a few hours' play far behind his professional competitor. Rarely, and much to his surprise, the neophyte may win. It is exactly the same in research. The untrained worker cannot successfully compete with the professional investigator, especially when the latter is abetted by a highly skilled co-operating organization. This is true even though the individual investigator is well educated in other ways if he is inexperienced in research.

Failures among would-be research workers are frequently traceable to this lack of proper training. Indeed, educators generally seem quite vague about what constitutes proper training for research. Many students, presumably trained for this vocation, are unable to achieve results or to keep up with others after they leave the universities to enter upon their careers. That is a serious situation, particularly when, as now, demand for qualified research men far exceeds supply.

The fault lies largely in lack of both understanding and appreciation by instructors of methods successfully employed in industrial laboratories. That is perhaps a direct consequence of too great reliance by educators on the literature alone as their source of material. One can read with the utmost diligence all the journals publishing researches and yet learn little of value about the methods employed in industry. The principal publications of industrial laboratories are patents and these scrupulously avoid suggesting the research methods by which the described result was reached. Even journal articles and papers from industrial sources commonly undergo the most rigid scrutiny by the patent staff and are revised to eradicate any hint of method that might help a competitor. Certainly it is unique to find published anywhere, whether from industrial or academic sources, any references to methods and measures which failed. Yet failures are often more instructive than successes, and the very human frailty of skipping lightly over errors, or ignoring them entirely, does not supply the student with the instructive value of the omitted material.

If we attempt to investigate the pedagogy of research, we encounter the shocking fact that no such thing exists in the universities. Usually the professor in charge of a group of research students follows one of two plans. Perhaps the more common practice is to tell each student, preferably once a day, just what he is to do during that day and how he is to do it. In other words, the student serves the instructor as an extra pair of hands. These finally become deft enough in two or three years to accomplish easily and quickly the manual labor required in investigation. The student is thus trained as a technician, but not at all in research.

Though this method is simple and satisfactory to the instructor, it falls short of teaching research methods to the student. He is likely to leave the university feeling that he has not been allowed to "play" with the machine, that the growth of his individuality has been hampered, and cherishing a desire to do things in his own way without detailed daily instructions. This is especially true of young men possessing natural aptitude for research who enjoy developing their own ideas. The student seldom receives from such instruction any clear idea of methods; if he does, it is usually quite accidental.

A few students are so antagonized by this treatment that they go to great lengths to prove the professor's scheme worthless, and one of their own far superior. These students are "Bolsheviks" and become foci of agitation and irritation for all around them, a particularly unfortunate trait in any organization. However, their "educational resistance" and their antagonism to suggestions foster a peculiar frame of mind which, even though unhealthy, puts them in a position really to learn research. Sometimes these individuals develop into geniuses, but seldom do they become good organization men, an essential characteristic in industrial research.

A second method of teaching research is to give the student a problem and let him alone. This technique has been carried to extremes on the assumption that a student will never learn the art of research by having someone else do his thinking for him. He must therefore be forced to think for himself.

This resembles the old fashioned method of teaching a neophyte to swim by throwing him off the end of a wharf. When he is about to sink for the last time, it is necessary to dive in and fish him out. The operation is repeated until the trainee of his own accord develops a method of operating his hands and legs that holds him up, and brings him back to the wharf.

As a method of instructing swimmers, this is no more adequate than its analogue in research. Often the student is sent to the library to look up everything he can find on a particular subject. He must then make his own selection of what he should do, and throughout he is permitted and encouraged to try out his own ideas, regardless of their probable value. When an idea has proved fruitless, as quite often happens, he is told to search the literature once more for a better one. The process is repeated until some sort of result is produced. This method develops the individual who already knows instinctively how problems can be solved. Furthermore, exceptional students with good mental stamina and ardent ambition develop wonderfully under this treatment. Others, whose potential value in research may be even greater, become discouraged and quit in the absence of sympathetic encouragement.

A more nearly ideal approach would tell a student, "Your problem falls within such a class. Problems of this particular nature have been solved satisfactorily in minimum time if a certain general procedure is followed." If he can be shown a standardized procedure for each type of research, the young man does not face a stone wall, nor does he feel it necessary to run to his instructor every hour to ask what to do next. In other words, a general scheme of research which the student can complete by adding the details would give him confidence, especially if he could see more than one way of reaching a satisfactory solution of a problem.

An example will illustrate. Assume the problem of preventing the formation of calcium sulfate scale in a boiler. If the instructor allows the student to believe that such problems are indefinite, and that no way exists to determine beforehand the physical or chemical characteristics of a compound that will suppress scaling, the student would feel hopeless from the beginning. Perhaps any one of a thousand different chemical compounds would serve. Lacking any theory, the student's only recourse is to the "shot gun" Edisonian method which we shall discuss in detail later. This would require developing a test, stocking the laboratory with these thousand compounds, and then putting one after another through the test. The solution becomes even more hopeless when we realize that concentration may be important, and it may therefore be necessary to test each individual compound at a great many different concentrations. This could require several years' work and lead to an absolutely negative outcome.

On the other hand, preliminary analysis by the instructor (or by the student) might suggest that problems of this nature could be solved by controlling the crystal growth of the scale, and that substances most strongly affecting growth of crystals from a water solution also tend to concentrate at the metal-liquid interface. Furthermore, substances tending to concentrate at this interface are known to decrease the surface tension of the solution. This provides a theory as a basis to start work. The original thousand possible compounds are narrowed by a process of reasoning alone to one class: surface tension depressors. Selecting for initial test something used before for a similar purpose, namely tannic acid, the student performs preliminary experiments and finds that this compound has a distinct favorable effect. But the basic conditions of the problem do not require a structure as complicated as tannic acid, which seems to be unstable. Apparently, tannic acid undergoes hydrolysis yielding gallic acid as one of the reaction products. This simpler compound, when tried, proves more effective. Pyrogallol, a compound of relatively simple structure but still meeting the basic requirements, proves best of all in further tests.

Thus a positive result is reached in a short time by first devising a theory based on experience or the literature. The investigation can continue along the same lines and perhaps uncover a reagent which will prevent the formation not only of calcium sulfate scale but of others as well. The student's ideas have now "risen to the dignity of an invention," and he may be amply rewarded for his pains and trouble.

In any event, he has learned something valuable about this type of research. Never has he been forced to lie awake nights and to cudgel his brain trying to conjure into being a marvelous inspiration that will overcome his difficulties. Furthermore, the manual labor has been relatively small, something that is bound to please any researcher, amateur or professional. Most important of all, the student is pleased with himself, and is given that soul-satisfying feeling that perhaps he may yet become an asset to the world in general and not a liability. The thrill of accomplishment thus experienced becomes a continuing goad to better work from then on.

If it were possible to lay down general principles applying to every class and type of research, a great step forward could be taken to reduce the gamble and to put industrial research on a productive basis. The only available method for discovering these general methods is to review in detail successful researches of others and to learn what characterized their methods and how these succeeded. This book is designed to apply this case method to successful research, and to survey a wide range of investigations to discover for future use the plans upon which they were conducted.

Chapter 2

The Dual Nature of Research

"All these (early flying) machines may be not inappropriately classified as devices of engineers to achieve flight by invention—call it practical experiment if you will—before the principles of dynamic motion had been studied. The practical man makes his machine first and lets experience decide whether its design is sound or not; the scientific man begins by investigating the principles involved in the problem, and then suggests how they may be met. The only satisfactory way to determine such principles is by experiment and calculations based upon the results." —Sir Richard Gregory

At the outset we must clearly differentiate two kinds of research, pure and applied. These are distinguished by their objectives and objective necessarily establishes the character of the work, often even in minor detail. We cannot here consider one more valuable, more important, more interesting or more fruitful than the other; that is not our present concern. Rather let us examine both to learn to use the methods of each when it is appropriate to do so.

Pure science is characterized by its aim to search out truth. If finding the truth should have practical results, all well and good, but the researcher is satisfied if his enlightened curiosity has reached a little nearer toward an answer to some of the great mass of questions about the meaning of life and our universe. Thus there can be no limitations of any kind placed upon the researcher in pure science, the philosopher, if you will. His imagination must be free and unfettered to range widely over his chosen field following up whatever clues he may discover and learning all he can, or cares to, about each. He must be free to redefine his objectives whenever it seems to him useful to do so, to narrow the scope of his investigation or to broaden it, to advance or to retreat with thought only for the problem in hand.

For our pure scientists are the great explorers. Theirs must always be the task of broadening our horizons. Others must follow after to develop the territory they have entered and explored.

This development of territory after it has been explored usually is undertaken for very definite purposes. The preliminary surveys of pure research indicate that results of utility and value may lie in a particular area and that these can be realized by further researches. Such subsequent researches thus have more or less clearly discernible and definable objectives. That at once characterizes them as what we differentiate as applied research.

Perhaps it would be more satisfactory to think of applied research as that undertaken for the purpose of attaining some useful objective in addition to, or aside from, the mere acquisition of knowledge for its own sake. The objective may be to solve some particular problem, as curing the tendency of a boiler water to form scale, or producing a billiard ball without ivory, or removing the stink from a particularly vile and refractory crude oil. While any of these highly practical researches may involve the most profound chemistry and physics, yet they are initiated for specific and definable purposes. They are pursued in order to reach some objective or objectives and not alone for the joy of the search.

In either case the methods of research may be much the same or they may contrast sharply, assuming quite individual aspects from the worker's point of view. The important difference is that the researcher in pure science is free to explore any by-paths that may attract him; while the worker in applied science must continually direct his attention and confine his energies to achieving his specified objective. In applied research questions of time and expense continually limit the freedom of the worker to follow his fancy into side issues. Even the most liberal management cannot totally ignore costs and probable return. Usually it is necessary that a worker in industrial research be able to show a reasonable probability of return from his excursions off the established line in order to justify himself in taking them.

In some ways the difference between pure research and that undertaken for utilitarian purposes is very much that between a scientist, properly so called, and an engineer. Sir Richard Gregory emphasizes this point in describing two approaches made toward the miners' safety lamp by Sir Humphry Davy, a recognized scientist, and by

George Stephenson, a contemporary engineer. Says Sir Richard in his well known book, "Discovery":

> "Industrial research is concerned not with the discovery of truth but with the production of something which will be of direct service to man and from which pecuniary profit may be secured. It is the province of the inventor rather than that of the man of science. Such research and that carried on with no ulterior motive are complementary to one another. Science has done its part when it has made a new discovery; constructive engineering renders good service when it shows how the discovery may be chained to the chariot of industrial advance. To foresee the possibilities of a discovery, to transform a laboratory experiment into the mechanical plant of a large works, or to apply it to the needs of ordinary life, require aptitudes not commonly possessed by the scientific investigator. The engineer usually has such practical purposes in mind; discoveries are to him things to be used and not ends in themselves, as they are to the man of science. He seeks not so much to know Nature as to circumvent her; and the research which he undertakes or organizes has for its object the artificial preparation of substances which are naturally rare, the production of a new process or the improvement of an old, the design of machines which will increase his power over her, and of instruments which will enable him to laugh at limitations of time and space.
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> "Research is necessary for these advances, but the spirit in which it is carried on is essentially different from that of the scientific worker. The engineer or the inventor first of all perceives a need and then endeavours to devise a means of meeting it. If he is of a scientific type of mind he will make an accurate analysis of the conditions to be fulfilled and then design his machine or instrument to fulfill them; but the usual way is to find practically what will perform the required functions, and to leave experience or scientific knowledge to indicate how improvements may be effected.
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> "The two methods may be illustrated by the discovery of the safety-lamp for miners. With no access to scientific works, or intercourse with scientific men, George Stephenson constructed a safety-lamp which, like Davy's, depended upon the principle that

the flame would not pass through tubes of small diameter and ignite explosive gases outside. Stephenson first made a lamp with a long chimney and a tube at the bottom to admit air for the flame. As this was found to give an unsteady flame, he corrected the defect by using several tubes of reduced diameter, instead of a single tube, to supply the air. This lamp was found to burn better than the first lamp, and was used with safety in a dangerous mine early in November, 1815. A few weeks later he had a third lamp constructed in which small holes in metal plates took the place of the tubes, but in this device he was forestalled by Davy, who presented to the public on November 9, 1815, his safety-lamp having wire gauze surrounding the flame.

"It is not our intention, however, to revive the angry controversy which arose over the respective claims of Stephenson and Davy as the discoverer of the miner's safety-lamp; all we wish to do is to use the invention to illustrate the different methods by which the same end may be reached. Stephenson made a lamp and then proceeded to test and perfect it; Davy, when he took up the problem of the cause and possible prevention of explosions in mines, first inquired into the nature of the explosive gases and of flame, and was soon able to announce his discovery 'that explosive mixtures of mine-damp will not pass through small apertures or tubes; and that if a lamp or lanthorn be made air-tight at the sides, and furnished with apertures to admit the air, it will not communicate flame to the outward atmosphere.' Davy discovered a principle and then constructed a lamp based upon it. Stephenson made a lamp and was led by it to a principle. Though there may be differences of opinion as to who was the inventor of the safety-lamp, the establishment of the principle of its construction was undoubtedly discovered by Davy, and was a notable advance of scientific knowledge. It was, however, left to practical men to devise the improvements which removed some of the defects of the lamp in its original form, and made it an efficient protection against the dangers of fire-damp in mines."

Thus the differences between the two great types of research, pure and applied, lie primarily in objectives and in the approach of the investigator to those objectives. These take their character from the point of view and the thinking of the person performing the research and are quite independent in other respects of the locale of the research or its sponsorship. Many of the universities have on occasion performed excellent industrial researches, and on the other hand, no brighter examples of pure scientific investigations can be found than those of Irving Langmuir, working in the industrial research laboratory of the General Electric Company. Langmuir's investigations into the realms of high vacua and of surface phenomena were planned and pursued in the most chaste spirit of pure science, and from his point of view it was only a side issue to the main researches that they turned out to exert profound effects on our whole civilization by supplying us with abundant, cheap light. On this subject of the character of research, Langmuir had this to say at the time he was awarded the Perkin Medal of the Society of Chemical Industry:

> "The leaders of industries are frequently conscious of the need of improvement in their processes, and even of the need of new discoveries or inventions which will extend their activities. It is thus logical, and often extremely profitable, to organize research laboratories to solve specific problems. Efficiency requires that the director shall assign to each worker a carefully planned program. Experiments which do not logically fit in with this program are to be discouraged. This type of industrial research, which should often be called engineering rather than research, has frequently been very successful in solving specific problems, but usually along lines already foreseen.
>
> "This method, however, has serious limitations. Directors are rare who can foresee the solutions sufficiently well to plan out a good campaign of attack in advance. Then, too, the best type of research man does not like to be told too definitely what must be the objects of his experiments. To him scientific curiosity is usually a greater incentive than the hope of commercially useful results. Fortunately, however, with proper encouragement, this curiosity itself is a guide that may lead to fundamental discoveries, and thus may solve the specific problems in still better ways than could have been reached by a direct attack; or may lead to valuable by-prod-

ucts in the form of new lines of activity for the industrial organization.

"Of course, no industrial laboratory should neglect the possibilities of the first and older method of organized industrial research. I wish, however, to dwell upon the merits of the second method in which pure science or scientific curiosity is the guide."

As the outstanding example of the industrial value of research in what can be properly called pure science, Langmuir detailed the history of his work in the development of the gas-filled incandescent electric lamp. This grew out of an excursion around the General Electric laboratory seeking some suitable subject for study during a summer vacation from his teaching duties at Stevens Institute.

"A large part of the laboratory staff was busily engaged in the development of drawn tungsten wire made by the then new Coolidge process. A serious difficulty was being experienced in overcoming the 'offsetting' of the filaments, a kind of brittleness which appeared only when the lamps were run on alternating current. Out of a large number of samples of wire, three had accidentally been produced which gave lamps that ran as well with alternating current as with direct current, but it was not known just what had made these wires so good. It seemed to me that there was one factor that had not been considered—that is, that the offsetting might possibly be due to impurities in the wire in the form of gases. I therefore suggested to Doctor Whitney that I would like to heat various samples of wire in high vacuum and measure the quantities of gas obtained in each case.

"In looking through the laboratory I had been particularly impressed with the remarkably good methods that were used for exhausting lamps. These methods were, I thought, far better than those known to scientific research workers. My desire to become more familiar with these methods was undoubtedly one of the factors that led me to select for my first research an investigation of the gas content of wires.

"After starting the measurements that I had planned, I found that the filaments gave off surprisingly large quantities of gas. Within a couple of weeks I realized that something was entirely wrong with my apparatus, because from a small filament in a couple of days I obtained a quantity of gas which had, at atmospheric pressure, a volume 7,000 times that of the filament from which it appeared to have come, and even then there was no indication that this gas evolution was going to stop. . . . I spent most of the summer in trying to find where this gas came from, and never did investigate the different samples of wire to see how much gas they contained.

"What I really learned during that summer was that glass surfaces which have not been heated a long time in vacuum slowly give off water vapor, and this reacts with a tungsten filament to produce hydrogen, and also that the vapors of vaseline from a ground-glass joint in the vacuum system give off hydrocarbon vapors, which produce hydrogen and carbon monoxide. . . .

"I was given first one assistant and then others to continue experiments on the sources of gas within vacuum apparatus, and a study of the effects produced by the introduction of various gases into tungsten filament lamps. The truth is that I was merely curious about the mysterious phenomena that occur in these lamps. Doctor Whitney had previously found that gases have a habit of disappearing in lamps, and no one knew where they went to, so I wanted to introduce each different kind of gas that I could lay my hands on into a lamp with a tungsten filament and find out definitely what happened to that gas. . . .

"For my study of the effect of gases, I had to devise new types of vacuum apparatus. I needed particularly to be able to analyze the small quantities of gas that existed in the tungsten lamp. With some of this special apparatus I was able to make a practically complete quantitative analysis of an amount of gas which would occupy about 1 cu. mm. at atmospheric pressure. In this sample of gas, we could determine the percentages of oxygen, hydrogen, nitrogen, carbon dioxide, carbon monoxide, and the inert gases.

"In regard to the fate of the different gases which I introduced into the lamp bulb, I found that no two gases acted alike. Oxygen attacked the filament and formed tungstic oxide, WO_3. That seemed simple enough, but the kinetics of the reaction presented many features of considerable scientific interest.

"In studying the effect of hydrogen very peculiar phenomena were observed. A limited amount of hydrogen disappeared and became adsorbed on the bulb, where it remained in a chemically active form, which was capable of reacting with oxygen at room temperature even long after the tungsten filament had been allowed to cool. This suggested hydrogen atoms and seemed to confirm some conclusions that I had already drawn from observations on the heat losses from tungsten filaments in hydrogen at atmospheric pressure. . . .

"By connecting a voltmeter and an ammeter to the tungsten filament which was being heated in hydrogen, I could determine the temperature from the resistance and also find the heat loss from the filament in watts. I wanted to see if anything abnormal happened when the temperature was raised to the extremes which were only possible with tungsten.

"The results greatly interested me, for they showed that the energy loss through the gas, which increased in proportion to the square of the temperature up to about 1800° K., increased at a much higher rate above that, until at the highest temperatures the energy varied in proportion to about the fifth power of the temperature. This result could be explained if the hydrogen at high temperatures were dissociated into atoms. The diffusion of the hydrogen atoms from the filament, and their recombination at a distance from it, would cause an enormous increase in heat conduction. . . .

"A large number of experiments, extending over several years, were made in this study of atomic hydrogen. Nearly all of these experiments would have seemed quite useless, or even foolish, to a man who was making a direct and logical attack on the problem of improving tungsten lamps.

"When nitrogen at low pressure was introduced into a bulb containing a tungsten filament at extremely high temperatures, such as 2800° K., the nitrogen disappeared at a rate which was independent of its pressure; in other words, here was a case of a reaction of zeroth order. This suggested that the reaction velocity was limited by the rate at which the tungsten evaporated from the filament. To check this hypothesis the rate of loss of weight of filaments at various temperatures was measured in good vacuum. This rate varied with the temperature in accordance with known thermodynamic laws, and since the rate per unit area was independent of the size of the filament, it was concluded that the loss of weight was really due to evaporation and not to chemical action of residual gases or to electric currents that passed from the filament to the surrounding space.

"A comparison of the rate of disappearance of nitrogen with the loss of weight in the filament showed that one molecule of nitrogen disappeared for every atom of tungsten that evaporated. A brown compound, WN_2, was formed which deposited on the bulb and decomposed when water vapor was introduced, forming ammonia gas.

"From time to time the question kept arising—how good would a lamp be if it had a perfect vacuum? And now, from studies of the character I have described, I began to have an answer. Hydrogen, oxygen, nitrogen, carbon monoxide, and in fact every gas that I introduced, with the exception of water vapor, did not produce blackening of the lamp bulb. The serious blackening that occurred with only small amounts of water vapor depended upon a cyclic reaction in which atomic hydrogen played an essential part. The water-vapor molecules coming in contact with the hot filament produce a volatile oxide of tungsten, and the hydrogen is liberated in atomic form. The volatile oxide deposits on the bulb where it is reduced to the metallic state by the atomic hydrogen, while the water vapor produced returns to the filament and causes the action to be repeated indefinitely. Thus, a minute quantity of water vapor may cause a relatively enormous amount of tungsten to be carried to the bulb.

"The question then arose whether the traces of water vapor, which might still exist in a well-exhausted lamp, were responsible for the blackening which limited the life or the efficiency of many of these lamps. We made some tests in which well-made lamps were kept completely immersed in liquid air during their life, so that there could be no possibility of water vapor coming in contact with the filament. The rate of blackening, however, was exactly the same as if no liquid air had been used.

"Having thus proved that the blackening of a well-made lamp was due solely to evaporation, I could conclude with certainty that the life of the lamp would not be appreciably improved even if we could produce a perfect vacuum."

At about this juncture, Langmuir became interested in the study of heating devices which continued and somewhat supplemented his previous work on filaments, including as it did heat losses from wires as well as from plane surfaces. His account continues:

"I was able to develop a theory of the heat losses which enabled me to calculate the loss from a wire of any size at any temperature in any gas, assuming, however, that the gas did not dissociate at high temperatures.

"Having now a definite theoretical basis on which to calculate the normal loss by convection, I was able to prove that the abnormal rate of heat loss previously observed with tungsten filaments at high temperatures in hydrogen was due to actual dissociation; in fact I was thus able to calculate the heat of dissociation and the degree of dissociation at different temperatures.

"However, to make sure of these conclusions I wished to make measurements of the heat losses in gases which could not possibly dissociate and therefore undertook experiments with heated tungsten wires in mercury vapor at atmospheric pressure. A little later I experimented with nitrogen to see if this gas dissociated at high temperatures, but found that it did not do so. In both of these gases the filaments could be maintained at temperatures close to the melting point for a far longer time than if heated in vacuum at the same temperature. Thus the rate of evaporation was greatly decreased by the gas, many of the evaporating tungsten atoms being brought back to the filament after striking the gas molecules.

"By this time I was familiar with all the harmful effects which gas can produce in contact with filaments and knew under what conditions these bad effects could be avoided. In particular, I realized the importance of avoiding even almost infinitesimal traces of water vapor. Thus, when I found a marked effect of mercury vapor and nitrogen in reducing the rate of evaporation, it occurred to me that it might be possible to operate a tungsten filament in gas at atmospheric pressure and obtain a long useful life. Of course, it would be necessary to raise the temperature far above that at which the filament could be operated in vacuum in order to compensate for the serious loss in efficiency due to convection resulting from the rise in filament temperature. Whether or not the increased rate of evaporation, due to this increase in temperature, would more than offset the decrease in the rate due to the gas was a matter that could only be tested by experiment.

"In connection with my studies of the heat losses from filaments of various diameters at incandescent temperatures, I had found that the heat loss increased only very slowly with the diameter, so that the loss per unit area from a small filament was enormously greater than from a large filament. Calculations showed that it was hopeless to get practical lamps with filaments in nitrogen, if these filaments were of very small diameter. For example, a filament 1 mil in diameter, which corresponds to an ordinary 25-watt lamp, if run in nitrogen at atmospheric pressure would consume 4.8 watts per candle at a temperature of 2400° K., which would give 1 watt per candle with a filament in vacuum. This great loss in efficiency is due to the cooling effect of gas. To bring back the efficiency of the gas-filled lamp to that of the vacuum lamp, it would be necessary to raise the temperature from 2400° to 3000° K., which would have caused a 2000-fold increase in the rate of evaporation, and such an increase could certainly not be compensated for by the effect of the gas in retarding the evaporation.

"With filaments of much larger diameter, however, the effect of the gas in decreasing the efficiency was not nearly so marked. We therefore constructed lamps having filaments of large diameter in the form of a single loop and filled these lamps with nitrogen at atmospheric pressure. We ran these lamps with a filament temperature so high that, in spite of the gas, the efficiency corresponded to about 0.8 watt per candle, instead of the usual 1 watt per candle at which we tested our vacuum lamps. We were disappointed to find that these lamps blackened much more rapidly than vacuum lamps of similar efficiency so that the total useful life of the lamp was short.

"This result, which is what most lamp engineers would have expected, seemed to indicate that the rise in temperature necessary to offset the heat losses by the gas increased the evaporation by more than the amount of the reduction in evaporation due to the gas. If I had not previously become so familiar with the behavior of various gases, this discouraging result might easily have stopped further experimenting in this direction. However, I noticed that the bulb had blackened during the short life of the lamp, whereas from my knowledge of the interaction of tungsten and nitrogen I had expected a deposit of a clear brown color. I felt that the black deposit, therefore, could mean only one thing, water vapor, notwithstanding the fact that to avoid this water vapor we had taken precautions which were greater, I believe, than had ever been used before for the preparation of moisture-free gases and glass surfaces. We were thus led to take still greater precautions and use still larger bulbs so that the glass surfaces could not become overheated by the convection currents in the gas that rose from the filament. We were then soon able to make lamps having a life of over 1000 hours with an efficiency about 30 to 40 per cent better than could have been obtained with filaments in vacuum.

"As I look back upon these experiments I think that we were very fortunate at that time in not having had at our disposal a supply of argon gas. From theoretical reasons I had concluded that argon should be better than nitrogen, and if I had had argon I should probably have tried it first. If these lamps had blackened because of traces of water vapor, I would naturally have attributed this to the increase in evaporation caused by the high temperature, and would have had no reason for suspecting that water vapor was the cause of the trouble, for, of course, in argon a brown deposit would not be expected in any case.

"The lamps that we were able to make in this way, with an improved efficiency, were limited to those which took a current of 5 amperes or more, so that the method was not applicable for 110-volt lamps with less than 500 watts. Some time later, however, it occurred to me that the benefits derived from the large diameter of the filament could be obtained with one of the smaller diameter by coiling the filament in the form of a helix, bringing the turns of the helix very close together. In this way, and by the use of improved tungsten filaments that do not sag so readily at high temperatures, and by using argon instead of nitrogen, it has gradually been possible to construct gas-filled lamps which are better than vacuum lamps down to about 40 or 50 watts. These smaller lamps, although not much better in efficiency than the vacuum lamp, have the advantage of giving a much whiter light. In the case of the larger lamps, the use of the gas filling, together with the special construction of the lamp, more than doubles the efficiency.

"The invention of the gas-filled lamp is thus nearly a direct result of experiments made for the purpose of studying atomic hydrogen. I had no other object in view when I first heated tungsten filaments in gases at atmospheric pressure. Even at the time that I made these experiments at higher pressures, they would have seemed to me useless if my prime object had been to improve the tungsten lamp."

Chapter 3

Stating the Problem

> *"Our mind is not likely to give us a clear answer to any particular problem unless we set it a clear question, and we are more likely to notice the significance of any new piece of evidence, or new association of ideas, if we have formed a definite conception of a case to be proved or disproved."*[1] —Graham Wallas

Perhaps the most important step in any research is to understand the problem at the beginning. Understanding it is an essential prerequisite to stating it clearly and correctly. The significance of the terms in which an industrial problem is stated has been suggested but not elaborated in a previous chapter in discussing boiler scale. Control of the crystallization of calcium sulfate from boiler water to prevent scale in the boiler may be stated in almost any number of ways; the terms depend upon who is making the statement and for what purpose. The stockholders would think of boiler scale only if it became a question of dividends. The directors might think of it as affecting efficiency of operation. To the president, it would be a matter of the diligence of the works manager and the works manager would look to the superintendent, who in turn would question the engineer. Finally, at long last, the director of research might be given the problem, but most probably in the form of a question of the efficiency of the power plant.

At this point a great many solutions are still possible: the plant might purchase power; it might seek a new source of boiler water; it might exchange steam turbines for diesel engines; it might install a water treating plant; it might change the blow-down cycle of the boilers to throw out much of the scale as it is formed; and finally it might initiate a search for a method of flocculating calcium sulfate to prevent it from scaling inside of the boiler, as we have noted.

Only when the problem is stated in some such terms as these last is it a proper subject to turn over to an individual in the research department as soluble by the methods of research. It must already have undergone a succession of narrowing operations to bring both problem and solution into focus.

In whatever form the problem reaches the research department, someone must at that point scrutinize and analyze it, and state or restate it in such terms that its solution becomes practical. It is impossible to overestimate the importance of this step in the process of research. Every research laboratory is cluttered with problems left unsolved. Presumably these are beyond or outside the abilities or skills of the available workers, but much more likely they have not been stated in practicable terms.

Ability to accept problems in the most general terms and then to restate, analyze and subdivide them is a skill of the highest value in any organization. Furthermore, possession of this skill somewhere in the organization, preferably in both management and research, is an inescapable necessity for efficient functioning of a research department. Research may supply information to management to help decide between purchased or produced power, between steam and diesel, and between other like alternatives, but these are primarily problems of management and not of research. Not only must it be possible to break problems down into parts that can be handled, but management, whose function it is to subdivide and assign tasks, must be able to understand what the whole thing is about and how it functions.

Lack of such understanding by management sometimes leads to weird results. A company president once posed this problem to me to suggest the value of cooperating with him. Said he: "I have an idea for a paint remover that will avoid all extant patents and make them useless. The mixtures present patents suggest simply soften the paint; you still have to remove it afterward. My new remover would actually take the paint off the wall so that it could be swept up from the floor." "Well," said I, "that is a valuable property and should create a great demand. What do you want me to do about it?" "Oh," said my friend, "I want you to tell me what to put in it!"

Even though that problem was all solved a quarter of a century ago, except for the essential detail of what to put in the product to make it function in that way, nothing of the kind has yet appeared on the market. Attempts to state the problem of such a composition in a form that can be solved suggest the reasons for this. Such a composition might be based on either of two kinds of softening agents already well known and widely used in paint and varnish removers: alkalies that would saponify the organic acids and thus convert them into water-soluble form; or organic solvents that would dissolve, swell or soften the film to be removed.

The use of alkalies to dissolve paint films is well known. Metal parts can be completely cleaned by dipping in a caustic lye of an appropriate concentration and temperature to dissolve the coating at hand. There is even an effective alkali remover for application to large objects (too large to immerse) which consists of a strong caustic lye to which a starch has been added for the purpose of holding the lye in a moist, and hence active, condition against the paint surface. If lye alone is spread on a surface, the solution drains off or its water content quickly evaporates and leaves the caustic dry and unreactive in contact with the incompletely attacked paint film. Adding starch to the lye before applying it to the paint film changes both its adhesion to the surface and its moisture holding characteristic; and the starch-lye holds the caustic in a moist layer on the surface to be cleaned. Because the starch swells in the lye, it also shrinks greatly as it dries. Thus if a caustic-starch paste of the kind suggested is applied to a surface and allowed to dry on it, the resulting layer will pull up into concave chips through the greater contraction of the outer surface because of its more rapid drying.

That would seem to indicate one direction for investigation, but unfortunately the caustic-starch paste remover has several apparently insuperable drawbacks to its general application. Most important of these is the attack of the caustic in such a mixture on wood and the difficulty of removing all the caustic from the wood itself after the oil paint film has been softened and removed. Caustic roughens the surface of wood, a serious fault expensive to correct if the surface is to be refinished, and any slight residue of alkali in or on the surface would injure the new finish applied over it. Washing woodwork with water, necessary to remove caustic, may also injure the wood surface for re-finishing.

When a caustic-starch paste remover is applied to metal surfaces, for which it is admirably suited, the paste and the old paint film, now practically saponified, can be easily, quickly and completely flushed off with water without injury to the surface, which need only dry to be in ideal condition for refinishing.

A possibility also interesting would produce some such effect with a paste based on organic solvents instead of water and utilizing the solvent effects of organic compounds instead of the saponifying action of lye. The present well known paint and varnish removers are formulated to include mixed solvents capable of softening and/or dissolving the paint film, and in addition a non-volatile constituent to retard the evaporation of the solvent mixture.

Nitrocellulose, for instance, and vulcanized rubber have the property of swelling in certain organic solvents, much as starch does in alkali, and might thus be employed under some yet unknown conditions to produce an effect of the kind desired.

The drawback of course is that the curling action of unequal drying of either type of material requires that the curling film approach dryness, whereas the softening of the paint film requires the moist condition produced by a relatively high concentration of solvent. Furthermore, the adhesion between the softened paint film that is to be pulled off and the drying layer of paste may be considerably less than the adhesion of the paint film, even when substantially dissolved by the remover, to the surface from which it is to be removed. Preliminary experiments along these lines at the time proved too discouraging to justify further pursuit of the idea.

Obviously, such a paint remover must perform a service of a value enough greater than that of existing materials of the kind to pay for both the added cost of the improved product used in the operation and the research, development and sales expense required to put it in the user's hands. That requires a knowledge of the possible users, the purposes for which they might employ the product and the value it might be to them in competition with other materials and methods for reaching the same results. In the case in point, even a cursory examination reveals the possibilities of profit to be too small to justify an extensive research.

While that problem can be reasonably pigeon-holed on the basis of such an examination and analysis, that by no means indicates that it must be permanently interred among the totally dead. At any time that the researcher learns of some new information or the property of some new or unfamiliar stuff that might contribute to its solution, the problem can be brought out for re-examination and reanalysis.

An organic compound, for example, having solvent properties combined with those of a base strong enough to react with linoxyn but not strong enough to "raise the grain" of wood might very well change the whole picture and completely nullify all previous estimates of the matter.

Actually that problem belongs in the same pigeon-hole with one seriously proposed to the late Allen Rogers during the extreme shortage of fast dyes during World War I. A visitor one afternoon sought the professor's help on what he said was an important problem. It had to do, he said, with a fast black dye that would resist any amount of any kind of mistreatment without fading. Dr. Rogers was immediately interested and asked for details. The visitor then insisted that every precaution be taken against eavesdroppers, and only when he was fully assured on this point and convinced of the trustworthiness of the professor did he reveal his idea. "Carbon," said he, "is absolutely permanently black and it blacks everything it touches. It should be able to impart this permanent blackness to a fabric immersed in a solution of carbon. What I want you to tell me, Dr. Rogers, is some good cheap solvent for carbon that will serve that purpose!"

It is hardly necessary to point out that the only known solvent for carbon is molten iron and that molten iron is hardly the kind of stuff one would choose for a dye bath to dye milady's nylons.

There is, of course, the possibility, not yet even remotely approached, that some method might be devised of creating a bond like that presumed to exist in rubber compounds between the excessively fine colloidal particles of gas carbon and the molecules comprising the filaments of textile fabrics. One might thus approach the ideal permanent black dye by establishing an electrical, or colloidal, or chemical, bond between carbon particles of almost molecular dimensions and the huge molecules of textile fibers. This might be direct or through some intermediate stuff acting as a mordant. All of which is interesting speculation but hardly significant industrially in the face of the extreme permanence and cheapness of modern vat dyes.

Far more unsolved research problems are left in some such form than in any other. Actually, of course, they are not, and sometimes as in these instances cannot become, proper research problems. For that purpose, they must be initiated entirely anew from the beginning and put into terms that make soluble problems of them. That re-examination can be undertaken best and most profitably whenever an important scientific advance opens new possibilities of successful attack on a variety of hitherto unsolved problems. The electron microscope, for instance, provided an eye far more deeply penetrating than had ever before been available to microscopists and thus justified a re-examination of problems involving what had previously been considered colloidal and amorphous particles. A number of puzzling questions about pigments were at once solved by electron examinations. The development of pH measuring techniques supplied immediate answers to great numbers of problems that had previously been abandoned as insoluble but which readily yielded to control of pH of the environment. Problems of tanning, fermentation and other processes involving proteins yielded readily to this treatment.

Often the statement of a problem requires the light that some alien instrument or technique can shed upon it before it can be intelligible and soluble. T. F. Bradley's research on the alkali isomerization of drying oils is a case in point. The problem was to increase the unsaturation of fatty oils, or the conjugation of their double bonds, to such an extent that plentiful non-drying oils could be made to replace drying oils unobtainable because of war.

Two types of structure characterize the best drying oils and seem closely coupled with the drying property: double bonds (unsaturation) and conjugation of double bonds (that is, pairs of double bonds connected to neighboring carbon atoms). While unsaturation is essential to drying, conjugation enormously enhances the drying property imparted by each unit of unsaturation. Now, while unsaturation is readily and accurately determined as the iodine number, chemical determination of degree of conjugation is not simple nor do the results have any considerable degree of precision. In fact, analyses for degree of conjugation by chemical methods are little more than guided guesses and results are at best only rough approximations.

Now, the method of isomerization under investigation by Bradley consisted of heating the fatty acid with an excess of alkali. Theory indicated that this reaction would succeed, but the change in conjugation effected by this treatment in the early stages of the research was less than the limit of error of the method of its determination. Under the circumstances no trends were anywhere discernible among the analyses from a long series of tests.

Thus it was that the whole line of investigation was about to be abandoned when the far more accurate and penetrating ultraviolet spectroscopic method of determining conjugation was tried. Immediately a trend became apparent from the reanalyses of samples already prepared and this trend indicated the direction subsequent experiments must take to produce the desired result. Following the new direction led to prompt success.

An obviously vital step in any successful research, usually the first one, is an examination of all available literature bearing on the subject. Careful reading of available pertinent journal articles and reference books usually provides a basis of judgment on which a problem can be correctly stated for the quickest and easiest solution. Sometimes, the literature supplies a complete solution which needs only to be tested under the specified special conditions to be ready for use. In any case, known data culled from the work of others circumscribe the unknown area and thus limit the amount of speculation and experiment needed to reach the required solution. Moreover, the findings and conclusions of others in the same or closely related fields will always help the research worker to understand his own problem better and to clarify his own thinking about it.

Literature searches immediately establish what may be called the level of the known and unknown respecting a particular problem. In the paint remover problem analyzed above, the literature at once reveals many solvents that alone or in mixtures will soften paint films, a number of alkalies capable of saponifying linoxyn with various degrees of speed and completeness, and a number of additives that would maintain the surface wetted with either solvent or lye in a moist condition. But nothing found is apparently likely to guide the investigator to a composition capable of reducing the old paint film to non-adherent chips or powder.

In any case, the value of certain experiments becomes evident to the researcher from his survey of the literature. When these have been carefully thought out, designed in detail and finally performed, the results are likely to stimulate further thinking and may very well suggest new lines of reading in the literature which were not obvious and hence were neglected in the first search.

This suggests the most important general method employed in industrial research organizations: a series of resorts alternately to the literature and to the laboratory. By this method the problem is narrowed by successive steps and the solution is made gradually more obvious until the final result becomes practically inescapable. At each stage in the process the problem can be restated in the light of the greater information available, and thus it can be substantially clarified and the research progressively limited. In this way, too, the field of inquiry in the literature becomes progressively narrowed and the objective of the search clearer as one step in the process of solution follows another. Thus the process of research reduces itself to a succession of statements of the problem ever more precisely focussed upon the solution as information accumulated bit by bit shrinks the unknown area around the objective.

A specific application of this general principle is the development of accelerators for the vulcanization of rubber.

George Oenslager entered the rubber industry in 1905 at a time when the industry itself did not know that it had problems a chemist might solve. Indeed, at that time the rubber industry had scarcely become conscious of itself as an entity having problems; but already rubber manufacturers had learned that different types and grades of rubber behaved differently in finished goods. So it was that Oenslager's first problem stated to him in the most general terms involved utilizing low-grade, and hence low-priced, rubbers economically. Neither the prospective researcher nor the management which assigned him the problem was particularly sanguine of attaining the announced goal, but both expected to learn by the attempt. In accepting the Perkin Medal for his work, Oenslager described his experiences in stating and restating this broad problem by successive stages toward its solution:

> "Realizing that the physical properties of vulcanized rubber were determined by the type of crude rubber used in the mixture, Marks concluded that there must be some reason why Fine Para after vulcanization was much superior to any other type of rubber. He noted that of the two rubbers obtained from the same tree, Islands Fine Para by evaporation, and Islands Coarse by spontaneous coagulation of the latex, the Islands Fine was faster in cure and gave superior qualities after vulcanization. He also noted that Up-River Fine Para and Manicoba rubbers, both obtained by the evaporation of latex, were fast in their rate of vulcanization and gave high-grade vulcanized products. From this he reasoned that,

possibly during coagulation, as a result of fermentation, certain materials naturally occurring in the latex were either destroyed or were removed with the serum which separates during coagulation. These materials, perhaps small in amount, might be responsible for the superior quality of Fine Para. He therefore extracted the acetone-soluble constituents from some Fine Para rubber, amounting to about 2 per cent by weight. The extracted rubber, on being mixed with sulfur and vulcanized, proved to be poorer in quality than the unextracted rubber. On adding the acetone-soluble material from Fine Para to a mixture containing Coarse Para and sulfur, the rate of cure was increased and the quality greatly improved. This fundamental experiment convinced him that perhaps the cheaper grades of rubber, and in particular rubber extracted from Pontianac, could be improved in quality after vulcanization by the addition to the crude rubber of materials then unknown. The problem of improving the quality of articles made from extracted Pontianac rubber was assigned to me as research chemist in 1905. The reward in case of success was most alluring. If it were possible to manufacture first-quality goods from the 10-ton daily production of cheap rubber from Pontianac, there was a potential saving of around a dollar per pound of rubber, two thousand dollars a ton, or twenty thousand dollars a day.

"The first question considered was: Does the extracted rubber have the same chemical composition as Fine Para? After freeing it from the 4 per cent of organic dirt, 5 per cent of mineral matter, and 5 per cent of resinous material which it usually contained, the clean, transparent rubber, now of a pale yellow color, had practically the same proportions of carbon, oxygen, and hydrogen as Fine Para rubber. Thinking that possibly the mastication of the extracted Pontianac rubber could result in partial oxidation, which might be the cause of its inferior qualities after vulcanization, systematic analyses of the rubber were made before and after mastication. No important change in chemical composition was found. Many other experiments were carried out in order to familiarize myself with the chemistry of rubber.

"It was now thought desirable to carry out a systematic study of the effect of adding a great variety of typical organic compounds to simple mixtures of rubber, zinc oxide, and sulfur, and to note the results of heating for varying periods of time at different temperatures. In other words, endeavors were being made to find out whether or not there were catalysts of the reaction between rubber and sulfur other than white lead, litharge, lime, and magnesia, which had been in common use in the industry. It did not then seem reasonable to me that the oxides or hydroxides of three elements—calcium, magnesium, and lead—could be the only compounds which would act as catalysts for the vulcanization of rubber, a change which, in common with the chemists of that day, I attributed exclusively to a chemical combination between rubber and sulfur. It was my intention to experiment with at least one compound of all the commonly available elements and later with typical organic compounds.

"The first compounding and curing experiments were conducted with materials then available in the laboratory. A suitable formula was chosen closely approximating that commonly used in the manufacture of tire treads at that time, calling for 100 parts of Fine Para rubber, 62.5 parts of zinc oxide, and 6.25 parts of sulfur. Such a mixture develops its maximum tensile strength of about 2800 pounds per square inch when vulcanized 90 minutes at 287° F. In this mixture, the Fine Para was replaced with Corinto rubber, a Central American rubber which cured very slowly and had poor physical properties after vulcanization, and to it was added such materials as barium sulfide, zinc dust, aluminum powder, tin dust, lead powder, red phosphorus, antimony trisulfide, silver sulfide, mercuric sulfide, and many other materials. It was hoped that the added sulfides or, more probably, those formed in the rubber mixture by combination with sulfur under the conditions which obtained during vulcanization, would further react to form polysulfides and that these might be active catalysts or sulfur carriers. All these materials, and many others, were found to be of little or no value as catalysts of the reaction. One material was found, however, which had remarkable properties—namely, mercuric iodide. When incorporated in small amounts into the standard rubber batch, it had a profound effect on the rate of cure; for example, a mixture containing 100 parts of Corinto rubber, 60 parts of zinc oxide, and 10 parts of sulfur would not give a good, technically cured product when heated for 2 hours at 291° F. The maximum tensile strength was only 1200 pounds per square inch. When, however, 2.5 per cent of mercuric iodide, based on the weight of the rubber, was added to the batch, a product having a maximum tensile strength of 2600 pounds per square inch was obtained by vulcanization in the short time of 20 minutes. This substance was apparently a powerful catalyst for the rubber-sulfur reaction, and its effect on vulcanizing a number of the important grades of rubber was studied.

"The amount required to produce a definite degree of cure in a definite period of time at a definite temperature varied with the grade of the rubber, being smallest with the fast-curing and largest with the slow-curing rubbers. Even extracted Pontianac rubber (which gave a very poor, technically cured product in a mixture containing only rubber, zinc oxide, and sulfur) gave an excellent product upon the addition of a few per cent of mercuric iodide, closely approaching the highest grades of rubber in quality. After further experiments with mercurous and mercuric bromides and chlorides, mercuric iodide was found to be the most satisfactory material of all which were tried.

"Here was a distinct step in advance. A substance had been found which, when added in small amount to any of the common rubbers, would cause them to cure at the same rate under identical conditions, and yield products having approximately the same physical properties in the vulcanized state. Also, it was found that, by decreasing the sulfur below the amount then in common use and increasing the amount of catalyst, the physical properties (tensile strength for example) could be greatly improved. Mercuric iodide, therefore, not only hastened the vulcanization of the slow-curing rubbers but also imparted to them in the vulcanized state the remarkably fine physical properties of high-grade rubbers, which litharge, lime, and magnesia had failed to do.

"These experiments showed that tremendous profit could be made if through the use of mercuric iodide the cheaper grades of rubber could be substituted for the more expensive varieties. The fact was not overlooked that mercuric iodide might act as a carrier for oxygen as well as for sulfur and consequently hasten the deterioration of the vulcanized product. However, lacking the laboratory aging tests now commonly used for quickly measuring deterioration, the enormous economies at stake induced the company to manufacture in April, 1906, a limited number of solid and pneumatic tires containing mercuric iodide and cheap grades of rubber in order to ascertain how they would perform in service. Because of overcure or, more probably, because oxidation was promoted by the mercuric iodide, many of of these pneumatic tires failed badly in service.

"Nevertheless, the results of the work with mercuric iodide were very encouraging because they demonstrated that at least one material had been found which, when used in small quantities, would produce the desired effect on vulcanization. It was believed that only time and persistent experiments were required to find others. It was obvious that the poisonous characteristics of mercuric iodide made its use an extremely undesirable industrial hazard and that something less injurious to workmen would have to be found. Therefore, without awaiting the results from the experimental tires, and believing that the survey of the field of inorganic compounds had been sufficiently thorough for the time being, I turned my attention to organic compounds. When one considers that materials such as lime, litharge, and magnesia, long used as catalysts or accelerators for the reaction between rubber and sulfur, are basic in character, it would seem natural to conclude that an organic base completely soluble in rubber might be a more satisfactory catalyst. Aniline, being one of the simplest, commonest, and cheapest of the organic bases, was the first which I investigated. This material was found to have marked value as an accelerator when used in the tread recipe to the extent of between 4 and 6 per cent on the weight of the rubber. Since the basic properties of aniline are due to the amino radical, it was deemed necessary to determine the significance of the amino group of organic compounds in their action as catalysts of vulcanization. Various nitrogenous bases were employed in the study. Toluidine and xylidine gave good results; naphthylamine in comparison gave poor results. Replacement of the hydrogen atoms of the amino groups with organic radicals seemed to decrease the catalytic action; dimethylaniline and diphenylamine were found to be only slightly active, if at all. If to the amino group was attached a carbonyl group, as in acetamide or acetanilide, the activity was greatly decreased. Materials such as phenylhydrazine containing an $-NHNH_2$ group, and hydrazobenzene, containing an $-NH{\cdot}NH-$ group, were inactive. Quinoline gave fair results; urea gave excellent results, as did also hexamethylenetetramine. It was observed that not all compounds containing nitrogen were useful as accelerators, but of those which had value, the activity appeared to be related to the presence of amino nitrogen.

"At the same time, the search for good catalysts included various other types of compounds. Typical materials such as naphthalene and anthracene, iodoform and phenyl iodide, mono- and dinitrobenzene, benzaldehyde, phenyl sulfocyanate, gallic acid, tannic acid, phenol, ethyl oxalate, azobenzene, phthalimide—all were tested and found lacking in desirable properties as accelerators of vulcanization. Tetraethyl lead gave excellent results. It was later discovered that compounds containing the nitroso group were active. Nitrosodimethylaniline, for example, was found to be exceedingly powerful, much more so than aniline. When mixed with various wild rubbers in the standard tread recipe to the extent of about 0.5 per cent, it caused them to cure in about 15 minutes at 287° F., with the development of a maximum tensile strength of about 2800 pounds per square inch. This appeared to be a remarkable accelerator, and careful consideration was given to its adoption. There was one serious objection: When used in a rubber batch, it stained yellow everything with which it came in contact. Even the hands of the workmen were colored a rich yellow, a stain which was difficult to remove with soap and water. Hence this material was not considered commercially desirable.

"Attention was again turned to aniline, which seemed to offer fairly satisfactory possibilities as a commercial accelerator. It was cheap but toxic when inhaled or brought in contact with the skin. Could it not be combined with some other material to form a solid body low in toxicity which preferably would melt at the temperature of vulcanization to form a liquid soluble in the rubber? It was hoped that such a material might be even more effective as an accelerator than aniline itself. The chemical having these desired properties was found to be thiocarbanilide, the reaction product of aniline with carbon disulfide. When it was mixed with various wild rubbers, zinc oxide, and sulfur, the rate of cure was greatly increased and the physical properties as evidenced by high tensile strength were remarkably good. Even the extracted Pontianac rubber, which, when mixed with zinc oxide and sulfur, would not give under any condition of vulcanization a product having high commercial value, responded strikingly to this accelerator. For example, if 3 per cent of thiocarbanilide was added to the standard tread batch, a maximum tensile strength of 2,500 pounds per square inch was developed on vulcanization for 60 minutes at 287° F. On doubling the amount of thiocarbanilide, the time of vulcanization was reduced to 10 minutes and a tensile strength of 3,000 pounds per square inch was developed. The tremendous decrease in time of cure which was effected by the use of this accelerator gave promise of great commercial value, but of equal importance were the improvement in physical properties of rubber so vulcanized, and the more uniform behavior of various grades of rubber when cured with this accelerator.

"It now became necessary to choose the best chemical for experiments on a commercial scale. Such a material should be reasonably cheap, nontoxic, either a liquid or a solid easily reduced to a fine powder, reasonably powerful as an accelerator, and easily manufactured by employees with but limited intelligence. Thiocarbanilide seemed at that time to meet these requirements, and accordingly a small plant was built for its manufacture. In September, 1906, this material and also aniline were employed experimentally in the manufacture of tires. Thiocarbanilide was used as the accelerator in the tread portion of the tire and aniline in the rubber compound which was calendered on the fabric.

"In view of the unfavorable experience in the use of mercuric iodide, careful attention was centered at this time on any tendency toward rapid perishing on aging resulting from the use of these two accelerators. Samples of vulcanized rubber containing varying amounts of accelerator and sulfur, cured for varying periods of time, were stored in the dark and were also exposed to the outside atmosphere for a period of nearly a year. Examinations were made periodically of the physical properties of these samples. At the same time, sections of tires were stored away for aging tests and were periodically examined. It became apparent that these two materials were not only accelerators of vulcanization, but also good preservatives of vulcanized rubber; in modern terms, they were fair antioxidants. Tires were put into service in different parts of the country where they were exposed to varying climatic and road conditions. From time to time, as the promise of success became more apparent, larger and larger numbers of tires were manufactured containing these two accelerators and the cheaper grades of rubber. Finally, in the latter part of 1907 aniline and thiocarbanilide were used in all the tires manufactured by The Diamond Rubber Company, as well as in the better grades of solid tires and mechanical goods. At that time my active interest in the discovery of new accelerators ceased, and henceforth I turned my attention to their manufacture and practical application.

"The research work above described developed some surprising results. The original purpose was to find some ingredient which would impart to rubber goods made from the cheaper grades of rubber the superior wearing qualities then obtainable only from Fine Para. While this was being accomplished, it was discovered that these same ingredients imparted to compositions made from the best grades of rubber a 20 per cent increase in tensile strength and a material reduction in the time of cure. Today, for example, some articles such as automobile inner tubes are being cured in as short a period as 7 minutes; passenger car tires which formerly required 3 hours now require only a one-hour cure.

"Later, as a result of the growth and development of the plantation industry, the price advantage of the wild rubbers was reversed in favor of the plantation grades. There still remained, however, the technical advantage of improved physical properties and shorter periods of cure which resulted from the use of organic accelerators in rubber products."

Other illustrations will appear later of the extreme importance of stating each research problem clearly and of the value of that step oft-repeated in approaching the goal.

Chapter 4

Two Basic Methods of Research

"One must use common sense even when doing research work."
—Wilder D. Bancroft

Research is primarily a mental activity based on physical processes of investigation. It is necessary to observe accurately but it is utterly essential to reason carefully from observations. Without both observation and deduction from it, the research fails. A number of eminent scientists have from time to time emphasized one or other of these two phases of research but no successful worker in the field has ever become so without employing both. It is, of course, true that several researchers may approach an utterly new problem quite differently, emphasizing either the theoretical or the experimental side. One approach will succeed about as often as the other, and either alone is equally likely to be misleading under other circumstances.

Thomas A. Edison was an eminent proponent of the Baconian "try-it-and-see" school of research, and the method of pure experiment has come to be better known today by his name than by that of Francis Bacon. The Edisonian method consists in trying everything, watching the results closely and hoping—even sometimes praying—for light. As observations are piled upon each other their very mass is expected to lead to the right answer. Actually multitudes of answers most often all clamor for recognition. To find the right one becomes somewhat like seeking a needle in a haystack; every straw must be inspected to see whether the needle is in it. On the basis of the law of probability, the average investigation will require half of all the possible straws to be tested and inspected.

Frequently, this is the only method available to the researcher entering upon an entirely new field, as Oenslager did in rubber and as Edison did in undertaking to find a filament for his incandescent lamp. The story of Edison's search for a material from which to produce a carbon filament within the lamp which would provide light and at the same time withstand the various hazards of operation is too well known to require repetition here. Suffice it to say that the search penetrated into most parts of the world and into animal, vegetable and mineral kingdoms. The only thread of theory extending through the whole was the permanence of carbon under high temperature. The final result of the search, a reasonably good carbon filament, was incomparably short of the present tungsten filament in every respect, but, of course, the subsequent research leading through tantalum to tungsten was undertaken only after the pioneer search for the carbon filament had succeeded! We have already considered some aspects of Langmuir's part in that search and will discuss other phases later.

The opposite point of view is represented in the Aristotelian method championed in recent years particularly by Wilder D. Bancroft, eminent physical chemist and long time editor of the *Journal of Physical Chemistry*. Whereas the Edisonian method amasses great accumulations of facts in the hope finally of reaching a theory that will help the search along, Bancroft begins with the formulation of a theory and continues with a search for facts that will bolster it and confirm it. Bancroft has repeatedly asserted the sanctity of theory even in the face of experimental contradiction and constantly insisted on a re-examination of all experiments and observations which failed to conform to the preconceived theory. Only under the strongest compulsion, he maintains, should a researcher abandon a well conceived and carefully thought out theory, and then only for another one. Without a theory to connect them, he has said, facts might as well not exist since they have no individual meanings. That goes somewhat farther than Aristotle, who scarcely recognized experiments at all.

Obviously for the purpose of illustration these two theories of research as noted here have been stripped of all modifiers and qualifications that make them usable. Actually, there are times when one approach will succeed and others when it will as surely fail. The reasonable approach to solving any problem in the overwhelming majority of cases combines a due mixture of both methods. When the whole matter is new and no clues are discernible in the available literature, then the only reasonable attack on the problem is to try everything that suggests itself, being careful to observe results with minute care. When results have begun to accumulate in some volume, a serious effort should be made to bring some sort of order out of their probable chaos. As soon as a pattern is discernible, even dimly, a theory can be formulated to supply a plan to go forward. The sooner this can be done, by all means the better, since a vast amount of needless labor can be saved thereby.

Obviously, the method of pure experiment recognizes no experience or previously accumulated data on the subject of the research. The researcher is expected in the extreme case to ignore, so far as it is possible for him to do so, any preconceived notions and any ideas previously formulated on any basis except specifically designed experiments. That is, of course, quite impossible since no one can keep his mind blank for long on any subject of his active thinking. And, too, it would be folly to attempt such a thing if there were the slightest possibility of succeeding.

On the other hand, the advocate of theory unshakable by experiment takes exactly the opposite view: only one's experience and his non-specific experiments can properly lead to a true solution of any problem. That is quite as fallacious and untenable when so stated as the opposite view, but it has much to commend it when tempered with common sense and judgment. More reasonably stated, the Bancroft method requires greater reliance on experiences that have undergone a process of mental digestion, examination and evaluation, than upon new observations which have not yet had time to acquire perspective. The distinction is between seasoned judgment and snap decisions.

Our restatement and re-emphasis of the Bancroft idea retains the caution against allowing ourselves to be swayed by any small number of experiments that appear to violate a logical rule. All experimental work must consider and allow for misleading experiments whose outcomes point to conclusions at violent odds with experience and judgment. So too, must the logician with equal vigor avoid complacency which leaps over great areas of experimental contradiction of his theory in the belief that theory is far stronger than observation.

The literature abounds in examples of both types of approaches. But seldom can a researcher forego building, modifying and rebuilding his theory as his experiments proceed and only in the rarest instances can theoreticians refrain from testing their theories experimentally as they are built up. We have already noted at work Langmuir, essentially a theorist, and Oenslager, who built primarily on experiment.

What are perhaps the most satisfying examples of the two basic procedures are described by one man, Thomas Midgley, Jr.

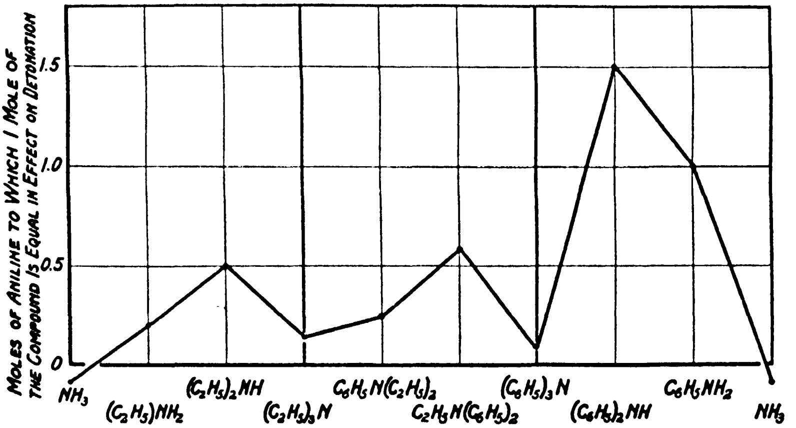
Midgley's discovery of the effectiveness of tetraethyl lead in inhibiting fuel knock in internal combustion engines must rank as a classic example of the value of the Edisonian method in exploring an unknown field for a property previously unrecognized. However, as soon as accumulated evidence permitted, conclusions were drawn and theories formulated to guide and direct further research. A great mass of experimental data had to be determined and digested in this case before any possibility appeared of connecting observations with any kind of helpful theory.

The reason for this lies in the nature of the problem. In essence, it was required to provide a chemical background for the conclusion of theoretical thermodynamics that the efficiency of an internal combustion engine would be enhanced by raising the pressure on the gas-air mixture at the instant of explosion. So far as it was possible to go in raising compression pressures, thermodynamic theory was valid, but even a small increase of pressure beyond a highly variable critical point caused a profound change in the nature of the explosion. At low initial pressures, an orderly rise of the pressure resulted from the explosion; but this became a very different phenomenon when the initial pressure was raised above the critical value. Under the new conditions, the pressure rose in regular fashion for a time, and then when the fuel charge was partly consumed, the remainder detonated at a much faster rate without contributing to the useful work done by the first part of the explosion. A fragmentary few data suggested that this "knock" is a function not only of initial pressures but also of the fuel itself. Kerosene produced less power and more knock than gasoline in the same engine.

Thus the problems facing Midgley were to learn the reason for the difference between gasoline and kerosene and to find a fuel of such a character that the enhanced power output of the higher compression engine would not be dissipated in knock. Nothing actually defined either the knock itself or the quality sought in the fuel. They were simply two unknowns related to each other in some indeterminate manner. Consequently, it was first necessary to devise a means of measuring knock and then to measure the effects of great numbers of different modifiers of the fuel in an effort to find some basis for theory to guide further search.

The measuring device which Midgley developed is an ingenious instrument consisting of a pin which detonation causes to bounce off a thin plate closing an opening into the engine cylinder. In regular operation the force of the explosions is not great enough to bounce the pin, but when detonation or knocking occurs, the sharp rise of cylinder pressure causes the pin to bounce high enough to close an electrical circuit. The current flowing through the circuit is proportional to the severity of the knock and it is integrated by electrolyzing water. That method of integrating the current curve was chosen in preference to existing instrumental methods because of the short duration of each pulse of current which might not overcome the inertia of a conventional watt-hour meter.

The results of great numbers of measurements of different fuels and different addenda were summarized by Midgley in his Perkin Medal address:



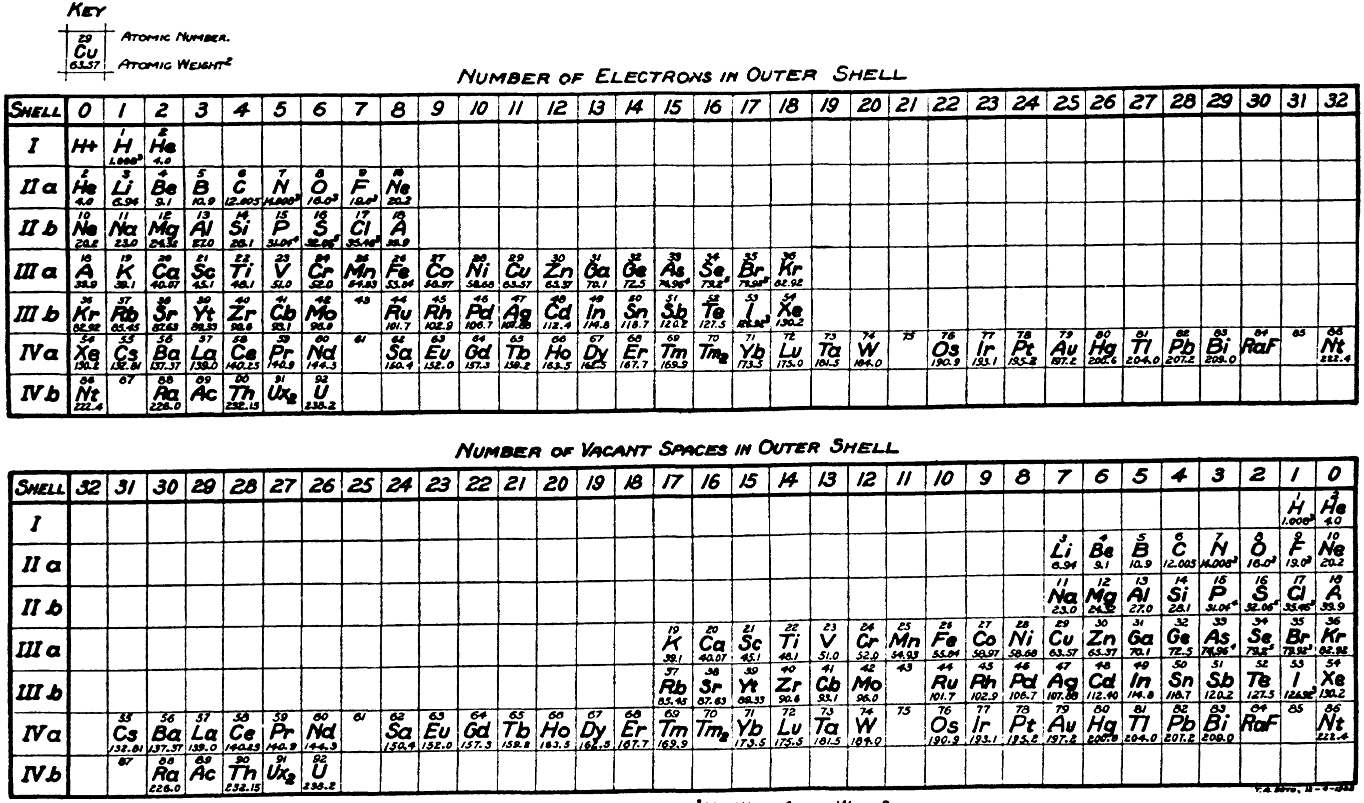
From *Ind. & Eng. Chem.* **29**, p. 242 (1937)

FIGURE 1. Influence of the groups attached to the atom on the antiknock effect of nitrogen.

"In the search for a material with which to control knocking in an internal combustion engine, the following determinations were arrived at by the Edisonian method:

"1. Elemental iodine, dissolved in motor fuel in very small quantities, greatly enhanced the antiknock characteristics of the fuel (the basic discovery).

"2. Oil-soluble iodine compounds had a similar, though modified effect.



KEY

29 Cu 63.57	ATOMIC NUMBER. ATOMIC WEIGHT[2]

NUMBER OF ELECTRONS IN OUTER SHELL

SHELL	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
I	H+	1 H 1.008[3]	2 He 4.0																														
II a	2 He 4.0	3 Li 6.94	4 Be 9.1	5 B 10.9	6 C 12.005	7 N 14.008[3]	8 O 16.0[3]	9 F 19.0[3]	10 Ne 20.2																								
II b	10 Ne 20.2	11 Na 23.0	12 Mg 24.32	13 Al 27.0	14 Si 28.1	15 P 31.04[4]	16 S 32.06[5]	17 Cl 35.46[3]	18 A 39.9																								
III a	18 A 39.9	19 K 39.1	20 Ca 40.07	21 Sc 45.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 70.1	32 Ge 72.5	33 As 74.96[4]	34 Se 79.2[5]	35 Br 79.92[3]	36 Kr 82.92														
III b	36 Kr 82.92	37 Rb 85.45	38 Sr 87.63	39 Yt 88.33	40 Zr 90.6	41 Cb 93.1	42 Mo 96.0	43	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.88	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92[3]	54 Xe 130.2														
IV a	54 Xe 130.2	55 Cs 132.81	56 Ba 137.37	57 La 139.0	58 Ce 140.25	59 Pr 140.9	60 Nd 144.3	61	62 Sa 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 159.2	66 Ho 163.5	67 Dy 162.5	68 Er 167.7	69 Tm 169.9	70 Tm$_2$	71 Yb 173.5	72 Lu 175.0	73 Ta 181.5	74 W 184.0	75	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.2	83 Bi 208.0	84 RaF	85	86 Nt 222.4
IV b	86 Nt 222.4	87	88 Ra 226.0	89 Ac	90 Th 232.15	91 Ux$_2$	92 U 238.2																										

NUMBER OF VACANT SPACES IN OUTER SHELL

SHELL	32	31	30	29	28	27	26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
I																																1 H 1.008[3]	2 He 4.0
II a																										3 Li 6.94	4 Be 9.1	5 B 10.9	6 C 12.005	7 N 14.008[3]	8 O 16.0[3]	9 F 19.0[3]	10 Ne 20.2
II b																										11 Na 23.0	12 Mg 24.32	13 Al 27.0	14 Si 28.1	15 P 31.04[4]	16 S 32.06[5]	17 Cl 35.46[3]	18 A 39.9
III a																19 K 39.1	20 Ca 40.07	21 Sc 45.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 70.1	32 Ge 72.5	33 As 74.96[4]	34 Se 79.2[5]	35 Br 79.92[3]	36 Kr 82.92
III b																37 Rb 85.45	38 Sr 87.63	39 Yt 88.33	40 Zr 90.6	41 Cb 93.1	42 Mo 96.0	43	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.88	48 Cd 112.40	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92[3]	54 Xe 130.2
IV a		55 Cs 132.81	56 Ba 137.37	57 La 139.0	58 Ce 140.25	59 Pr 140.9	60 Nd 144.3	61	62 Sa 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 159.2	66 Ho 163.5	67 Dy 162.5	68 Er 167.7	69 Tm 169.9	70 Tm$_2$	71 Yb 173.5	72 Lu 175.5	73 Ta 181.5	74 W 184.0	75	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.2	83 Bi 208.0	84 RaF	85	86 Nt 222.4
IV b		87	88 Ra 226.0	89 Ac	90 Th 232.15	91 Ux$_2$	92 U 238.2																										

[1] J. AM. CHEM. SOC. 41, 868 (1919).
[2] ATOMIC WEIGHTS 1921, J. AM. CHEM. SOC. 42, 1763 (1920); EMBODYING ALSO THE CHANGES LATER RECOMMENDED. J. AM. CHEM. SOC. 44, 427 (1922).
[3] MOL. WT. = ATOMIC WT. x 2.
[4] MOL. WT. = ATOMIC WT. x 4.
[5] MOL. WT. = ATOMIC WT. x 8.

From *Ind. & Eng. Chem.* 29, p. 241 (1937)

FIGURE 2. A periodic system based on the Langmuir theory of atomic structure and an arrangement by R. E. Wilson.

"3. Aniline, its homologs, and some other nitrogenous compounds were effective, though their effectiveness varied over a wide range depending upon the hydrocarbon radicals attached to the nitrogen (Figure 1).

"4. Bromine, carbon tetrachloride, nitric acid, hydrochloric acid, nitrites, and nitro compounds in general increased knocking when added to the fuel and air mixture.

"5. Selenium oxychloride was extremely effective as an antiknock material.

"6. A large number of compounds of other elements had shown no effect.

"With these facts before us, we profitably abandoned the Edisonian method in favor of a correlation procedure based on the periodic table. What had seemed at times a hopeless quest, covering many years and costing a considerable amount of money, rapidly turned into a 'fox hunt.' Predictions began fulfilling themselves instead of fizzling. Diethyl selenide was prepared and worked as expected; diethyl telluride next fulfilled our predictions, and seemingly our wildest dreams of success had been realized. There are, however,

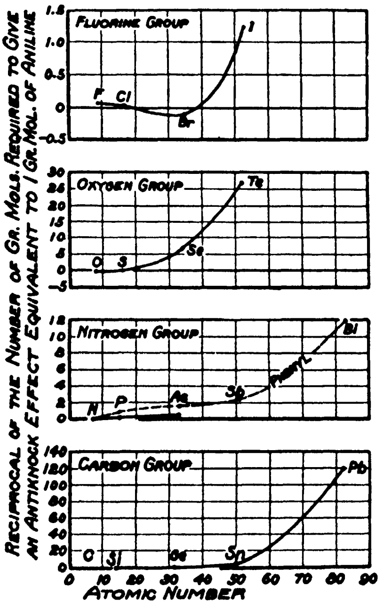


FIGURE 3. Detonation-influencing effects of the ethyl compounds of four groups of elements.

From *Ind. & Eng. Chem.* 29, p. 244 (1937) good reasons for not using tellurium compounds. A systematic survey was then conducted using a periodic arrangement suggested by R. E. Wilson (Figure 2). The ethyl and phenyl derivatives of the elements on the right of the arrangement according to vacant places were prepared and their effects measured in motor operation.

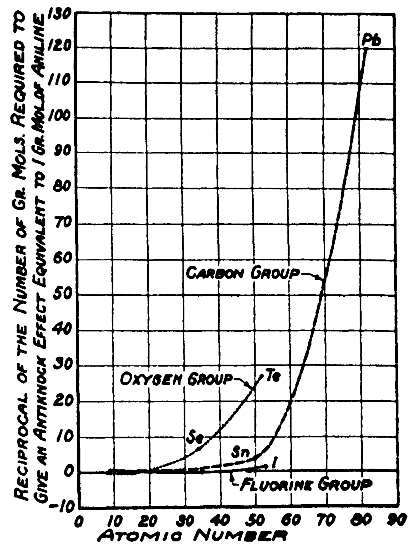


FIGURE 4. Curves of fluorine, oxygen, and carbon groups of Figure 3 plotted to the same scale.

From *Ind. & Eng. Chem.* 29, p. 244 (1937)

The results, plotted as antiknock effect *vs.* atomic number are shown in Figures 3 and 4. Tin was the first element investigated from the group immediately to the left of those previously reported. Its ethyl derivative was studied. This compound exhibited a much more powerful effect than had been expected. We thereupon predicted that tetraethyl lead would solve the problem. The record of the past decade has borne out that prediction."

Midgley provides a perfect example of the Bancroft or Aristotelian method in his research leading to the fluorinated hydrocarbons as safe refrigerants. Whereas his search for knock-suppressing tetraethyl lead consumed half a dozen years and required thousands of experiments, the search for a nontoxic, nonflammable refrigerant was completed in three days with only confirmatory experiments made after the solution of the problem had been reached. Here is his account of this research presented as showing "the use of the periodic table in connection with the development of the organic fluorides as refrigerants."

"In the preceding case, we were tracing a hitherto unknown property through the periodic table to discover in which element it would become maximum. This required much synthetic chemistry and presented many difficulties in properly evaluating the results, all of which took years to accomplish. The case of the refrigerants was distinctly different. We were looking simply for a compound, or a group of compounds, in which would be combined certain well-known properties. This was accomplished in three days.

"I was in the laboratory one morning and called Kettering in Detroit about something of minor importance. After we had finished this discussion, he said: 'Midge, I was talking with Lester Keilholtz last night and we came to the conclusion that the refrigeration industry needs a new refrigerant if they ever expect to get anywhere. So I told Lester that I would call you and have you see him to talk it over. He is leaving for Dayton tonight.' L. S. Keilholtz was chief engineer of Frigidaire at that time. We spent the next morning in his office discussing this problem. What was wanted was obvious—a nontoxic, nonflammable refrigerant. On leaving Keilholtz, I expressed myself as very doubtful that we would be able to find a single substance suited to the task but that there might be some hope of greatly reducing the existing hazards by using mixtures where nonflammable but toxic materials would be mixed with nontoxic, flammable compounds to give a mixture substantially nonflammable and considerably less toxic than the refrigerants then commonly employed.

"In this frame of mind, I returned to our laboratory where I found A. L. Henne and Robert MacNary waiting to have lunch with me. We discussed the problem during lunch and I have Henne's word that my skepticism of solving the problem with a single compound intrigued his interest so much that he gave up his free afternoon and he, MacNary, and I went to the library and started to work.

"The desired combination of properties was a boiling point between 0° and −40° C., stability, nontoxicity, and nonflammability.

International Critical Tables gave us a partial summary of the volatile organic compounds. The now proved mistake that carbon tetrafluoride boiled at −15° C. struck us in the face and started us thinking about fluorine. No one could doubt at that time that it was terribly toxic, probably too toxic to use even with isobutane. Perhaps we could add some chlorine compound with beneficial results. Henne suggested chlorofluorides as a class to be investigated further. And so the discussion ran.

"Recognizing that the International Critical Table list was very incomplete, I decided to bring into play the periodic table. Perhaps volatility could be related to it in some way. It takes but a fraction of a second to see that this is true. In the arrangement according to vacant places in Figure 2, the elements on the right-hand side are the only ones which make compounds sufficiently volatile for the purpose in hand. In fact, only a certain number of these (Figure 5) need be considered. Volatile compounds of boron, silicon, phosphorus, arsenic, antimony, bismuth, selenium, tellurium, and iodine are all too unstable and toxic to consider. The inert gases are too low in boiling point. Now look over the remaining elements. Every refrigerant used has been made from combinations of these elements. Flammability decreases from left to right. Toxicity (in general) decreases from the heavy elements at the bottom to the lighter elements at the top. These two desiderata focus on fluorine. It was an exciting deduction. Seemingly no one previously had considered it possible that fluorine might be nontoxic in some of its

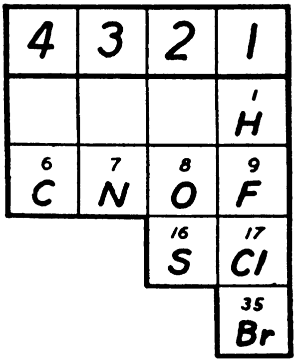


FIGURE 5. Enlarged portion of vacant-space arrangement of Figure 2.

From *Ind. & Eng. Chem.* 29, p. 244 (1937) compounds. This possibility had certainly been disregarded by the refrigeration engineers. If the problem before us were solvable by the use of a single compound, then that compound would certainly contain fluorine. The heats of formation between the halogens and carbon were checked. They increase from iodine to fluorine, thus indicating a high degree of stability for fluorine-carbon compounds. Everything looked right except that old fear of hydrofluoric acid burns. As it turns out, hydrofluoric acid burns are a special case. Actually gaseous hydrofluoric acid is less toxic than hydrochloric acid, but we didn't know it that afternoon. Next came methods of preparation. Carbon tetrafluoride seemed rather hard to make. And then how could dichlorodifluoromethane boil at −20° C. and carbon tetrafluoride at −15° C.? It just didn't make sense. Plottings of boiling points, hunting for data, corrections, slide rules, log paper, eraser dirt, pencil shavings, and all the rest of the paraphernalia that takes the place of tea leaves, and crystal spheres in the life of the scientific clairvoyant, were brought into play. We decided that carbon tetrafluoride boiled at about −136° C. or else it was a very special kind of substance. (Not long after this a publication on the subject appeared. Carbon tetrafluoride boils at −128° not −15° C.) Feeling pretty certain at the time that −15° C. was wrong and that it was a sizable research problem to make carbon tetrafluoride, we selected dichloromonofluoromethane as the starting point for experimentation. I called one of the chemical supply houses by telephone and ordered five one-ounce bottles of antimony trifluoride. I believe this was all there was in the country at the time. . . .

"The five one-ounce bottles of antimony trifluoride arrived. One was taken at random, and a few grams of dichloromonofluromethane were prepared. A guinea pig was placed under a bell jar with it and, much to the surprise of the physician in charge, didn't suddenly gasp and die. In fact, it wasn't even irritated. Our predictions were fulfilled. We then took another bottle and made a few more grams and tried it again. This time the animal did what the physician expected. We repeated again but this time we smelled the material first. The answer was phosgene; a simple-caustic wash was all that was needed to make it perfectly safe. Then we examined the two remaining bottles of antimony trifluoride. They were not pure. In fact, they were both badly contaminated with a double salt containing water of crystallization. This makes phosgene in ample quantities as an impurity. Of five bottles marked 'antimony trifluoride,' one had really contained good material. We had chosen that one by accident for our first trial. Had we chosen any one of the other four, the animal would have died as expected by everyone else in the world except ourselves. I believe we would have given up what would then have seemed a 'bum hunch.' "

No better examples than these exist of the two basic methods of research, the one relying primarily on experiments in great numbers to lead to a solution, and the other depending quite as definitely on a theory based primarily on experience, whether of the researcher himself or of others recorded in the literature. Midgley did not emphasize this aspect of the two researches in describing them but clearly these differences are obvious from even these brief descriptions.

These accounts also indicate the most important applications and usefulness of the two methods. Vast numbers of experiments or observations are necessary in exploring hitherto unknown or unexplored fields or subjects. We have already noted how this method was used by Oenslager in arriving at the important family of vulcanization accelerators for rubber. Darwin finally reached his theory of evolution from consideration and digestion of thousands upon thousands of observations. Hippocrates followed the same method in his pioneering of medicine. Actually Darwin's active accumulation of observations extended over a period of some twenty years. He tells the story in these words:

"By collecting all the facts which bore in any way on the variation of animals and plants under domestication and nature, some light might perhaps be thrown on the whole subject. My first note-book was opened in July 1837. I worked on true Baconian principles, and, without any theory, collected facts on a wholesale scale, more especially with respect to domesticated productions, by printed inquiries, by conversation with skilfull breeders and gardeners, and by extensive reading. When I see the list of books of all kinds which I read and abstracted, including whole series of Journals and Transactions, I am surprised at my industry. I soon perceived that selection was the keystone of man's success in making useful races of animals and plants. But how selection could be applied to organisms living in a state of nature remained for some time a mystery to me.

"In October 1838—that is, fifteen months after I had begun my systematic enquiry—I happened to read for amusement Malthus on population, and being well prepared to appreciate the struggle for existence which everywhere goes on from long-continued observation of the habits of animals and plants, it at once struck me that under these circumstances favourable variations would tend to be preserved, and unfavourable ones to be destroyed. The result of this would be the formation of new species.

"Here, then, I had at last got a theory by which to work; but I was so anxious to avoid prejudice that I determined not for some time to write even the briefest sketch of it. In June, 1842, I first allowed myself the satisfaction of writing a very brief abstract of my theory in pencil in 35 pages; and this was enlarged during the summer of 1844 into one of 230 pages, which I had fairly copied out and still possess.

"But at that time I overlooked one problem of great importance; and it is astonishing to me, except on the principle of Columbus and his egg, how I could have overlooked it and its solution. This problem is the tendency in organic beings descended from the same stock to diverge greatly in character as they become modified. That they have diverged greatly is obvious from the manner in which species of all kinds can be classed under genera, genera under families, families under sub-orders, and so forth; and I can remember the very spot in the road, whilst in my carriage, when to my joy the solution occurred to me; and this was long after I had come to Down. The solution, as I believe, is that the modified offspring of all dominant and increasing forms tend to become adapted to many and highly diversified places in the economy of nature."

While we ordinarily forget that Hippocrates was an important research worker in the earliest days of medicine, it is undeniable that his great value to humanity lay in researches into the nature of disease upon which treatment of patients was later systematized. He was reaching out for general theories to connect and give meaning to the immense numbers of observations of patients and symptoms which had to serve as experiments in that early day of medicine. L. J. Henderson tells us about it:

> "In order to construct a useful conceptual scheme, Hippocrates proceeded to analyze the phenomenon, as he abstractly conceived it, into elements. . . . To this analysis and the resulting elaboration of the theory we owe the survival of such words as 'crisis' and 'coction.' But the theory, having served its purpose is obsolete, like Ptolemy's astronomy. . . .
>
> "Throughout a great part of his work Hippocrates is thus moving step by step toward the widest generalizations within his reach. In great part, he is seeking a natural history of acute disease or at least of those acute diseases that were prevalent among his patients. His success was great, and the whole history of science goes far to support the view that such a methodical procedure is a necessary step in the development of a science that deals with similarly complex and various phenomena."

Examples of following out an initially conceived theory as the pattern of research abound throughout the literature of science and engineering. Indeed, the rarest phenomenon in all published research is the successful worker who is willing afterward to admit that he did not have from the beginning of the search, or near it, a reasonably clear, if not actually pellucid, theory leading directly to the successful outcome. Usually a theory can be formulated in a totally new field, as we have seen, only after considerable experimentation has cleared a way for it. The number and range of the experiments prerequisite to theorizing in any investigation are in inverse ratio to the amount of exploration done by oneself or one's predecessors in the same or a closely related field. That is not always true. As we have seen in the researches of Langmuir in high vacua, some minds are capable of leaping from little evidence and few experiments to theories of the greatest value. Less brilliant minds, or those at least unendowed with this invaluable gift of generalizing, must amass more evidence before they can draw useful conclusions.

Perhaps that is well, for even that master theorist, Albert Einstein, recognizes that "No amount of experimentation can ever prove me right; a single experiment may at any time prove me wrong." Thomas Huxley saw in that "the great tragedy of science—the slaying of a beautiful hypothesis by a single ugly fact."

So it will perhaps be well to end this discussion of the two great methods of research on somewhat the same note of caution that initiated it. Paul Sabatier, whose discoveries in the pure science of catalytic hydrogenation have had enormous industrial consequences once said:

"The theory of temporary compounds furnished by the catalyst has constantly guided me in these various labors; it is these indications to which I owe all by new results. I shall retain these theories until the day when I find them irreconcilable with the well-established observed facts. Theories should never have the pretension of being indestructible. As has been said by Henri Poincaré, 'A theory is good only as long as it is useful'!"

Chapter 5

Thinking Out the Problem

"*We don't solve a technical problem or make an invention in the laboratory. We do these things in our heads. All this laboratory apparatus is simply to help us get an understanding of the problem we are working on.*" —Charles F. Kettering

"*With accurate experiment and observation to work upon, imagination becomes the architect of physical theory. Newton's passage from a falling apple to a falling moon was an act of the prepared imagination. Out of the facts of chemistry, the constructive imagination of Dalton formed the atomic theory. Davy was richly endowed with the imaginative faculty, while with Faraday its exercise was incessant, preceding, accompanying and guiding his experiments. His strength and fertility as a discoverer are to be referred in great part to the stimulus of the imagination.*" —John Tyndall

In the preceding chapters, we have suggested the mental process which is the vital essence of every research. Whatever may be one's views on the most effective proportion between observation, reading and experiment, there is no possible avoidance of, or short cut around, the reasoning process of research. This alone can bring cause into due relation with its effect and lead to the final solution of the problem. Whereas anyone can learn to perform the various physical operations of research, not every mind is capable of the original thinking essential to success. Yet latent ability to think clearly and along original lines is far more common than one usually supposes and it is a talent which can be cultivated and trained. Quite as readily as other personal skills, one's mental faculty can be sharpened and strengthened by exercise and practice. We cannot here delve into the psychological depths of this subject, but an examination of some of the aspects of the thought process is pertinent.

The basic case was stated by Hans Zinsser:

"It is an erroneous impression, fostered by sensational popular biography, that scientific discovery is often made by inspiration—a sort of *coup de foudre*—from on high. This is rarely the case. Even Archimedes' sudden inspiration in the bathtub; Newton's experience in the apple orchard; Descartes' geometrical discoveries in his bed; Darwin's flash of lucidity on reading a passage in Malthus; Kekule's vision of the closed carbon ring which came to him on top of a London bus; and Einstein's brilliant solution of the Michelson puzzle in the patent office in Berne, were not messages out of the blue. They were the final co-ordinations by minds of genius of innumerable accumulated facts and impressions which lesser men could grasp only in their uncorrelated isolation, but which—by them—were seen in entirety and integrated into general principles. The scientist takes off from the manifold observations of predecessors, and shows his intelligence, if any, by his ability to discriminate between the important and the negligible, by selecting here and there the significant stepping-stones that will lead across the difficulties to new understanding. The one who places the last stone and steps across to the *terra firma* of accomplished discovery gets all the credit. Only the initiated know and honor those whose patient integrity and devotion to exact observation have made the last step possible."

Thought proceeds in chain fashion through a series of associations of ideas. Progression from one idea or mental picture to the next in the chain is ordinarily so swift that a succession of ideas will have flashed through the mind in the smallest conscious interval of time. A sudden interruption of this progression sometimes yields a reasonable consequent, but more often when thus taken from its context, any single idea seems utterly unrelated to what has gone before and what comes after. The uncontrolled flash of images in this fashion follows a pattern based on the mind's history and the fortuitous interruption of the chain at intervals provides the psychoanalyst with data from which to reconstruct this history. While the series of associations projected by any mind is individual and characteristic of that mind, psychologists are able to discern and distinguish important broad classes of mental reactions and aptitudes.

Just as the past history of a mind can be reconstructed from its present reactions, so, too, can its present or future reactions be determined, or at least fore-shadowed, by the training and experience which it has been given. It is quite difficult, if not actually impossible, for a mind ignorant of the multiplication table, for instance, to associate or relate to each other the numbers 2 and 4. Further mathematical training will permit 16 to be readily associated with 2 and 4 as the fourth power of two or the second power of four, for example, a feat quite impossible to one who knows only multiplication. The trained mind thus acquires, or better achieves, an enlarged number of methods of associating ideas from the greater variety of the things, situations and relationships with which it is familiar. The process of training itself, particularly that of learning new facts, gives the mind practice in relating the various ideas it absorbs because only by association can it retain usefully what it learns. Thus the ordinary processes of education early reveal whether or not a particular mind possesses an ability to associate ideas readily. If the student possesses this faculty, education sharpens and strengthens it, and at the same time provides it with material on which to work.

Viewed in this light, the entire process of education from its very inception can be considered as leading toward research as its ultimate goal. Not that it must necessarily reach that point to be successful, but rather that it leads the student as far along that path as his abilities and inclinations suggest or permit. Nor are long years of education in every case necessarily prerequisite to original thinking. That is manifestly true, since some of the most brilliant associations of ideas into inventions of the most profound significance have been the apparently fortuitous products of unschooled minds.

While such things can happen, and do, the chance that they will is slender and tenuous in the extreme. One should not in reason rely upon the occurrence of an event so improbable; the slender chance of success makes the odds against it far too great to be considered in industrial research. As the training of the mind in question expands, so too does the probability rise that it will be able to achieve useful new associations of ideas and also that it will be able to solve a particular problem.

Henri Poincairé expands the idea:

"An isolated fact can be observed by all eyes; by those of the ordinary person as well as of the wise. But it is the true physicist alone who may see the bond which unites several facts among which the relationship is important, though obscure. The story of Newton's apple is probably not true, but it is symbolical; so let us think of it as true. Well, we must believe that many before Newton had seen apples fall, but they made no deduction. Facts are sterile until there are minds capable of choosing between them and discerning those which conceal something and recognizing that which is concealed; minds which under the bare fact see the soul of the fact."

Reduced to its simplest terms, then, the mental activity of research consists of countless trial associations of the several parts of the available data until a combination is realized, or clearly foreseen, through which the desired result can be attained. In the course of such trial associations, gaps in data are usually apparent and the researcher must resort to the literature or to experiment to supply the missing pieces. Not infrequently, it is possible to foresee the outcome of learning some particular bit of information before it is reached, and the researcher can then postulate the next step to be either of two alternatives, depending on whether the teaching of the experiment is positive or negative.

The outstanding example of this guessing and duplicating research was the vast program of both research and development which led to the atomic bomb. At every juncture, the outcome of the next step was guessed and the subsequent step undertaken at once. This next step was always designed to answer the next question whichever way the immediate investigation pointed. The time factor was dominant at all points and thus all the links in the chains of both research and development were being forged simultaneously. The strange and fascinating story of how the various pairs of alternatives proved out is sketched, but not fully told, in the official Smyth Report, which all men should read thoughtfully.

Obviously one's ability to form the vast numbers of mental associations commonly required in research depends to a significant extent upon natural aptitude; but also vital is one's quickness in forming associations, a faculty which can be developed and greatly enhanced by practice. Thus it is that research workers, particularly the most successful of the clan, are inveterate puzzle solvers and spend their leisure time engaged, rightly or wrongly, in some pastime requiring the same kind of skill as their daily occupations. Such hobbies as chess, bridge, cryptography, deciphering Mayan inscriptions, reading or writing detective stories, and the many other pursuits requiring intense mental effort find their most enthusiastic devotees among successful research workers. So closely does solving puzzles resemble research in its mental requirements that personnel departments and research directors often use puzzles of one kind or another as part of the tests given applicants to determine their fitness for research positions. These puzzles may be part of, or supplement, more orthodox psychological tests. One type that requires a high degree of associative skill and mental quickness gives the solver a number of apparently unrelated facts to reassemble to give a true picture of a certain situation, wherein the similarity to research problems is greater than appears on the surface. Far more often than not, the data gathered in the early stages of a research appear quite as disperse and incomplete. Fortunately for those of us whose minds are baffled by such fragmentary and disordered data, it is usually possible in a research to dig out a few more facts experimentally to complete the picture, or at least to bring its outlines into some kind of focus. Fortunately, too, in neither pursuit is there any prohibition against assuming an answer on the basis of any available facts and then subjecting it to the test of fitting with the other facts. Indeed, no better method can be applied to the usual problems of research or puzzledom.

The successive steps in the solution of any problem follow the pattern commonly described for promoting original thought. The steps are:

(1) Accumulate all possible facts bearing upon the problem in hand. Study them and impress them on the mind.

(2) Digest and synthesize these facts into a solution, either complete and final, or interim and representing a stage of progress toward the ultimate solution. Obviously, few problems can be solved at one trial and hence piecemeal solutions are the rule.

(3) Repeat these steps alternately as often as necessary, with each repetition appropriately modifying the operation to take into account each bit of progress, however small, that has been made before.

It is hardly necessary to present any arguments for bringing to bear upon the problem each fact that can be mustered; even the mind needs raw material to keep going and facts are the raw material of research.

Three important sources of facts are at the command of the researcher: experience, observation and experiment.

Within the term "experience," I would include any fact which is available from the past. This would include one's own personal experience, and other data dug from the tremendous wealth of the experiences of others treasured in the literature of science. Nor should the bits gathered from personal contacts with other workers be overlooked, since these are often our most valuable helps.

Observation performs a vital function when the conditions governing an event are beyond immediate control. Astronomical investigations and many, if not all, researches into geological, biological and genetic subjects, for example, permit the researcher to exercise negligible control over the events he studies. He must, therefore, use all his powers to observe every factor and every variable affecting his particular problem.

Experiment acquires value only when pertinent data are completely observed and significant conditions are controlled to the extent that they may affect the result.

In listing these three essential sources of facts, their order is purely fortuitous and is by no means intended to establish an order of importance of these three sources. Rather they are and should be cognate in the researcher's mind, to be called into play whenever and however circumstances dictate. Furthermore, in establishing equal values for these several sources of facts, it is essential also to recognize that all are equally likely to prove misleading. No other experience has been acquired by any one under exactly the circumstances of the particular research in hand. No other observer or experimenter has worked to exactly the present specifications. Even the experiments one designs and performs for oneself with the utmost care are quite as likely to mislead as to guide the reasoning processes.

The accumulation of facts by one or all of these methods obviously must follow the pattern most acceptable to the person who is to use them, and that best adapted to the problem of the moment. Long and detailed searches of the literature may be rendered quite unnecessary by the early discovery that there is no such ample literature; or a comparatively brief search may turn up material of such pertinence and value that immediate recourse to experiment is strongly indicated to test the application of the findings to the present problem. This might very well be the discovery in the literature of exactly the data needed. Observation may be impractical in any particular case, (such, for instance, as seeing a process operating in a competitor's plant) and thus the prospective observer is thrown back upon his own resources of experiment and imagination to reach some useful conclusion.

The great volume of literature currently available on practically every imaginable subject encourages one to initiate, and even complete, a research in the library. Our scientific forebears had no such convenient help at hand, but always had to begin by formulating theories of their own and testing them by experiments designed for the purpose. Both methods are as useful today as ever.

Leonardo da Vinci stated his basic method of research thus:

> "In treating any particular subject I would first of all make some experiments, because my design is first to refer to experiments and then to demonstrate why bodies are constrained to act in such a manner. This is the method we ought to follow in investigating the phenomena of Nature. Theory is the general, experiments are the soldiers. Experiment is the interpreter of the artifices of Nature. It is never wrong; but our judgment is sometimes deceived because we are expecting results which experiment refuses to give. We must consult experiment and vary the circumstances, till we have deduced general laws, for it alone can furnish us with them."

And Leonardo's personal success in such widely varied fields attests the value of his method.

Francis Bacon, the great advocate of the experimental method, freely criticized those who, as was the fashion in his day and before, relied wholly on speculation:

> "For all those who before me have applied themselves to the invention of arts have but cast a glance or two upon facts and examples and experience, and straightway proceeded, as if invention were nothing more than an exercise of thought, to invoke their own spirits to give them oracles. I, on the contrary, dwelling purely and constantly among the facts of nature, withdraw my intellect from them no further than may suffice to let the images and rays of natural objects meet in a point, as they do in the sense of vision;

whence it follows that the strength and excellency of the wit has but little to do in the matter. . . .

"Now what the sciences stand in need of is a form of induction which shall analyse experience and take it to pieces, and by a due process of exclusion and rejection lead to an inevitable conclusion. And if that ordinary mode of judgment practised by the logicians was so laborious, and found exercise for such great wits, how much more labour must we be prepared to bestow upon this other, which is extracted not merely out of the depths of the mind, but out of the very bowels of nature. . . .

"If we begin with certainties, we shall end in doubts; but if we begin with doubts, and are patient in them, we shall end in certainties."

We have already noted that the view, which Bacon thus vigorously attacked, the method of pure logic, scarcely, if at all, defiled by experiment, still exists to this day in full vigor. But so too does Bacon's method. Let us, however, look upon these differences as signs of mental health and vigor and not as establishing one or the other as an unalterable law of research to which we must constantly and consistently adhere under all circumstances. We have already examined the two in an earlier chapter but it remains to illustrate and to clarify their applications.

Whatever one may be bent upon doing, the necessity of providing oneself with a bountiful supply of facts and experience at the outset is constantly emphasized. Thomas Hobbes looked at the problem of original thinking from a point of view that appears somewhat archaic to modern eyes, but nonetheless his conclusions are completely sound today. If for "prophecy" one reads "invention," or even "the advancement of science," the following excerpt from his "Of Man" becomes highly pertinent:

"The best prophet naturally is the best guesser; and the best guesser he that is most versed and studied in the matters he guesses at, for he hath most 'signs' to guess by.

"A 'sign' is the event antecedent, of the consequent; and, contrarily, the consequent of the antecedent, when the like consequences have been observed before; and the oftener they have been observed, the less uncertain is the sign. And therefore he that has most experience in any kind of business has most signs whereby to guess at the future time, and consequently is the most prudent; and so much more prudent that he that is new in that kind of business as not to be equalled by any advantage of natural and extemporary wit; though perhaps many young men think the contrary."

Graham Wallas continues this thought into the second stage of the research utilizing a further quotation from Hobbes:

> "The educated man has learnt, and can voluntarily or habitually follow out, rules as to the order in which he shall direct his attention to the successive elements in a problem. Hobbes referred to this fact when in the *Leviathian* he described 'regulated thought' and contrasted it with that 'wild ranging of the mind' which occurs when the thought-process is undirected. Regulated thought is, he says, a 'seeking.' 'Sometimes,' for instance, 'a man seeks what he has lost. . . . Sometimes a man knows a place determinate, within the compass whereof he is to seek; and then his thoughts run over all the parts thereof, in the same manner as one would sweep a room to find a jewel; or as a spaniel ranges the field till he finds a scent; or as a man should run over the alphabet, to start a rhyme.' A spaniel with the brain of an educated human being could not, by a direct effort of will, scent a partridge in a distant part of the field. But he could so 'quarter' the field by a preliminary voluntary arrangement that the less-voluntary process of smelling would be given every chance of successfully taking place."

Perhaps it is short of complimentary to compare our great researchers to a spaniel, but nevertheless the figurative quartering of the field of interest in search of facts, and clues to connect them, falls precisely into the mental pattern and activity of every successful researcher.

Whenever and however one obtains his basic facts, each must be suspect to the researcher until its validity has been conclusively proved. Too often we assume that some mere notion is a fact and true simply because someone else before us has done so. Our habitual discarding of the livers of animals, the bran of wheat and the peelings of potatoes required the most extensive investigations into nutrition backed by tremendous publicity and enforced by the regimentation of a World War to prove and to correct the wastefulness of our habits. Research cannot succeed when its progress is hampered by cherished ideas which the researcher refuses to submit to test and proof.

Orderly and successful research develops on quite the opposite attitude, according to George Sarton, who sums up his views:

> "Establish the facts by direct, frequent, and careful observations, and check them repeatedly one against the other; these facts will be your premises. When many variables are related, find out what happens when only one is allowed to vary, the others remaining constant. Multiply such experiments as much as you can, and make them with the utmost precision in your power. Draw your conclusions and express them in mathematical language if possible. Apply all your mathematical resources to the transformation of the equations; confront the new equations thus obtained with reality. That is, see what they mean, which group of facts they represent. Make new experiments on the basis of these new facts, etc. And repeat the process as often as may be necessary."

An obvious and usually convenient method of getting order out of apparently chaotic numerical data is to plot them. We have already seen how this method guided Midgley to tetraethyl lead in his search for a compound to suppress knock in gasoline engines. When straight numerical coordinates do not yield an orderly curve, logarithmic or semi-logarithmic coordinates often solve the difficulty. This comparatively simple method often reveals relations, as well as inconsistencies, in data which may well be the keys to the solution of the problem.

Charles Darwin developed to a high degree his faculty of continually and carefully observing living things and of drawing every possible observation from each experiment and each opportunity. He considered himself especially good at "noticing things which easily escape attention, and observing them carefully. My industry has been nearly as great as it could have been in the observation and collection of facts. What is far more important, my love of natural science has been steady and ardent."

His son, Francis Darwin, gives us this important insight into his illustrious father's methods:

"He wished to learn as much as possible from an experiment so that he did not confine himself to observing the single point to which the experiment was directed, and his power of seeing a number of other things was wonderful.

"There was one quality of mind which seemed to be of special and extreme advantage in leading him to make discoveries. It was the power of never letting exceptions pass unnoticed. Everybody notices a fact as an exception when it is striking or frequent, but he had a special instinct for arresting an exception. A point apparently slight and unconnected with his present work is passed over by many a man almost unconsciously with some half-considered explanation, which is in fact no explanation. It was just these things that he seized on to make a start from. In a certain sense there is nothing special in this procedure, many discoveries being made by means of it. I only mention it because, as I watched him at work the value of this power to an experimenter was so strongly impressed upon me."

J.B.A. Dumas emphasized differences between events observed and deliberately planned experiments. Says he:

"The art of observation and that of experimentation are very distinct. In the first case, the fact may either proceed from logical reasons or be mere good fortune; it is sufficient to have some penetration and the sense of truth in order to profit by it. But the art of experimentation leads from the first to the last link of the chain, without hesitation and without a blank, making successive use of Reason which suggests an alternative, and of Experience, which decides on it, until, starting from a faint glimmer, the full blaze of light is reached."

An astoundingly high percentage of industrial research problems yield to the processes we have described of learning and marshalling facts and then drawing conclusions from them. Not infrequently the process is cyclic, as we have indicated, and requires several cycles of search, experiment and coordination of the findings. Usually one is able thus to simplify the problem in successive stages until the final solution is obvious and inescapable.

Sometimes that does not happen. The cycle fails to simplify the problem or to narrow the area in which a solution might reasonably be sought. Something more is necessary. Original thinking only can bridge the gap and that sometimes requires a complete change of procedure. Psychologists tell us that what the conscious mind cannot or will not do is sometimes easy for the subconscious mind. They point out that great numbers of discoveries, inventions and developments spring directly from the seeming inspiration which characterizes the successful working of the subconscious mind. Furthermore, the method of bringing this invaluable agency into action is simple and quite well understood. It consists of three steps. Two of these will already have been taken by the research worker before he faces a blank wall after several cycles of the processes described above. The first is to charge the mind with all the information bearing on the subject of the search that one can lay hands upon. The second grows logically from that and consists in collating and coordinating the accumulated information as far as and in every way possible. It is important to utilize *all* sources of raw material, experience, literature and experiment, in the accumulating process and to place no limitations as to practicability upon the patterns into which this material may be grouped. It is usually impossible to predict practicability surely and easy to prove it later.

This last condition is usually impractical to realize in conscious thinking because the conscious mind tends always to work in cycles, to wear grooves of repetitive thinking and to follow them endlessly. That cyclic following of worn ruts of thought builds up the insurmountable stone wall that separates us from our objectives and defeats our efforts to get ahead. Presumably the value of our subconscious minds lies in their freedom from ruts, or in their ability to rise above them and to reach conclusions impossible for rut-bound thought.

When given an opportunity, the subconscious mind is capable of the most amazing feats and in the end presents our conscious mind with a flash of inspiration, the "flash of genius" of the patent law, with minimum apparent effort. The process of final inspiration resembles nothing so much as the charging of an electrical condenser. Toward the end the rate of charging becomes extremely slow, but ultimately it builds up a charge great enough to overcome the resistance of the system in a lightning-like flash. The first part of the charge may be imparted at whatever speed the individual mind finds adaptable and in ordinary course this rapidly imparted charge alone may raise the potential to the point of rupture. Thus in our ordinary thinking, we reach the mental potential needed for the conclusion by quite ordinary processes. When, however, our usual faculties are unable to reach the mental potential required to solve some intricate or abstruse situation, we can to advantage utilize the power of our subconscious minds to add by tiny increments the last tiny part of the charge needed to achieve the result.

The analogy between original thinking and building up an electrical potential is somewhat closer than appears at first blush. As we have noted, the thinking process consists basically in fitting together enormous numbers of combinations of elements in the mind until the whole presents a satisfactory overall pattern, which is the solution to the problem. Multitudes of indications must finally point in the same direction. In an electrical sense, the gross charge on a body can be considered to be built up by the concordant arrangement of innumerable tiny charges of the magnitude of those on electrons. In both cases the result is achieved by aligning great numbers of infinitesimal forces (mental or electrical) in such a way that the resultant of their operation is the sum of all of them.

Just as electrical charges can only be built up to great magnitude by preventing any of the accumulating charges from leaking away, so the exercise of great mental power requires that the process be allowed to proceed without interruption or mental disturbance. A state of mental insulation that fosters the mind's subconscious activity is most easily achieved by relaxing mental tensions. This need not require physical isolation. The circumstances conducive to this state differ for different individuals, but all have in common the idea of blocking out annoying and disturbing thoughts and inducing mental relaxation by whatever method may be individually most effective.

Sometimes a state of mental rest is created by the simple process of isolation, or by physical rest, or by some kind of activity, either mental or physical, that is quite different from those of every day. While the greatest variety of circumstances have been credited by various individuals with heightening their mental powers, these have only two aspects in common: relaxation of mental tensions and exclusion of irritating and disturbing extraneous thoughts.

The circumstances of revelation and inspiration possess astonishing variety. Platt and Baker made a particular study of the subject of original thinking among research men and reported their findings in the *Journal of Chemical Education* in 1931 (volume 8, page 1969). Their method was to question several hundred successful research workers and then to collate the answers. In their study are noted cases where the requisite degree of mental insulation was achieved by such varied acts as: walking briskly downtown in anticipation of a beefsteak dinner; riding a train before dawn; resting and loafing on the beach; sitting at a desk idly thinking of other matters; dodging through automobile traffic; awakening in the morning; dressing after a bath in the ocean; dozing after a hard day's work; sitting in church; shaving; riding in an automobile; listening to fine music; and many others equally various.

On this subject, Barrett Wendell said:

> "My method of clearing my ideas is by no means the only one. I have known people who could do it best by talking; by putting somebody else in a comfortable chair and making him listen to their efforts to discover what they really think. I have known others who could really do best by sitting still and pondering in apparent idleness; others who could do best by walking alone in the open air; others, by stating to themselves the problems they wish to solve, and then going about all manner of business, trusting from experience to something they call unconscious cerebration. Each man, I take it, must find his own method; at different times each man may find different methods the best."

Graham Wallas cautioned against false relaxation that can come from surrendering our own thinking processes to those of some one else. Said he:

> "Perhaps the most dangerous substitute for bodily and mental relaxation during the stage of incubation is neither violent exercise nor routine administration, but the habit of industrious passive reading. Schopenhauer wrote that 'to put away one's own original

thoughts in order to take up a book is the sin against the Holy Ghost.' During the century from 1760 to 1360, many of the best brains in England were prevented from acting with full efficiency by the way in which Greek and Latin classics were then read."

The processes of original thinking are thus the same wherever they may be employed and whatever may be their purposes. James W. Young, in his "A Technique for Producing Ideas," applies the foregoing considerations to the creation of advertising copy. He outlines the process as consisting of the same three steps: accumulation, digestion or incubation, and finally inspiration or synthesis.

Obviously, a clear understanding of this matter is of the utmost importance to every research worker and to everyone concerned in any way directly or indirectly with the effectiveness of research. As the minimum essentials, the researcher must be provided by his employer or through his own efforts: (1) with facilities for accumulating facts and experiences by reading, by personal contact and by experiment; (2) with opportunity to digest and collate these facts under circumstances conducive to the optimum exercise of his mental powers and favorable to inspiration or synthesis from them; and (3) with the necessary means to prove and elaborate the results of these supreme mental processes.

While it is possible to achieve tremendous feats of imagination under quite deplorable conditions, modern industry cannot risk the uncertainty of such miracles. Rather it must create and maintain the most favorable conditions for research to invite inspiration. Even then industry frequently becomes impatient that developments of world-shaking consequence cannot be delivered every hour on the hour. Although it is difficult to persuade research men to admit such a thing, it is also possible to provide too much ease and too great convenience for the researcher. In the extreme case, the process of relaxation and incubation may become so pleasant that the time of the researchers may be so whole-heartedly devoted to this phase of the operation (with neglect of the cognate activities of experiment and proof) that nothing at all is accomplished. One great research laboratory is said to approach this condition so closely that its inmates commonly speak of it as the "plush-lined rut."

Obviously here, as in every other phase of research, common sense must govern. Relaxation must be limited before it leads to mental flabbiness, and rigorous austerity must equally be avoided lest it lead to mental sterility. Research, as all things, profits most from following a happy medium between the two.

Chapter 6

Process Research

"Tyndall emphasized the extreme value of the two little words 'as if' when used by the scientific mind, showing how, from things seen, a scientific imagination can lay bare things unseen and make possible discoveries of great value. Discoveries often come by accident, but the imaginative mind sees in these discoveries future possibilities. The imaginative mind, following out discoveries so made, is led into unlimited fields of usefulness. We must not think, however, of imagination as being the sole factor, although it is probably the principal factor, in the production of valuable materials. There must be energy, concentration, and persistence, which will carry such a mind across the Jordan into the promised land. Nevertheless, the imagination is the most important factor here, because, without it, there would be no promised land." —Gustave W. Thompson

A common problem of industrial research is to develop an entirely new process for the manufacture of some known compound or product. A study of procedures that have successfully solved even widely different problems of this kind reveals the amazing fact that the steps taken in each are almost identical quite regardless of the nature of the process. These are the steps in order:

(1) Determine the need and state the broad problem.
(2) Review the literature thoroughly.
(3) Select what seems to be the best method to be examined in detail, the one holding the most promise of development.
(4) List all factors involved in this particular reaction or series of reactions. Include not only temperature, pressure, and concentration of individual elements but also the physical and chemical properties of each substance that enters the reaction and the possible effects of catalysts and impurities.
(5) List the obvious methods of varying each factor. Note that

what is obvious to one investigator may not be obvious to another.

(6) Select one or more factors to be varied successively, one at a time, with all others held constant.

(7) Select methods of varying these factors on the basis of unusual familiarity with the technical facts.

(8) Experiment, and collect and study the resulting data.

Of course, the chances are that the first factor selected and the first means of varying this factor will not solve the problem. Commonly several methods of varying the selected factor must be tried, and other, even secondary, factors must be varied before ultimate success is attained.

A somewhat similar series of steps were stated by William A. Hamor as characterizing institutional research. After noting the initial steps that must be taken by the newcomer in orienting himself in the institution, Dr. Hamor suggests that successively the researcher:

gets history of problem
surveys literature
defines problem
studies attack
suggests solution
determines needed data
selects methods
outlines program
enters experimental stage
tests solvability
verifies findings
collects data
systematizes data
analyzes data
appraises results
makes deductions
reaches conclusions
tests conclusions
plans development

While these several steps are unquestionably vital, there is still another phase of the research that cannot be neglected. That is, at more or less frequent, and above all regular intervals, the researcher must draw up a report covering what work has been done, and what conclusions may be drawn from it. In the light of the latest experiments, literature readings and just plain thinking out the problem, the report must formulate the best statement of what the problem now is. This last is necessarily the next question that the research must answer. This phase of the research has been suggested in a previous chapter where we noted that the progress of a research is nothing more nor less than a consecutive series of statements of just what the problem has come to be. While it is usually necessary for the researcher to keep someone else—his colleagues, his superiors or his backers—informed of his progress for reasons of business or policy, it is vital to his own efficiency that he draw up frequent reports to himself, if not to others.

The usefulness of this general plan of attack on a research problem can be best appreciated by considering examples which illustrate its applications. Several of these accounts follow Keyes' analyses closely, especially ethyl acetate, absolute alcohol and electroplating aluminum.

After World War I, a producer of ethyl alcohol and acetone, both required in munitions manufacture, was left with excessive stocks on hand. Ethyl alcohol was particularly abundant since the acetone had been made from calcium acetate, which in turn was made from acetic acid produced by the fermentation of dilute ethyl alcohol.

The company not only had on hand large stocks of alcohol, acetic acid and acetone, but it also had a large (and unfortunately idle) capacity for producing them all. Investigation of possible markets for these products in peace revealed, among other things, a possible demand for substantial quantities of ethyl acetate which could be made from ethyl alcohol and acetic acid. It seemed logical, therefore, to seek out the best possible method of manufacturing ethyl acetate from the available raw materials, 95 per cent alcohol and dilute (10 per cent) acetic acid.

The literature disclosed the fact that to make ethyl acetate from alcohol and acetic acid, it is necessary, or at least desirable, to have 100 per cent alcohol and 100 per cent acetic acid. These two compounds react in the presence of fairly high concentrations of a strong dehydrating agent, such as sulfuric acid. The yields, however, are rather low (around 60 per cent) probably because concentrated sulfuric acid destroys (oxidizes) these anhydrous organic compounds. Although sulfuric acid is a well-known dehydrating agent, it seemed possible that it might also be a catalyst. If so, lower concentrations could be effective. A series of experiments were first made to determine the most useful concentration of sulfuric acid. The hypothesis of catalytic action for the acid proved correct, since a concentration of sulfuric acid as low as 2 to 3 per cent brings the reaction in a mixture of 95 per cent alcohol and 10 per cent acetic acid to equilibrium in a comparatively short time. In other words, large quantities and high concentrations of sulfuric acid are not necessary.

This established the existence of a reasonably rapid reaction between 95 per cent alcohol and 10 per cent acetic acid in the presence of 3 per cent sulfuric acid to form ethyl acetate and water. The next factor worth investigating was the concentration of the two reactants. Quite obviously anyone trained in physical chemistry would utilize the law of mass action by increasing the concentration of one or the other to force the reaction in the desired direction. Alcohol was chosen because it was simpler under existing conditions to increase its concentration than to raise that of acetic acid. A decrease in the concentration of one of the reaction products in the reacting zones should produce a similar effect. The research organization engaged on this problem was thoroughly familiar with the theories of distillation and fractionation and with the practical operation of fractionating columns. It was thought possible to decrease the concentration of products in the reaction by carrying it out in an ordinary fractionating column. Again the literature was searched, and an azeotropic mixture was found to be formed by the alcohol, ethyl acetate, and water. This ternary constant-boiling mixture has a boiling point lower than that of the familiar binary constant-boiling mixture of 96 per cent by volume of alcohol with 4 per cent by volume of water, and this in turn has a lower boiling point than any single component of the system. Therefore, if the reaction mixture is fed into the side of an ordinary fractionating column, a large proportion of the overhead product (that is, the more volatile constituent) consists of this ternary mixture and the column can be so regulated that only water and sulfuric acid leave it at the bottom. This possibility was tried experimentally and the results confirmed the surmise. Incidentally, an excess of alcohol introduced into the feed gave a product which showed no acetic acid. All of the acid had reacted; in other words, the yields were 100 per cent based on the acetic acid fed into the column.

At this point a process had been devised operating at a satisfactory rate and giving 100 per cent yields on the basis of one of the constituents. The problem of converting the constituents at hand into pure ethyl acetate had been partly solved, and all that remained was to separate the products from the mixture in pure form. This also presented difficulties and required further research.

The azeotropic mixture contained all of the acetate formed and any attempt to separate it by simple fractional distillation would necessarily fail. The distillate would always be the original constant-boiling ternary mixture (consisting of 83 per cent ethyl acetate, 9 per cent alcohol, and 8 per cent water), and the residue would contain only the excess alcohol and water accidentally accompanying the azeotrope.

The problem of breaking down the azeotropic ternary mixture had to be solved before it was possible to concentrate the final product, ethyl acetate. From the literature, it was learned that in a mixture of three liquids one component usually acts as a blending agent for the other two. Addition of an excess of either liquid, not the blending agent, to such a ternary mixture reduces the concentration of the blending agent, and thereby separates the mixture into two liquid phases. In this particular case, one phase should contain a greater percentage of the ethyl acetate than the other. Experiment showed that adding water to the condensate from the top of the fractionating column caused a separation into two layers, the upper containing approximately 94 per cent ethyl acetate, 4 per cent water, and 2 per cent alcohol. The lower layer, consisting primarily of alcohol and water, contained a minor percentage of ethyl acetate. Incidentally, this lower layer was returned to the fractionating column onto a particular plate where the composition was approximately the same.

Thus the percentage of ethyl acetate was raised from 80 to 94 per cent. This was accomplished by operating with the concentration factor, and by using a well-known principle regarding the mutual solubilities of liquids.

In order to remove the final traces of alcohol and water from the mixture and thus to obtain practically 100 per cent ethyl acetate, it was only necessary to pass this mixture into another fractionating column. Ethyl acetate was in excess of the amount required to form the ternary mixture with the alcohol present. Consequently, from the top of the column came the constant-boiling ternary mixture (since it possessed the lowest boiling point of any constituent), and this was returned to the separator where more water was added to repeat the process. At the bottom of this column appeared the finished product, approximately 100 per cent ethyl acetate. Once more the factor of concentrations of the constituents had served and the well-known principle of fractional distillation was utilized to change these concentrations as desired.

In brief, this problem was solved by manipulation of the conditions of chemical and physical equilibrium by the application of common methods plus the utilization of specific knowledge regarding the physical and chemical behavior of our reactants. Note too how each successive step brought a new statement of the problem that narrowed it progressively.

Obviously, the key to this solution lay in the fact that sulfuric acid plays a catalytic, rather than a dehydrating, role in the reaction of ethyl alcohol with acetic acid. This had to be learned by experiments undertaken, in this case, because the raw materials available were expensive to concentrate and to dehydrate—steps that would have been necessary if the reaction would not occur between them as they were. Distillation techniques were familiar to the organization faced with this problem and the necessary equipment was readily available. Furthermore, distillation as a method of changing concentrations of constituents already present in a mixture is preferred to salting out or extraction methods, which introduce extraneous substances and increase the expense of the operation. The reasoning behind the steps suggested is readily apparent from the solubilities of the constituents in one another and the boiling points of mixtures.

The development of the Twitchell process for hydrolyzing fats to yield glycerin and fatty acids is somewhat similar in its basic chemistry. Ernst Twitchell, in accepting the Perkin Medal in 1917, described his research thus:

"The first suggestion which led to my discovery of a special catalyzer for hydrolizing fats came to me in studying the so-called *acidification process*. This was one of the oldest methods used in candle factories for separating glycerol from fatty acids. It consisted in treating the fat at a fairly high temperature, over 100° C., with a small amount of concentrated sulfuric acid; 4 per cent or considerably less could be used; the product was then boiled with an excess of water. The result is a layer of fatty acids floating on the acid water containing the glycerol.

"This reaction could not be explained by the assumption that there is a combination of sulfuric acid with the fat or fatty acid and glycerol, which decomposes during the subsequent operation of boiling with water, because there was not enough sulfuric acid to combine with all of the fat. I have seen various theories given to explain the acidification process, some quite absurd. For instance, in one textbook it is stated that fats consist of minute globules surrounded by membranes and that the function of the sulfuric acid is simply to char and destroy these membranes, leaving the fat in a condition to be hydrolyzed by water at 100° C. Another theory I have frequently seen, even in recent articles, is that compounds are formed which cause the fat to emulsify with water, and the idea evidently is that if a good enough emulsion is obtained, hydrolysis will take place even at 100° C. I have seen this theory given to account for the action of my hydrolyzing reagent. As a matter of fact, fats do not hydrolyze at 100° C., practically speaking, with water alone, even though they may be perfectly emulsified. At higher temperatures than 100° C., and under pressure, hydrolysis takes place, as is illustrated in the autoclave process of separating glycerol.

"In the course of practical experiments with the acidification process I found that I could reduce the amount of sulfuric acid used very considerably and yet obtain complete decomposition; but often the boiling with water had to be decidedly prolonged. It seemed clear that there was some catalytic agent which caused the reaction between the fat and the water in this process of boiling, and it would naturally occur to anyone that this catalyzer was probably some sulfur compound produced by the action of sulfuric acid on fat. I found that compounds of this nature could be roughly separated from the fat which contained them by treating with petroleum ether in which they were insoluble. They could be further purified by solution in ether and extraction with water and were easily identified as sulfonic acids by their acidity, the formation of potassium sulfate on fusion with caustic potash, and other characteristics.

"It occurred to me to prepare this catalyzer outside of the body of the fat, thus avoiding the action of the sulfuric acid in forming with the fat undesirable compounds, in charring, discoloring and partially destroying it.

"As these sulfonic acids were probably produced by the action of the sulfuric acid on the oleic acid constituent of the fat, I first studied the results of the action of sulfuric acid on pure oleic acid under various conditions of temperature, quantity, etc.

"The action of sulfuric acid on oleic acid at low temperatures, as was known, produces a compound of sulfuric acid, stearosulfuric acid, an acid sulfuric ester. This was not the catalyst that I was seeking. It very probably has all the properties of a catalyst for the hydrolysis of fats except one: it is decomposed on boiling with water; and as the hydrolysis of a fat hardly takes place at all under any circumstances at a lower temperature than 100° C., it is plain that this compound would not serve my purpose.

"The compounds obtained on treating oleic acid with sulfuric acid at a temperature of 100° C. or over are not sulfuric acid compounds but are true sulfonic acids. The principal one seemed to be derived from two molecules of oleic acid and contained one sulfonic acid group and one carboxyl group.

"I have never seen this sulfonic acid described, but believe that I had in my hands a fairly pure compound of the composition $C_{17}H_{34}(SO_3H)COO \cdot C_{17}H_{34}COOH$. This was my first hydrolyzing reagent or 'saponifier.' But as it was difficult to prepare commercially in fair yield and of any degree of purity, I dropped further investigation along this line on the accidental discovery of the fatty aromatic sulfonic acids, described in the *Journal of the American Chemical Society*, January, 1900.

"In this research the most important question was: What properties must a substance have to act as a catalyzer to accelerate the hydrolysis of fats? My views on this subject I have partially expressed in my paper, 'A Reagent in the Chemistry of Fats,' where I say that it must be a strong acid, one dissociated strongly in water giving a considerable concentration of hydrogen ions, and then it must be soluble in both fat and water and cause the one to dissolve in the other.

"The only bodies that I can at present conceive to have the desired properties are sulfonic acids containing higher fatty radicals. They have the physical character of fats or oils, yet are soluble in water forming soapy solutions, and yet are strong acids.

"As I have said, the discovery of the fatty aromatic sulfonic acids was made by accident. I had a mixture of oleic acid and benzene which I treated with an excess of sulfuric acid and then poured the mass into water. I was not surprised to find an oily layer floating on the acid water, and when I found this oil to be soluble in pure water, that also did not surprise me, as I supposed I had simply stearosulfuric acid; but when I found that after boiling for half an hour with water it still remained soluble, I felt sure that I had sulfonic acid, and the analysis of the product confirmed my conclusion. This is the compound which has been put to practical use in the separation of glycerol and fatty acids. Instead of benzene, naphthalene is used with oleic acid in the manufacture of the commercial article. This 'saponifier,' when added in the proportion of half a per cent or less to fat boiling with water in an open tank, will cause the separation of the glycerol.

"Besides the compound containing the stearic radicals and a sulfonic group (the first which I found to have the catalytic property) and the fatty aromatic sulfonic acids, I have also prepared my hydrolyzing reagents by treating oleic acid at 200-220° C. with sulfur, or in the cold with sulfur chloride (S_2Cl_2), and then oxidizing with nitric acid, potassium permanganate, bromine or other oxidizing agent. The resulting compound contained one sulfonic and one carboxyl group and its molecular weight and other properties showed it to be a sulfonic acid of the stearic radical.

"Besides its use in hydrolyzing fats, my catalytic agent has been applied to other less important ones. A catalyst, which would accelerate the hydrolysis of an ester in the presence of an excess of water, would also accelerate the esterification of a fatty acid and an alcohol on the removal of the water formed. Fatty acids can be made to combine with glycerol and other alcohols of high boiling point by simply treating a mixture of the two with a small quantity of the reagent and evaporating the water formed at 100° C."

The steps by which Charles M. Hall was led to the development of the production of aluminum supplies an excellent example of this method of attack as it succeeded in an entirely different field. The story in Hall's own words was told by him in accepting the Perkin Medal in 1911. Here it is in part:

"I read about Deville's work in France, and found the statement that every clay bank was a mine of aluminum and that the metal was as costly as silver. I soon after began to think of processes for making aluminum cheaply. I remember my first experiment was to try to reduce aluminum from clay by means of carbon at a high temperature. I made a mixture of clay with carbon and ignited it in a mixture of charcoal with chlorate of potassium. It is needless to say that no aluminum was produced. I thought of cheapening the chloride of aluminum then used as the basis for aluminum manufacture, and tried to make it by heating chloride of calcium and chloride of magnesium with clay, following the analogy by which iron chloride is produced when common salt is thrown into a porcelain kiln. A little later, I worked with pure alumina and tried to find some catalytic agent which would make it possible to reduce alumina with carbon at a high temperature. I tried mixtures of alumina and carbon with barium salts, with cryolite, and with carbonate of soda, hoping to get a double reaction by which the final result would be aluminum. I remember buying some metallic sodium and trying to reduce cryolite but obtained very poor results. I made some aluminum sulfide but found it very unpromising as a source of aluminum then, as it has been ever since.

"On a later occasion I tried to electrolyze a solution of aluminum salt in water, but found nothing but a deposit of hydroxide on the negative electrode. I did not give a great deal of time to these experiments, as I was then a student in college and was working on three or four attempted inventions.

"I had studied something of thermochemistry, and gradually the idea formed itself in my mind that if I could get a solution of alumina in something which contained no water, and in a solvent which was chemically more stable than the alumina, this would probably give a bath from which aluminum could be obtained by electrolysis.

"In February, 1886, I began to experiment on this plan. The first thing in which I tried to dissolve alumina for electrolysis was fluorspar, but I found that its fusing point was too high. I next made some magnesium fluoride, but found this also to have a rather high fusing point. I then took some cryolite, and found that it melted easily and in the molten condition dissolved alumina in large proportions. I rigged up a little electric battery—mostly borrowed from my professor of chemistry, Professor Jewett of Oberlin College, where I had graduated the previous summer. I melted some cryolite in a clay crucible and dissolved alumina in it and passed an electric current through the molten mass for about two hours. When I poured out the melted mass I found no aluminum. It then occurred to me that the operation might be interfered with by impurities, principally silica, dissolved from the clay crucible. I next made a carbon crucible, enclosed it in a clay crucible, and repeated the experiment with better success. After passing the current for about two hours I poured out the material and found a number of small globules of aluminum. I was then quite sure that I had discovered the process that I was after.

"I undertook to broaden and improve the method, and found that I could use, instead of cryolite, other double fluorides, particularly a double fluoride of potassium and aluminum. The most important change, however, which I made at this time, was in the material used as an anode. I wanted to get rid of the burning up of the carbon anodes. I tried a platinum anode and found that it seemed to work all right, but it was too expensive. I discovered that if I used a fusible bath of a potassium double fluoride with a sodium double fluoride, I could use a copper anode, which immediately became coated with a thin film of copper oxide and acted like a permanent platinum anode. This was not a step in advance as I had hoped, because more or less copper got into the reduced aluminum, and the use of a copper anode led me to use very fusible baths, which on the whole did not work as well as the less fusible baths. It is probable that this change delayed a successful result for a year or two.

"When worked on a small scale, this process with any of the baths I have mentioned, and with either copper or carbon anodes, is not apparently promising. The ampere efficiency is low, sometimes zero, and the bath, whether composed of sodium or potassium salt, becomes filled with a black substance which accumulates and renders the process very difficult. I presume that my friend, Dr. Héroult, who invented the process independently in France about the same time, encountered the same difficulties. In spite of the difficulties mentioned, however, I had great faith in the theoretical possibilities of the process, and believed that the practical obstacles could be overcome, so I stuck to it from the start.

"In December, 1886, I returned to my home in Oberlin, continued my study, and found that a bath composed of a very fusible double fluoride of aluminum and potassium, with copper anodes, worked much better than anything I had before tried. I have a number of buttons of aluminum made by this method at that time. The larger one was made with current from a galvanic battery on December 7, 1886, and weighs about 8 grams."

From this point, Hall, like most inventors, became much involved in efforts to obtain backing for his idea. He failed to interest a Cleveland group in his process and later for a period of a year he worked with the Cowles Electric Smelting & Aluminum Company at Lockport, New York. Of his work there, Hall says:

"The baths which I used at Lockport worked well for a few days, but after a time became less efficient. I finally worked out a system by which the difficulties were overcome. This was by making a bath consisting partly of calcium fluoride, or fluorspar, and adding 3 or 4 per cent of calcium chloride, and using carbon anodes. I reasoned that chlorine was evolved and burned up the objectionable compound which spoiled the bath. After finally overcoming these difficulties, I made several pounds of aluminum in small crucibles. I showed this to Mr. Alfred Cowles, but he was not interested.

"I then sent Mr. Romaine Cole to Pittsburgh, to get together the gentlemen who formed the Pittsburgh Reduction Company, now the Aluminum Company of America. We started in the summer of 1888 to build and operate a commercial plant on Smallman Street in Pittsburgh. We had at our disposal about fifty horsepower in electrical current of 2,000 amperes. It took a few weeks after starting to get the dimensions of our baths just right, and then the difficulties which I have referred to disappeared as if by magic. The clogging and spoiling of the bath, which had caused trouble for the last three years, did not occur on a large scale. No calcium chloride was required. It seems that this is a process (unlike a good many others) which works badly on a small scale and well on a large scale. I accounted for this by the fact that on a large scale the electrodes are further separated and there is less circulation between the positive and negative electrodes to lower the efficiency and favor the formation of the clogging black compound. We also found, as I had predicted nearly three years before and had stated in a patent application filed two years before, that on a commercial scale no external heat was required to keep our baths in fusion. This was a great advantage, but I believe that it resulted from a law of nature and not from any invention, as we did not use any excess of current for maintaining fusion, but only the normal current and voltage for electrolytic purposes. The use of the electric current for fusing and heating in connection with electrolysis had been disclosed and published almost a century before."

This account of Hall's work provides a clue to another problem, that of electroplating with the metal. Aluminum could obviously not be electroplated from watery solutions nor could such a plate be applied to ordinary objects in a fused salt bath without undue risk of damage to them by the high temperature of the bath.

The marked tendency for the freshly deposited aluminum to react with water and to go promptly back into solution with the liberation of hydrogen obviously requires an electrolyte that contains no water and no compound with replaceable hydrogen. Of course, the electrolyte must conduct electricity and should contain besides aluminum no positively charged ion which can be easily neutralized at the cathode. Therefore, the attack should be directed toward finding a satisfactory electrolyte meeting these basic conditions. Simple reasoning suggests this as the factor upon which to operate, just as Hall did. Other factors may also be considered. For example, a common electrolyte might be changed by the addition of a reagent to be found which would prevent liberation of hydrogen at the particular potential at which aluminum could be deposited. Careful study, however, led to the belief that a liquid radically different from water is the most logical electrolyte. Fused anhydrous salts were ruled out by the effects on the work in hand of the required high temperature.

The Grignard reagent (compound of magnesium, an alkyl group or groups, and a halogen) dissolved in anhydrous ether is familiar. Such a compound is an electrolyte and will conduct electricity. Also familiar is the distinct similarity in chemical properties between magnesium and aluminum. Therefore, it may be possible to make an electrolyte of the compound of aluminum, an alkyl group and a halogen. Simple examples of such compounds are diethyl aluminum iodide and ethyl aluminum di-iodide. The structures of such compounds include no easily removable or mobile hydrogen atoms. If such a compound would conduct electricity, probably only aluminum would appear at the cathode. The compound was then prepared, anhydrous ether added, the whole placed in a dry cell with a copper cathode and an aluminum anode, and the current started. Surprisingly, no aluminum was deposited on the copper cathode, but instead a gas appeared, which analysis showed to be hydrogen. Going back over the reasoning revealed no flaws. The hydrogen thus must have come from some compound other than the particular one prepared as the electrolyte. In other words, an impurity was present. The only logical impurity is water. Evidently the solution had absorbed a certain amount of water, and perhaps was continually absorbing water from the atmosphere. In order to rectify this difficulty, the obvious thing to do was to prepare the electrolyte once more under anhydrous conditions and to cover the cell. When the process was started, dry air was passed across the top of the electrolyte to prevent any moisture entering the chamber. The result, after a few minutes of operation, was a deposit of finely crystalline aluminum on the copper cathode. Obviously this was the right track.

However, the operation was not satisfactory because the electrolyte is depleted as deposition continues, and no aluminum dissolves from the anode. This initial, although partial, success prompted continued study of the electrolyte. The basic specifications for the electrolyte must be met, but apparently by a different compound, possibly a complex compound containing not only aluminum, an alkyl group and a halogen, but nitrogen as well. Such metallo-organic compounds are well known, and many of them have been recognized to be polar in nature; that is, they should conduct electricity in a manner similar to a water solution. The simplest compound of this type is a combination of aluminum, an ethyl group, ammonia, and a halogen, such as iodine or bromine. The compound should have a low melting point to allow the process to go at a reasonable temperature. Experiments indicated that tetraethyl ammonium bromide added to aluminum bromide will produce a conducting liquid. Further experiments showed that, provided this liquid is kept dry, electrolysis will take place depositing aluminum on a copper cathode, and at the same time the solution will regenerate itself by dissolving away the aluminum anode.

This solution of the problem described depends largely on the specialized knowledge of the research worker engaged upon it. In other words, it would have been impossible to obtain a satisfactory electrolyte for plating aluminum if the investigators had not been thoroughly trained in fundamental organic chemistry. But the properties of the Grignard reagent are well known to every student familiar with elementary organic principles. Furthermore, in this particular case the investigator who proposed the use of the nitrogen complex was not an organic chemist, but had been trained in physical chemistry. His proposal was based not on any knowledge of this type of compound, but rather on his knowledge of the atomic structure of nitrogen. He reasoned that such a compound could be produced and that its properties would make it useful for this particular purpose.

This is an excellent illustration of the necessity, or at least desirability, of carrying on research in a cooperative organization and spirit rather than by giving a problem to an individual and expecting him to produce satisfactory results based solely on his personal knowledge of the subject. In other words, rarely does one research worker have sufficient fundamental information to select the proper factor and the proper method of varying this factor to give a satisfactory outcome.

Often when following this general method the first attack fails, and this forces the operator to seek another line of investigation. Even when the factor has been chosen for variation, the first method of varying it may prove entirely unsatisfactory. The wise research worker will then try a different method, or perhaps initiate an attack from a different direction.

The development of a process for removing sulfur dioxide from flue gases illustrates this point. Water could obviously not be used successfully to scrub flue gases containing 0.3 per cent sulfur dioxide because of the high partial pressure of sulfur dioxide in water solution, even when very dilute. The factor selected to be varied was the solution, and the first method of varying the solution tried was to add catalysts to promote reaction between sulfur dioxide and oxygen dissolved in the water. Sulfuric acid so formed has, even in concentrated solution, a very low partial pressure. If such a scheme could be used, the amount of water necessary to scrub the large quantities of gas (a million cubic feet per minute) might be relatively small and the operation, commercially feasible. Unfortunately, considerable experimentation revealed no practicable way of raising the rate of solution of oxygen in water to the point of producing a solution containing appreciable amounts of sulfuric acid. Other difficulties appeared such as inhibitors dissolved in the water solution from the flue gases. This plan failed because the required commercial equipment, being of low capacity, would be enormous and on that ground alone commercially unfeasible even if the process could operate.

A second attempt was based on producing a slightly alkaline solution which would therefore absorb sulfur dioxide quite readily. Heating this solution frees sulfur dioxide. The solution is an absorbent when cold but at a somewhat higher temperature will liberate an appreciable part of the dissolved sulfur dioxide. Inhibitors present in the flue gas which prevent the formation of sulfates now work to the advantage of the process.

Study revealed that this process had other distinct advantages over the sulfuric acid process. The product in this case is sulfur dioxide, which can be liquefied and sold directly with an existing and probable market for the large amount produced. On the other hand, the very dilute sulfuric acid that might be produced in the first process could not be sold for any purpose and at the same time was difficult of disposal as a waste material.

This general method of process research applies equally well to chemical and physical processes. The physical process of producing anhydrous ethyl alcohol from the 96 per cent product, for example, involves no chemical reactions, but this problem can be readily solved by the method already illustrated. Constant-boiling ternary mixtures, readily formed by alcohol and water with a third substance, have water and alcohol contents in considerably different ratios from the 4:96 proportion of their binary constant-boiling mixture. All that is necessary is to feed into the side of a fractionating column a binary mixture of alcohol and water plus the quantity of the third substance to form a ternary azeotrope. Benzene is conveniently used. Out of the bottom of the column, when properly adjusted, will come 100 per cent alcohol, and from the top a ternary mixture approaching the composition of the constant-boiling mixture of the three constituents.

As noted above, the alcohol and benzene in the constant-boiling mixture can be recovered by cutting down the percentage of the blending agent, in this case alcohol, by adding an excess of one of the other constituents, for example, water. A system of two liquid phases appears with most of the benzene in the upper layer and most of the alcohol and water in the lower.

Of course, the entire process can only be made efficient by recovering all of the alcohol and all of the benzene. This can be done by the standard procedure. The water layer containing most of the alcohol and a little of the benzene is fed to a second fractionating column. Off the top of this column comes the ternary constant-boiling mixture which is returned to the separator. From the bottom comes the excess alcohol and water. This mixture, in turn, can be sent to a third fractionating column, yielding the constant-boiling binary mixture of alcohol and water, which can be sent back to the feed plate of the dehydrating column. From the bottom comes the excess water. The benzene layer can be sent to a fourth fractionating column, off the top of which will come the constant-boiling ternary mixture (as it has the lowest boiling point) to be returned from the separator. From the bottom of this column comes fairly pure benzene to be returned to the feed plate in the dehydrating column. We now have a process which uses as a raw material 96 per cent alcohol and gives as products, anhydrous alcohol and water. The simplicity of this research lies in the fact that it is entirely physical in nature and it is unnecessary for the research worker to employ any method of changing the factor of concentration other than that previously discussed.

Langmuir has repeatedly proved himself a master of the art of selecting just the right property or condition to be varied and then of getting the greatest possible good from his experiments. Our previous quotations from his published work suggest something of his method. Undoubtedly the extraordinary quality of his mind has much to do with this facility, but this faculty quite clearly shows itself in his penetrating and painstaking analysis of the problem before him at the beginning of the research. Obviously he does not content himself with varying one condition solely because it is easy when another, more difficult to handle might lead to quicker and surer conclusions. He suggested one of his valuable methods when he told about investigating the effect of extreme vacuum in incandescent lamps:

> "It was the universal opinion among the lamp engineers with whom I came in contact that if only a much better vacuum could be produced in a lamp, a better lamp would result. Doctor Whitney, particularly, believed that every effort should be made to improve the vacuum, for all laboratory experience seemed to indicate that this was the hopeful line of attack on the problem of a better lamp. However, I really didn't know how to produce a better vacuum, and instead proposed to study the bad effects of gases by putting gases in the lamp. I hoped that in this way I would become so familiar with these effects of gas that I could extrapolate to zero gas pressure, and thus predict, without really trying it, how good the lamp would be if we could produce a perfect vacuum.
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> "This principle of research I have found extremely useful on many occasions. When it is suspected that some useful result is to be obtained by avoiding certain undesired factors, but it is found that these factors are very difficult to avoid, then it is a good plan to increase deliberately each of these factors in turn so as to exaggerate their bad effects, and thus become so familiar with them that one can determine whether it is really worth-while avoiding them. For example, if you have in lamps a vacuum as good as you

know how to produce, but suspect that the lamps would be better if you had a vacuum, say, 100 times as good, it may be the best policy, instead of attempting to devise methods of improving this vacuum, to spoil the vacuum deliberately in known ways, and you may then find that no improvement in vacuum is needed or, just how much better the vacuum needs to be."

Obviously this basic thinking and method of experiment can be applied to a wide variety of conditions—purity, concentration, temperature, pressure, pH, electric and magnetic effects, as well as vacuum—whenever the extreme is difficult or impractical to reach.

Related, but different enough to be enlightening, is the problem described by Landis of concentrating the rare gases of the atmosphere for use in the early gas-filled incandescent lamps. This particular research failed as the basis of a commercial venture but it is nevertheless worth examining.

"On November 14, 1914, the American Cyanamid Company accepted an order from the National Lamp Works of the General Electric Company to deliver 5,000 cubic feet of argon at the rate of 100 to 200 cubic feet per day, the concentration of argon in the mixture shipped to be more than 20 per cent. Deliveries actually started in December, 1914, and continued through to May, 1915, totaling in all nearly 8,000 cubic feet of argon. As far as we know, it was the first commercial contract for this gas made anywhere in the world. . . .

"In the cyanamide ovens at that time, we were able to utilize only about 50 per cent of the nitrogen led into them, and this was by no means uniform throughout the 40-hour nitrification period. During the starting-up period the ovens were flushed with nitrogen before the heater unit was turned on. Again the ovens were cooled under nitrogen. Consequently both the beginning and the end periods showed rather low nitrogen absorption, whereas in the more active portion of the cycle there were undoubtedly times at which up to 80 per cent of the nitrogen was going into the carbide. These ovens floated on the nitrogen line, and regulation was accomplished by manipulation of a vent in the cover of the oven.

"During nitrification a number of side reactions took place. The paper liner and tube distilled. Residual water vapor and decomposition products of carbide both produced foreign gas. Consequently, the vent gases were not pure nitrogen and argon, but a very complex mixture; for example, taking the most active period of nitrification, about 20 hours after starting, the percentage composition of the mixture was: argon, 6; hydrogen, 24.7; oxygen, 3.2. Nitrogen and undetermined constituents made up the balance. These complex waste gases from the cyanamide ovens make complications in argon recovery.

"In the preliminary discussion with Dr. Whitney it was pointed out that the mere collection of the waste gases from the vents of the cyanamide ovens would be of little help in the solution of his problem. Air carries approximately 0.9 per cent argon. After removal of the oxygen, the concentration is increased to 1.2 per cent. The ovens as a whole extracted about 50 per cent of the nitrogen, which would give a maximum concentration of around 2.5 per cent argon. But actually because of the introduction of foreign gases the argon concentration will be less than this figure. Therefore, in the regular cyanamide practice as of that time, argon concentration was hardly worth consideration. It was recognized, however, that during the most active period of nitrification, some 18 to 25 hours after the start of the ovens, there should be a much higher concentration of argon in the vent gases; samples were actually obtained from individual ovens showing as high as 6 per cent of this desired gas.

"One great difficulty was our lack of a quick and effective means of determining argon concentration. For a long time we were forced to ship gas samples to Schenectady for analysis, and the delay occasioned by this procedure greatly slowed up progress in the development of the most promising method of approach to a solution of the problem. It was not until December, 1914, that we obtained from Schenectady an apparatus that enabled us to make rapid and reasonably precise determinations.

"Naturally it occurred to us that we might improve this concentration by connecting cyanamide ovens in series, passing the vent gases from one to the next. Strange to say this did not yield improved results. The gas current picked up large volumes of foreign gases which reduced the nitrogen concentration to a point where it was difficult to maintain temperatures in the ovens because of slowing up of the reaction. We improved this condition, however, by starting nitrification in an adjacent bank of ovens. When they had reached the active period and were at full temperature, we would pick them up and drop them into the series-connected ovens; in this way the heat stored in the hot mass of carbide and cyanamide was utilized to carry on fixation at lower nitrogen concentrations, but even then we had difficulty in obtaining much above 10 per cent argon, calculated to argon-nitrogen mixture.

"The next modification was to break the connections in our series of ovens and insert in the line a small copper purifier such as was used in the nitrogen plant. This was a piece of 12-inch pipe about 6 feet long and filled with copper mass. It was built into a furnace structure and could be heated externally by gas flame. The final arrangement consisted of four ovens in series, then the purifier with its scrubbing equipment, and two additional ovens in series with a second purifier and a scrubbing and drying equipment. We kept these purifiers oxidized so that most of the copper was in the form of copper oxide. This would burn the hydrocarbons to carbon dioxide and water vapor, which were removed by caustic scrubbers and lime dryers. With this system we began to approach a 20 per cent argon-nitrogen mixture, but beyond that point we could not go with the cyanamide ovens.

"Although the contract called for a gas containing 20 per cent argon minimum, pressure was brought to bear to increase this concentration as high as possible. An additional absorption unit was constructed consisting of a horizontal pipe built into a furnace, into which we charged carbide. This was externally heated by gas and enabled us to continue nitrogen absorption independent of the heat generated by the reaction. We also studied the possibility of catalysts in the carbide, and finally determined that a mixture of calcium fluoride and calcium chloride did have a beneficial effect when added to the extent of about 10 per cent of the carbide charged into the final absorber. The apparatus, however, proved quite impractical on large-scale continuous operation.

"Sitting in the lunch room at Niagara Falls one day, I had a sudden hunch as to a more effective piece of apparatus for final absorption of nitrogen. I picked up a heavy stoneware saucer, such as is ordinarily found in plant lunchrooms, sent it to a local foundry, and had a large number of castings made with this saucer as a pattern. A hole was drilled in the center, and we strung these castings on a long iron rod, spacing them with ordinary pipe nipples. Four of these units were assembled. A furnace was built into which four steel pipes were set vertically and arranged for gas heating. These pipes were connected together in series.

"In operation the crane would pick up the 'Christmas tree,' as our string of saucers was called, and lower it slowly into the pipe from the top. A funnel charged with carbide would fill these saucers as they were lowered into the pipe. The caps were replaced and the unit was put into operation. It required only a few minutes to load such a furnace. This, then, became the tail end of our absorption system, and we found we could run the argon content up to 90 per cent and above without difficulty. When the carbide was exhausted, it was a simple matter to lift the saucers from the pipe; the spent carbide was discharged merely by laying the saucers on their sides on the ground and rapping them with a hammer, when they were ready for replacement.

"This final absorption apparatus was also followed by a copper purifier with its caustic scrubber and lime dryer. Next the gases were sent to the compressor which filled them into the steel bottles in which they were shipped to the lamp company.

"The plant actually commenced operation and shipment in December, 1914. By March we were producing better than 2,000 cubic feet of argon per month. All told, we shipped a little under 8,000 cubic feet of argon, most of which was better than 80 per cent concentration.

"From the commercial standpoint we spent about $2,500 for labor and materials in assembling the unit. This included expenditures for alterations during an experimental period and before signing the contract. In addition we borrowed from the storeroom meters and blowers; considerable stocks of this equipment were carried, since they were standard in the nitrogen plant. There was little or no wear and tear upon them during this short period of operation. We received $1.25 per cubic foot for the argon under the contract, and as nearly as the accountants could determine, the operation just about broke even when it was wound up in May, 1915.

"It has been mentioned that in the discussion with Dr. Whitney we did not believe the cyanamide process could offer any solution to this argon problem. The contribution of the routine oven operation as noted was only to double the argon content, hardly enough to make it of moment. From that point onward it called for special manipulation, all of which interfered to some degree with cyanamide production. For example, the transfer of a hot can of carbide from one oven to another involved oxidation and consequent loss of efficiency. This amounted only to 2 to 3 per cent, but it was nevertheless an item to be considered. Of much greater moment, however, was the fact that the copper process of producing nitrogen had become obsolete by this time. Improvements in the liquid air machinery and a better knowledge of safe operation about a cyanamide plant spelled the end of the copper retort, for the liquid air process could be operated to produce a higher quality nitrogen at about one third the cost of that by the copper process as it was set up at Niagara Falls.

"Up to the signing of that argon contract, the development of the fundamentals in the operating plant had been very slow. There was no great driving force behind it, and when one considers that the gas samples had to be shipped 300 miles to Schenectady for analysis, one can understand the relatively slow progress in these early stages. But when two commercial men had signed a contract to produce something that neither knew very much about and under specifications far beyond anything that had yet been attained in the unorganized exploratory work, there was an entirely new aspect. It was a strong moral, if not a legal, obligation to make good. But even at this point the argon venture was only an incident, for two much more important problems had to be solved at the same time, both resulting in large operating units to be completed and put into operation before the summer of 1915, and both concerning entirely different materials. The war in Europe was forcing performance on a record scale and at a record pace."

An important example of process research was given by Edward Weston, when as part of his Perkin Medal address in 1915 he described his pioneering in the electroplating of nickel. To understand his description, one must realize that there was a time long ago when the electroplating of nickel was industrially new and that the work here described preceded its general adoption as a commercial practice.

"At that time the art of nickel plating had just begun, and very little was known about the chemical, electro chemical or even the mechanical conditions necessary to carry it on successfully. Moreover, the public knew practically nothing about the properties of the metal nickel, or the advantages to be derived from coating articles with it. In other words, the public had to be educated to use nickel-plated articles, and those who undertook to practice the art had to learn much about the conditions which had to be complied with in order to prepare successfully, plate and finish the various metals and combinations of metals to which nickel might be advantageously applied for protective or for ornamental purposes.

"In general, there was no difficulty with the nickel solutions. The solutions when properly used gave good results. The trouble was mainly due to using methods that were similar to those employed in depositing silver, but silver, as you know, is a very soft metal, whereas deposited nickel is very hard. Electro-deposited silver is *burnished* with a burnishing tool, which, with the aid of a little lubricant, is worked backwards and forwards until a lustrous finish is obtained. The last operation is just to touch the surface lightly on a very soft canton-flannel buff covered with a little rouge and water. A nickel deposit, however, cannot be burnished. It is too hard; consequently it must be polished. The processes then employed in preparing the articles for nickel plating were mechanical. The articles, after they came from the buffs, were dipped in hot or boiling solution of caustic potash, in order to saponify whatever grease might remain on the surface. The article was kept in the potash bath until not only the fat was saponified, but a rather dark coating of oxide was formed on its surface. It was withdrawn from the hot potash solution and was scoured with a common plater's brush, dipped in rather fine pumice stone.

"You can imagine exactly what would take place under these circumstances with a soft metal like brass. Of course, it would be scratched very badly. The article was then washed in water and placed either directly in the bath or immersed in a solution intended to remove the last faint trace of oxide which might have been formed on the surface of the metal during the operation of scouring.

"In the processes then employed the standard voltage recommended was two volts, that is, two Snee cells, which gave very closely approaching two volts under ordinary conditions of their use. That recommendation was fundamentally wrong because, as chemists, you can readily see that what was necessary was to cover the inferior metal as quickly as possible after it was placed in the solution, because if this was not done, secondary reactions were apt to take place between the inferior metal and the nickel in solution, and then the adhesive characteristics of the coating were lost. Hence, in reality one of the most important things was to increase the voltage and quickly coat the whole article with a film of nickel, transfer it to a bath in which the voltage was lower, and let the deposit go on until it reached thickness. If the article was very large or irregular in shape or was a long distance from the operation, parts of the surface would get covered with secondary compounds and any attempt at polishing would cause flaking. Now, when we plated that relatively rough surface we were, of course, compelled to put on a sufficient coat to cover up those scratches.

"We lost a very large percentage of the nickel in this way and also a very great deal of time in carefully polishing the nickel coat. The remedy would seem to be obvious—chemical cleaning and putting on the soft metal before placing it in the bath just as good a finish as was wanted on the nickel after polishing. However, I was told that chemical cleaning would spoil the plating solutions, since the claim in the patent was that potash or soda would ruin the solutions. That induced me to take up the question of what the influence of these substances was, and, of course, I found that really they did no harm. The chemical method of cleaning was adopted entirely and is still in use except that the cleansing of iron or steel articles or other metals not readily acted upon by caustic potash or soda is done by the aid of electrolysis.

"It then occurred to me that we ought to be able to get softer nickel, but at first the only way I could do it was by reducing the rate of deposition, keeping down the tendency of the evolution of hydrogen at the cathode. Some years later I was rewarded by finding a solution which yielded a nickel deposit with characteristics closely approaching those of good copper. It could be rolled and drawn and I called it 'malleable nickel.' I think that was the first time malleable nickel had been produced by the electrolytic cathode. It was done by using a *single* salt of nickel, at that time a subject for considerable disagreement among chemists. Beckold actually produced and exhibited before the French Academy of Sciences samples produced by deposition from a sulfate of nickel solution, and later from a solution of a double sulfate of nickel and potassium; he then stated that it was perfectly easy to get from either of these solutions the required amount of metal. Now it is a rather strange thing that he did not continue his investigation a little longer and discover that his solutions were limited to one or possibly three sheets.

"No single salt of nickel that I know can be used for depositing nickel commercially, and no double sulfate of nickel and potassium or any other alkali can be used for depositing nickel, and for a time the cause of it was quite a mystery to me. The supposition was that electrolysis of the double salt would deposit the potassium together with the nickel at the cathode. However, that is not possible, for the potassium would attack the water and cause the formation of caustic potash, which would, in turn, take the acid radical and precipitate its equivalent of nickel on the cathode. But what did take place was this: If you take a solution of a single salt of nickel—chloride, sulfate, bromide or iodide—and electrolyze it you will first get exactly what Beckold did—a good deposit of metallic nickel. But after a while the deposit takes on a darker and darker color, until at last there is a little tint of green on the surface of the cathode; when that begins, more and more hydrogen is evolved at the cathode until finally the cathode is being covered slowly with a very green salt. But the addition of a little sulfuric acid to the solution causes it to begin depositing nickel again. Now, although all the single nickel salts give an acid reaction to litmus paper, if you electrolyze the solution until you get the green deposit on the cathode you will find that the solution is in a basic condition. To test the accuracy of the conclusion drawn from my experiments, that it was simply because of the basic condition of the solution and not because of any foreign substance, I electrolyzed a specially pure solution of nickel sulfate and before the deposit began to turn acid I added a little freshly precipitated hydroxide of nickel; instantly the deposit became green; I added a little acid and it became metallic nickel. Not satisfied with this I prepared extraordinarily pure nickel, taking great precautions to exclude every trace of potash, soda, alumina and lime, and I found that the solution acted exactly as did my first solution and the commercial sort. That led to the invention of a nickel anode and a new solution and gave me my really first great start.

"The anode was made from grain nickel mixed with the minimum amount of carbon with a binder of tar or pitch, the whole thing being submitted to hydraulic pressure. After a long period of use if you broke the nickel-carbon electrode up you were rather astonished to find that although you had taken an enormous amount of nickel out of the electrode there was apparently no change in the size of the grains. The only difference observable was to be detected by the use of some sharp-pointed instrument and then you could dig in and cut it out in a powdered condition. There is a colloid form of nickel and a crystalline one, and if you use a large cast anode for some time it will look just the same in size as it was originally even after you have used it for a year, but it will bend exactly like a piece of flexible sandstone. Examine it under a glass, and you will note that the colloidal portion has been dissolved out and only the crystals are left.

"The solution used was sulfate of nickel or chloride of nickel, to which boric acid had been added. I could have added any other acid and prevented the precipitation of the salt of nickel at the cathode and the change in the chemical condition of the solution, and, of course, got along fairly well, but there were certain pretty good sound reasons why I should not. If I added another acid which had a tendency to attack the positive metal to be coated I would have secondary reactions set up immediately upon my putting the electropositive metal into the bath, and it turned out that boric acid was the most suitable. The patent was unfortunately drawn so that afterwards others put in acetic acid. You can put in other acids—just keep the solution slightly acid and it will go.

"Colloids in a nickel solution are often very dangerous, especially in the ordinary double sulfate solution or double chloride solution. I learned that in about 1870. Under the direction of a New York chemist, a firm in Newark had started a small nickel-plating plant, but after it had been running a short time it began to give an extremely black, powdery deposit and large amounts of hydrogen. They could not get a regular metallic deposit. The chemist, who had furnished the solution, the anodes and I think also the batteries, was threatened with a suit and asked me if I could help him. I cross-examined the workmen at the plant but no one would admit doing anything to the solution; yet, I could not correct it. Then I questioned them even more closely and finally they admitted that the tank had leaked and that they had saved the solution by transferring it to a barrel—a clean alcohol barrel. I could not imagine what there could be in an alcohol barrel except possibly some organic matter, probably glue. So I made a solution of permanganate of potash, stirred it into the plating solution until I got just the pinkish tinge, put an article in with an electrode, and the thing was all right. Several times thereafter I had similar experiences, and an investigation showed that as much as 0.1 per cent of foreign matter in the form of gelatin ruins a plating solution."

When, as now, gasoline is available everywhere in quantities that are equal to every demand, it is difficult to imagine that it was not always plentiful. First step to magnify the quantities of volatile fuel available from crude oil, and hence to insure plenty of gasoline, was the cracking process which was developed to commercial success by

William M. Burton. He described this development in accepting the Perkin Medal for 1922:

"The low-boiling fractions of petroleum naturally came into use (for powering internal combustion engines) and up to about 1910 the supply of this fuel was sufficient to meet the demand. In fact, the automobile provided an outlet for the sale of these products which, to some extent, had been a drug on the market in the oil world. The older refiners in the country will remember when these so-called naphtha products were thrown away and allowed to run down the streams adjacent to the refineries, thereby causing a willful waste and a fire menace to the surrounding neighborhood.

"Prior to 1910 the average yield of naphtha or gasoline products from crude oil in the United States was about eleven per cent, this yield representing only the amount of such products (of the quality desired at that time) normally present in the crude petroleum, their separation being secured by ordinary methods of distillation at atmospheric pressure; and, further, this small yield was sufficient to furnish all that was needed for gasoline stoves and other industrial purposes prior to the advent of the internal combustion engine for transportation purposes.

"When the automobile came into general use, however, it was perfectly clear that the normal yield of naphtha products suitable for fuel in self-propelled vehicles would not be nearly enough. At that time our refineries were selling about forty per cent of the products of crude oil for use as fuel and for gas-making purposes in lieu of coal. The remaining sixty per cent represented the normal yield of naphtha and gasoline, illuminating and lubricating oils.

"The above-mentioned forty per cent fuel and gas oil comprised fractions boiling between 225° and 375° C. These oils could, if necessary, be withdrawn from the market, and our problem was to convert them so far as possible into fractions boiling between 40° and 200° C., the product to be equal in quality to normal naphtha products and the yield and operating expense to be commercially practicable.

"Our first experiments were directed toward making a suitable product by superheating the high-boiling vapors as such, but without pressure, somewhat along the practice observed in making Pintsch gas. We soon found, however, that this so-called 'cracking' in the vapor phase required a temperature so high that the aliphatic hydrocarbons contained in the petroleum were largely converted into cyclic and aromatic bodies and fixed gases, unsuited for our purpose. The yield was poor and the quality most undesirable. Obviously our problem included the proposition of reducing the molecular weight without changing the general structure.

"We next tried the use of various reagents and catalyzers, such as aluminum chloride and ferric oxide. Anhydrous aluminum chloride, indeed, produced some rather remarkable results. The yield and quality of naphtha products were fairly satisfactory but there was a substantial loss of oil in the operations, and the first cost of the anhydrous aluminum chloride, as well as the difficulty in recovering it from the residues, rendered this plan unattractive.

"Nearly thirty years ago Sir Boverton Redwood and Professor Dewar in England patented a pressure distilling process for the purpose of increasing the yield of kerosene oil from the residues of Russian crude petroleum, but it never was applied industrially. It has been known, therefore, for some years that distilling petroleum under pressure served to break down the high-boiling fractions into low-boiling fractions but, as far as we could learn, no one had ever done it on a large scale and, in fact, such a proposition could not commend itself to a practical refiner because of the obvious dangers from explosions and fires.

"But having tried everything else that suggested itself, we attacked the problem of distilling petroleum in considerable quantities (8,000 to 12,000 gallons) under pressure of about five atmospheres. Our first still was of a welded design and was planned to handle 100 gallons of the high-boiling fractions. Obviously, the raw material first to be tried consisted of the so-called fuel oil, or reduced crude, meaning the residue of crude oil after the more valuable products had been removed. We soon found that we could not work profitably with this product; when distilled with or without pressure it produced quantities of coke that deposited on the bottom of the still and caused a red-hot bottom that would not stand any rise in pressure. The next proposition comprised the use of high-boiling distillates from the crude, *viz.*, oils boiling from 225° C. upwards. We distilled these distillates at a pressure of about five atmospheres and were thereby able to hold down the temperature to a moderate figure, the cracking being done in the so-called liquid phase. We found to our intense gratification that the low-boiling fractions produced belonged mostly to the paraffin series, which were easily deodorized and finished into products suitable for sale. Further, the yield of salable liquid was good and the production of fixed gases and coke was small.

"Experimentally, therefore, our work was successful. But the big problem remained to be solved. Could we build large equipment that would, in a practical way, secure the desired results and at the same time be durable and reasonably free from the fire hazard that always attends operations in an oil refinery? Some of our practical men said we could, but more of them said we couldn't. In this case, however, the majority was overruled and we immediately prepared plans and specifications for a still eight feet in diameter and twenty feet long, built of one-half inch mild steel plate, which would charge 6,000 gallons of raw material. It had a safety factor of 5, the working pressure to be 100 pounds and the bursting pressure 500 pounds.

"The still was built and charged, with many misgivings on the part of the doubters, but with boldness and confidence exhibited by the rest of us. As soon as we had the still hot and pressure began to develop, we encountered our first difficulty. The still was built in a workmanlike manner and would have made a good steam boiler, but rivets and seams leaked badly under oil pressure where they would not under steam pressure. It was difficult to induce boiler-makers to calk the leaks while the still was hot and under pressure, but we found men bold enough to do it, and the first run was sufficiently encouraging to induce us to proceed further. But the leaks persisted until Nature came to our aid, and when the minute portions of oil in the leaks gradually carbonized, they closed without our aid.

"The experiments with the large still proved our results with the small one: *viz.*, the yield of suitable gasoline fractions was good; the loss was trifling; the cost was reasonable; and the fire hazard under close caution and supervision was not excessive. Further, we were astonished to find that the residue remaining in the still contained substantial quantities of asphaltine actually created (from a distillate containing none of it) by distillation under pressure.

"We learned early in the work that operating at moderate pressure required a substantial dephlegmating system that would return to the still fractions boiling too high for our purpose, and allow the others to pass on.

"A suitable safety valve that would operate properly with oil vapors at high temperature had to be devised. After making a number of runs with our 8 by 20 still, and in view of the fact that the demand for gasoline was increasing at a rapid rate, we asked for an appropriation of one million dollars to build sixty pressure stills eight feet in diameter and thirty feet long, each charging 8,000 gallons of raw material. Considerable argument was required to convince any of our directors that such a revolutionary proposition could possibly be successful, but finally they voted in favor of it, and we went ahead. . . .

"Innumerable minor difficulties arose. We had solved the big points, but there were many smaller ones. For successful results we must operate with the oil at temperatures from 370° to 400° C. in the still. At 450° C. steel begins to lose its tensile strength and its capacity to withstand pressure. It is clear, therefore, that with this narrow margin great caution must be exercised to prevent overheating. The human element enters here, as it does in every feature of pressure-still operation, but we operated over eight years with hundreds of these stills in daily use, and manufactured millions of barrels of gasoline by this method before we had a fatal accident."

Colin G. Fink gives us a quite different example of process research. He utilizes modern electrochemical technique in a process he designed to restore to very near their pristine condition metal art objects whose original beauty had been destroyed by corrosion through the ages. In his Perkin Medal address, Dr. Fink tells of some of his chemical processing of utterly priceless museum specimens:

"Objects of copper and bronze exposed to the elements react with them to form oxides, chlorides, sulfates, and carbonates. In the past it has been the practice to remove these products of disintegration, collecting often as a thick crust on the surface of the metal object, either by the use of small chisels or by dipping the whole object into acid. In the course of our studies we discovered that details of design are retained by the crust and, accordingly, it was necessary to develop a method which would restore the detail. It occurred to us that, since the corrosion of metals was due to electrolytic action, it might be possible to reverse this action and reduce the oxides, sulfates, chlorides, and carbonates back to metal. When the objects were made cathode in dilute acid solutions, the local action was so severe that the crust dissolved and was not reduced to metal. It became necessary to use a weak solution in which copper showed very low solubility. The solution we finally adopted and which has been used for a number of years is a 2 per cent sodium hydrate solution. At first we were concerned about obtaining the proper electrical contact, but it soon developed that merely wrapping a soft, annealed copper wire over the surface of the object and connecting this to the cathode bar was all that was necessary. As anode we have used iron and nickel, but we prefer to use platinum. There are always appreciable quantities of chlorides present in most of the crusts, and these chlorides attack the iron or nickel anode. The heavier the incrustation, the lower the current density we use. It is important not to try to hasten matters, as such procedure will generally mean destruction and loss of valuable detail. Many thousands of objects have been restored by this process and a number of interesting facts have been brought to light. An interesting phenomenon is the decuprification of objects made of silver-copper alloys. During the process of corrosion, while the object is buried in the soil, both copper and silver in the surface of the object migrate some distance from the surface. But at one stage during the migration the silver metal is reprecipitated as metallic silver, and the curious fact is that this reprecipitated as metallic silver reproduces faithfully on a slightly enlarged scale the details the artist originally engraved upon the silver-copper alloy article.

"Although the application of thin foils of gold and silver to articles of copper and bronze was known to the ancients, as many museum specimens testify, it was only two years ago (1932) that we discovered that the Egyptians knew how to deposit a film of antimony on copper by chemical methods. It came about in the cleaning of an ewer and a basin of the fifth or sixth dynasty (about 2,500 or 2,000 B. C.) belonging to the Egyptian Department of the Metropolitan Museum of Art. During the cleaning operation, we discovered a white, silvery plating on the surface of both the ewer and the basin, and, on careful analysis, we found present in this coating also a small amount of iron. The assumption that the antimony might have been applied by a fire process was soon dispelled and the presence of the iron gave us a clue. After numerous trials, starting with those chemicals available to the Egyptians five thousand years ago, we were able to reproduce this antimony plate on copper by either of the following two methods: According to method 1 we used 20 grams of 'natron,' 1 gram of antimony sulfide, and 100 cc. of water. The natron was artificially made according to an average of the analyses given by Lucas. (Na_2CO_3, 48.7; $NaHCO_3$, 19.4; NaCl, 15.4; Na_2SO_4, 21.1). Antimony sulfide was used by the young ladies of Egypt to darken their eyebrows. The solution of natron and antimony sulfide was brought to boiling and pieces of bright copper were immersed in it. Within a short time, a silvery coating was deposited on the copper. This deposit took a good polish on a cotton buff. The reaction is probably due to interaction between metallic copper and sodium thioantimonite. The plate is relatively hard; evidence of this is shown also in the fact that the antimony bottoms of the ewer and basin had not worn off during the life of the articles before they were buried in a tomb thousands of years ago, and both articles showed much wear, so that they were evidently not new when put into the grave where they were found.

"The second chemical method of applying the antimony coat which the Egyptians may have used was as follows: To 1 liter of vinegar we added 200 grams of sodium chloride and 5 grams of antimony oxide. The copper articles, held in contact with iron, when immersed in the bath, acquired a beautiful coating of antimony. The principle involved is really electrolytic but could easily have been accidentally or empirically discovered and applied. There is no question about the vinegar and the salt having been known to the Egyptians. There may be some doubt about the iron. It will be recalled that Egypt sculptured her masterpieces, not with the aid of steel, but with hardened copper. Nevertheless, meteoric iron was available and known to the Egyptians for over a thousand years before the period of the ewer and basin in question. Why the antimony plating of the Egyptians had not been recorded heretofore is due to the fact that methods of restoration in the past have been too radical, and the thin, silvery coating escaped notice and detection."

Chapter 7

Product Research

"Necessity is not the mother of invention; knowledge and experiment are its parents. This is clearly seen to be the case of many industrial discoveries; high-speed cutting tools were not a necessity which preceded, but an application which followed, the discovery of the properties of tungsten-chromium-iron alloys; so, too, the use of titanium arc lamps and vanadium in steel were sequels to the industrial preparation of these metals, and not discoveries made by sheer force of necessity." —W. R. Whitney

New chemical products developed to meet existing needs have often proved highly profitable by providing the basis for entirely new industries. Ductile tungsten, rayon, cellophane, neoprene, Freon, nylon and a host of others illustrate the point.

Methods of attack used in this type of research vary widely probably because research workers who seek to produce new substances have, at the start, no clear picture of the kind of compound or mixture they seek. In fact, there are cases where the investigators apparently had no particular compound as their objective and no plan of producing a new substance. In other words, they have not stated their problem clearly and the final result may even be the by-product of another investigation. Often the incentive back of such work is an extension of the sales field of some product or products.

If an investigator wishes to develop a new chemical substance for a particular purpose, his method of attack should be based on the following steps:

(1) List the faults of the present products; a list of virtues is also desirable.

(2) List similar products or those having properties that might be valuable in the particular use.

(3) Select from this list a product having the fewest faults for the particular purpose.

(4) Modify this product either fundamentally or by mixing with others to eliminate faults and enhance virtues.

Obviously the steps involved in a product research are the same as those of a process research once the basic problem has been clearly stated. Indeed these two classifications of research overlap and interlock so completely that the distinction between them is more imaginary than real. Certainly there is no value to a process except through the product it yields; nor can one easily conceive a product without some process by which it is made. The difference for our present purposes between product and process research lies in the approach to the problem: whether production and the efficiency of the plant be the paramount issue, or whether the needs of the user of the product are controlling.

Edison's search for a material that would produce the carbon filaments of the earliest incandescent lamps has already been noted in passing. The outcome of that initial search was a material, the fibers of bamboo, that could be carbonized to yield a char that would hold together in a form resembling wire. That was the outcome of a world-wide search and many thousands of experiments. It was fairly successful, but still left a great deal to be desired. One of the workers who undertook to find a better filament for electric lamps was Edward Weston, who discusses his research as follows:

"With the incandescent lamp, the smaller the candle power the smaller the filaments must be. It does not make any difference whether they are in series or multiples. Here the chemical difficulties were vastly greater than the mechanical. You could never make a commercially successful incandescent lamp filament out of untreated paper or thread by the carbonizing method. For instance, with paper there is no uniform density. Moreover, tensile strengths and thicknesses of paper are variables and very thin strips give different amounts of electrical resistance per unit of length. The total resistance of the loop is one thing, but the total resistance of every loop of a given candle power should be exactly the same, and the total amount of matter in the separate lamps should be exactly the same. But there must not be slight resistance in some sections of a loop and large resistance somewhere else, *i.e.*, the loop must be entirely homogeneous. You will see at once that paper or wood fiber, in which the fibers differ, can not possibly furnish a material that will give an evenly distributed electrical resistance. Bamboo is better than any of the other fibers. If gelatin paper is used, you get a gelatinized fiber, as it binds the fibers of paper together and helps, but if you pass the current through such a loop in a vacuum, the loop will become hot in some spots and will remain cool in others. But if you have a defective loop made from any of these substances, and put it into a hydrocarbon vapor and pass a current through it, the hydrocarbon vapor will be dissociated, and you will have a deposit of carbon forming on the hot spots, so that finally the loop will be repaired and will glow all over uniformly. The next step is to continue the deposition of carbon all over the loop so as to bring the resistance to exactly what you want it before it goes into the lamp. Thus you have chemical control of the resistance, not only of the bad spots, but of the loop as a whole.

"However, when filaments were treated by the hydrocarbon method they always failed at one spot—the initial weak spot that you first saw and tried to remove. We put a lamp between the poles of a powerful permanent magnet and passed an alternating current through it, and the loop vibrated at a rate corresponding with the rate of alternation of the dynamo. That was a severe test but it showed us whether we had completely eliminated the defective spots, because when the loop began to vibrate, any weak spots would show. On obtaining the perfect lamp it became necessary to try to raise the efficiency of the lamp in order to increase the possibility of commercial competing with materials like gas.

"I then took up the problem of producing the structureless carbon, a homogeneous thread of uniform cross section, and of uniform electric resistance from end to end for any given section. That was a chemical problem, of course. At first I attempted to dissolve cellulose. After various expedients, finally including squirting through small openings, I finally came back to collodion film. If you pour a solution of pyroxylin in ether and alcohol on a glass plate it leaves behind a beautiful thin horny film. It has great strength if the cotton from which the colloaion is made is good—about 16,000 to 20,000 pounds per square inch. Its tensile strength closely approaches that of some of the poorer metals and some of the rare, good metals. But if you attempt to use a filament of this material for an incandescent lamp the double solvent causes trouble. The alcohol-ether does not hold the pyroxylin in solution quite as well as it should, and shrinkage and pockmarking happen. We got over that by putting a frame of wood around the glass plate on which the liquid was poured and covering the top of the frame of wood with a very thin but very good filter paper. The vapor of the ether and alcohol traveled slowly through the filter paper and left a perfectly smooth film. Another way was to dissolve the pyroxylin in methyl alcohol and allow the solvent to evaporate. But this absorbed moisture from the atmosphere and caused a precipitate so that the film would turn milky—a result of cooling pyroxylin in a finely divided state in the film—called 'chilling' in varnishes. A tray of anhydrous calcium chloride over the plate absorbed the vapor and allowed it to evaporate without the interference of moisture. We finally used ammonium sulfide hydrate to convert the material back again to cellulose.

"After we got the film in that shape the next thing was to get the gases out of it without getting little explosions in the solid substance. That gave a lot of trouble. We placed the films in the usual apparatus for baking them and raised the temperature slowly and got films, but the bulk of them would be full of little volcanoes, caused by explosions of gas. We analyzed the gases and then we got along all right. That filament slowly displaced everything else. The process was later modified by squirting cellulose dissolved in chloride of zinc through a very fine tube into alcohol; the homogeneous carbon filaments were obtained."

This type of filament gave way later to the metallic tungsten filament made possible by the perfection of processes for drawing tungsten. This development, particularly the part played in it by Langmuir, has already been described.

John H. Long, manager of sales research for Hercules Powder

Company, presented a penetrating analysis of product research to a group of experts in this field. He recognized three types of product research.

"First is a product and no market. Can it be used? Can it be offered at a profit by the seller with benefits to the prospective customer? Next is a market and no product. A customer wants something. Can it be developed from available raw materials, and be produced with facilities with which we are most familiar and which are available to us? Third is no product and no market, but an idea.

"*(I) A Product but No Market*

"In the normal processes of turning out 'oil for the lamps of China,' or turpentine for the house painters of America, or coke for the blast furnaces of industry, something is left over after the crude raw materials have been refined. The question then naturally arises: is there anything in the residue that can be of value to somebody else? . . .

"A number of years ago, a change was made in the process by which Hercules extracted rosin, turpentine, and pine oil from the stump-wood of the cutover longleaf pine forests of the South. After recovery of the distillable terpene hydrocarbons and terpene alcohols, the residual resin component was of a somewhat different character than that obtained previously. When it was put through our regular solvent refining operation, a new type of dark resinous material was recovered in addition to the usual grades of pale wood rosin.

"The yield of the new resin was substantial. But we hadn't the slightest idea what to do with it. Our major problem was to get it out of the way. For a short time, it was burned. However, since we are optimistic as well as thrifty, this practice was soon abandoned in favor of pumping the molten resin to open storage bins. While we persistently studied the resin, the capacity of the storage bins was expanded time and again.

"Today, that accumulated surplus has gone to market. The resin, that at first appeared to be useless, is now a regular article of commerce. We have given it the trade name of 'Vinsol.' It serves the needs of such diverse industries as paper and steel, asphalt and glass, phonograph records and Portland cement.

"*(II) A Market but No Product*

"Next is the case of a known market, but no product. That is quite different. The production of toluene by the petroleum industry is a beautiful example. I will cite two from our experience.

"The first begins with the fact that the enterprising chemist always has been intrigued by the possibility of synthesizing the economically important constituents of natural essential oils. Here is a clear case of a known market; one that always has been and probably always will be. The demand, relatively, is great. The supply of natural oils is limited. And, in times of commercial unbalance such as those caused by war, the supply may be reduced to zero.

"Let us take, for example, oil of anise and its commercially valuable derivative, anethole. As you know, practically all the oil of anise which the essential oil people have had to work on in years past was imported from China. Came Pearl Harbor; the supply was shut off overnight. But the market—the demand—didn't change a great deal, as far as the buyers of anethole in this country were concerned. A dozen industries—toothpaste, dog food, bakeries, confectioners, perfumers—continued to maintain that demand.

"Therefore, the possibility of making anethole from some basic material other than anise seed appeared to be decidedly worthwhile. It was apparent that none of the natural base material could be imported for some time to come. And, perhaps, even when it was again available in quantity, the economics of supply and demand would still leave open an opportunity.

"The situation was this: (1) we had an established position with the essential oil industry; our terpene derivatives were being used as intermediates in the manufacture of a variety of essential oils; (2) the essential oil industry had been producing anethole from imported oil of anise, the supply of which had been cut off, and the markets for anethole in a number of industries had been established;

and (3) Hercules chemists knew that anethole might be derived from terpenes by several methods.

"The first step, obviously, was to analyze the market. Were the potentials great enough, in both physical and dollar volume, to justify experimental work for the purpose of determining production costs? We found that they were ample. At the same time, we found out what quality of anethole the market wanted.

"The next step was to check potential supplies of raw material for assurance that they would be adequate at reasonable prices, and would not be jeopardized except by cataclysm.

"We had to assure ourselves, too, that the patent situation was clear and not likely to subject us to infringement or interference suits.

"Then came the experimental work to determine costs as well as production methods. This showed the possibility of establishing profitable production without exorbitant investment.

"So, we went ahead with larger-scale pilot plant production. Everything checked. And the anethole produced duplicated the natural product. Equipment was then installed for production on a commercial scale, and the product is now being sold in worthwhile quantities.

"Isoprene is another case of a market but no product. The question again was whether or not we could and should produce for that market. In 1942, isoprene had a market in the production of certain types of synthetic rubbers. It also appeared that isoprene might be the key to get one of the Government's synthetic rubber processes into early operation. Although Hercules was not producing isoprene, we had prepared it from time to time in the laboratory by the thermal cracking of terpenes, as part of a continuing fundamental research program. But we also recognized that it was possible to prepare isoprene from raw materials other than terpenes, including certain low-molecular-weight hydrocarbons from petroleum refinery operations.

"With this background, a survey was undertaken to learn more about the needs of the synthetic rubber producers. Not only did we want to know what quantity of isoprene would be needed and its price, but we wanted to know what quality of isoprene was being used, and what hazards, if any, would be associated with its manufacture, shipment, and storage. Finally, we wanted to learn whether the petroleum industry, with its wealth of 'know-how' on thermal cracking, might not be a more logical producer of isoprene for the known market.

"One of the facts brought out in this survey was that isoprene was present in the product-stream from certain oil refinery operations. Another was that relative to terpenes, suitable hydrocarbons from petroleum refinery operations were considerably less expensive and many times greater in supply. On the other hand, one advantage we could see was that an operation based on terpenes would have a lower processing cost, by virtue of a lower-cost purification step, than that of a process based on petroleum hydrocarbons. On the basis of these facts, we were inclined to be less enthusiastic about the economic possibilities, but we were urged by the Government to continue our experimental work. Eventually, we were ready for pilot plant testing.

"Through cooperative arrangements with several companies in the petroleum industry, use was made of their thermal cracking pilot plants. There we learned what would be required in the way of a commercial plant and what would be the probable cost of isoprene production from terpenes. Also, we were able to make, for our prospective customers, sufficient isoprene to confirm the fact that it not only met specifications, but also was usable in their polymerization process.

"About this time, the urgent need for large volume production of isoprene disappeared, because of a change in the Government's synthetic rubber program. Therefore, the product was abandoned.

"*(III) No Market and No Product*

"The third is in many ways the most interesting, most intriguing, and most difficult type of product research. It is little more than an ephemeral idea that, if such and such could be made, would it be any good for this and that?

"Such ideas may originate either with the chemical manufacturing company, or with the customer of the chemical manufacturer.

"When they start in the chemical manufacturer's plant or laboratory, it is often because some chemist has thought of a novel chemical reaction, or prepared a chemical with certain unique properties. To be important, it must have valuable properties, properties that can be sold at a profit because they can benefit the buyer.

"All sorts of variations are possible. The customer wants to lower production costs. Or he wants to improve his product. The chemical he wants may never find its way into the end product—a frother in an ore flotation process, for example. Or it may be an important factor in controlling the physical properties of the end product—a stabilizer to maintain the initial clarity or color of plastics; or something to improve the durability of an automobile finish. Sometimes, the customer may have little knowledge of the chemistry of the new product he wants. Other times, he may have analyzed his problem so completely that he knows what chemical and physical properties are needed to give the performance characteristics he requires. He may even have made the chemical in his own laboratory but, for any one of a number of reasons, he may feel that you are the more logical producer.

"In any event, wherever the idea originates the chemical manufacturer's problem is a tough one; there is a feeling that something should be done, but there is no product and no market. And there won't be until something is done about it.

"General managers are not in the habit of approving expenditures without more justification than that.

"Extremely close liaison must be maintained between the potential customer and your research department in work of this type, because it involves two variables, each of which can get out of hand easily—each of which can, in effect, turn and oppose the other. These two variables are product development and market development. In the beginning, one of these variables should be put in the 'deep freeze' compartment, turning *exploration* into either simple market development or simple product development channels.

"The procedure followed with Resin 731 is a good example of this freezing and unfreezing of the market and product variables. It also is an example of a development which could not have succeeded without close liaison between our own research department and our prospective customer.

"When war came, and industry tackled the job of producing synthetic rubber in unprecedented volume, it was evident that large quantities of soap would be needed for the emulsion polymerization of the butadiene-styrene type of synthetic rubber, GR-S. Fatty acid soaps, derived from high-grade fats, had been used in the manufacture of this copolymer before the war: but, if a suitable substitute could be found, a worth-while quantity—amounting to some 100,000,000 lbs.—of fats and oils could be conserved for other purposes.

"Hercules was producing rosin and rosin soaps for use in a number of industrial processes, including emulsification. Consequently, arrangements were made to have these established products tested against fatty acid soap. It was a clean-cut case of market development, and here again the testing was carried out by prospective users.

"The results from this short-lived market development program showed that, while rosin soaps would emulsify butadiene and styrene, at the end of the reaction cycle most of the styrene and butadiene failed to polymerize; the yield of synthetic rubber was disappointingly low. It was obvious that a reduction in the projected output of synthetic rubber could not be tolerated; that the polymerization plants, then under construction, had been designed to operate under a set of conditions which could not be met when our regular rosin soaps were substituted for fatty acid soaps.

"Several rays of hope caused us to unfreeze the product variable, to start an exploration program, and to establish and maintain an effective liaison between our research department and the producers of synthetic rubber. In the first place, some of the rosin soaps were not as poor in their performance as others; the polymerization was extremely sensitive to certain types of known chemicals which inhibited reaction; and new inhibitors were being discovered every day. *Perhaps* the rosin soaps contained inhibitors which could be removed. Secondly, the synthetic rubber was less tacky than natural rubber, causing difficulties in tire manufacture; this was thought to be aggravated by the presence of fatty acid, as a result of using fatty acid soap in the polymerization. *Perhaps* a more tacky rubber would result if the polymer contained rosin, a known tack promoter. And finally, the supply of rosin was large, its price was low relative to fatty acids, and savings might therefore be realized by the synthetic rubber producer.

"So, the exploration job got under way, with the research department preparing a series of resin acids, derived from rosin. The samples which were finally selected and submitted for testing are probably the purest that have ever been made. Several of the resin acids, when converted to soap, gave as high a yield of polymer as the most active fatty acid soaps in the standard polymerization recipe, under standard conditions of reaction. Further, it was indicated that the new synthetic rubber was, as had been hoped, a more tacky product; yet it was comparable to the older product in other respects. It appeared that a market had been found, that we should freeze this variable and not go looking for other market possibilities, and that we should develop the product.

"This product development job was just about as short-lived as the market development job on our established rosin soap products. We found conclusively that cost of producing several of the resin acids was exorbitant, another of the resin acids would require plant equipment which could not be obtained during the war, and in the case of another, an intermediate raw material was not available in sufficient quantity. It was necessary again to classify the problem as one of exploration.

"There is no need to review each step in the history of this effort. But eventually we were ready for pilot plant production on Resin 731, a material which satisfied the requirements of this market.

"A commercial scale plant was then built to supply enough Resin 731 for an annual production of about 100,000 long tons of the new synthetic rubber, officially designated as GR-S-10, or 'rosin-rubber.' The job with Resin 731 is in the market development stage again—the product variable has been frozen. We are now working with other customers to develop new markets for our product."

The huge surpluses of both materials and capacity for producing them which were left idle at the close of World War I were important stimuli to product development. A similar situation has followed World War II involving other products. We have already discussed in a preceding chapter the development of a process to utilize excesses of ethyl alcohol and dilute acetic acid to produce ethyl acetate. That was only part of the story which ties in with the development of nitrocellulose lacquers, also from surpluses.

After World War I vast quantities of nitrocellulose, solvents, plasticizers and diluents left from smokeless powder production filled warehouses in this country. Our industrial plants housed equipment to produce these chemicals in enormous quantities. No market for them existed. The pigmented varnish of the day was extremely unsatisfactory for painting automobiles. A durable finish required many coats of a rather costly varnish to be applied and each given plenty of time to dry before the next was put on. The process took two weeks or so. This meant that the automobile industry must have in its plants two weeks' output of automobiles at all times undergoing the process of finishing. The cost in tied-up capital was terrific quite aside from the expense of the process itself. Quite naturally the automobile companies and the producers of nitrocellulose and solvents embarked upon researches on their apparently separate problems. Soon they got together and directed joint research toward producing a pigmented nitrocellulose lacquer which would dry rapidly and at the same time yield a durable finish. The great fault of older lacquers, not usable for automobile finishing, was the very high viscosity of the lacquer solution when it contained appreciable quantities of nitrocellulose. The development of the so called low-viscosity nitrocellulose yielding fluid instead of jelly-like solutions, and new and better solvents made possible modern lacquer and its utilization as an automobile finish. The time for finishing a car was reduced by the new lacquers from two weeks or more to a couple of hours. It is even related that Charles F. Kettering played a practical joke on a paint manufacturer by having his automobile completely refinished in a new color during a long luncheon.

Pigmented lacquer of the type first used had little or no brilliancy when applied to the automobile. An ingenious attempt to avoid this difficulty was the substitution of bright and light colored pigments for the carbon black and dark blue pigments inherited from the older varnish coatings. The surface was still dull, but it gave the casual observer an impression of gloss from its light and brilliant color. Eventually, the public demanded more gloss, and it was produced by a change in gum content and of the plasticizer in the lacquer.

Nitrocellulose lacquer, although a vast improvement over the older varnishes and enamels, was nevertheless too expensive to be wholly satisfactory. About 75 per cent of the lacquer was solvent or a combination of solvents whose sole function was to liquefy the nitrocellulose until it was applied and then evaporate from the surface as the lacquer dried. In other words, approximately 75 per cent of the material was thrown away, and the coating left on the automobile from considerable quantities of lacquer was very thin. Furthermore, evaporation of the solvent from the surface tended to form a skin over the surface which must be punctured for the solvent underneath to get out. The final film, especially one unpigmented, was often full of holes which allowed water vapor and oxygen to pass readily through to corrode the metal below. Clearly nitrocellulose lacquers were far from ideal.

Subsequent attempts succeeded in revolutionizing the finishing of automobiles again. The successful attack was based on the solution of synthetic resins in an unpolymerized state in drying oils in much the same way that natural resins (the copals) were dissolved in oil to yield varnishes. Bakelite, a condensation product of aldehyde and phenol, was studied early. If such a condensation product could be incorporated with lacquer and a drying oil, the investigators reasoned, the combination might produce a finish quite as durable as modern lacquers but at the same time yield a film considerably thicker and far more brilliant in appearance. The hope was that a reaction between the synthetic resin and the drying oil might tend to speed up the setting of the oil without interfering with the initial formation of a film by the evaporation of some solvent from the nitrocellulose solution present. This nitrocellulose solution was introduced to speed up the initial drying, or the setting rate, and the other constituents were intended to retard final drying or setting to allow a smooth glossy surface to form. This hope was realized. The actual chemical reactions involved are not known, but obviously the synthetic resin reacts with the unsaturated oil fairly rapidly, but still slowly enough to produce a smooth and glossy surface. Subsequent developments have employed other resin-forming compounds instead of the phenol-aldehyde product mentioned. Several families of quick-drying finishes possessing high durability are based on the different synthetic resins: the alkyd, urea-aldehyde, and melamine-aldehyde families, among others.

John Wesley Hyatt was primarily concerned with a product research when he set out to win the $10,000 prize that had been posted in his day to reward the inventor of a satisfactory substitute for ivory billiard balls. Although the billiard balls that he made were of indifferent usefulness, the value of Celluloid, the first synthetic plastic, had been tremendous. Mr. Hyatt has this to say on the subject in his acceptance of the Perkin Medal for his many contributions to industrial science:

"My results have been obtained mainly by persistent and many times mistaken experiments. Some successful experiments I might never have made if I had been familiar with the danger theories of some learned men.

"My earliest experiments in nitrocellulose were incited by accidentally finding a dried bit of collodion the size and thickness of my thumb nail, and by my very earnest efforts to find a substitute for ivory billiard balls. From the first, it was apparent that a semiliquid solution of nitrocellulose, three-fourths of the bulk of which was a volatile liquid and the final solid from which was less than one-fourth the mass of the original mixture, was far from being adapted to the manufacture of solid articles, and that I must initially produce a solid solution by mechanical means. The only useful solvent known to me at that time was a mixture of alcohol and sulfuric ether; with the old formula (about equal parts of ether and alcohol) I mixed in a closed mill a thick paste of soluble cotton, made by the old firm of Charles Cooper & Co. After mixing, the cover of the mill was removed and the mass evaporated down to a thick dough, which was then forced accurately around the ball (made of another substance), and allowed to dry. This I found resulted in a rather brittle coating, owing, as I found, to the unequal evaporation, leaving only the alcohol, a poor solvent by itself, at the final shrinkage. This was remedied by using only the least amount of alcohol (five parts ether to one alcohol) necessary as a solvent. Even this coating shrunk to less than half of its original thickness and required to be dried immersed in water under several hundred pounds' pressure per square inch to insure its solidity and freedom from bubbles. It became necessary to strain the mass by forcing it through a very fine sieve to exclude the unnitrated fibers. All these difficulties stood in the way of success, except in high-priced articles like billiard balls. Other seriously objectionable features became apparent. In order to secure strength and beauty, only coloring pigments were added, and in the least quantity; consequently a lighted cigar applied would at once result in a serious flame, and occasionally the violent contact of the balls would produce a mild explosion like a percussion guncap. We had a letter from a billiard saloon proprietor in Colorado, mentioning this fact and saying he did not care so much about it, but that instantly every man in the room pulled a gun.

"I next had a small beating engine made, to pulp the nitrocellulose. In one experiment I placed a small quantity of this dried pulp in a strong cylinder and forced quickly a minimum quantity of liquid solvent into it with pressure. The result was a solid substance, as hard as sole-leather, which soon dried, leaving a fine, hard disc about three-fourths of an inch in diameter and one-half an inch thick. While no explosion ever resulted from this, there was real danger to be feared, and the matter was dropped.

"My brother, I. S. Hyatt, joined with me at that time, and finding it stated in some patents to which I was referred, that a little camphor added to the liquid solvent was beneficial we conceived the idea that it might be possible to mechanically mix solvents with the pulp and coloring matter while wet, then absorb the moisture by blotting papers under pressure, and finally submit the mass to heat and pressure.

"To our surprise, we noticed a slightly solvent action of the precipitated and washed camphor upon the pulp, even before the heat and pressure, and without other solvent we succeeded in producing a transparent slab one-fourth of an inch thick, fine, and as hard as a piece of wood."

Some research workers achieve success, as Hyatt did, by clinging with unshakable determination to a single objective. Others are equally successful through following diverse threads revealed in the course of their investigations. Charles F. Burgess belongs to the second group. He suggested the concatenation of ideas frequently encountered in research by his descriptive account of how a search for a new bandaging material led him into the field of sound deadening and silencers. He said:

"During World War I, cotton became scarce and almost unobtainable even for such important uses as surgical dressings on the battle front. It was suggested at a laboratory conference that a good substitute could be made from wood pulp. This was entered as a project, an emergency measure. Rapid progress was made. In the process as evolved, a white bleached pulp was first converted by special disintegrating machines into what resembled a snow storm of cellulose fibers. This came into contact with a cloud or mist of adhesive, the combined material settling quietly on a moving screen, then passing through a drier, and emerging as a thick sheet of porous structure, well adapted to the specification of a surgical absorbent bandage.

"Before regular production was started, the war stopped and the material became unnecessary. Seeking a method of salvaging this development, we studied the properties of the material and its adaptability to other uses. An outstanding characteristic was its heat-insulating property; another its ability to absorb sound. To develop a commercial use as a building material, it was necessary greatly to reduce the cost, which was done by eliminating the bleaching operation and by using a cheaper grade of material—pulp-mill screenings. Thus evolved the commercial product known as Balsam Wool.

"The adaption of the porous cellulose material to sound-deadening purposes introduced us to new problems requiring solution. It became desirable to develop a protective covering which would give rigidity and permanency to the wall surfaces on which the absorbent was applied.

"A discovery (simple enough to be important) was then made:

that when sound waves strike a metal plate perforated with small holes and backed with sound absorbent material, the metallic surface does not reflect the sound. In fact, evidence points to a greater effectiveness of a sound-absorbent material if faced by a perforated metal plate than without it. The metal screen thus affords a surface which may be painted and decorated, as well as giving strength and fire-resistant qualities. This type of structure is now extensively used in architectural acoustic treatment.

"In an attempt to apply the perforated-plate idea to the quieting of the exhaust of gas engines, perforated sheet iron was formed into a tube and surrounded by a heat-resistant absorbent material, such as steel wool held in place by an outer iron cylinder. By conducting the pulsating exhaust gases through the inner pipe, an almost complete removal of sound was produced, and with no back pressure.

"Thus by a series of steps, the original attempt to make bandages for wounded soldiers evolved finally into the production of mufflers for absorbing noise and increasing the efficiency of automobile engines. But those steps, thus lightly touched upon, covered a period of fourteen years of continuous effort. One factor that made for slow progress was the necessity of developing instruments and methods for measurement and analysis of sound waves."

The Frasch method of desulfurizing petroleum could properly be considered as developed from a process research, but its greatest significance was necessarily in the improvement of a product through purification so that it may quite as reasonably be placed in the product research category. The problem was to improve Canadian petroleum so that it would have a market value and so that products made from it could be marketed through customary channels. The problem was soon narrowed to a search for a method of removing sulfur compounds from the oil and finally even to sulfur compounds of a particular type that could not be removed by the customary treatments with sulfuric acid used before. Herman Frasch tells us this about his development:

"This dreadful odor of Canadian oil, which the Canadians called 'skunk,' arose from a peculiar hydrocarbon-sulfur compound, and the clouding of the lamp chimney was due to its sulfur content.

The sulfur in the oil burned into sulfuric acid, which condensed against the lamp chimney, and any unconsumed carbon or organic particles in the air would adhere thereto and form this objectionable soot. To remove the sulfur from the oil completely meant the elimination of the smoke as well as color and odor, and when this was effected the oil furnished an illuminant equal in quality to the best Pennsylvania.

"To free petroleum of elementary sulfur or hydrogen sulfide presents comparatively little difficulty, but the sulfur compound which is the cause of this offensive odor is very stable and cannot be broken up into hydrogen sulfide or any other sulfur compound which can be eliminated. It was because of the presence of this peculiar compound that Canadian oil for so many years resisted all the efforts made to refine it.

"This sulfur compound has the peculiarity of dissolving a number of metallic oxides. When the oil is saturated with all the oxide it can carry in solution, the disagreeable odor disappears. It reappears, however, if an attempt is made to free the solution of its metal. I found that this solution of metal in petroleum has an intense affinity for sulfur, and also that when a portion of the sulfur has been precipitated with the metal as a sulfide, additional quantities of metal oxide can go into solution. If more oxide than that necessary to precipitate all the sulfur is added to the petroleum while it is being distilled, a complete desulfurization of the petroleum is effected.

"When this petroleum solution is made with water-white petroleum distillate, which has been freed of elementary sulfur and hydrogen sulfide, the solutions assume colors characteristic of each metal. The lead solution is a canary yellow; mercury, orange; copper, blood-red; silver, brown.

"I selected copper as the metal most suitable—first because it dissolves in the petroleum, and in the second place because of the readiness with which the sulfide of copper can be reconverted into oxide.

"In desulfurizing petroleum, the oxide of copper is mixed with the petroleum distillate in a still supplied with an upright shaft and arms radiating therefrom, to keep the oxide in agitation during the process of distillation, flexible chains attached to the arms being used to prevent the copper from adhering to the bottom of the still. One hundred thousand pounds of oxide of copper are used for the first charge of 2,000 barrels of distillate. After 80 per cent has been distilled off, a new charge of distillate is added with an additional charge of 30,000 pounds of copper, which is followed by two further runs, so that about 200,000 pounds of copper material are in the still when the fourth run is made. The residuum is pumped through a filter press, and the solid product of the filter press has the oil adhering thereto burned off. The dry mixture of oxide and sulfide of copper is then put into a roasting furnace, where it is desulfurized to 1 per cent or less.

"A variation of my method treats the vapor coming from a still charged with crude petroleum, and consists in passing the vapor through two brushes made of No. 10 steel wire, the brushes being 5½ feet in diameter and 16 feet long. They are inserted into a shell which is almost the same diameter as the brush, and the requisite amounts of copper and heavy oil are pumped into two shells, each containing one brush. The vapor passes in series, first around the shell to prevent condensation; then through the shells on to the condenser. The brushes are made to revolve at about six revolutions per minute. These wires are immersed continually in this oxide of copper magma, the shells containing the brushes are surrounded by the vapor coming from the still, and as the temperatures of the vapors increase, anything condensed thereon during the prior period is reevaporated by the hotter vapor following."

Another type of product research which has been successful is exemplified by the development of "two-type" solvents for nitrocellulose employed in the lacquers described above. For many years mixtures of alcohol with ether or an ester were recognized as better solvents for nitrocellulose than any single compound. Quite logically, then, a molecule containing both an alcohol and an ether group or an ester and an alcohol group should be an excellent solvent. Experiments proved that true. The ethyl ether of ethylene glycol and ethyl lactate are specific examples of such "two-type" solvents.

Perhaps the most productive type of product research is based on suggestion. A new compound never made before, or made only for a specific purpose in very small amounts, has unique properties and is produced on a generous scale. Sometimes a new process is employed. Liberal samples are distributed among research organizations who might be interested. Its physical and chemical properties are well publicized in articles and advertising. In the course of time, someone working in another organization is almost sure to find a real use for the particularly urgent need. A case in point is the development by the petroleum industry of furfural as a selective solvent for refining lubricants, a use never suspected by the producers of furfural.

However, if the problem is to produce a new substance for a specific purpose, the original method of attack outlined above is the only feasible one. Success or failure largely depends on the second step: listing all possible substitutes for the old compound or mixture. Experience has shown that the broader the view in preparing this listing, the more likely is success. D. B. Keyes supplies this example: in seeking a substitute for tincture of iodine as antiseptic, one group of investigators suggested the mixture used in analytical chemistry, of potassium iodide, potassium iodate, and an acid salt (the one finally selected was anhydrous aluminum sulfate). When dissolved in water, this particular mixture reacts to liberate free iodine. This particular dry mixture could be formed into tablets which would yield an antiseptic solution when placed in water. The faults of the tincture of iodine were recognized as: first, a usual excess concentration of iodine tends to burn the flesh and do more harm than good; and, second, the alcohol used as a solvent irritates the wound. The iodine content of the new mixture could be controlled, and hence that of the water. This, with the absence of alcohol, should make it an effective and practical antiseptic. This proved to be the case.

Compounds or mixtures closely similar to the substances already used are the most likely ones to put on the list for consideration. On the other hand, compounds having little similarity, especially those never used for a similar purpose, are the most difficult to discover. Often products well known in one field possess possibilities in another if one can only discover them. Compounds or mixtures of this kind more often prove successful bases for future development.

Typical of the development of mixtures is the work done by Edward Weston in perfecting electrical resistance alloys required particularly in his electrical instruments, but also important in a great number of other applications.

"The alloys at our disposal for electrical measurement work were German silver and platinum silver, which was too expensive for use. German silver generally gave a resistance about thirteen times that of copper and a temperature coefficient of 0.004433. 'German silver,' of course, is only a common term for an alloy composed of a mixture of zinc, copper and nickel. German silver is used in the arts for all sorts of purposes, and is on the market with the nickel content varying from 4 per cent to 18 per cent. I found out quite early that it varied very much in resistance, and the temperature coefficient varied; so I took up the subject very carefully and found that if I increased the percentage of nickel in the German silver I increased the specific resistance, and reduced the temperature coefficient, both by nearly the same proportion. We went over the field carefully and made standard German silver, in which we used 30 per cent nickel; it had twenty-eight times the specific resistance of copper (about thirteen as given by Madison) and the temperature coefficient was almost half that of copper. These temperature coefficients were, of course, of very great importance to the electrical engineer and to other people in using electrical apparatus, because it was necessary where electrical instruments were used to give true results, whereas the results obtained from other alloys varied. The very best German silver that we could make was not good enough for instrument work, nor was it good enough for standard. It had to be used with very great care, and you had to be very careful about measurements. You can scarcely imagine what that means in a laboratory where thousands of electrical measurements are made in a day. Even the labor of calculating was frequently enormous and delayed the investigations, so that it became very urgent to try to find something that would give better results. I took a large number of alloys, and out of all that I examined there was nothing which gave such a high specific resistance as manganilin, the resistance-giving metal of all metals. Nickel stands next to it. Nickel gives very high specific resistance, not only with copper but with other metals. On the other hand, the nickel alloys do not give as good a temperature coefficient as these manganilin alloys, and what is worse, they have a relatively high thermoelectrical effect against copper and other metals."

Many developments undertaken under the compulsion of World War II involved amazingly efficient researches leading to new processes, new products and new equipment. Outstanding, of course, was the spectacular development of atomic fission and the production of an atomic bomb. That actually was the culmination of literally thousands of separate researches converging upon a single objective—a military weapon of a power beyond imagination. The overall story of the coordination of all of these separate endeavors into a single gigantic project is recounted in the official report, "Atomic Energy for Military Purposes" by Henry D. Smyth. It would serve no good purpose to repeat parts of that discussion here, but every research worker will wish to study that report carefully in the full original version, and not in paraphrase or condensation. Besides the excitement of the facts themselves and their now known consequences, the report describes in fascinating detail the integration of the multitude of separate researches into a unified whole.

Expediency requires much technical detail of that and other wartime researches bearing on military affairs to be secret, but occasionally reports are released in sufficient length to illustrate useful methods employed in the researches leading to results of military value. A case in point is the development of the thickening agents used to make gelled gasoline for incendiary purposes, as described by Louis F. Fieser and his coworkers in the Gibbs Laboratory of Harvard University:

"The background for the research was provided by an interesting series of circumstances starting, in the summer of 1941, with an exploration of possible military uses of divinylacetylene. This hydrocarbon is capable of undergoing peroxidation to products that have occasionally exhibited either explosive or inflammatory properties, but our attempts to produce material of regularly destructive character were without avail. . . .

"Major Gerard Rambaut, of the British Air Ministry, encouraged the continuation of work on incendiary gels; he told of the parallel development of rubber-benzene gels in England. . . .

"Burning tests soon provided evidence that the gels from divinylacetylene, even when fortified with chlorates or nitrates, were more spectacular than effective. Rubber gels proved to be better; consequently, extensive studies were made in the fall and winter of 1941 on the preparation and incendiary properties of 6-8 per cent gels of smoked sheet, crepe, and latex rubber in gasolines, naphthas, and other less available hydrocarbon fuels. . . .

"Then came Pearl Harbor and the sudden cancellation of rubber from the list of available stores. In response to a request received a few days later from the chief of the Technical Division, Chemical Warfare Service, work on rubber gels was stopped at once, and an empirical search for some other gelling agent was started.

"The requirements were severe. The thickening agent had to be compounded from abundantly available starting materials (eventual production reached a scale of about 75 million pounds per year). The gel had to be easily ignitible and burn efficiently, and be sufficiently tough and stringy to withstand the blast of an explosive charge and not shatter. It could not thin out at 150° F. or become brittle at −40° F., and had to be stable in storage and withstand cyclic temperature changes and shaking. A further specification was that the process of preparing the gel be adaptable to a simple field-filling operation. Actually, the plans were later changed and the bombs for which Napalm and other gels were designed were all loaded at the site of manufacture or in local arsenals. However, the early insistence on field filling turned out to have been a fortunate decision when gelled fuels came to be used in flame throwers and belly tanks.

"The known metal soaps initially appeared unpromising; for example, aluminum stearate can be incorporated into gasoline satisfactorily only by heat-treatment, and the resulting gels are hard and friable and lack the adhesive and cohesive properties desired. The first gels that seemed to have some of the character of the rubber gels with which we were familiar were two samples prepared by a cooperating group of Arthur D. Little, Inc. One was an 8 per cent gel of aluminum naphthenate in gasoline prepared by a heating process. The other was a 5 per cent gel prepared in the cold from an alcohol-washed aluminum naphthenate. Both gels seemed to have the stringy consistency desired, but the first was incompatible with the field-filling requirement and the second was soon ruled out by a report from a manufacturer indicating that the alcohol washing could not be conducted on a large scale without great loss and expense. We, therefore, sought comparable agents or combinations capable of low-temperature gelation, or some method of incorporating the commercially available soft gums of aluminum naphthenate or aluminum oleate into gasoline without recourse to special processing or heat treatment. Attention was directed to a product marketed under the name 'aluminum palmitate' because of the manufacturer's claim that this soap would form gels with hydrocarbons at low temperatures. Actually, gelation in gasoline was found to proceed very slowly at room temperature and the gels proved to be feeble and unstable. However, it was observed (January 23, 1942) that the addition of a free fatty acid caused rapid setting to a full-bodied thermostable gel. Unsaturated acids, such as oleic or oleic-linoleic, seemed particularly efficacious as plasticizers, and hence the gels obtained from the combination of the supposed 'palmitate' and 'enic' acid were designated Palmene gels. It was next found (January 29, 1942) that a combination of aluminum naphthenate with the same 'aluminum palmitate' could be easily incorporated into gasoline to form a promising gel, and we termed this naphthenate-'palmitate' combination a Napalm gel. Subsequently, it developed that the supposed 'aluminum palmitate' was actually the aluminum soap of the total fatty acids of coconut oil, and that the specific gelling quality is due to a high content of lauric, not palmitic, acid. . . .

"Gels in gasoline or kerosene were prepared by mixing the aluminum soap of the total coconut oil acids (*e.g.* 'aluminum palmitate' Metasap) with the fuel to produce a slurry, adding the fatty acid component, and agitating the mixture at ordinary temperature (15-25° C.) for a short time, either by stirring or by cyclizing through a gear pump homogenizer. An initial stiff gel is produced in less than one hour and changes to a more stringy consistency in about 15 hours. Successful formulations in gasoline contained 5-9 per cent aluminum coconut oil acid soap (Al-COA) and 2-5 per cent of Armour's Neo Fat 3R (40 per cent oleic, 60 per cent linoleic). A 7 per cent Al-COA-4 per cent Neo Fat 3R gel withstood cycling between −40° and 52° C., showed good body and stringiness throughout this range, and in the standard burning test had an average value of 402 (grams of wood destroyed) as compared with the value of 492 for 6 per cent crepe rubber in the same commercial grade of motor gasoline. The addition of 2 per cent lampblack to the same gel raised the burning test value to 531. . . . The best formulation found for a bomb filling contained 9 per cent Al-COA soap, 5 per cent Neo-Fat 3R, and 2 per cent lampblack; this gel was fairly tough and durable and probably suitable for a tail-ejection bomb, but dropping tests conducted in the M-47 bomb at Edgewood Arsenal on February 25, 1942, showed that the gel was not stringy and tough enough to withstand a black powder explosion.

"In another series the acid component was kept constant, and the composition of the aluminum soap was varied. The results showed that lauric acid is a key component of the soap but that synthetic acids offer some promise of serving as substitutes."

A long series of tests with a variety of materials and numerous modifications of the technique of preparation led the group to these general conclusions:

"The better Napalm, Oleopalm, and Palmene soaps have in common the ability to form hydrocarbon gels at ordinary temperature and to produce gels that are remarkably indifferent to high and low temperatures. Thus the gelling agents, regardless of the physical form or the procedure by which they are incorporated into gasoline, all appear to have the same general functional characteristics. Uniformity is also evident in chemical make-up, for these soaps of the general Napalm type can be considered as compounded from two distinctive components. One is aluminum laurate or a saturated fatty acid soap containing at least 40-50 per cent of this substance or of a functionally related acid soap; this component is a relatively high-melting solid that, by itself, produces only thin and unstable gels. The second component is an aluminum soap or soaps selected from the group including cycloparaffinic and unsaturated acids—that is, an aluminum naphthenate, oleate, oleate-linoleate, etc. By itself, the aluminum soap comprising the second component is either a resinous gum or a low-melting solid, and most soaps of this type yield hydrocarbon gels only by heat treatment or by special processing; the resulting gels are not full-bodied. The combination of an aluminum soap of the laurate type with one or more soaps of the naphthenate-oleate type gives a thickening agent of distinctive and superior properties not found in either component and when prepared by the precipitation process, the soap is a solid of sufficiently high softening point to withstand elevated drying and storage temperatures.

"The Napalm-type gels were developed to meet an urgent requirement for even a makeshift substitute for rubber gels. Actually, they surpass rubber gels in incendiary effectiveness; they are applicable for use in flame throwers whereas rubbers gels are not; and the greater speed and simplicity of preparation of the gels have opened other fields of application. Although the new aluminum soap gels are very sensitive to the peptizing action of water and many other substances, fortunately they possess remarkable stability in storage, whereas rubber gels suffer syneresis on standing for a few months. Thus original samples of all the classes of gels described in this article have, in 1946, the same outward character they had when made up in the early months of 1942."

What on their face appear to be abstruse speculations of no reasonable application to industrial problems often lead active minds to important commercial developments. John J. Grebe, thinking from the point of view of theoretical physics, conceives all natural phenomena to lie in a continuous scale of cyclic or vibrational frequencies ranging from infinitesimal electromagnetic waves to vast astronomical cycles measured in terms of thousands, even perhaps millions, of years. The continuity and applications of this cyclic scale was the subject of Grebe's address accepting the Chemical Industry Medal in 1943. In it he pointed out valuable application of this concept, and the conclusions to be drawn from it, to the important problem of electrical insulation now seriously complicated by the expanding range of frequencies employed in radar, television and like modern electronic developments. The development of polystyrene for such applications, he described thus:

"Although we had excellent infrared equipment available, we lacked facilities for going down below that in the scale of frequency. It was necessary to find out what molecules or groups of atoms could be excited into resonant vibrations by the decreasing frequencies. We tried for several years to build a satisfactory shock-excited impulse generator and transient analyzing device capable of detecting absorption bands in this region. We planned to have a complete series of these for decreasing frequency ranges. Here again the war interrupted. While we have good equipment, it is far from what we hoped to have.

"Electrical currents in this wide range of frequency require pure hydrocarbon polymers, particularly polystyrene, for insulation. A generally desirable low dielectric constant is inherent in this type of polymer. It was necessary to eliminate all impurities and addition agents that might have any electromagnetically excited resonant frequency from 60 cycles up to the highest frequency for which vacuum tubes and magnetrons could be built. In optics these desirable properties would be called a low index of refraction and high transparency. The glass industry knows what a tough time it has to produce glass that is highly transparent in the visible region, which covers only about one octave. What a job we cut out for ourselves when we wanted transparency over a range of 86 octaves corresponding to a piano keyboard 50 feet long!

"Our work was started because we had years of manufacturing experience in both aliphatic and aromatic hydrocarbons, and we felt that this background could be best used in developing a range of products in the alkylated aromatic family. Styrene had been known for a hundred years, but the price was $1.25 per pound and the product was of very poor quality. We knew it could ultimately be produced to be one of our cheapest and most versatile plastics. In fact, we think of polystyrene as the cast iron, and its copolymers as the steel, of the plastics industry.

"On the other hand, there was much to be said against it. Almost all the properties that we had been looking for could be obtained in the form of one of the other plastics currently produced, with the big exception of the electrical properties. In addition, a competent chemical company had put a large amount of research into this project and had given it up. Other laboratories had worked on styrene and abandoned it. So, with two strikes against it, the styrene program was pushed ahead, principally because we realized the absolute need of very pure hydrocarbon dielectrics for the expanding field of high-frequency communication. All other materials would absorb too much through the oscillation of polar groups in various resonant frequency ranges.

"Some of the difficulties of alkylating benzene and dehydrogenating the ethyl benzene were surmounted. Then the fun began. The purer the raw materials the more difficulties we had with polymerization during distillation. The discovery of methods of inhibiting polymerization throughout the entire distillation equipment overcame most of these problems. This is one of the best examples of controlling naturally occurring cycles. Inhibitors capture the activated molecules and shorten their lives. This permits normal life to go on among the rest of the molecular population. Now, one wonders why it took more than a decade of intensive work to bring the production of styrene by our processes to a rate of approximately 200,000 tons per year.

"During the many trials and setbacks encountered in this project the question would arise whether we were on the right track. Those two strikes on the styrene project were constantly before our eyes. Fortunately, this struggle was won, not only for the important applications in high-grade dielectrics that were tremendously important in the war, but in addition, for the unexpectedly large synthetic rubber program. Most of the capacity goes for this use. The management of our company let us continue with our research on the single argument that it was to be of increasing importance to ultra high-frequency radio communication.

"Pure styrene was so precious in connection with the early radio locator work of the British that they made it from phenyl ethyl alcohol at a great cost. Even the slightest impurities interfere with satisfactory use of such insulators for a wide frequency range."

Chapter 8

Equipment Research

"The increase of net incomes, estimated in commodities, which is always the consequence of improved machinery, will lead to new savings and accumulations. These savings are annual."

—David Ricardo

Often changes are required in the design of equipment to adapt it to perform some new and different function. Usually existing, standard equipment is to be altered and that imposes limitations which do not hamper the development of entirely new equipment for some newly important purpose. Rarely must the new equipment utilize new physical forces or processes. Much more often equipment from another industry or process can be adapted to function well under the new conditions. In chemical production, a vessel or tool used for one specific reaction—perhaps standardized for that purpose—can be readily modified to suit an entirely different reaction.

The general methods of research outlined above also serve here. The problem now involves a machine or tool of known and easily determined characteristics, and the methods of changing these are as well known as those of a chemical reaction. The faults and virtues of the equipment are also known or as readily measurable as those of a new chemical product.

Both process and equipment research are based on three general rules:

First, learn all of the fundamental requirements for the process or the machine and the special conditions that must be met, particularly those which depend on specific economic considerations.

Secondly, select a line of research as far removed as possible from past, present, or future activities of any competitor so far as these are known. If possible, do not compete at all, since to do so only courts touble later. When competition enters research, the element of resources plays an important role. Wealth and man-power determine success for as was once said about the outcome of battles, "Fortune is always on the side of the largest battalions." That is also true of research. The successful conclusion to similar researches by competitors is generally reached first by the organization with the more men and more money to spend. In other words, the attack on a research problem should be based on the broadest view possible; and if the problem warrants it, the program should be planned along lines radically different from any attempted before. The principle is by no means intended to rule out analogy, which here as elsewhere is the researcher's most powerful tool. Rather one should seek his analogies in non-competitive fields.

The third principle is: do only one thing at a time. In modifying a process or a machine, certain conditions must be met. One should not attempt to meet them all at once. For example, if the problem is to increase the output or capacity of a reactor and at the same time to increase its efficiency of operation, it is wise not to attempt both at once.

A common fault of young researchers, impressed with the importance of economy, is to omit from the program certain modifications because they seem to be too expensive. Many important inventions have been unduly delayed by this view of the research. A famous chemical engineer once said: "I don't care whether my research men start by setting up in the laboratory a diamond-studded machine with platinum trimmings, provided the thing really works." That is a useful view to take of any equipment development.

Much equipment research is aimed, as we have noted, at increased efficiency of existing types; labor saving is the best name for it despite the usually low labor costs in chemical plants. Herbert H. Dow describes the steps by which equipment research built up the American bromine industry with all its ramifications.

"The most conspicuous labor-savers in a chemical plant are: (1) larger equipment, to cut down the expense of chemical control and operating labor per unit of product; (2) automatic analysis, to save the labor expense of chemists making routine analytical tests at regular intervals and to secure results more quickly and more exactly, with the chance of error due to the personal factor reduced; (3) automatic operation of the equipment, which is governed by the automatic analyzer; all leading to the final desideratum, (4) a continuous process which is both automatically controlled and operated. There are, of course, other means for labor-saving, such as the economic application of human motion study, the coordination of supplies, and other ways for increasing the effectiveness of the human element, but such measures are less important in operating large-sized chemical equipment having a very large output per man employed as direct labor than in the case of machine processes involving manual operations. We shall consider, here, therefore, only the large factors in labor-saving which make it possible to pay higher wages and at the same time give the consumer more for his money and also increase dividends.

"The one most important way to lower the labor cost of manufacture in a chemical plant is, doubtless, to increase the capacity of the individual apparatus unit wherever practicable. This is usually accomplished by first increasing the size of the units; then substituting a continuous process when the size is large enough to justify it, provided quick methods of analysis and control have been developed; and finally substituting automatic control for manual control.

"In a product made on any ordinary machine tool it becomes necessary to increase the number of tools in proportion to the output, then to increase the number of operators in proportion to the number of tools employed, except that expensive automatic machinery can be used for very large scale production. In the case of chemical manufacturing many of the steps involved are capable of being handled in enormously larger units than is now customary without any increased cost of plant per unit of output and with no increase in labor costs, irrespective of the amount turned out. This is a great advantage that a chemical process has over a mechanical one, and applies to containers, mixers, fractionating columns, vacuum pans, gravity types of filters, and practically every continuous process.

"Let us suppose we are treating a 100-gallon tank with the proper chemicals to carry out a certain chemical process. A small laboratory and a chemist are necessary in order to know the amount of treating material to be added. If the size of the tank were increased from 100 gallons to 1,000 gallons, the same chemist and the same laboratory would accomplish that same end, but the unit labor cost of doing the treating would only be about one-tenth what it was with the smaller container, and yet even 1,000-gallon tanks are puny compared with the 4,000,000-gallon tanks used for oil storage. Why stop even with the practice of the oil man? The waterworks reservoir is infinitely larger than an oil tank. Apparently the size is limited only by the amount of material it is desired to produce, which in turn is limited by the demands of the market. Of course, it would be entirely feasible for a man to agitate the contents of a 100-gallon tank by hand. It is obvious that the 1,000-gallon tank should require a mechanical agitator, and as the size goes up to that of the largest oil tank and then to reservoir dimensions, real engineering of a different order would have to be employed, but probably a continuous process would supersede the big containers and reaction vessels long before the larger dimensions were attained.

"A concrete example of the evolution of the oldest process of the Dow Chemical Company will illustrate the development that is going on in all of our methods of manufacture.

"The Dow process in outline is as follows: The brine is oxidized to set the bromine free. The brine then has a light orange color, a strong odor of bromine, and is corrosive. This brine, without heating is passed down through a tower in contact with an air current that removes the bromine by blowing out. The bromine-laden air is then brought into contact with iron or an alkali solution and the bromine is thereby extracted from the air. This made a big saving in fuel required for evaporating the brine, which was the principal expense item by the old process.

"In the first plant started in 1889 bleaching powder was used as the oxidizing agent. The brine was treated in large containers until analysis showed that the bromine was substantially all set free, and was then drawn off to a blowing-out tower that worked continuously.

"The next step was to eliminate the big containers and make the whole process continuous and simultaneously substitute electrolytic oxidation for the bleaching powder and acid. This was accomplished by passing the brine through electrolytic cells located at a higher level than the top of the blowing-out towers, whereby the bromine-laden corrosive brine would not have to be pumped and would flow by gravity through the towers as its bromine was being removed. It is a very simple matter to make an analysis for free halogen in brine, and if the determination showed too much oxidation, either the flow of brine was increased or the current used by the cells was decreased.

"The first method was to vary the amount of brine in accordance with the indications of the titrations, but later it was found more convenient and reliable to vary the electric current. This was most easily accomplished by changing the speed of the engine driving the electric generator, and for many years thereafter the operator changed the weights on the governor each half hour in accordance with the indications given by the brine analysis.

"In 1894, a laboratory equipment was so arranged as to give galvanometer indications of the amount of free chlorine in the bromine in this brine. The operation of this apparatus was based on the fact that chlorine in solution would produce a higher voltage than bromine. Designs were worked up for utilizing these variations in voltage to vary the speed of the engine automatically, thereby controlling the amount of oxidation of the brine; but it was not until many years afterwards that equipment was finally perfected that would accomplish this purpose in an entirely satisfactory way. Reliable equipment now on the market greatly facilitates the working out of such problems. This oxidation-potential equipment now appears to have found quite general application; in fact, it is comparable with equipment for hydrogen-ion control.

"In retrospect, the bromine plant development consisted of substituting a continuous process for large containers in the first step of oxidation. The second step was changed from a batch blowing to a continuous process on the drafting board before the first plant was built. Then followed the substitution of automatic, continuous analysis for periodic titrations, and its application to suitable mechanism to make the analyzer automatically control the oxidation.

"The details of working this out are somewhat difficult to explain, but the principle involved can better be illustrated by a corresponding, although not altogether similar, process now operating continuously in our Epsom salt plant.

"Magnesium hydroxide for many years had been a by-product, and much thought was given to possible means for utilizing it. The process finally adopted is as follows:

"Sulfur dioxide gas is absorbed in magnesium hydroxide to form magnesium sulfite or magnesium acid sulfite. This mixture is then oxidized to sulfate by blowing with air. We found that the acidity or alkalinity—or in other words, the hydrogen-ion concentration—of the magnesium sulfite solution was of utmost importance in carrying out the oxidation. It is well known that the oxidations of salts of lime, magnesium, iron, manganese, etc., are most easily attained in an alkaline medium as in the re-oxidation of manganese salts in the Weldon process. In the present case, however, although an alkaline condition would be desirable for effecting the oxidation, the magnesium sulfite unfortunately is almost insoluble in an alkaline solution and consequently would escape oxidation at a satisfactory rate when the suspension was blown with air. On the other hand, magnesium acid sulfite is readily soluble, but the acidity of the solution retards and may even stop the oxidation completely. In this dilemma we were finally led to a solution of the problem by discovery that a mixture of normal sulfite and acid sulfite within a narrow range of composition could be oxidized at a sufficiently rapid rate to make the process commercially feasible. It was important, however, to maintain the composition of mixture within the prescribed limits, if the oxidation were to be effected successfully.

"At this point, the question arose—how to maintain the correct ratio of normal sulfite to bisulfite, when the proportions were constantly changing as the oxidation proceeded. Chemical analysis and control were hopeless. In the first place, the mixture was of a muddy consistency, hard to filter, and incapable of showing a good end point with any known indicator. Then again, if a suitable indicator could have been found which would have made possible a sufficiently accurate titration, the usual methods of chemical analysis would have been too slow. Before the results could have been obtained, the composition of the mixture would have changed materially. However, the optimum ratio of normal sulfite to acid sulfite corresponds to a certain definite acidity of the solution, that is, to a definite hydrogen-ion concentration. By devising an instrument which would record almost instantaneously the hydrogen-ion concentration of the mixture in the oxidation tank, it became possible to follow the progress of the reaction closely and to maintain the correct hydrogen-ion concentration by suitable additions of magnesium hydroxide. Although the development of a satisfactory recorder required more time than was anticipated, the object was successfully accomplished. Now it has been so far improved that the recorder is caused to actuate a motor-operated valve which controls the feed of magnesium hydroxide added to the liquor. The whole operation of controlling the progress of the oxidation and the proper additions of hydroxide to maintain the correct acidity is carried out automatically. When the batch is finished, requiring about 8 hours, a workman opens a valve to empty the tank and then refills with fresh mixture to start the next batch. At other times, no operating labor is required except for occasional inspection. The automatic recorder functions accurately and without sleeping. It is not going too far to say that this process would have been a failure but for the creation of automatic recording and control means, which have proved to be indispensable for maintaining the uniform conditioning required for successful operation. . . .

"Each one of the four vital factors in labor-saving in a chemical plant is well exemplified in the epsom salt process. We use equipment of such size that it can run for an 8-hour period before dumping the batch. The analysis of the batch is automatically recorded continuously, presenting on a chart a clear history of the progress of the reaction. The automatic analyzer is employed to actuate valves to control the flow of materials added to the batch. Finally, the complete cycle of the process is carried out continuously and automatically without manual operation of any kind except to open a valve to dump the finished batch. In fact, it would no doubt require the exercise of but a little more ingenuity to contrive means to control the valves for emptying and refilling the tank, thus dispensing entirely with manual labor or operation. Perhaps we will come to that, but we are still old-fashioned enough to believe that a process should have some one to look after it, at least once in every 8 hours."

The Dow bromine process is employed today not only to recover bromine from brine but also to produce this element from sea water.

A review of chemical equipment development reveals the great power of analogy, that consistent success has come to those who have modified to their use equipment employed by another industry for a somewhat different purpose. Many examples illustrate this. The x-ray machine was originally used to inspect bones or metallic objects within the human body. When a child swallowed a button, the x-ray machine located it and at least afforded the parents the satisfaction of knowing what had happened to the missing button. Today the x-ray machine is so widely used in industry that it is impossible to cover all of its useful applications in a single volume. The machine itself has been greatly modified and the method of its operation has been changed to meet special conditions. These modifications have required considerable skill and thought and research extending over a long period. The process continues and broadens the x-ray's value.

The synthesis of methanol from carbon monoxide and hydrogen was developed commercially to utilize high-pressure and high-temperature equipment originally designed for the fixation of nitrogen. Germany's capacity for synthesizing ammonia at the end of World War I was far beyond reasonably possible paece time requirements. Quite logically, this stimulated the interest of men familiar with the design and operation of this equipment in applying it for other purposes. Methanol synthesis uses the ammonia equipment with changes only of raw materials and catalyst.

The Dorr thickener and classifier, originally designed to meet metallurgical needs are today employed in slightly modified forms in a great many industries from biscuit manufacture to sewage disposal.

Consider the problem of developing a dryer for the extremely delicate and sensitive high explosive, tetranitroaniline, required in World War I but extremely difficult to supply because of frequent trouble in the dryers. For safety's sake TNA was handled with 15 per cent or higher moisture content, but this had to be removed before the beautiful fine green crystals could be loaded into depth bombs for the Navy. Tray dryers had caused trouble for two reasons: (1) the extremely fine crystalline powder would fly about as a dust when dry in even weak air currents and (2) some decomposition occurs whenever TNA is warmed in presence of moisture. The problem thus became to dry the powder without warming it and under conditions which would completely obviate the creation of extremely hazardous flying dust. Furthermore, like many highly nitrated compounds, TNA easily assumes a static electric charge even when the dried powder is simply dropped a few feet through dry air. After much cogitation, the investigator decided to try an arrangement based on the familiar Buchner funnel, since he feared dusting above all other hazards and this seemed to avoid that danger completely. Warmed air was drawn downward by a vacuum through a layer of the fine crystals held on a filter cloth. When the arrangement was tried through successively larger units, it was found not only to prevent dusting but it also completely avoided heating the explosive crystals until they were completely dried by the warm air current. Drying occurs in such an arrangement at a temperature actually below the atmosphere since the moist crystals are kept cool by the evaporation of their water content until that has all been carried away by the air stream. A series of thermometers inserted into the mass showed an initial drop of temperature when the air stream was turned on and began to rise only at the instant that drying was completed. The electric charge on the powder was safely carried off by a grounded metal screen in the mass. Thus a modified Buchner funnel overcame the three principal hazards in drying TNA, previously an extremely dangerous process.

Standard equipment is frequently altered to improve its operation, but even more often the flow schemes of processes employing standard equipment can be radically changed to give improved yields and capacities. An excellent example is the development of the cracking unit, consisting of a combination of high-pressure reaction chamber, pipe heaters, and fractionating columns. Each individual component of this system has been greatly improved from the original designs, but even more important is the improved arrangement of these components into systems of greatly enhanced efficiency. Consider the use of columns and evaporators for flashing tar, of a separate furnace as a "viscosity breaker," of a combination pipe heater or furnace for simultaneous "naphtha reforming" and heating and cracking, and of bubble towers for stripping feed, fractionating product and controlling recycle stock; all of these have contributed materially to the efficiency of modern cracking plants.

A simpler example is the bubble cap fractionating columns used to replace film or packed towers for recovering natural gasoline. The advantages of the columns are now so obvious that it is hard to understand why the industry took so long to adopt them. Only strong economic pressure from competitors forced the natural gasoline industry to adopt the preferred equipment. Of course, some modification of the bubble cap column was necessary to adapt it for this particular use. The same thing is true of carbon dioxide absorption, but that industry too has been slow to adopt the efficient bubble cap column. These modifications might conceivably have constituted invention, but even at that the industry was painfully slow to see the importance of this line of research.

Research on apparatus often produces equipment resembling some existing design even though the investigators were entirely unconscious of copying. This happens frequently, especially in chemical practice. The reason is obvious. Chemical industry requires its equipment to perform no complicated mechanical feats, but rather to channel and control an increasing or decreasing flow of energy or material. The equipment design problems of chemical industry are thus largely confined to the transfer of material or heat. Chemical reactions sometimes absorb, but more generally emit heat. This must be removed from the reaction zone at a controlled rate to maintain optimum conditions and to avoid undesirable reactions. The designer is usually required to remove this heat as fast as it is released, as in the many nitration reactions. Sometimes the problem is to heat a fluid to reaction temperature in minimum time; more often the final products must be cooled as rapidly as possible after reaction. These conditions are typefied by catalytic vapor phase oxidations. The reasons for similarities in the basic design of equipment for even the most different chemical reactions are thus obvious from their similar function.

The absorption of a gas by a liquid, a case of material flow, may occur under two basic sets of conditions, depending on whether the gas is slightly or highly soluble in the liquid. In the first case, the liquid film at the interface is the important factor in equipment design; in the second, the gas film controls. The character of the chemical reaction that may take place in either phase will thus not greatly influence the basic design requirements.

An example is the development of a contactor for gaseous oxygen and an organic liquid (alcohol). The result was similar to equipment that had been commonly used before. This case involves a slightly soluble gas and that emphasizes the liquid film at the interface, whose thickness must be reduced to a minimum. The case has been analyzed by Keyes.

The original device developed for this particular reaction was a high speed stirrer consisting of two circular plates a few thousandths of an inch apart submerged in the liquid and running at approximately ten thousand revolutions per minute. Gas and liquid were admitted through an opening in the lower plate and were shot out at the periphery between the plates by centrifugal force. The shearing action of the plates broke up the oxygen into extremely small bubbles which traveled rapidly throughout the body of the liquid. On a small scale this device was highly satisfactory, but a large-scale unit having the same peripheral speed involved serious engineering problems.

A second much simpler device consisted of two tubes set at right angles with open ends together. The liquid was forced through one and gas through the other. This device could operate in the liquid and had a shearing action similar to the high-speed stirrer. Considerable experimentation later revealed the same action could be had from a fine slit in the center of a pipe with gas forced in one end and liquid in the other. In other words, the device is an ordinary leak in a pipe.

A further development injected the liquid and the gas against a revolving disc set just above the inlet openings with a clearance of only a few thousandths of an inch. The disc was run at about 10,000 revolutions per minute. This device, also satisfactory on a laboratory scale, was a rather simple type of colloid mill.

Another attempt was a stationary cone inserted in a cone-shaped base with the inlets at the apex of the cone. This was clearly a "cracked" valve, but it was less satisfactory than the moving devices.

This apparatus was changed by rotating the cone rapidly. The clearance was a few thousandths of an inch, the speed was high as before, and an effective heating chamber was placed around the stationary base. This was, of course, a modification of the colloid mill, and gave thorough contact between gas and liquid.

Occasionally a method can be found to get around the high resistance of the films at the interface in a gas absorber and thus raise capacity of existing scrubbers without facing the difficulties inherent in the various mechanical contactors. An example is the MacKee-Winter process [U. S. Patent 2,043,109 (June 2, 1936)] for absorption of carbon dioxide from the flue gas. This method differs from the usual absorption of carbon dioxide in an alkali carbonate-bicarbonate lye principally in the introduction of ammonia into the flue gas stream to react with the carbon dioxide and allow it to pass the interface as the very soluble ammonium bicarbonate. Whatever may be the exact mechanism involved, the gas phase reaction as part of the absorption process substantially raises the overall capacity of an absorption system per cubic foot of tower or per square foot of active absorbing surface. This is important since the low rate of absorption of gas in carbonate lye prevents any reasonable approach to equilibrium in a practicable absorber. The increase in output is particularly great when the feed gas has a relatively low carbon dioxide content. Naturally certain changes are necessary in the system to keep the ammonia in the active part of the system.

The possibility has also been suggested that the resistance to absorption interposed by the liquid film can be materially reduced by the introduction of substances into the absorbing solution which lower its surface tension.

Often a particular piece of equipment or machine could have been designed for a specific purpose years before it was. This is particularly true in the chemical field. The reason is that many investigators start to work without having a clear idea of just what is necessary to satisfy the particular requirements. They do not first state the problem clearly and thus they lose sight of their objective. It is self-evident that success in any research requires as an absolute essential at the outset to know the problem and objective exactly and in detail. A common cause of failure is to forget the fundamental problem. The investigator not infrequently becomes so intensely absorbed in some minor aspect of the main problem that he is able to effect improvement in only one step of a series and misses the opportunity to improve the whole series. Some years ago, the efficiency of the compressor used to liquefy ammonia in ice production was greatly improved. To realize this increased efficiency required changes in operating conditions of the plant, but when these were made, production of ice dropped, instead of rising, despite the enhanced efficiency of the compressor.

In developing a new piece of equipment, the researcher must learn all the fundamental requirements and must never forget them throughout the entire development.

Often the research worker may so rivet his attention on one line of reasoning and direct his efforts toward one method of solving his problem that he misses a simpler and generally more satisfactory solution. The handling of waste aniline water in the production of aniline is a case in point. When this industry was new in the United States just after World War I, the habit was to recover the aniline oil dissolved in the process water around the plant by steam distillation. Since aniline is soluble in water to the extent of about 3 to 5 per cent, the recovery of this amount from the large volumes of water used around the plant, particularly for steam distillation, forms an important part of the plant's output. Some, but by no means all, of this water could be returned to the reducers. As production of the early plants grew, batch steam distillation of aniline water was rather naturally displaced by a continuous process employing a bubble-cap column, until a point was reached when the capacity of available stills was overwhelmed by the growing amounts of aniline water poured forth from the plant. Much time and energy were spent in a futile effort to amplify the capacity of the stills at hand to carry the swelling input before the simple and highly effective method was hit upon of using the excess aniline water to wash the nitrobenzene raw material going into the aniline reducers. In this way the aniline of the aniline water was returned to the process with the minimum expenditure of energy, and with no significant change in the plant's equipment. Nitrobenzene at that time was washed several times with water in a counter-current scheme and it was necessary only to substitute aniline water for well water entering that system, adding soda ash to it as to the well water to insure complete neutralization of the nitrobenzene before it entered the reducers. Not only was the substantial expenditure for column stills originally believed necessary avoided by this change of method, but at the same time the recovery of aniline from waste water was so integrated with the overall process that it ceased thereafter to be a problem, since quantity of nitrobenzene to be washed, quantity of aniline water available and output of aniline are all mutually dependent variables.

Adaptation by Frederick G. Cottrell of a high-tension electric field to the precipitation of clouds of dust or mist illustrates a vital consideration often overlooked by research workers. Obviously, a great deal of preliminary development must have been done before any particular research or invention can succeed. Cottrell's electrical precipitator was quite impossible until, for instance, a dependable source of high-voltage electricity was available to him. This Cottrell carefully points out in reviewing attempts employing the identical principle that failed to accomplish his objective even a few years before he succeeded. These failures had been under the direction of no less a person than Sir Oliver Lodge so that they did not fail from the researcher's want of ability.

It is no reflection on Cottrell's genius to point out that development of alternating-current techniques and equipment had of necessity to precede his work to insure its success. He required an electrical field of such high voltage that it could only be realized by stepping up an alternating current through a transformer. He further needed a dependable and efficient rectifier to convert the product of the transformer into direct current still at high voltage. This he found in the synchronous motor which was still comparatively new when Cottrell used it around 1906. Obviously this development of equipment had to be built upon what had been done before by others. It was clearly a synthesis for highly practical purposes of elements already existing. Timing was an essential element in success, and had Cottrell not found the key to the solution of this problem, it is highly likely that someone else would have done so at nearly the same time. When an urgent need and the elements that can be integrated to satisfy it exist, sooner or later someone is impelled to assemble them. In 1911, Cottrell described his research leading up to the successful electrical precipitator thus:

> "The removal of suspended particles, from gases, by the aid of electric discharges is by no means a new idea. As early as 1824 we find it suggested by Hohlfeld as a means of suppressing ordinary smoke, and again a quarter of a century later by Guitard. These suggestions, which do not seem to have stimulated any practical study of the question, were soon entirely forgotten and only brought

to light again by Sir Oliver Lodge many years after he himself had independently rediscovered the same phenomena and brought them to public attention in 1886. The first recorded attempt to apply these principles commercially appears to have been made at the Dee Bank Lead Works. The general principle of electrical precipitation of suspended matter was at this time patented by Alfred C. Walker of the above firm in several countries, but these patents have long since expired. The apparatus was described as consisting of a system of metallic points situated in the flue from the lead furnaces and excited from two Wimshurst influence machines with glass plates 5 ft. in diameter, each machine being driven by a one-horsepower steam engine.

"The apparatus undoubtedly did not in practice fulfill expectations as we find nothing further of it in the literature. The most apparent weakness of the project lay perhaps in the reliance on the Wimshurst machine, which had then just been brought out and from which a great deal more was anticipated than has been justified by experience, at least as far as commercial applications are concerned.

"Some four years ago (1907) while studying various methods for the removal of acid mists in the contact sulfuric acid process, the author had occasion to repeat the early experiments of Lodge and became convinced of the possibility of developing them into commercial realities. The work described here may fairly be considered as simply the reduction to engineering practice of the fundamental processes long since laid open to us by the splendid pioneer work of Lodge, a feat vastly easier today than at the time of Lodge and Walker's original attempt.

"The precipitation of suspended matter whether in gases or liquids may be accelerated by electricity in the form of either direct or alternating current, but the mode of action and the type of problem to which each is best applicable differ in certain important respects.

"Where an alternating electromotive force is applied to a suspension, the action consists for the most part in an agglomeration of the suspended particles into larger aggregates in the body of the suspending medium and a consequently more rapid settling of these aggregates by gravity.

"Thus if powerful Hertzian waves are sent out into foggy air the alternating fields set up in space cause an agglomeration of the particles of liquid into larger drops which then settle much more rapidly. Considerable work aimed at the application of this phenomenon to dispelling fog on land and sea has recently been done in France and England but very little on definite results has yet been published. The field appears, however, one of considerable promise. Another application of alternating current along these lines is found in a process now in use in the California oil fields for separating emulsified water from crude oil. This process grew out of the work here described.

"Alternating current may thus be used to advantage where the masses of gas or liquid to be treated are fairly quiescent and where a simple agglomeration of the suspended particles into larger aggregates is sufficient to effect separation by gravity or otherwise.

"In the large volumes of rapidly moving gases in smelter flues the agglomerating and settling process is, however, too slow even when the flues are expanded into dust chambers as large as are commercially feasible. In such cases direct current methods are particularly important.

"If we bring a needle point connected to one side of a high-potential direct-current line opposite to a flat plate connected to the other side of the line, the air space between becomes highly charged with electricity of the same sign as the needle point irrespective of whether this is positive or negative. Any insulated body brought into this space instantly receives a charge of the same sign. If this body is free to move, as in the case of a floating particle, it will be attracted to the plate of opposite charge and will move at a rate proportional to its charge and the potential gradient between the point and plate.

"Even if there are no visible suspended particles the gas molecules themselves undergo this same process, as is evidenced by a strong wind from the point to the plate even in perfectly transparent gases. The old familiar experiment of blowing out a candle flame by presenting it to such a charged point is simply another illustration of the same phenomenon.

"The first step toward practicability was of necessity a commercially feasible source of high-tension direct-current. The obstacles to building direct-current generators for high voltages lie chiefly in difficulties of insulation, and if this is avoided as to individual machines by working a large number in series the multiplication of adjustments and moving parts causes trouble. On the other hand, high-potential alternating-current technique has in late years been worked out most thoroughly, and commercial apparatus up to 100,000 volts is available in the market. The mercury arc rectifier has been made practical for series arc lighting service up to some 5,000 volts direct current, but although higher voltage units were at one time attempted by the electrical companies they were later withdrawn from the market as unsuited to practical operating conditions. For high voltages they seem, like static machines, to work well under the careful management and light duty of the laboratory but to fail in practice. This is particularly so in the application to metallurgical and chemical work where the electrodes in the flues have to be placed close together and worked near the potential of disruptive discharge. This discharge places more severe loads upon generating apparatus than series arc lighting, to which the rectifier seems particularly well adapted. . . .

"The procedure actually used in our installations consists in transforming the alternating current from an ordinary lighting or power circuit up to some 20,000 or 30,000 volts and then commutating this high potential current into an intermittent direct current by means of a special rotary contact-maker driven by a synchronous motor. This direct current is applied to a system of electrodes in the flue carrying the gases to be treated.

"The electrodes of two types correspond to the plate and point in the experiment above cited. The plate presents no special problem as any smooth conducting surface will answer the purpose. The pointed or discharge electrodes are quite otherwise and working out practical forms for these proved the key to much of the success thus far obtained.

"In laboratory experiments when the discharge from a single point (or a few such) is being studied, fine sewing needles or even wire bristles answer very well. But when it is attempted to multiply such discharge points in order to treat uniformly a large mass of rapidly moving gas at moderate temperatures, great difficulty is met in obtaining a powerful and, at the same time, effective distribution of current.

"The clue to the solution of this difficulty came from an almost accidental observation. I was working one evening in the twilight when the efficiency of the different points could be roughly judged by the pale luminous discharge from them. Under the particular conditions employed at the time, this glow only became appreciable when the points had approached the plates almost to within the distance for disruptive discharge; but a piece of cotton-covered magnet wire, which carried the current and was widely separated from any other conductor of opposite polarity, showed a beautiful uniform purple glow along its whole length. The explanation lay in the fact that every loose fiber of the cotton insulation, although a relatively poor conductor, acted as a discharge point for this high potential current. The cotton's fineness and sharpness, of course, far exceeded that of the sharpest needle or thinnest metallic wire. Acting on this suggestion, it was found that a piece of this cotton-covered wire when used as a discharge electrode at ordinary temperature proved far more effective in precipitating the sulfuric acid mists than any system of metallic points which it had been possible to construct. Perhaps the greatest advantage thus gained lay in the less accurate spacing demanded between the electrodes of opposite polarity in order to secure a reasonably uniform discharge.

"Practice, of course, demanded a more durable material than cotton and this has been found in fine filaments of asbestos and scales of mica, supplying the discharge points or edges of the excessive fineness required. These materials are twisted up with wires or otherwise fastened to suitable metallic supports to form the discharge electrodes. The current has to pass only a short distance by surface leakage over them, the slight deposit of moisture or acid fume naturally settling on them serving to effect the conduction. If the gases do not supply such a coating, then the material must be treated before being placed in the flue.

"The construction and arrangement of the electrodes, as also of the chamber containing them, naturally vary widely with the conditions to be fulfilled."

Quite as important as new equipment are the instruments required to control operations. Herbert H. Dow tells of an interesting and effective makeshift, as we would now call it, which served as an important instrument in the early days of the bromine industry.

"In 1893 the bromide plant had absorption towers that did not completely absorb all the bromine except when alkali had been recently added, and if there was too much conversion of the alkali into bromide and bromate there would be a big loss of bromine into the escaping air. In order to know whether the night shift had gone to sleep and let the alkali get too near saturation before replenishing it, the following device was installed:

"A very fine iron wire was stretched across the air outlet. If the bromine came through in abnormal amounts it would corrode the wire thus reducing its cross section enough to increase materially the electrical resistance, and it was the intention to devise instruments that would record this resistance. (This was before the days when good and cheap automatic recording apparatus was available.) However, it was found that the resistance would change only very slightly under some circumstances and under others the wire would be eaten entirely through, thereby preventing any further record being made. So the plans were changed, and instead of using an elaborate equipment, the wire simply supported a weight; then, if bromine came out at any time during the night in a sufficient volume to weaken the wire materially, it would break off and drop the weight and thereby prove that the operators were not attending to their business.

"This piece of apparatus was in use for some time, but later the absorption equipment was made so large and contained such a volume of alkali that it could not go far wrong between quitting time and

> morning, even if it were neglected; consequently the corroding wire was abandoned."

While no one today would be likely to choose such an instrument, the kind of ingenuity which went into devising it brings even better returns today.

Compelling reasons for prosecuting a particular research may develop from the most diverse causes, and investigations and developments initiated for what may seem to be trivial first causes need not be themselves trivial. William P. Jesse, of the Argonne National Laboratory, relates how a physicist's reactions to the rigors of a geological field expedition prompted him to develop a valuable instrument for radioactive measurements:

> "The Geiger-Müller counter proved itself of great use in locating outcroppings of uranium ore by means of the gamma rays emitted and also in making assays of sample specimens picked up by the prospecting party in the field. During the early part of the war, this then comparatively new method was tried out by one geological party. The Geiger-Müller set then available weighed about 40 lb. Apparently these geologists were equally skilled as psychologists, since they took along a physicist to operate the instrument. After the perspiring physicist had carried for days the 40-lb. set over windfalls on trails, through swamps and up steep hills, he returned to his laboratory with the unquenchable resolve to build a much lighter set. Through his efforts and those of other physicists following him, a set is now available weighing less than 2 lb. It can be easily carried in the coat pocket, since it is not much larger than a small camera. In the future small sets of this sort should be useful in hospitals for such purposes as finding lost radium capsules."

Chapter 9

The Progressive Development of an Idea

"Science is built up of successive solutions given to questions of ever increasing subtlety approaching nearer and nearer towards the very essence of phenomena." —Justus von Liebig

In the preceding chapters we have looked at individual researches and have analyzed a number of them. It seems also profitable to examine the evolution of an investigation developing over a long period of time and through the work of a number of successive persons and groups. The synthesis of rubber is such a research and the several different stages of its progress will provide an index of the way a search initially entering a broad open field gradually narrows and finally focusses upon minor details that were totally undiscernible a short time before. By progressive intermediate steps the searcher advances from the nebulous generality with which a research begins through successive narrowings of the field of investigation. Finally, he must solve many little problems whose very existence and nature could not be suspected at the beginning, but which are utterly essential and contribute immensely to final success. Looking into rubber synthesis provides a series of glimpses at a large subject over a long time that can very well correspond to the regular reports an investigator should make to acquaint others with his progress, but even more important to clarify his own thinking. The stages of rubber synthesis that we shall examine can be considered as quite representative of those through which any successful research must pass before it can succeed, even though the timing may be entirely different.

Among the great and pressing problems of the second quarter of the twentieth century, none has demanded more of research than the large scale production of synthetic rubber-like materials. During the century following Goodyear's discovery of the vulcanization process, the question of synthesizing rubber went through several important stages. In its earliest phase the composition of rubber and its synthesis were mere academic problems totally lacking economic pressure to force their solution. Rubber to meet demands for it was reasonably available first from wild tropical forests and later from plantations in the East Indies and southeastern Asia.

The great Michael Faraday had determined even before Goodyear's day that rubber consisted of carbon and hydrogen. Later several investigators confirmed the fact that rubber could be broken down by heat to yield isoprene, C_5H_8, and hence it seemed highly probable that rubber itself was composed of some polymer or assembly of isoprene units. Proof of this was adduced by William A. Tilden (later Sir William) in 1892 when he found that some samples of isoprene he had prepared had reverted to rubber. He has this to say on the subject:

> "When isoprene is brought into contact with strong acids, aqueous hydrochloric acid for example, it is converted into a tough elastic solid, which has been examined by G. Bourchardat and by myself; it appears to be true India rubber.
>
> "Specimens of isoprene were made from several terpenes in the course of my work on those compounds, and some of them I have preserved. I was surprised a few weeks ago at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In place of a limpid colourless liquid the bottle contained a dense syrup, in which were floating several large masses of solid of a yellowish colour. Upon examination this turned out to be India rubber. The change of isoprene by spontaneous polymerization has not to my knowledge been observed before. I can only account for it by the hypothesis that a small quantity of acetic or formic acid had been produced by the oxidizing action of the air and that the presence of this compound had been the means of transforming the rest. The liquid was acid to test paper, and yielded a small portion of unchanged isoprene.
>
> "The artificial India rubber, like natural rubber, appears to consist of two substances, one of which is more soluble in benzene or in carbon bisulfide than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characters with a similar preparation from Para rubber. The artificial

rubber unites with sulfur in the same way as ordinary rubber, forming a tough elastic compound.

"The constitutional formula of isoprene is not known with certainty, but it must be selected from the five following formulae:—

$$\left.\begin{array}{l} CH_3CH_2CH{=}C{=}CH_2 \\ CH_3CH{=}C{=}CHCH_3 \\ (CH_3)_2C{=}C{=}CH_2 \end{array}\right\} \begin{array}{l} \textit{Derivatives of allene,} \\ \quad CH_2{=}C{=}CH_2 \end{array}$$

$$\left.\begin{array}{l} CH_3CH{=}CH{-}CH{=}CH_2 \\ CH_2{=}CCH_3{-}CH{=}CH_2 \end{array}\right\} \begin{array}{l} \textit{Derived from crotonylene,} \\ \quad CH_2{=}CH{-}CH{=}CH_2 \end{array}$$

"It is obvious that compounds such as these containing doubly-linked carbon may polymerize in a variety of ways, and in the present condition of our knowledge of the constitution, even of isoprene, it would be idle to speculate as to which out of the numerous possible arrangements would correspond to the constitution of caoutchouc."

While that represents an important step toward the synthesis of rubber, no further progress came of it at the time nor for a considerable period afterward. Tilden had here learned that polymerization of a compound takes place and he had narrowed its structure down to one of five possibilities. Included among them are the basic elements now successfully used for polymerization to synthetic elastomers.

But nothing serious came of this early beginning for the important reason that it was premature. Existing sources of natural rubber satisfactorily met needs even after the advent of the automobile created demands of new magnitude and of new urgency. Occasional disturbances interfered with the orderly supply and demand for rubber, but by and large there was no serious urge to seek out synthetic when natural rubber was plentiful and cheap.

The Germans took a somewhat different view of the matter, and although others were content to depend upon plantations in remote tropical regions, the German nation preferred to develop home industries through synthesis. Rubber to such a point of view offered no greater difficulty than indigo which had been synthesized with signal success. Thus German chemists and German industry were already well along with the problem of synthesizing rubbery materials, or so they thought, when the blockade of Germany imposed by the Allies in World War I required home production of rubber as well as every other possible commodity to support the German war machine. So it was that Germany fostered a rudimentary industry turning out an unsatisfactory product. K. Gottlob was intimate with this practically throughout its life and soon after the war's end described his experiences in this manner in *India Rubber Journal*:

"I myself have been engaged for almost eight years on the study of synthetic rubber, more especially on rendering the synthetic product applicable to the manufacture of rubber goods. It was my duty, as chemist to the Farbenfabriken vorm. Friedrich Bayer and Co., to introduce the methyl rubber made by this firm under my management during the war into the manufacture of India-rubber goods and cables. . . .

"I was very much interested in the paper of C. Harries in 1910. I knew that the solution of this problem, making India rubber synthetically, must not only be of great practical interest (raw rubber was then very expensive and gradually rose to 25 marks per kg.), but that it was above all a scientific event of the first rank, to synthesize, even if only in the laboratory, a substance of such complicated composition, a colloid the structure of which was still not clear. . . .

"I became very desirous of taking part in this work in some way and to collaborate, according to my ability, in the solution of the problem. Naturally, I first turned my attention to the manufacture of isoprenes, which earlier chemists tried to obtain by the destructive distillation of turpentine.

"The study of this earlier work convinced me that the small yields which had been obtained up till then were mainly to be attributed to the unstable nature of isoprene at high temperatures. The point clearly was to remove the isoprene formed rapidly from the mixture.

"I sought to solve this problem by dipping a piece of silund in a flask filled with turpentine and heating it to incandescence by an electric current. By this means I was able to raise the yield of isoprene boiling at 32-34 deg. C. from 7 per cent to about 30 per cent. In this work Herr Karl Miksch assisted me very effectively.

"The isoprene so obtained I tried to polymerize by adding acetic acid at an elevated temperature in a closed tube, and actually obtained, even if the yield was only small, a few grains of a perfectly transparent pasty substance which was very similar to clear plantation rubber purified by solution in benzol and precipitation with alcohol. I could not make any experiments in vulcanization on account of the small quantity of the substance and lack of small experimental apparatus.

"Using dipentenes or limonenes instead of turpentine as the raw material, I found, gave a far greater yield of isoprene (over 50 per cent).

"I applied for a patent on the process and at the same time turned to my former teacher, C. Harries, to give me a suggestion as to the possibilities of my patent.

"Thereupon I heard from him that he was himself engaged in quite similar work and had decomposed turpentine vapor by means of the incandescent metal filament of a glow lamp from which the glass had been removed.

"The process was thus essentially similar to mine; only as careful investigation subsequently showed, it had the disadvantage of giving somewhat lower yields. Moreover, the incandescent wire became very brittle if carbon deposited upon it. In accordance with an agreement, C. Harries and I published the new process (see *Annalen*, 383, 228). On his advice I turned, in order to carry out my process, to the Farbenfabriken vorm. Friedr. Bayer and Co., of Elberfeld. I was required by this firm to test and demonstrate the process again there, and I took the opportunity of also investigating a number of other terpenes to determine their yield of isoprene under pyrogenous decomposition by my method. I could in no case obtain a higher yield than that obtained with dipentene. The firm acquired my patent; at the same time I decided, in the summer of 1911, to give up my previous post and to devote myself, as chemist of the dye works, entirely to the study of synthetic rubber. I may mention, moreover, that the production of isoprenes from terpenes by Merling's synthesis and that of the Badische Anilin und Soda Fabrik is left far behind, so that they can no longer be of importance when the price of India rubber becomes normal again. Nevertheless, it had, and had long retained, its value for the investigation, since by suitably enlarging the apparatus according to my process it permitted fairly large quantities of isoprenes to be made from turpentine with a yield of roughly 30 to 36 per cent. The process is also suitable for the production of erythrenes, *e.g.*, from petroleum or cyclophenol.

"When I came to Elberfeld in the summer of 1911 synthetic India rubber had long been 'discovered.' Drs. Fritz Hofmann and Coutelle had worked on the problem since 1907 and in 1909 they had reached the stage of taking a patent for the 'polymerization of hydrocarbons with conjugated double bonds by simple heating in a closed tube with or without the addition of means for accelerating the polymerization.' Polymerization by metallic sodium had been discovered independently by C. Harries, of the Farbenfabriken, and by two English chemists, Mathews and Strange.

"From the scientific and the patent sides the ground was quite well prepared, erythrene-, isoprene- and methylisoprene-rubbers were known, the latter also in a modification as Kondakow's product, and still other kinds. Technically none of them were then useful, and what was submitted to me when I came in, in unvulcanized and especially in vulcanized samples, was not very encouraging and led me to the conclusion that the most important problem to be solved was not to discover a new synthesis of the hydrocarbons which formed the raw materials, but rather improvement of the methods of polymerization and vulcanization. This also best suited my laboratory, which at my suggestion was provided with small experimental rollers, presses and an apparatus for testing the tensile strength of soft rubber (Schopper).

"I then had only one or two small samples of erythrene rubber available. They were quite elastic, but very easily broken, almost friable.

"The vulcanized isoprene samples were not much better. They were certainly quite elastic, but had, in addition to a very unpleasant odour, a very low tensile strength, which scarcely amounted to a few kgms. per sq. mm. Still worse were erythrene- and isoprene-rubbers obtained with metallic sodium.

"To me the most interesting was methylisoprene rubber or methyl rubber. It was in two modifications. One, resulting from polymerization under heat, was then very much in the ascendant;

the yield was almost quantitative, the behaviour, the appearance and the elasticity in the unvulcanized condition so beautiful, that one actually became enthusiastic. This enthusiasm, however, ceased directly you wished to vulcanize the material. It would not vulcanize at all. The fact was very remarkable. This beautiful material could be worked so well on the rollers and could not be rolled dead. It took up quite smoothly 10 and 18 per cent, and even more, of sulfur. But after vulcanization for two or three hours at 4 atmospheres it became a quite inelastic, dead, soft and leathery mass, which no longer had anything in common with rubber. On the testing machine this material showed little strengh, but much permanent extension.

"If this material is allowed to stand in the air before vulcanization for any length of time, the vulcanized product is still worse; the extension rises to far above 1,000 per cent, the strength fails to 1-2 kgs. and less per sq. mm. Finally if the material stands long unprotected, it becomes no longer capable of vulcanization by reason of the advanced oxidation; it yielded a sticky material of unpleasant odour. Furthermore, all vulcanized articles made therefrom were sticky; even those originally dry became sticky in a very short time. In a few days a packet of small valves under the action of air and light was converted into an inseparable mass, which left only resin-like oxidation products when heated.

"The polymers obtained cold behaved in a similar manner. This product had previously been known for a long time by the Russian, Kondakow; he even supposed that it had some relation to rubber, but he never investigated it. This cold polymerization product, which in itself had no rubber-like appearance, can be drawn out quite well into sheets on hot rollers, and mixed with sulfur. The vulcanized product appeared to me (if the material had not been too much oxidized previously) to be somewhat better and more durable; however, it was not usable. Even the sodium-methyl rubber, which in a raw condition presented a beautiful transparent rubber-like appearance and was elastic, was after vulcanization in no way better, but was much worse than the other two kinds.

"Since all the means usual in the rubber industry, the addition of chalk, litharge and the like, were fruitless, I finally began to investigate the vulcanized product for combined sulfur. I found that this amount was in all cases far below the standard for natural rubber, and at most only a few tenths per cent; the vulcanized products obtained from Kondakow's material were certainly somewhat worse.

"All this so considerably lowered my hopes (based on my laboratory experiments) of supplying the dye works with useful vulcanized products from their beautiful raw materials that I devoted myself more and more to the study of isoprene rubber.

"I was much astonished that the dye works laid themselves out for the manufacture of large quantities of hot polymerization products of methyl rubber, for which they had found a market. As I knew one India-rubber works had made experiments with this material and had used it as a substitute for motor tire cover mixings. Contrary to my expectation, these experiments turned out well, so that some German princes had their cars fitted with these tires. I could not bring my experiments into line with these results and could not understand when the works declared themselves ready to accept larger quantities. Some claims were made, since the tires, after being allowed to stand a short time, became hard and useless. I received instructions to investigate the matter at the India-rubber works.

"What I saw there was nothing new to me, for the samples submitted to me were just as hard and brittle as those I made myself. The only things that interested me were some samples of hard rubber combs which I had an opportunity of seeing. On account of the low vulcanizing capacity of the hot polymerization products of methyl rubber it had not yet occurred to me to make hard rubber from it.

"In any case the first attempt which had been made to bring artificial rubber on the market had ended in a heavy failure, and the disappointment was all the greater as the maintenance of the scientific India-rubber laboratory (to which at times fifteen chemists were attached) called for an annual expenditure of hundreds of thousands of marks, and as the apparatus erected in the meantime for the manufacture of methyl rubber had swallowed up further hundreds of thousands.

"The future of synthetic India rubber then hung on a thread—certainly on a very strong one—the invincible optimism of the general manager, C. Duisberg, who then already deserved the Bunsen Medal (which was awarded him seven years later for the introduction of artificial rubber). He infected the others with his optimism, and the work went on.

"I myself was also optimistic; I recognized the product as useless at this stage, but believed it capable of improvement. It was merely unfinished. Just at this time I made some fresh observations which supported my optimism.

"In the first place, I succeeded in considerably improving the hot polymerization products of isoprene and in increasing the yields obtained by polymerizing the isoprene in a closed vessel, shaking it with an aqueous solution or emulsion of albumen and similar substances.

"At one stroke I was able to raise the yield to 80 per cent, by this special form of the Hofmann method; above all, the vulcanized products were far better and were not much behind those obtained from a medium regenerated or a third quality natural rubber.

"Even methyl rubber made strides and experiments were made by Messrs. Hofmann, Delbruch and Meisenburg to reduce the oxidizability thereof by the addition of suitable agents. The addition of organic bases and substances of the phenol class appeared advantageous in this respect.

"Among the basic substances suggested by Dr. Hofmann for preventing oxidation was piperidine. This base was added occasionally to a methyl rubber (cold polymerization product) on the rollers, then 10 per cent of sulfur was mixed in, and a valve was vulcanized by me from this mixture in the press for one hour at 4 atmospheres.

"This valve differed considerably in appearance from all the finished products which I had seen up till then. It was no longer a whitish or dirty grey semi-soft material, but was almost black, somewhat transparent, elastic when warm, very stiff and leathery cold, and very similar to hard rubber. In order to explain this remarkable result I determined the combined sulfur in it and found that a few per cent of sulfur were combined, many times the amount previously found.

"This experiment was repeated several times with material obtained from different quarters; in each case I obtained the same result. Moreover, it appeared that the material treated with piperidene in a raw state, if it was kept cool and in closed vessels, showed very little tendency to oxidize and the vulcanized products were far more durable. I should have pursued further this wonderful effect of the piperidene if the absolute inelasticity of the vulcanized product had not deterred me from expecting anything from the matter; I hoped everything then from the isoprene rubber.

"Only when the above-mentioned failure with the first batch of methyl rubber occurred I took up the matter again in order to prosecute it in two directions. In the first place, I wished to try to introduce in the rubber works in question, instead of the warm polymerization products heretofore used there, a cold polymerization product treated with piperidine as a substitute for a motor tire cover mixture, after I had convinced myself that this product could be used to an almost unlimited degree in admixture with natural rubber.

"This certainly miscarried for various reasons. In the first place this kind of methyl rubber is very dry, and even externally it does not give quite a rubber-like impression; moreover, the works with whom we were working had become cautious by reason of the loss incurred and did not wish to undertake experiments.

"I might anticipate that only two years afterward—shortly before the outbreak of the war—this and another firm were prepared to resume the experiments for making soft rubber from methyl rubber. Some methyl rubber outer covers were again made. But these experiments also came to nothing. The dye works in peace times did not find customers for their methyl rubber nor for hard rubber, although there the conditions were much more favorable.

"The rapidly supervening brittleness of the hard rubber made before from methyl rubber, and also its low strength, I attributed to the fact that in the vulcanization of 8-10 hours at 4 atmospheres, not sufficient sulfur was combined. I assumed that, if it were possible to saturate all the double bonds with sulfur, the oxidizability of the finished hard rubber must cease.

"Added piperidine appeared to me to render this possible and in this way I actually obtained what was, in my opinion, a quite useful hard rubber, and this most easily from methyl rubber produced by cold polymerization. Since I lacked apparatus for testing, I got my firm to come to an agreement with a large hard rubber works.

"The matter did not begin very favorably, for our material was clearly not quite fully polymerized and also contained some volatile hydrocarbon, and began to burn on the rollers. Only the extraordinary determination of the technical manager of the works prevented them from being burnt out in the first experiments with artificial rubber.

"As an accelerator of vulcanization we then employed a somewhat less volatile piperidine derivative, which proved quite useful. With about 1 per cent of this accelerator and an addition of sulfur of about 50 per cent, the material vulcanized faultlessly in the normal time of 8-10 hours, and gave a hard rubber which externally differed in no way from the best Para hard rubber. When in thin plates it was transparent with a red colour.

"The mechanical tests showed that its tensile strength and hardness were only slightly less than the best Para hard rubber, and its elasticity was not much behind; on the other hand, its dielectric strength and its resistance to heat in the first experiments were quite as good and in some cases splendid. . . .

"After all it was usable, and I hoped then that the dye works with some assistance from the hard rubber works would be able to reduce its material to the same price as average plantation rubber. But in this I was wrong. . . . No order for even a gram of methyl rubber was given by any firm up to the outbreak of the war (World War I).

"The situation was all the more discouraging since even scientifically no new decisive success had been achieved, and since also my isoprene rubber polymerization had shown no result worth mentioning. . . .

"In 1913 I described the problem of synthetic rubber, so far as it related to polymerization, etc., as twofold, *viz.*: (1) making useful vulcanization products (practical rubber goods) from the polymerization products then known; and (2) polymerizing the butadienes, more especially isoprene, to a rubber chemically and physically the same as natural rubber and where possible superior to it. The second problem, which at that time I considered the more difficult one was not solved up to the spring of 1918, and as far as I know is not today (1920). The first has, by the necessity of the times, been somewhat forcibly brought to a solution; that is goods were made during the war from methyl rubber which will certainly not be made from it when normal supplies of natural rubber become available again. Nevertheless I believe that methyl rubber, and perhaps isoprene rubber too, will be kept on the market at a not excessive price for many reasons. This would be important for Germany for many reasons, not the least being intrinsic value."

This venture had thus practically ceased to exist before growing demand created by the fast-multiplying horde of automobiles and dislocations in the world's economy rendered natural sources of rubber unsatisfactory. Monopolistic control of plantations plus the vulnerability of the long and attenuated lines of transportation over which rubber must be brought to market ultimately concentrated renewed attention on the problem in the late '20's. Obviously the new attack on the problem at that time derived considerable benefit from the narrowing of the field of search by the researches and developments we have considered.

In 1925 a British restrictive plan of operating the rubber plantations raised the New York spot price of rubber from 11 cents per pound to $1.23 per pound in a few months. This demonstrated the need of some protection for the United States, by far the largest user of rubber, and encouraged active research on the problem of synthesis. A leader in that research was the late Wallace H. Carothers of the du Pont company who pioneered the production of chloroprene rubber. Shortly after the first commercial production of the new material, Carothers summarized the status of the problem as he saw it at that time. His discussion follows:

"Two objectives in attempts to synthesize rubber are (1) to discover or demonstrate completely the structure of rubber and explain its properties in terms of this structure, and (2) to produce artificially a commercially acceptable substitute. The second of these objectives is now an accomplished fact, but the first is far from having been achieved.

"The difficulties in this connection can be illustrated by first viewing the facts in the light of the assumption that rubber hydrocarbon is a chemical individual in the usual sense—*i.e.*, that it is made up of identically similar molecules capable of being represented by a single definite formula. If this were true it should be possible to infer the structure by a study of chemical behavior and then to make a rational synthesis—that is, from known starting materials to build up by known and deliberately controlled steps the supposed structure. If the synthetic product was then exactly identical in all its properties with the natural product, the structure of the latter would be proved.

"What is sometimes referred to as the synthesis of rubber consists essentially in this: Isoprene on standing passes slowly into an elastic solid having the chemical composition and many of the chemical reactions of rubber. But although this material is elastic, it is not physically identical with rubber; few experts in the field would mistake it for rubber. The product synthesized, then, is probably not rubber; and, even if it were the synthesis is not rational. It is a spontaneous or accidental transformation of unknown mechanism from which little can be inferred concerning the structure of the product.

"The question then arises as to how one can determine whether a given sample of material is rubber. The determination of identity is complicated by the fact that rubber is lacking in easily measured and sharply characteristic physical properties. Moreover, those properties that can be measured—*e.g.*, plasticity—are not necessarily the same for different samples or even for the same sample at different times. The result is that there must be considerable latitude in the specifications as to what constitutes rubber, and it is almost impossible to set any definite numerical limit for a given property. This lack of definition unfortunately makes it possible to designate as rubber-like almost any material having any appreciable degree of resilience and elastic extensibility; partially polymerized styrene is said to be rubber-like, and so are some aqueous dispersions of starch, gelatin, and sodium silicate. It is in this sense that many of the so-called synthetic rubbers are physically rubber-like. Chemically those derived from isoprene resemble rubber very closely, but so also do chicle, balata, and guttapercha which also have resilience and elastic extensibility but are not called 'rubber' because they do not possess these properties in sufficient degree.

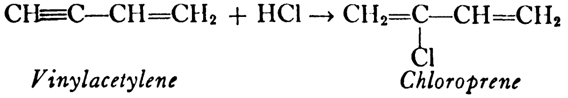
"In spite of the looseness with which the term 'rubber-like' is used, rubber is a unique material. When vulcanized it possesses an extraordinary degree of elastic extensibility combined with great strength. No other type of material (with the exception of those noted below) remotely approaches it in the magnitude of these combined properties. Rubber is also unique in the nature of the patterns that it furnishes when examined by x-rays. Unstretched samples yield a diffuse pattern characteristic of amorphous materials; stretched samples furnish a point diagram characteristic of fibrous crystals. The fiber diagram disappears instantly when the sample is released from stress. The unique properties of rubber are: great strength combined with an elastic extensibility of about 900 per cent, and instantaneously reversible fiber orientation.

"It is now generally recognized that the physical variability of rubber is inherent in (or at least reconcilable with) its chemical structure. Rubber molecules are long chains or threadlike structures built by the regular 1,4-combination of units having the formula $-CH_2-C(CH_3)=CH-CH_2-$. Chemical properties are conditioned by the presence of this unit, but the physical properties are determined by the average length of the chains and the way in which the individual lengths are distributed about the average. Geometrical isomerism due to the presence of the double bonds may also come into play. When isoprene polymerizes, its molecules apparently unite to form chains similar to those indicated above. But if the product is to approach rubber in its properties, the unions must occur regularly 1,4-(without inversions) and the configurations about the double bonds must be the same as those in natural rubber, as must also the average length of the chains and the distribution about the average.

"The complete description of rubber in terms of molecular structure (distribution of lengths, geometrical state, etc.) has not yet been accomplished; the mechanism of the polymerization of isoprene is unknown. Practical approach to the synthetic rubber problem must therefore be highly empirical. Starting with the historically important observation that isoprene on standing is transformed to an elastic solid, the attempt is made to modify favorably the properties of the product by controlling the conditions under which the transformation occurs. The enormously extensive experiments in this direction with isoprene, and with the related compounds, butadiene and dimethylbutadiene, have no doubt led to improved products, but, so far as any published information goes, they have never led to anything closely approaching rubber.

"The possibility was early recognized that some dienes might be found whose polymerization would yield products much superior to those obtained from isoprene, but the exploration of this possibility was hampered by the dearth of suitable methods for synthesizing dienes.

"Revolutionary progress in this direction recently became possible with the discovery of a simple process for preparing vinylacetylene. The latter is an especially suitable starting material for the synthesis of new types of dienes. Among the new dienes obtained from it are chloroprene and bromoprene:



$$CH{\equiv}C{-}CH{=}CH_2 + HCl \rightarrow CH_2{=}\underset{\large Cl}{\underset{|}{C}}{-}CH{=}CH_2$$

Vinylacetylene *Chloroprene*

These compounds polymerize several hundred times as rapidly as does isoprene, and they lead directly to products which are equal to rubber in strength and elastic extensibility. Moreover the products exhibit instantaneously reversible fiber orientation. Polychloroprene and polybromoprene are therefore the first synthetic products that equal rubber in those qualities which make rubber unique, and in this important sense they are the only true synthetic rubbers yet known.

"The field of synthetic rubber still presents many unsolved or incompletely solved problems. Among these may be mentioned the following:

"*Development of Satisfactory Methods for Physically Characterizing Rubber in Significant Numerical Units.* If there were, for example, two properties, x and y, simply measurable on small samples and such that together they furnished a numerical indication of quality, cumulative progress in the study of rubbers would not be so difficult. Obviously important practical indications of quality are extensibility and breaking strength, but these properties must be measured on the rubber after it is vulcanized, and the values obtained will depend partly upon a very complicated set of factors which constitute the conditions of vulcanization. The difficulties here are to a large extent inherent in the nature of rubber and are presented also by other macromolecular materials. The problem of physically characterizing such materials in significant numerical units is of the utmost importance to the whole field of resins, plastics, and fibers, and it should receive more attention jointly from physicists and chemists. Meanwhile, in future studies of synthetic rubber, quantitative data must be obtained whenever possible, since the accumulation of systematic information is impossible without quantitative data.

"Complete determination of the molecular structure of rubber will probably have to await the development of more information concerning macromolecular compounds generally.

"*Relation Between Physical Behavior and Molecular Structure.* It is quite certain that high strength requires the presence of very long molecules while elastic extensibility implies low internal viscosity, but these conditions are certainly not sufficient. Solution of this problem will obviously require more knowledge concerning the structure of rubber, and the study of synthetic materials of more or less known structure may be expected ultimately to throw considerable light on it.

"*Influence of Structure on Diene Polymerization.* Dienes vary greatly in their ease of polymerization and in the nature of the product. The fact that chloroprene and bromoprene are so much superior to isoprene emphasizes the importance of completely exploring the relation between structure and polymerization of dienes. Some data bearing on this point are presented in Table I. If the inferences from these data can be relied upon it appears that the

Table I. Estimated Relative Speeds of Polymerization of Various Dienes at 25° C. Compared with Isoprene (According to Carothers[b])

Compound	*Position and Nature of Substituent*				*Estd. Speed*[a]	*Character of Polymer*
	C══	══C──	──C══	══C		
1	...	Cl	Cl	...	2000	Hard, not extensible
2	...	I	...	...	1500	Rubber-like under certain conditions
3	...	Br	...	...	1000	Good rubber
4	...	Cl	...	...	700	Excellent rubber
5	...	Cl	CH_3	...	500	Fair rubber but low extensibility
6	Cl	Cl	Cl	...	120	Soft, elastic
7	...	C_6H_5	...	...	90	Soft
8	CH_3	Cl	...	...	30	Soft
9	C_2H_5	Cl	...	...	30	Soft
10	C_4H_9	Cl	...	...	10	Soft
11	C_7H_{15}	Cl	...	...	10	Soft
12	...	C_7H_{15}	...	...	9	Soft
13	Cl	...	...	...	7	Soft, sticky
14	...	CH_3	CH_3	...	3	Fair rubber but low extensibility
15	CH_3	CH_3	Cl	...	1.5	Soft
16	...	CH_3	...	...	1.0	Fair rubber
17	...	...	...	...	0.8	Fair rubber
18	CH_3	...	...	...	0.3	....
19	CH_3	CH_3	...	...	Probably <1	
20	$(CH_3)_2$	...	...	...	↓	....
21	CH_3	...	CH_3	...		....
22	CH_3	...	...	CH_3		....
23	$(CH_3)_2$	...	CH_3	...		....
24	$(CH_3)_2$	...	...	CH_3		....
25	CH_3	CH_3	CH_3	CH_3		....
26	$(CH_3)_2$	...	...	$(CH_3)_2$		....

[a] The estimated speeds are based on calculated unimolecular reaction velocity constants. The data from which the constants are derived suffer from a very large factor of uncertainty owing to the fact that, for dienes, the rate of polymerization varies considerably with the history of the sample and with conditions (amount of exposure to light and air) which are not specified or controlled in all of the experiments. These uncertainties are, however, thought to be insufficient to affect the order of magnitude of the indicated numbers.

[b] *Ind. Eng. Chem.*, **26**, 30 (1934).

best dienes will be of the type $CH_2=CX-CH=CH_2$ in which 'X' is an activating group other than alkyl or aryl.

"*Control of Diene Polymerization.* The product obtained spontaneously and accidentally from isoprene is so much like natural rubber in some ways that it is difficult to believe that it will always be impossible to control the reaction in such a way as to obtain a product fully equal to natural rubber. In the absence of simple objective measures of physical quality, progress in this direction must of necessity be slow. Another complication arises from the fact that dienes are enormously susceptible to catalytic effects not only in the speed of their polymerization, but also in the physical properties of the products. Exact reproducibility is therefore possible only under the most elaborately controlled conditions, and one of the conditions that must be controlled is the amount of exposure of the diene to air and light. In spite of the enormous amount of work implied by the voluminous patent literature, the factors indicated above have been generally ignored. Exact indications concerning the effect of conditions on the nature of products obtained from diene polymerizations are exceedingly meager. The possibility still remains of so controlling such reactions as to obtain improved products.

"*Mechanism of Diene Polymerization.* If the mechanism of diene polymerizations were sufficiently understood, a theoretical attack on the control of such reactions would become possible.

"*Synthesis of Rubber-Like Materials by Other Reactions than Diene Polymerization.* One method of attacking the synthetic rubber problem would be to synthesize giant molecules of known structure, study the relation between physical behavior and structure, and from inferences thus established proceed to the synthesis of materials having the required structure. The deliberate and rational synthesis of sufficiently large molecules having a completely known structure is at present impossible, but an approach to this ideal is found in reactions of condensation polymerization which proceed by a definitely known mechanism and lead to products whose general structural plan can be certainly inferred. Some of the complications and obscurity inherent in reactions of addition polymerization are thus immediately dispensed with and a clearer theoretical approach is made possible. It may be expected that this method of approach will ultimately throw considerable light on the relation between structure and rubber-like properties.

"Table I shows the influence of structural variations on the relative speeds of polymerization of various dienes and on the nature of the products. Very little quantitative significance can be attached to the numbers presented because they are derived by calculations sometimes involving extrapolations from data of uncertain reproducibility. The numbers, however, indicate relative degrees of magnitude.

"The three types of substituent groups present are halogen, phenyl, and alkyl. Comparison of the β-monosubstituted derivatives shows that all of these groups have an accelerating effect; methyl is very feeble, heptyl is appreciably stronger, phenyl is much stronger, and the halogens are very much stronger in the increasing order: chlorine, bromine, iodine. The full activating effect is manifested only if the group is on the β- or γ-carbon atom. Alkyl on the terminal carbon inhibits, and it depresses the activating effect of a group on the β-carbon. It appears that to obtain a high rate of polymerization the terminal carbons must be free of any substituents. A substituent at the γ-carbon atom generally reinforces the effect of one already present at the β-carbon, but these disubstituted dienes (Cl,Cl; CH_3,Cl; and CH_3,CH_3) all yield products that are deficient in extensibility. Another specific effect is that due to phenyl. β-Phenylbutadiene polymerizes quite rapidly, but the product is mostly the crystalline dimer. The small amount of higher polymer formed is soft and probably has a relatively low molecular weight. The formation of dimers is always a competing reaction in the synthesis of rubber from dienes, and it rapidly becomes more serious the higher the temperature used. At ordinary temperatures the rate of dimer formation from isoprene and chloroprene is roughly the same, but the temperatures required to obtain 50 per cent polymerization of the two dienes in 10 days are respectively about 90° and 25° C., and the percentages of dimer in the products at these temperatures are about 40 and < 1. This fact gives additional emphasis to the importance of a high rate of polymerization."

World War II took the problem of synthetic rubber immediately out of the class of mere interest and made its solution an urgent necessity. The development of many phases of hydrocarbon chemistry by the petroleum industry had meanwhile provided much additional information on which the industrial solution of the problem could be based. The accomplishments of the production program built upon quickly accelerated research and development were astounding. Also important in the situation and especially interesting in its bearings on the present discussion of research methods, is the great change in outlook of the leaders of research in the field.

Here we have for comparison a statement of the problem a decade later by another outstanding man. A comparison of Carothers' views then and now cannot be made because of his deplorable death before synthetic rubber had become a world wide problem. However, Waldo Semon was a key person in what we may call the post-Carothers development of the industry and his views are therefore highly significant. Dr. Semon's Charles Goodyear Memorial Lecture of 1944 supplies the following:

"Natural rubber is only one member of a wide class of materials that have the property of elasticity, characterized by the ability, after being stretched 200 per cent to 1,000 per cent, of being able to return forcibly and rapidly to substantially their original dimensions. Thus, rubber is a generic term and should be considered as one of the typical states of matter in the same class with crystals, fibers, glasses, and resins. Any material composed of a tangle of long linear molecules subject to lateral molecular motion similar to that in a liquid may be termed a 'rubber.' The plasticity and cold-flow characteristics are determined largely by the physical and chemical forces exerted in the molecules. If the linear molecules in the tangle are not restricted by crystalline forces, hydrogen bonding, or cross linking, the product is a thermoplastic material that can be worked on mills and molded into various shapes. Many rubber-like materials are permanently thermoplastic and not capable of being cross linked. Thus these materials cannot be vulcanized. Typical is high molecular-weight polyisobutylene.

"For greatest commercial value, a rubber should be capable of vulcanization—that is, after it has been formed into the desired shape it should be possible to cause some chemical change to occur so that the linear molecules are no longer free but are cross bonded or netted together to restrict plastic flow. In the case of natural rubber, the common way of obtaining this result is to react the rubber with sulfur. Actually, the amount of chemical reaction that needs to occur to change a rubber from a thermoplastic moldable material to a product that will retain its shape is relatively small. Half of one per cent of combined sulfur will cause such a change.

"To aid in visualizing these phenomena let us compare a single molecule of natural rubber to a rope 1 inch in diameter and 300 to 1,000 feet long, with knots tied every 4 inches. A piece of rubber might be compared to a tangle made up of these long molecules similar to the tangle of fibers that is typical of a boll of cotton. If this cotton is pulled out between fingers, the individual fibers tend to become more or less parallel and if the pulling is continued far enough the fibers straighten out perfectly parallel as in the carding of cotton. A similar effect occurs with rubber. As the sample is elongated, there is an orienting of the molecules. After sufficient elongation, flow occurs and the sample pulls apart. However, if the stress is removed before flow occurs the lateral molecular motion tends to cause the rubber to return to its original form.

"Now, if we dip a boll of cotton in dilute glue and allow it to dry, the fibers where they cross are stuck together or restricted in their action. When the sample is now pulled between the fingers the fibers as before tend to assume parallel positions. However, the slip or pulling apart no longer occurs unless the bonds or the fiber is broken. This structure is characteristic of vulcanized rubber.

"From this introduction it should be apparent that it is not necessary to duplicate the precise chemical structure of natural rubber in order to have a synthetic rubber-like material. It is merely necessary to build up long molecular chains which retain lateral molecular freedom. Theoretically this can be done in a large number of ways. Two types of simple organic molecules that can be caused to join together by polymerization are vinyl compounds ($CH_2=C-$) and conjugated dienes.

"The conjugated dienes can polymerize 1,2- or 1,4- or in any mixture of the two. However, for each diene molecule that enters into the structure, there is one double bond remaining, unless netting or cyclization has occurred. This double bond is reactive and makes possible vulcanization of such polymers by convenient reactions. If the polymer is made solely from diene there is a tremendous amount of unsaturation in the molecule, more than is actually required to give satisfactory vulcanization. Hence, the idea developed that advantages can be obtained by copolymerizing vinyl compounds and dienes in the same molecule. The nitrile rubbers, GR-S, and butyl rubbers are all typical of such copolymers, in which the diene portion of the molecule contributes vulcanizing properties and the vinyl portion of the molecule contributes to the elastic and plastic properties.

"The problem of devising a commercial synthetic rubber resolves itself into making a large number of polymers and copolymers of vinyl compounds and dienes under varying conditions and evaluating the polymers as rubbers. This polymerization can be carried out either undiluted in mass, in solvent solution, or in emulsion. All methods were tried in the laboratory. However, it soon developed that the control possible with emulsion polymerization warranted major effort on this process.

"Some idea of the tremendous amount of work required in the research on and selection of synthetic rubbers may be gathered from the fact that prior to Pearl Harbor there were prepared and evaluated in our laboratory 14,492 different synthetic rubbers. Of these less than 100 were considered worthy of pilot-plant trial for commercial development. The total number that have been produced and used on a commercial scale is only about a dozen.

"Butadiene forms the main basis for the molecular chain of the butadiene synthetic rubbers. The double bond remaining after the polymerization is responsible for the ability of the synthetic rubber to vulcanize. While the butadiene could be replaced in whole or in part by other dienes such as isoprene, dimethyl butadiene, or methyl pentadiene, butadiene as the sole diene yields rubber having the lowest hysteresis, highest rebound, and best low-temperature characteristics.

"Butadiene of high purity is required if the polymerization is to proceed rapidly to yield a uniform high quality rubber.

"While it is necessary that the butadiene used should polymerize rapidly and completely, nevertheless, this butadiene has to be stored and handled under conditions that would normally cause considerable polymerization. This paradox can be solved by adding to the butadiene in storage an inhibitor such as a mercaptan, an aromatic amine, or a phenol, and removing it before use.

"The function of the vinyl compound used as a comonomer is to increase the tensile strength and improve the plasticity of the copolymer.

"Styrene, the comonomer used in making GR-S, is cheap, readily purified, and gives a copolymer that is miscible with natural rubber.

"Acrylonitrile as the comonomer forms a nitrile rubber characterized by high tensile strength and low swelling in oils. Such rubbers are not miscible with natural rubber or with many other copolymers, and hence are usually considered specialty rubbers.

"Acrylate, methacrylate, or allyl esters as comonomers give high-grade rubbers.

"In some cases it is desirable to use more than one comonomer in a recipe.

"The ratio of diene to comonomer has an important effect on the processing characteristics of the polymers obtained. This ratio rather than the details of the polymerization controls the hysteresis, low-temperature properties, and oil resistance of the synthetic rubbers.

"In emulsion polymerization, water is the dispersing medium in which to carry out the reaction. It also keeps the rubber fluid, so that the heat of reaction can be controlled by repeated passage of the reacting mixture over the cooling surface.

"The fatty acid soap or other emulsifying agent used in the emulsion polymerization process serves to solubilize the reactants, so that the reaction starts in monomer oriented in the micelles.

"The most efficient solubilizing agents are soaps which form micelles at the temperature of the reaction. If the polymerization is to be run at a low temperature, soaps which are fairly soluble in water are required—namely, the myristates and oleates. At a higher temperature, less soluble soaps such as the palmitates and stearates are preferable.

"Many emulsifying agents are valueless for initiating polymerization. However, many of these do have real value in a polymerization recipe, since they may improve the stability of the latex and prevent build-up of polymer on the reaction vessel and pipes. Examples of these materials include sodium lauryl sulfate, sodium alkyl benzene sulfonates, and sodium dialkyl naphthalene sulfonates.

"Certain surface-active agents have been found to control the growth of the polymer chain.

"Polymerization accelerators are minor additives to the polymerization recipe which accelerate polymerization, first, by removing the inhibitors, or second, by combining with and making more active the usual initiators of polymerization.

"In carrying out a polymerization all of the major ingredients may be added and then thoroughly mixed. The reaction can then be started by a more or less 'trigger' action by adding the initiator. Polymerization initiators function by some chemical reaction which generates hot spots of sufficient local energy to start chain formation. Oxidation of one of the many reducing agents present in most polymerization mixtures, either as impurities, as monomers, or ingredients added purposely, such as the modifiers, will serve. The oxidizing agent to be used depends upon the temperature of the polymerization. At a low temperature, stabilized hydrogen peroxide is extremely satisfactory. At higher temperatures, more stable oxidation agents give better results.

"In general, with any specific system the lower the temperature of polymerization, the higher the quality of the resultant rubber. However, polymerization proceeds more slowly at lower temperatures; and, practically, it is necessary to operate at a high enough temperature to complete the reaction in a reasonable time. Polymerization, however, will occur in the entire range between 0° and 100° C. . . .

"Polymerization is a typical autocatalytic reaction characterized in general by an S-shaped curve. Usually, there is an induction period in which the reaction starts off slowly, gathering speed until it reaches a constant and maximum rate which is maintained until the reactants are approximately 75 to 80 per cent consumed. Thereafter, the rate drops. For example, a reaction may go 75 per cent to completion in 14 hours, yet require 30 hours to reach 95 per cent.

"In the manufacture of synthetic rubber latex, highly efficient agitation is not required. The main reason for agitation is to obtain gross mixing of the monomers with the aqueous phase and to bring the contents periodically in contact with the cool surface, to remove the heat of polymerization. . . .

"The rubber in the latex from which the monomers have been removed is still highly reactive chemically. In order to prevent isomerization, cyclicizing, or oxidation when the rubber comes in contact with the air, it is necessary to incorporate in the rubber from 1 to 3 per cent of antioxidant. This can be done conveniently by dispersing the antioxidant in water and stirring it with latex. . . .

"Most synthetic rubber is used today on equipment originally designed for natural rubber. Hence, the latex must be coagulated, washed, and dried to be in a form that can be handled on rubber mills."

Comparison of the views of these leaders emphasizes the progressive narrowing of the problem. Every research should proceed in that way whether it is a minor matter that one man can complete in a matter of hours, or if, as here, it is a world problem that has occupied an army of research men over more than a generation.

Every research should in a very real sense proceed after the fashion of light rays approaching a focus through a lens. Each experiment must narrow the field of possible solution a little even if by only a barely perceptible amount. The cumulative effect of several successive narrowings thus brings the solution of the problem into clearer and clearer focus as more and more information converges upon it. Finally the solution becomes inescapable.

Chapter 10

Three Illustrative Researches

"*A great part of every man's life must be employed in collecting materials for the exercise of genius. Invention, strictly speaking, is little more than a new combination of those images which have been previously gathered and deposited in the memory; nothing can come of nothing; he who has laid up no material can produce no combinations. The more extensive, therefore, your acquaintance is with the works of those who have excelled, the more extensive will be your powers of invention, and, what may appear still more like a paradox, the more original will be your conceptions.*"

—Sir Joshua Reynolds

In what has gone before, we have examined the characteristics of research as it is practiced for the benefit of industry. We have inspected it from the points of view of many successful practitioners of the art and we have attempted to reveal an underlying pattern that will help others who undertake to explore the borderlands of knowledge and to apply their findings to the very practical purposes of industry. But throughout our investigation it is always clear that, whatever pattern there may be, the business of discovery and its creative application can never be reduced to rote; there will always and inevitably be a vast amount of room for the exercise of all the imagination the researcher can muster. No one can gainsay the value of imagination, and its younger brother, ingenuity, to every researcher in meeting changing situations as his quest develops. Our review of significant researches demonstrates beyond peradventure the importance of meeting situations as they arise and of being prepared with a variety of attacks in case the changed direction of the research requires it. Quite obviously no single scheme of attack can succeed in solving every problem and the searcher who is best equipped with the greatest variety of methods is most likely to solve the greatest number of problems and them with the least waste of effort. To meet that need, this discussion has developed as many pertinent examples of variety of attack as it has been possible to include.

The three researches discussed in this chapter bring out three further and quite different aspects of the business of solving problems through research. The first example shows how an industry was rescued from failure by logical analysis of the causes of failure and their correction by the application of penetrating scientific investigation. Just as the original plan which led to failure seemed the obvious one to follow in the beginning, so does the method which converted the original failure into subsequent success. The difference lay in stating the problem in two different ways before undertaking its solution. The questions involved were primarily economic in spite of scientific bearings. Every step was taken under the eager watchfulness of the financial backers of the enterprise. That necessarily gave character to the work.

In striking contrast to this was the development of the important field of catalytic hydrogenation by Paul Sabatier, professor of chemistry at Toulouse, France. This work, for which Prof. Sabatier received the Nobel Prize in Chemistry in 1912, was undertaken and pursued throughout for its own intrinsic interest and quite without thought or regard for any economic or commercial implications it might have. Actually the principles developed by Sabatier have profoundly affected the usefulness and value of, among other things, the great bulk of the world's vegetable oil supplies and thus an important share of a vital food. But these considerations in no way affected the professor's thinking nor his eager pursuit of science for its own sake alone. Others following after took the subsequent steps to adapt and develop Sabatier's work to commercial purposes. Obviously these circumstances profoundly affected the research itself.

Finally, the researches of Robert R. Williams leading to the commercial synthesis of vitamin B_1, thiamin, sprang from humanitarian motives that seem to be as nearly pure altruism as one is likely to meet in this modern age. From its early stages this investigation was pursued as the extra-curricular activity of a man who combined scientific with humanitarian attainments. Remembrance of poignant scenes witnessed in childhood and youth of suffering of mothers and babies afflicted with beriberi supplied a potent driving force for more than a quarter century of research. Inevitably the whole enterprise took its character from these facts.

Not only do these three researches possess certain intrinsic interest of their own, but they also illustrate three different approaches to the solution of research problems. Nothing more is necessary to account for their inclusion here.

The problem of recovering potash, borax and other values from the alkaline brine of Searles Lake in the Mohave Desert, California, is described by John E. Teeple in his American Chemical Society Monograph on the subject:

"By 1912 the California Trona Company had in hand as the result of all investigations a voluminous report on the utilization of the brine (of Searles Lake) for the manufacture of potash, borax, soda ash, and sulfate of soda. The general method was the one which seems to make an appeal to almost any chemist the first time the problem is proposed to him, *i.e.*, carbonate the liquors and so remove all of the sodium carbonate as sodium bicarbonate or trona. This is filtered off and calcined to make soda ash. The filtrate is then subjected to successive evaporation, filtration and crystallization steps to obtain potash, borax and sodium sulfate, all dependent of course on the fact that the solubility of potassium chloride increases very much with temperature, that of sodium chloride remains almost stationary, and that of sodium sulfate has a definite curve that does not coincide with either.

"The report was probably unduly optimistic; the operations can be performed in the laboratory and the separation made without any question, but from a commercial point of view one can see that the report failed to take account of a good many rather important factors. The people who were interested in the California Trona Company and in the money that had been advanced to it were expert in mining matters, but not particularly strong on chemical manufacture. Therefore they could not be expected to foresee the difficulties, but they did take the very sensible step of passing the report to a very well-known firm of consulting chemists for confirmation and advice. Unfortunately the report of this firm likewise was unduly optimistic. As a result, the American Trona Corporation, which by this time had been organized to take over all the assets of the receivership as successor to California Trona Company and the bondholders, determined to build a preliminary plant to operate then on a small scale at Trona. By the end of 1914 the plant was finished on the same site that had been occupied by the California Trona plant, and before that by the San Bernardino Borax Mining plant. By that time, too, the Trona Railway, about thirty-five miles long, had been built to connect the plant with the Southern Pacific Railroad at Searles Station. Then the plant started on its preliminary run. Something went wrong. I do not know just what, nor have I been able to find any report or record in the archives. There apparently is nothing but tradition to rely on. Something went wrong. The trial run was never finished, the plant was abandoned, the process given up, and several hundred thousand dollars had disappeared—a total loss.

"This might seem to be an excellent opportunity for criticism, but I have none to offer. The company officials had apparently made careful investigation, and so far as they could learn had selected suitable men for the work and given them the facilities for carrying it out. The original proposer of the process and the plant had apparently done the best he knew how after careful investigation. The consultants had gone through a novel and difficult problem, had carried out the different steps themselves on a small scale and found nothing to prevent successful operation. Notwithstanding, the thing had not turned out well. All three parties to the transaction had been mistaken. But this is not an unusual situation even with the best of men and of corporations. It is cited here because it is typical of what so often occurs during the birth of a new enterprise or a new development. The problem at first looks simple, delightfully easy, just as this problem did, and almost any chemist would have undertaken it with a feeling of confidence and a sense of merely taking a short stroll before breakfast through a pleasant path in the woods. Soon the path begins to meander, obstructions arise, detours must be made, and before he realizes it his simple path has become a complicated maze of bypaths all apparently leading nowhere. Instead of being a peaceful stroller he has become a desperate struggler. The ones who do not die here keep on struggling until they finally emerge on good roads leading in a definite direction and things are again perfectly simple. This is the natural course of almost any novel enterprise, and this development of a potash industry is no different from the others. In 1912 it was strolling. There were a number of paths and they all looked straight and easy. In 1919 when I first saw it, it was still struggling, and now in 1928 it is on clear highways. All the participants in the incident related above have ceased any connection with the potash industry long ago and so the tale may be used to point a moral. The moral is, don't underestimate the difficulties of a new enterprise, and the fact is that we probably will the very next time a new enterprise presents itself. My only criticism begins at the point where the plant failed. There was no record of what happened. At that point there could be nothing to represent all the money that had been spent excepting information, and the information was not recorded."

From this point a new beginning had to be made which would not duplicate the failure of its predecessor. Teeple continues:

"It is obvious that any recovery of potash from a brine such as that at Searles Lake must involve concentration, that is, an increase in the percentage of potash either in salts or in liquor in relation both to water and to the other salts. The two plants operating on the lake had learned that they could get such an increase in percentage of potash in the brine by triple-effect evaporation at sufficiently high temperatures. This removed water by evaporation and salted out sodium carbonate, sulfate and chloride. The resulting concentrated liquor when cooled precipitated a salt rich enough in potash to market during the War (World War I) but it was known that considerable quantities of potash were lost with the waste salts. It was even known that the presence of sodium carbonate or mother liquors had some influence at times on the amount of potash that was lost in this way. Since, however, potash was known to be lost in three different ways, it was very difficult to get accurate figures from plant operation. First, the liquor foamed very badly in the pans and carried over potash to the condensers or to the belts of the other pans; second, potash in some combination apparently became insoluble in the liquors and actually precipitated along with the sodium chloride and sulfate; and, third, there was great difficulty in freeing the waste salts from the adhering liquors which were rich in potash. Consequently recoveries were comparatively small. An examination of the analysis (of the brine) indicates that at a minimum it is necessary to evaporate about 13½ pounds of water and separate and discard about 6 pounds of other salts in order to recover 1 pound of dry potassium chloride. In good triple-effect evaporation we expect to evaporate about 2.2 pounds of water from 1 pound of steam, so that we would expect to use a little over 6 pounds of steam to recover 1 pound of potash.

"Burning fuel oil of, say, 150,000 B.t.u. per gallon in a boiler house of reasonable efficiency we might expect to produce 120 or 130 pounds of steam from a gallon of fuel oil. Combining these figures we get a theoretical result of 100 gallons of fuel oil required at a minimum to furnish the steam needed for evaporating the water from 1 ton of potassium chloride if we have complete recoveries. Needless to say there are no 100 per cent operations in a plant. Actual practice does not approach very close to this figure. Actual consumption during the war period (World War I) was probably nearer 1,000 gallons per ton of potash than it was to the theoretical 100. I have frequently seen it well over 1,500. This consumption of several times the necessary amount of oil for evaporation could apparently be materially reduced by three different lines of attack, in addition, of course, to the ordinary improvements from increased efficiency in machinery. First, to stop the foaming in the pans and consequent loss of potash from entrainment; second, to improve the separation and washing of waste salts and thus prevent loss of potash adhering to these salts in the form of brines on which work had been done; third, to study the equilibrium conditions in the pans themselves and so to avoid the possibility of the liquors becoming saturated with some potash salt and precipitating it among the waste salts. The first two problems seemed to be essentially questions of plant operation. The third one very clearly demanded long laboratory study of solubilities, in terms for the layman, or of phase rule application as the chemist would say. Perhaps it would not be out of place to give the impression received in 1919 as quoted from a report which I wrote at that time:

" 'You have present only sodium and potassium combined as carbonates, bicarbonates, chlorides, sulfates, metaborates, and biborates, and at nearly every step of any process you have ever used or may use in the future, you are dealing with a solution that is saturated with respect to some one of these compounds, and so is salting it out; or you are dealing with a solution which is unsaturated with respect to one of them, and so is dissolving it.

" 'Before you began any operation or process six years ago, then, your natural course would have been to study these solubilities; to make solubility curves covering the range of temperature between, say, −20° C. and 110° C., and covering all reasonable variations in concentration of the individual constituents. Any good physical chemist could have done this for you. With such information in hand, you would be able to discuss any possible process intelligently. Without it you are entirely at sea. Notwithstanding the fundamental importance of such information for your work, I cannot find that any effort was ever made to obtain it until within a week or two of my visit to Trona. The work done in that last week or two was only preliminary, probably inaccurate, and covered only a couple of arbitrary conditions of the many possible ones; but notwithstanding, I gathered a more intelligent basis of judgment from these few curves than from any other single source at the plant.'

"These comments on lack of proper research work, when taken by themselves, may seem a bit rude and forceful, but in my experience clients desire to be told the plain truth. The statements would have been just as true regarding any other potash plant in America. For that matter, many other industries besides potash fall into the same error. To act first and do the considering afterward is rather typical of pioneer work, and America is still largely a nation of pioneers in business. A beautiful example came to my attention only a few years ago. We were all familiar with the roadside scene of a flat tire, a hand pump, and a man bathed in perspiration and profanity. An inventive genius, seeing these scenes often, conceived a brilliant business idea. Sell everyone a cylinder of compressed gas to carry in the car. No more hand pumping. Simply connect the gas cylinder to the tire, turn a cock, the tire in inflated, disconnect, and drive on. Now carbon dioxide is cheap, very compressible, and a small cylinder will hold a lot of it. There you have the idea on which an enormous business could be built. The next steps were patent application, company organized, financed, plant production arranged, cylinders bought, literature prepared, and then, but apparently not till then, someone tried it. Alas, a rubber tire will not hold carbon dioxide. That gas is just about as effective for inflating rubber tires as water is for filling a sieve.

"Naturally when I was invited to take some responsibility in rejuvenating the American Trona Corporation and in making my own recommendations effective, an intensive study of the equilibrium of the constituents in Searles Lake brine was one of the earliest tasks. The work began in 1919 and continued intermittently, as data were needed, through several years. This was a utilitarian study. An accuracy of ±0.3° C. was maintained. In analyses the accuracy required was usually ±0.3 per cent of the total. The limits of temperature checked were +20° to 110° C., and only those systems and those temperatures were studied which might throw some light on our problems of manufacture. The industrial man feels called upon to place rather definite limits about his research activities, while the scientist in pure research may roam gaily over any field that attracts him.

"The important constituents of Searles Lake from our point of view are the sulfates, chlorides, carbonates, bicarbonates, borates and metaborates of sodium and potassium, or Na, K, H, SO_4, CO_3, B_2O_4, Cl, H_2O, a seven-component system. A complete study of this would include

8 systems of 6 components
25 " " 5 "
39 " " 4 "
32 " " 3 "
12 " " 2 "

and there are, of course, several other components of interest in the lake besides these seven, such as phosphates, arsenates and bromides, for example. All of the twelve two-component systems were adequately studied long ago as can be seen from any handbook or table of solubilities. The same is true of many of the three-component systems. The information we needed, however, related chiefly to systems of four and five or more components, and this was almost a virgin field so far as it concerns the particular group of salts in Searles Lake. The little that had been published was by van't Hoff, D'Ans, and Blasdale, and covered only one four-component system (the chlorides and sulfates of potassium and sodium). The three investigators were not in entire accord with each other on that one system."

That analysis of the basic problem and the results of the long series of phase rule studies undertaken to implement it provided the basis for a successful enterprise supplying potash salts and borax in competition with other sources.

Contrast the direct, purposeful attack by which Teeple solved his problem with the leisurely but meticulous method which characterized Sabatier's progress toward catalytic hydrogenation of organic compounds. On a visit to this country in 1926 after his retirement from active life, Sabatier described his outstanding research to American chemists:

"Coming from l'Ecole Normale, where I had followed the lectures of Henri Sainte Claire Deville and performed my first laboratory work, I became an assistant of Berthelot at the College of France and was directed by him at first toward thermochemical matters. I naturally was obliged, under the influence of these two illustrious masters, to direct my researches toward general chemistry—thermochemistry, chemical equilibriums, reaction velocities, absorption spectra—and toward mineral chemistry—sulfides, selenides, chlorides, and hydrochlorides, nitrosulfuric acids, basic salts, etc.; and it would have astonished me greatly if, during the first twenty years of my scientific career, it had been predicted that I should work principally in organic chemistry and that in this field I should obtain the most important results.

"In 1890, Mond, Langer, and Quincke announced that by the direct action of carbon monoxide on very finely divided nickel, prepared by reduction from its oxide, there was obtained a volatile compound, nickel carbonyl, resulting from the fixation on the metal of incomplete (unsaturated) molecules of gas, and they indicated that reduced iron yielded an analagous compound. I was very much impressed with these results, and I asked myself if other incomplete gaseous molecules—nitric oxide, nitrous oxide, nitrogen peroxide, acetylene, ethylene—could not, in the manner of carbon monoxide, be fixed on nickel or on reduced iron, in giving well-defined, stable, and volatile products comparable to nickel carbonyl.

"With the collaboration of one of my pupils, M. Senderens, who had just undertaken his doctorate thesis, I tried first of all nitric oxide, NO, the incomplete character of which is so clearly affirmed by its spontaneous combination with oxygen. But our tests with nickel, cobalt, iron, and copper were negative and, at temperatures more or less high, would give only reduction of nitric oxide to nitrogen, with formation of protoxides NiO, CoO, FeO, and of the red suboxide, Cu_2O. We were not very fortunate with the nitrous oxide, N_2O. But in making the vapors of nitrogen peroxide, NO_2, act on copper recently reduced from its oxide, we observed that at ordinary temperature there is a regular fixation leading to a definite compound, solid and nonvolatile, nitrated copper, Cu_2NO_2. Reduced cobalt, reduced nickel, and reduced iron yield analogous reactions, but the products are less stable.

"We ended this work in 1896, and we were prepared to try the fixation of acetylene on the same metals when we learned from the *Comptes rendus* of the Academy of Sciences that the experiments had just been attempted by MM. Moissan and Moureu. Having turned a current of acetylene on slivers of iron, nickel, or cobalt recently reduced from their oxides by hydrogen and chilled in this gas, they observed a brilliant incandescence. The high temperature thus produced decomposed the greater part of the acetylene into hydrogen and a large amount of carbon which was not long in filling up the tube. The rest of the acetylene yielded liquid hydrocarbons, which closely resembled those which Berthelot had obtained by heating acetylene to dull redness in a bell inverted over mercury.

"According to the two scientists, the porous metal absorbs the acetylene with production of sufficient heat to cause its spontaneous destruction. As it is very endothermic, incandescence is reached and is maintained as long as the acetylene enters, and this incandescence determines the polymerization of the acetylene into liquid products. However, they neglected to analyze the free gas, which they judged to consist of hydrogen, and they examined the liquids only sufficiently to recognize the presence of benzene.

"This publication left me greatly disappointed and tended to destroy my hopes of fixation. But the explanation of the phenomena which the authors gave appeared to me inexact, and in my opinion they should be interpreted entirely differently.

"On the mechanism of catalytic actions in general, whatever might be their nature, my ideas were very different from those usually admitted—ideas which I owed certainly to the influence of my master, Berthelot. I thought, and I still think, that in all cases the catalyst acts with one of the agents of the reaction, or of products which could result from it, in yielding a temporary unstable compound. For example, in the case of porous platinum sponge acting on a mixture of hydrogen and oxygen, its catalytic activity for combining them is due, not to a physical condensation of the gas in the pores of the metal, causing a local elevation of temperature sufficient to unite them, but to a truly chemical combination at the surface of the platinum with the oxygen in a sort of suboxide, which acts immediately upon the oxidizable matter, here hydrogen, in producing some water and regenerating the metal, which indefinitely continues the same effects.

"In the experience of Moissan and Moureu, the cause of the phenomenon seemed to me to be the affinity of metal—nickel, cobalt, or iron—either for acetylene or for its constituents, carbon or hydrogen, extracted by them from the endothermic molecule of gas.

"Moreover, Moissan, who on account of his brilliant work on fluorine and on the electric furnace had withdrawn from organic chemistry, was not greatly interested in this reaction, which he considered solely as a curious experience. If he had analyzed the liquids, he would have discovered the saturated hydrocarbons unattacked by the sulfonitric mixture. If he had analyzed the gas, he would have recognized that the hydrogen is only present in a small proportion and that there is found a large proportion of ethane. Moreover, if he had taken the precaution, after reduction of the oxides by hydrogen, to cool them, not within this last gas but within a current of pure nitrogen, to eliminate the hydrogen condensed or combined in the metal, he would have found that the flow of acetylene no longer determined a spontaneous incandescence, and that to release it he would have to heat it to 300° C. This proves that the determining factor is hydrogen condensed on the porous metal, or rather the hydride which covered its surface.

"I did not wish, by scientific courtesy, to take up immediately the experience of Moissan and Moureau. Having learned from an authoritative source that they did not think of pursuing it, I decided the following year, in 1897, to begin it, not at first with acetylene, but with a hydrocarbon less violent in its reactions, ethylene, bivalent carbide, which permitted me to expect a fixation resembling that of nickel carbonyl.

"With M. Senderens, I directed a current of ethylene upon slivers of reduced nickel. No action was produced in the cold, but if the temperature was raised progressively, around 300° C., a brilliant incandescence of the metal was noticed, which disappeared in a voluminous deposit of black carbon, proving the destruction of the ethylene. But the gas which issued from the apparatus contained only a little hydrogen and was mainly ethane. The latter could only proceed from a hydrogenation of ethylene not destroyed, and this hydrogenation had been without doubt provoked by the presence of nickel. This permitted us to predict that the reduced nickel possessed the property of hydrogenizing ethylene.

"This we immediately verified. If a mixture of equal volumes of ethylene and hydrogen is conducted through a bundle of slivers of reduced nickel, very lightly heated (30° to 40° C. is sufficient), one-half the volume of pure ethane is obtained, and the reaction continues indefinitely without the necessity of heating and without an appreciable modification of the metal. At a higher temperature, around 150° to 180° C., it is still more rapid, and a few centimeters of metallic slivers are sufficient to accomplish it.

"Nickel obtained by the reduction of its oxide is also found to be a remarkable catalyst of hydrogenation of ethylene.

"The following year we discovered that it possesses the same power with respect to acetylene, which starting from the ordinary temperature is changed to ethylene, then to ethane, according as in the mixture of acetylene it is treated with its own volume or a double volume of hydrogen.

"We have, moreover, proved that reduced cobalt, iron, and copper, as well as finely divided platinum sponge, or black, possess an analogous but less energetic action.

"This special power of reduced nickel seemed to us so perfect that we thought of generalizing it, and we attacked a case of hydrogenation, which up to that time had not been realized by any method, that of benzene. Berthelot had attempted to effect it with his universal agent of hydrogenation, a concentrated solution of hydriodic acid at 250° C. But instead of cyclohexane, which boils at 81° C., he had prepared only its isomer, methylcyclopentane, which boils at 69° C. Under the influence of the hydriodic acid the hexagonal nucleus was transformed into a substituted pentagonal nucleus.

"It was with a real emotion that we proceeded to this decisive test. The benzene vapors, carried along by a current of hydrogen in excess, were directed over a bundle of reduced nickel, maintained at 200° C.; the gases issuing from the tube were sent to a U-tube surrounded by ice, within which the vapors of cyclohexane should be expected to condense to a liquid state. The operation seemed to proceed well from the beginning, the velocity of hydrogen issuing from the condenser tube seeming very little less than that at the entrance. But after boiling for a rather short time the gas ceased to pass, the U-tube was stopped up by the condensation of a solid product, which it seemed could only be benzene, solidifiable at 4° C. —that is to say, within the ice—whereas we had seen in the literature that cyclohexane, extracted from Caucasian petroleum by Markovnikov by means of 110° C. fractional distillations, was condensed to a solid which melted at −11° C. But our despair was of short duration and was changed to a very lively joy, when on opening the

U-tube we perceived, instead of the odor of the original benzene, the special intermediate odor between that of chloroform and that of the rose, which belongs to cyclohexane. The condensed product was cyclohexane, entirely pure, melting, not at −11° C. but above 6° C., absolutely unattacked by the sulfonitric mixture. The transformation of benzene had been complete.

"The power of finely divided nickel as a catalyst of direct hydrogenation was also demonstrated and, therefore, we had only to verify this power for the most diversified compounds.

"Thus all the compounds possessing a double ethylene linkage —hydrocarbons, alcohols, acids—take up very easily around 180° C. a molecule of hydrogen under the action of reduced nickel. All the unsaturated hydrocarbons of cyclic nuclei, homologous with benzene—polyphenyls, naphthalene, anthracene, etc.—easily take up hydrogen at their double bonds and are thus converted to the corresponding saturated hydrocarbons. The phenols furnish the cyclohexanic alcohols. Aniline and its homologs fix in the same manner six atoms of hydrogen for generating cyclohexylamine and similar amines. The aldehydes and the aliphatic acetones are, without any difficulty, changed to corresponding alcohols. The nitriles lead in the same way to the amines.

"With the same facility we have been able to realize the hydrogenations accompanying the simultaneous formation of water, synthesis of methane starting from the carbon monoxide or carbon dioxide, preparation of the amines starting from the nitro derivatives, from the amides or the oximes. . . .

"These direct fixations of hydrogen in the presence of reduced nickel in the neighborhood of 180° C. are usually very easy and frequently give very high efficiencies without any difficulty. But this is accomplished only by using carefully prepared nickel and pure hydrogen, and avoiding the presence of any substance capable of forming with the nickel a combination irreducible by hydrogen, thus diminishing the active surface of the catalyst. The role of such a substance is analogous to that of living microorganisms in fermentations. A poison introduced into the liquid kills the ferments and suppresses their useful action. In the same way, the metallic ferment, which is the nickel catalyst, is killed by traces of chlorine, bromine, and sulfur, and thus neglect of sufficient precautions explains the failure that so many chemists experience in certain hydrogenations, such as those of benzene and phenol.

"I should acknowledge that in this respect M. Senderens and I have had very good fortune. Naturally we were ignorant, at the beginning of our labor, of the extreme susceptibilities of the metal catalyst, and from the first, instead of ourselves preparing the oxide destined for the reduction, we made use of an oxide bought on the market, which fortunately was found good. By good fortune also, our benzene and our phenol, bought it is true as pure, were so in reality. But if there had been in the benzene a small portion of thiophene or of chlorobenzene, we would not have discovered any hydrogenation and, discouraged by this accidental failure, we would perhaps have attributed it to the direct impotence of nickel in this particularly difficult case of hydrogenation.

"Let me cite a very striking example. We prepared some cyclohexane by the direct hydrogenation of phenol. The reaction proceeded regularly for two days, interrupted each evening but resumed the following morning. The slight oxidation which the nickel was able to undergo during the night in the chilled tube was not a disadvantage, since at the temperature of operation, around 180° C., the oxide of nickel is converted to the metallic state. Suddenly we discovered that the phenol was no longer transformed, and the preparation resumed with new nickel and the same phenol gave again a negative result. I remember that during the operation, a little while before the check of the catalysis, I had uncorked a bottle of bromine not far from the vessel which contained the phenol. The traces of bromophenol dissolved by this latter rendered it incapable of being transformed into cyclohexanol.

"I have seen in these actions a succession of purely chemical phenomena. The hydrogen coming in contact with the nickel forms very quickly on the surface of each grain a very slight coating of a very definite hydride, such as NiH_2 or Ni_2H_4, dissociable and capable of yielding rapidly its hydrogen to hydrogenizable substances in regenerating the nickel, which continues indefinitely the same effect. The activity of this nickel should, moreover, be all the stronger as the surface of the grains increases in proportion to their mass.

"The liquid state of hydrogenizable material seems incompatible with the physical theory of the cavities where the compression of the gas determined the combination. On the contrary, it does not seem to be an obstacle to the formation of a temporary compound of the metal and hydrogen. In 1903, Mr. Crossley, of Warrington, England, asked me if I thought that the direct hydrogenation of olein and its transformation into stearin would be possible by reduced nickel working on the liquid olein. I answered in the affirmative, estimating that it would without doubt act violently enough so that the grains of nickel immersed in the olein would be constantly brought in contact with the hydrogen. This was the beginning of the great industry of the hardening of oils, which has been so greatly developed in certain countries and particularly in the United States.

"The hypothesis of the hydride of nickel formed directly by the hydrogen on the surface of the grains was remarkably supported by the observation of Schlenk and Weichselfalder, who were able, by the action of hydrogen on a colloidal solution of nickel, to prepare a brown flocculent hydride, NiH_4, which dried in the hydrogen becomes NiH_2, and which possessed remarkable abilities as a direct hydrogenizing agent. Another result of the theory of the temporary hydride is that it tends equally to produce at the beginning some substances which retain hydrogen only slightly. The hydride thus produced dissociates very quickly in liberating free hydrogen and regenerating nickel capable of reproducing indefinitely the same effect. We also foresaw that the nickel catalyst of hydrogenation would also be a catalyst of dehydrogenation, and that it would be the same with the other finely divided metals—copper, cobalt, iron, platinum. Experience has proved that this is very much the case."

Robert R. Williams first encountered the dread effects of beriberi, as we have noted, when as a young man he was employed as a research chemist in the Bureau of Science of the Philippine Islands. That was in 1910 just after the connection of rice polishings with beriberi had been established and announced, and that too was the beginning of 25 years of labor that culminated in his synthesis of thiamin. At that time Williams was working with the Army's Bureau of Tropical Medicine then actively studying the disease. Previously, as a child in India, he had seen the effects of hunger but only later knew it as beriberi. Here, in part, is Williams' account:

"Beriberi was very prevalent in Manila. There, as is usual elsewhere, it takes two forms of similar character except that the so-called wet type shows extensive edematous swelling of the extremities; in the dry type muscular atrophy is externally conspicuous. Lameness, ataxia, numbness of the extremities, and loss or exaggeration of patellar reflexes reveal a disturbance of the motor and sensory nerves. In its more acute stages there is labored breathing and cyanotic discoloration about the mouth and nose which suggest a disturbance of the respiratory function; this suggestion has been confirmed in recent years by the finding of pyruvic (*i.e.*, acetoformic) acid in beriberic blood and analogous to acetoacetic acid in diabetes. Hypertrophy of the right heart occurs and death ensues from heart failure.

"Especially destructive is the infantile form of the disease. About 25 years ago this form of the disease was first reproduced in puppies and thus identified by Andrews in Manila. For this purpose Andrews suckled puppies at the breast of human mothers who had just lost their babies of the then mysterious disease *taon*. The enlistment of these bereaved, poor, and ignorant mothers in the cause of science required some diplomacy. Andrews says one mother refused to nurse a puppy until its eyes were open. Infant mortality in Manila regularly reached the staggering figure of 50 or even 55 per cent. In contrast to western cities, mortality was much greater among breast-fed than among bottle-fed babies in spite of the unsanitary tropical milk supply. No more eloquent testimony to the deficiencies of the prevailing human dietaries could be found. Mothers who lacked an unknown element secreted a deficient milk. Later evidence suggests that it is also poisonous.

"Undertaking the work under such circumstances, it was natural that the chemist should be drawn into personal contact with the disease and, in company with his medical associates, test the progress of his chemical fractionations of rice polish not only upon experimental animals but upon human patients as well. The most prevalent form of beriberi is of a chronic or rudimentary type, most conspicuous among women of childbearing age. Treatment of such cases brings about a gradual improvement over periods of weeks or months. However, in acute beriberi, especially in infants, response is usually dramatic. On several occasions in the absence of a medical associate, I went at the call of a public health inspector to the Tondo slum district of Manila to attend without benefit of medical certificate reported cases of beriberi. Often I dosed the baby myself to be sure to get as much of my precious preparation inside and as little outside the baby as possible and sometimes sat down beside the anxious mother on the split bamboo floor of the little nipa shack to await results. Within as little as 3 hours I have seen the cessation of the weird, almost soundless crying which, due probably to paralysis of the larynx, is characteristic of the last stage of the malady. Easing of the gasping breathing soon followed, and then the smoothing of the wild-pulse, the fading of blue lips, a hungry nursing and peaceful sleep.

"Observing such profound effects, the young and impressionable chemist inevitably conceived the desire to know what was responsible for them. The crude rice polish preparations were variable and uncertain in their action, and their use could throw little light upon the function in the body of the beriberi-preventing substance which later came to be called vitamin. We know now that crude rice polish extracts contain only 1 part of vitamin in 50,000. The search was destined to last 25 years and to enlist the talents of biochemists in every civilized country of the world. Fortunately we did not know that then. Jansen in Java was the first to isolate the substance in pure form. Windaus in Germany 6 years later showed the presence of sulfur in the molecule. However, an efficient means of obtaining the substance in quantity for chemical study was still lacking. This we accomplished in 1933 using the methods of Funk, Seidell, and Jansen; these methods were reinforced by our own expedients, notably the use of quinine for the elution of the vitamin from fuller's earth which is used as an adsorbent in an early stage of the process. For years the sole objective of our work was increased efficiency of process so that we should at the end obtain enough vitamin to study it. Such work requires some patience and skill; it requires vastly more faith and courage, and a rigorous adherence in spite of disaster to one's ideal and objective. To the intestinal fortitude of those who joined me in this enterprise I pay just tribute. With these I include Seidell in America, Peters in England, Suzuki and Ohdake in Japan, and Jansen's group in Java, all of whom persistently hammered at this all-important objective through long and difficult years.

"At last we had in sight a gram or two of vitamin. We had to be sure it was pure; otherwise the analysis for carbon, hydrogen, nitrogen, and sulfur would only be misleading. Wrong information is worse than none at all. Its composition turned out to be $C_{12}H_{18}N_4SOCl_2$.

"In order to determine the structure, it was necessary to split the molecule into progressively smaller pieces until they could be recognized as previously known substances. Knowing the identity of each fragment, we might hope to learn how to put them together again to form artificially the original substance. In these phases of the project we enlisted first H. T. Clarke and later E. R. Buchman and J. K. Cline. Each contributed important ideas and skill in the study of structure and synthesis. This work is, therefore, the accomplishment of a group rather than of an individual.

"Over a period of 2 or 3 years we had worked up several tons of rice polish in 300-pound lots. Merck & Company then undertook the same process on a much larger scale and were soon providing not only for our experiments but also for others.

"We had the good fortune at the outset of the structural work to hit upon a useful cleavage reaction of the vitamin picked from our past experience in its isolation. In the presence of sodium sulfite at a pH of 5 the vitamin splits neatly and quantitatively without the loss of an atom according to Equation (1):

$$\text{(1)}\quad C_{12}H_{18}N_4OSCl_2 + Na_2SO_3 \rightarrow \underset{\text{I}}{C_6H_9N_3SO_3} + \underset{\text{II}}{C_6H_9NSO} + 2NaCl$$

$$\text{(2)}\quad \underset{\text{I}}{C_6H_9N_3SO_3} \xrightarrow{HCl} \underset{\text{III}}{C_6H_8N_2SO_4}(=C_6H_6N_2\cdot SO_3H\cdot OH) + NH_3$$

"Product I of the sulfite cleavage proved difficult to identify. It is insoluble in organic solvents, very sparingly soluble in water, readily soluble in alkali, and infusible up to 440° C. As shown in Equation (2), on reaction with aqueous hydrochloric acid, product I splits out ammonia and yields product III, also infusible crystalline substance. Product I or III yields sulfuric acid on heating with water at 200° C. and sulfurous acid on fusing with alkali, indicating the presence of a sulfonic group. Significant organic residues could not be isolated.

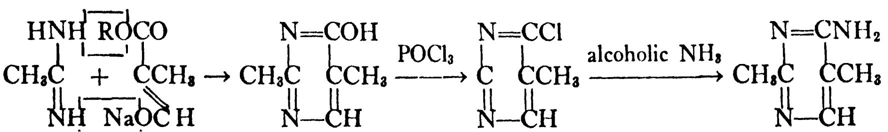
"We had long suspected from its ultraviolet absorption spectrum that product I, which we will call an aminosulfonic acid, contains the pyrimidine nucleus and that the amino group is in position 6. This conclusion was based not only on the absorption but also on the difficulty of splitting out ammonia, and the fact that this amino group, although primary, reacts with nitrous acid or with benzoyl chloride only under vigorous conditions. The task we were now facing was to find where the sulfonic group is located and where the extra two carbon atoms are in the aminosulfonic acid which has the composition $C_6H_9N_3SO_3$.

"The spectrum of this aminosulfonic acid is single-banded in acid solution; it shows vestiges of a second band in water solution and becomes definitely double-banded in alkali. A similar behavior with acid and alkali is observed in 6-aminopyrimidine and all its alkylated derivatives. This series of compounds, several of them new to chemistry, were synthesized for the purpose. For brevity we must omit many details and pass on to later experiments that supplied conclusive evidence.

"Equation (3) shows a reduction of the aminosulfonic acid with sodium in liquid ammonia,

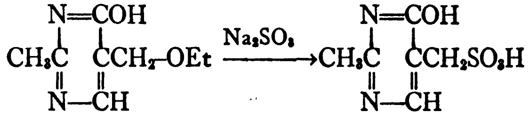
$$(3) \qquad C_6H_9N_3SO_3 + 2Na \rightarrow C_6H_9N_3 + Na_2SO_3$$

yielding a base $C_6H_9N_3$, whose picrate proved on mixed melting point to be identical with that of 2,5-dimethyl-6-aminopyrimidine, the synthesis of which is indicated in Equation (4):



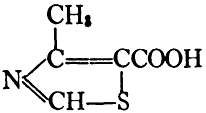
This valuable piece of evidence settled at once all question of the 6-aminopyrimidine grouping and also fixed the number and position of the side chains. Equation (5) indicates a synthesis which yielded 2-methyl-6-oxy-5-pyrimidine methylsulfonic acid:

(5)



This was proved by absorption spectrum and otherwise to be identical with the oxysulfonic acid (product III) derived from the vitamin. This settled the structure of the pyrimidine half of the vitamin.

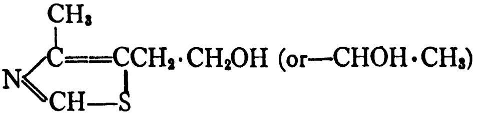
"We now return to the sulfite cleavage reaction and consider the other half of the molecule, although chronologically the work was done in the reverse order. Product II of the sulfite cleavage [Equation (1)] is a weakly basic oil and is chloroform-soluble. Nitric acid oxidation yields product IV. This product is identical with one previously obtained by Windaus by oxidizing the vitamin itself with nitric acid. Although Windaus regarded it as a pyrrole derivative, such an oxidation without loss of sulfur, as well as other facts, suggested to H. T. Clarke a thiazole nucleus. A literature search showed that the compound corresponded in melting point and composition to 4-methylthiazole-5-carboxy acid, synthetically prepared by Wohman in 1908:



IV. *4-Methyl-thiazole-5-carboxy acid*

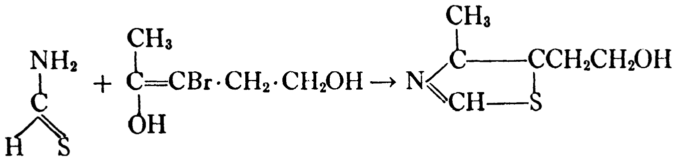
The thiazole nucleus had never before been found in nature. It is probably quite important to the physiological action of the vitamin.

"These findings enabled us to conclude that the original sulfite cleavage product must have one of two structures:



The latter could be excluded by the optical inactivity of our product. Its identity was confirmed by the following synthesis:

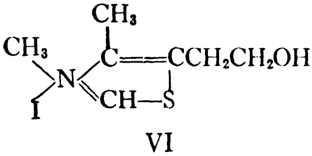
(6)



Thio-formamide *Bromoacetopropyl alcohol (enol)* V. *4-Methyl-5-(β-hydroxy) ethylthiazole*

"Having established the structure of the two fragments produced by sulfite cleavage, we shall consider the relationship of the two nuclei to one another. Obviously the sulfonic group serves as a flag to mark on the pyrimidine portion the original point at which the thiazole nucleus was attached to it. But which atom of the thiazole was involved in this linkage?

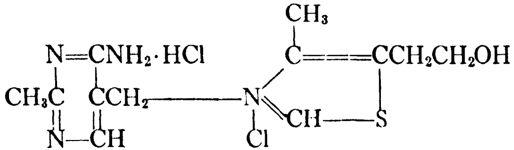
"We had noted that the vitamin whose habits suggest it to be a strong base is split by sulfite into a slightly acidic and a slightly basic substance. This loss of basicity by cleavage with a neutral reagent suggested the disruption of a quaternary ammonium base or a sulfonium base. Methyl iodide was found to add to the thiazole half of the vitamin molecule to produce a quaternary base in the familiar way. This methiodide (product VI) betrayed a peculiar and striking kinship to the vitamin:



VI

"Potentiometric titration of the quaternary methiodide, product VI, with alkali showed no sharp break when 1 mole was reached, and only after 2 moles had been added did the pH move upward, indicating the presence of an excess. In the case of the vitamin chloride, we are dealing with the salt of a diacid base, since there are two ionic chlorines in the molecules as we have seen in the empirical formula. On titrating this chloride with alkali, we found a sharp rise when 1 mole was reached, corresponding to the formation of neutral or monoacid salt, but from that point onward it behaved like the methiodide of the thiazole with no further break until a total of 3 moles had been added. The parallelism of the two compounds in respect to this extraordinary behavior left no doubt that the vitamin is a quaternary thiazole.

"With this piece of information, we can now write the complete formula of the vitamin:

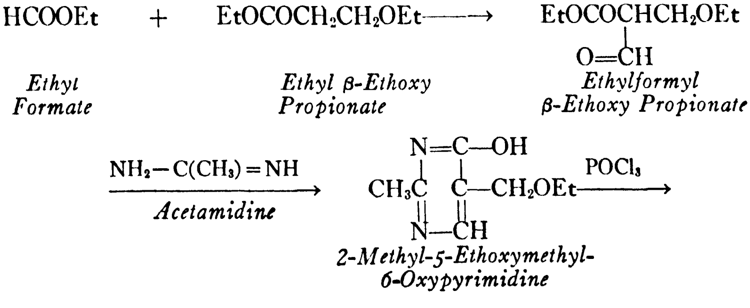


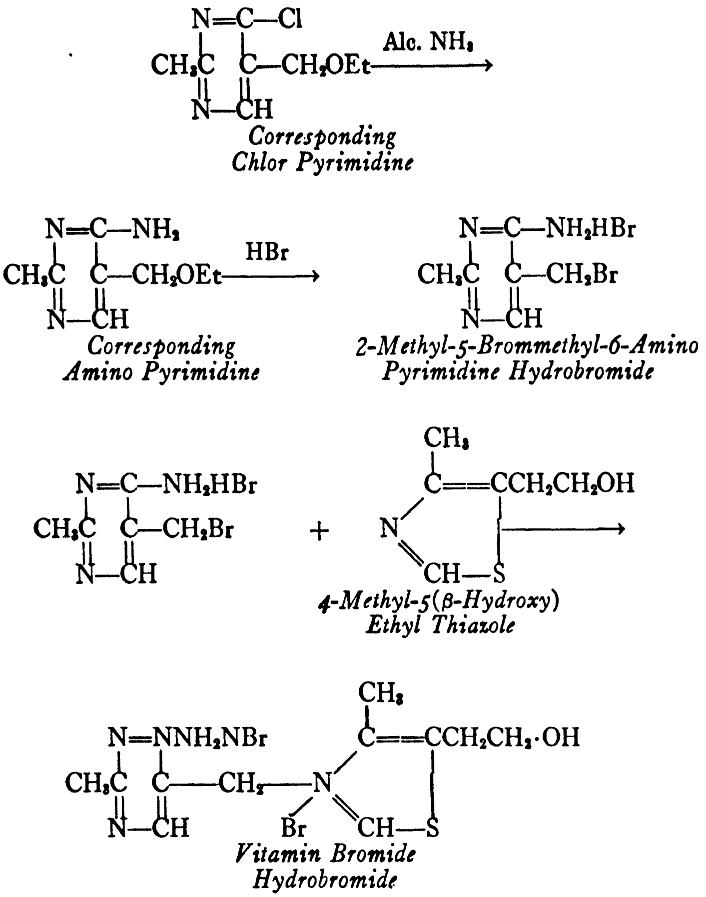
VII. *Vitamin chloride hydrochloride*

"The action of alkali may be explained as follows: One mole of alkali reacts with the diacid salt and liberates the monochloride; further addition of alkali begins to liberate the strong quaternary base, but this is not stable; the hydroxyl group goes over rapidly but not instantaneously to the 2-carbon atom to form the neutral pseudo base or carbinol. Such a process of migration of hydoxyl is well known in cyclic quaternary bases. In effect it uses up hydroxyl ions and prevents the pH from rising. Nor does the pH rise even when 2 moles have been added because quaternary thiazoles such as this undergo ring opening in alkaline solution, forming an acidic sulphydryl group. Only when this group is neutralized with a third mole of alkali does the alkalinity rise sharply. On adding an acid, the whole series of reactions undergoes reversal and the vitamin is regenerated.

"The confirmation of the structure by synthesis of the vitamin proceeds according to the following series of reactions:

Synthesis of Vitamin





Corresponding Chlor Pyrimidine

Corresponding Amino Pyrimidine

2-Methyl-5-Brommethyl-6-Amino Pyrimidine Hydrobromide

4-Methyl-5(β-Hydroxy) Ethyl Thiazole

Vitamin Bromide Hydrobromide

"The resulting bromide hydrobromide has the typical physiological properties of the vitamin and can be converted by shaking with silver chloride into the more familiar chloride hydrochloride, identical in every way with the natural product. Needless to say, the product can be produced much more cheaply by synthetic means. It is now commercially available in quantities corresponding to thousands of tons of rice polish. Its cost is a fraction of that of the natural substance in the pure state.

"The first trial of this synthetic product on polyneuritic rats represented the most tense and dramatic moment of 26 years of research. It was with much elation that I translated the conservative report of the pharmacologist into the message, 'The rats say yes.' "

Chapter 11

The Pilot Plant and What Happens There

"The most apparent and probably the most impressive differences between research today and forty years ago are the prodigious scale on which it is now conducted and the incredible diversity of activities to which the scientific method is applied. . . . We no longer await the explosions of inventive genius. Our present system of organized research places in the hands of genius all the facilities at our command, thus not only hastening his progress but providing the best means of translating his results promptly to utilitarian purposes. The system has further advantages. The cumulative results of the day-to-day application of scientific methods in our research laboratories has given mankind many of the beneficent things we did not have twenty, ten, or even five years ago." —Frederick M. Becket

Chemical processing involves numerous factors not well understood and hence difficult to evaluate. Theory and the operations of the laboratory are so far unable with certainty to convert a bare idea directly into a going manufacture. When in the exceptional case this is attempted, the operation of the full-scale plant is subject to such hazard from the failure of little things, and some not so little, that the cost of interruptions, spoiled goods and wasted time usually runs to many times the reasonable cost of the intermediate pilot plant step. The pilot plant, invented by the chemical industry to ease this transition from grams and ounces to pounds and tons, possesses other important values, as we shall see, and these must also be taken into consideration.

Baekeland described the pilot plant as an instrument to "make your mistakes on a small scale, so that your profits can be on a large one." Kettering characterized the pilot plant as "a bridge across the shirt-losing gap" between laboratory experiment and plant production.

In a very real sense the pilot plant is the halfway house of chemical industry, for all the different phases of industry meet here. Here the research chemist puts his reactions to their first test of production, but on a scale that avoids bankruptcy if they fail and destruction of the physical plant if they run wild. The plant operating departments can here subject their processes to searching scrutiny looking for improvements by varying operating conditions, and they can do this without interrupting regular production. By operating processes in the pilot plant on a scale large enough to give meaning to measurements taken from them, the engineering department can determine most, if not all, of the facts that it requires to arrive at an efficient design for the full scale production plant. Pilot plant operation can readily supply small quantities of a new product, or a new modification of an old one, for distribution by the sales department to prospective users; from these a dependable estimate can be made of market possibilities, covering quality, quantity and price of the product. When all of these data are assembled and correlated, management has available a penetrating analysis of all the facts on which to base its decisions in a specific situation.

Obviously then the pilot plant can, when properly used, safeguard the judgments of all concerned in the success of any enterprise. At the same time, it provides a reasonable and practical meeting ground for settling differences and forming policies for the future that is more logical than the usual conference room. Here every aspect of each problem can be studied with great care and here the interchange of ideas and points of view between the several groups constituting the company's staff can take place on the common ground of determined facts.

An instrument so potent for the good of an organization must of necessity be handled with skill and understanding if all its possibilities are to be realized. The pilot plant can yield abundantly if it is (1) amply equipped, (2) staffed by capable persons, and (3) well understood by all departments.

A genius might possibly be able to produce results from a pilot plant whose equipment is drawn entirely from the junk pile of the maintenance department's final discards. A genius might also be able to run a pilot plant effectively using only the part-time services of the janitor and the office boy with a call on the attention of the third assistant chemist on Lincoln's birthday and alternate Saturday afternoons. A genius who could do those things would certainly not worry about whether the sales and operating departments would use his findings or the engineering department know of his existence. But since we are far more interested in average research workers than in occasional geniuses, and in day-to-day performance than in miracles, it behooves us here to consider what constitutes adequacy of both equipment and personnel of the pilot plant to be fully effective.

Necessarily, the details of the pilot plant are determined by the general classifications into which its problems are likely to fall. The pilot plants of a glass works, of a petroleum refinery and of a dyestuff plant are totally different from each other except in their basic elements. For instance, each of the three would need space large enough to set up miniature duplicates of the principal units of equipment of the parent plant and room beyond that to allow these units to be moved about into various combinations. Furthermore, each unit as set up for work must be so situated that every part of it can be reached for measurements, alteration, cleaning, repair and any other purpose that the operator may be able to imagine. The working space of the pilot plant must be heated and ventilated adequately for its purposes and must be provided with all the services of the plant itself: water, sewer, steam, electricity, fuel gas, vacuum, air pressure, and any others available. Every reasonable and some unreasonable safety devices must be at hand. The equipment of the pilot plant must include as a minimum an adequate set of mechanical tools for setting up and dismantling any or all of its equipment, and every type of measuring (and preferably automatically recording) device and instrument that may reasonably bear on its problems. Finally some provision must be made for the assembly and recording of data, a desk at least in a separate room where records can be kept and calculations made.

Beyond these basic items, the pilot plant ordinarily duplicates the operating plant in miniature. Size is the most obvious difference, but in addition to that the essential flexibility of the pilot plant requires a generous use of unions and flanged connections on each unit and plenty of thermometer wells and other connections must provide for many gages and meters of various kinds. A number of tanks, preferably with round bottoms and demountable electric stirrers, and made of various materials for appropriate resistance to reagents, are generally invaluable as mixing vessels, storage vats and crystallizers. These particularly should be mounted on dolleys so that they can be easily moved about as they may be needed. Dolleys, too, are immensely convenient for mounting all of the pieces of equipment that are likely to require moving from place to place. Such large items as hydraulic presses, jacketted autoclaves, furnaces, and some of the other major pieces can be permanently mounted on solid foundations to advantage, flexibility depending on bringing up lighter items to be connected into the system as needed.

The personnel of the pilot plant staff is even more important than its physical equipment. The prime necessity is to provide a skeleton staff of one or more persons as may be required that will be permanently attached to the pilot plant. This staff must be experienced in as many aspects of the company's business as possible and certainly the director of the work must be thoroughly familiar with the points of view of research, production, sales and management. His inclination to go off the deep end in a research sense must be tempered by his desire in an operating sense to produce results as fast as needed; his salesman's optimism must be mixed with a generous share of management's conservatism. Obviously this individual must be so independent of each of these several divisions that none of them dominates him and that his thinking is not incompatible with any of them. Obviously such a person is impossible to find; but at least he is the one that should be searched for, and the compromise that is finally effected should be given a position as far as possible independent of each of the groups that will be his best customers, the company's departments.

Having installed a minimum permanent staff in the well equipped pilot plant, the next question is: how shall it function to best advantage? Necessarily someone from each of the other departments of the company interested in a particular problem must be available to solve it himself or with the assistance of others. When the pilot plant research approaches a point where some other department should be interested or should prepare to take over, then an appropriate person from that department should be available on loan. It is a mistake for any man whose primary interest is in some other department of the company to become permanently attached to the pilot staff. It is equally wrong not to send men from other departments into the pilot plant at reasonable intervals because each man can contribute to its effectiveness and each can learn something from it. M. C. Whitaker once emphasized the differences in men about the plant thus: "A man who is essentially a plant man is liable to be a nuisance in a research laboratory, and on the other hand, a man with research inclinations is a hazard to any production process." These two types of men can safely and effectively meet in the pilot plant. Here the research-minded man can experiment to his heart's content without interfering with the regular progress of raw material into the main production line and finished goods out of it to customers. The production man can see for his part equipment more substantial than the glassware of the laboratory and a certain orderly progress of affairs that can be influenced and adjusted with a wrench and a screw driver instead of a glass blower's lamp and a piece of rubber tubing.

Here, too, the salesman can acquire some acquaintance with, and respect for, the processes and equipment that give him a product to sell. He can even operate the process himself without fear of drawing on himself the management's Jovian lightnings should something fail to go just right. This familiarity with his own product and a nodding acquaintance with the problems of others in supplying it have never yet been known to mar a salesman's effectiveness.

Finally, the pilot plant provides an effective initiation for any person entering a company with the expectation of assuming some responsibility for its affairs at once or later. The pilot plant's very nature makes this function simple and easy as well as time-saving and effective. Visitors are always problems in an operating plant and neophytes who are not definitely training to become operators must be classed as visitors whatever their histories and expectations. The operating force can seldom shut down an operation just to show a visitor how it works and certainly this cannot be timed with the visitor's whims. On the other hand, a trainee in the pilot plant can be given under careful supervision useful work to do in connection with its operation and so earn his salt while learning.

The foregoing remarks belong more properly in a treatise addressed to management than in one for research people, but they are included here for what seems to be good and sufficient reasons.

No research can be considered complete until it has survived the test of at least pilot plant operation. Here the research man continues to foster and cherish his offspring, but here he must transfer it by degrees to others' care. Its stay in the pilot plant may be considered for a process to correspond to the period of adolescence in children. In infancy the research man has complete control of it in every respect, but in the pilot plant his infant must be put through a process of growing up, of passing from the secure dependence of the research laboratory to the hazardous maturity of operation for profit. Not only is the scale of operation undergoing tremendous enlargement, but at the same time the new process is acquiring a purpose only dimly imagined in the laboratory. Thus the research man must assume a certain responsibility for the way things go in the pilot plant and he cannot properly leave this entirely to others.

Normal routine would require that the research man (or one chosen from the group if several have participated in the investigation) leave the laboratory and take his brain-child into the pilot plant. Here appropriate steps put the new process into operation. The staff of the pilot plant participates with the researcher in this, and as the work develops, representatives of the engineering department are called in to help things along. At a later stage a designated person from the sales department and another from the operating department may be called in to contribute to the development. Naturally, the sales department has no particular interest in the development of a totally internal process which will not affect the products it has to sell. Nor will the production department show seriously active interest in a totally new product until the sales department reports some actual or potential interest in it from the company's customers. Thus the burden of proof continues to rest at the point of origin, the research department, until some probable value of the development has been demonstrated to others. All of this consumes considerable time, but it also makes important opportunities to study the new process, to determine its operating characteristics and to make enough of the product to develop some interest in it from potential customers and others than its parents in the research laboratory. The bugs in the process revealed by engineering and production and those in the product found by sales and customers are gradually cleared out.

Operations in the pilot plant require careful planning that they may cover successfully the interval between test tube and full scale plant, and reasonably give the findings meaning. Not only is the material of which pilot plant equipment is built more like that in the production plant than like laboratory glassware, but the increased scale of working introduces new and important differences. The basic fact is sometimes overlooked that the surface of a vessel, through which heat passes, increases as the square of the dimension, while the volume goes up as the cube of the dimension. Neglect of that shape-size relation is responsible for a great deal of trouble when one increases the scale of a process or operation, especially when the material of the surface exerts a catalytic or an anti-catalytic effect on the reaction. At the same time, numerous other aspects of the problem protrude as important in the pilot plant that were negligible in the laboratory.

The reaction of aniline with carbon disulfide to form thiocarbanilide and hydrogen sulfide, for example, goes smoothly in the laboratory. A 20 per cent or so excess of carbon disulfide amply converts all of the aniline and is readily removed by simple distillation when the process is complete. Furthermore, the excess of carbon disulfide keeps the mass in a mushy form that can be stirred to insure that no part of it escapes reaction. A reflux condenser of the ordinary laboratory type suffices to return the vaporized carbon disulfide to the process and the hydrogen sulfide escapes easily up the fume chimney. Yields from aniline are close to 100 per cent. Experiments with several metals introduced into the reacting mass showed no apparent catalytic effects but only the anticipated formation of sulfide. Aluminum seemed to be satisfactory for the construction of the reactor and a jacketted vessel to provide for steaming out the carbon disulfide at the end of the reaction seemed indicated. At that point the matter went to the pilot plant.

Because the pilot plant had no jacketted aluminum vessel at hand, a glass-lined kettle was used instead, and some pieces of aluminum were attached to the stirrer to give the effect of a metal vessel. The reactor was connected to a glass-lined condenser surrounded by cold water. The plan was to condense the carbon disulfide, allowing it to return to the reaction zone, and to vent the hydrogen sulfide. The original proposal was to burn the hydrogen sulfide high enough in the air so that the SO_2 would be safely diluted and carried away by the atmosphere.

That was a grave error of judgment from several points of view, but there would be no use experimenting if the result could be known in advance.

The first error was in estimating the quantity of sulfur dioxide to be disposed of in this way. The effectiveness of a laboratory fume hood in handling a few grams of sulfur, as either the dioxide or hydrogen sulfide itself, is no possible gage of what to expect when the pilot plant reaction turns out pounds and pounds of sulfur in either form. Furthermore, the excess condensing capacity always available in the laboratory Liebig condenser is seldom to be found in any pilot plant no matter how carefully planned. In this case, what had seemed ample in the laboratory proved entirely inadequate in the pilot plant, and instead of condensing and returning to the reaction all of the vaporizing carbon disulfide, the pilot plant condenser proved powerless to prevent the escape of great quantities of the vapor with the hydrogen sulfide going to waste. The sulfurous flame rising from the screen covering the end of the long vent tube was clearly consuming not only large volumes of hydrogen sulfide that it was supposed to handle, but it was obviously burning up further quantities of carbon disulfide that had no business to be thrown away.

What had been a mere trickle of hydrogen sulfide in the laboratory belched out of the vent as a great plume of flame all out of proportion. Reference to the usual tables showed the vapor pressure of carbon disulfide to be 127mm at 0° C., and 300mm at 20° C. (which happened to be close to the temperature of the cooling water at hand). Obviously, cooling the condenser further with ice or ice water would help, but even at 0° C. the exit gas would contain 16.7 per cent by volume of carbon disulfide and the waste hydrogen sulfide would carry with it about one-fifth of its volume of carbon disulfide. Translated to a weight basis, the carbon bisulfide lost at 0° C. would weigh almost half as much as the hydrogen sulfide thrown away (44.6 per cent). At 10° C., the carbon disulfide weighs 77.8 per cent as much as the hydrogen sulfide vented, and at 20° C. the figure becomes 145 per cent.

Some other attack must be devised. If economy did not insist upon it, the neighbors for miles around certainly would in no uncertain terms.

The problem clearly became one of finding a less objectionable form for discarding the hydrogen sulfide.

Inquiry revealed that the production department required sodium sulfide for certain of its operations and that this was used in solution containing excess alkali. That provided a simple answer to the problem and a warm solution of caustic soda readily absorbed the hydrogen sulfide while allowing the carbon disulfide vapor to go on to the condenser to be completely liquefied. Yields in terms of carbon disulfide went up at once from about 25 per cent to a not unreasonable figure of 85 per cent. In other words the key to the ultimate production problem was found in the form of the hydrogen sulfide disposal system and its location ahead of the carbon disulfide condenser instead of after it. After that arrangement was made, the determination of optimum conditions of reaction and relative proportions of the reactants for optimum yields was merely a matter of time.

And so a time came when the process was nearly ready for the big plant and when research, engineering and production were all reasonably well satisfied with it, if not actually enthusiastic. At this point, the sales department was asked to send a man over to watch our wonderful process turn out its beautiful product. Only then did it develop through the sales department that the principal potential buyers of our thiocarbanilide were already in the business of making it for themselves in plants representing substantial investments. In addition, they were buying their aniline raw material from us at a good price and a good profit to us, and had for years been in production. In other words, some one had set up a problem whose solution was not wanted at all. Fortunately, the pilot plant operation represented only a minor expenditure, but it had effectively prevented a major one that would have been equally useless.

Obviously, the several blunders made in this development were far less serious in their effects on the pilot plant scale than they would have been had they happened in a production plant. That, of course, in no wise excuses the researchers in this case from simply blundering ahead thoughtlessly and without a careful plan. Far too often the research man abandons his brains at the door of the pilot plant, and because he understands that it is the place to make mistakes, proceeds to make every reasonable error and some utterly unreasonable ones. The plant man and the engineer do the same thing and the pilot plant operator is the victim of them all.

Occasionally that attitude of outsiders has caused considerable trouble in the pilot plant, where this has grown into a substantial part of the whole plant with its own staff. In at least one case in the author's experience, friction developed to a shameful extent between the glass-and-rubber scientists on the one hand and the steel-and-monkey wrench pilot plant operators on the other. As a result the former set up a glass semi-pilot plant of their own which the pilot plant operators visited as need arose, and the scientists were allowed to visit the pilot plant from time to time. Neither could work with the other for long without trouble. Similar differences may also develop between pilot plant and the production department unless management takes care to prevent.

Such troubles are silly in the extreme and have no business to be. They sometimes arise because the value and function of the pilot plant are not understood by others. Too often the pilot plant is thought of as being an extension of the other fellow's territory reaching out toward one's own, when actually it is an independent entity between the two and belonging to neither, and to both.

Design of pilot plant processes to serve their purpose is an important study in itself. Unfortunately, too little attention has been paid to it, presumably on the assumption that the good sense of all concerned will arrive at a reasonable and effective compromise and that such a compromise will be the thing desired. Or course, it may or may not be. The mere fact that it is a compromise does not guarantee its value. Furthermore, the fact is repeatedly evident that failure can happen quite as readily between laboratory and pilot plant or between that and the full scale plant. And it is not impossible for a process to succeed in the full scale plant when it has previously failed in both laboratory and pilot plant; witness Hall's aluminum process discussed in Chapter 6, page 80.

The basic problem of the pilot plant process is to enlarge the laboratory reaction and to shrink the plant operation to give the intermediate pilot plant stage some logical and evaluable relation to each. Primarily this involves heat and material balances. We have already mentioned the volume-surface relation that must enter all such calculations. The operator must also consider and evaluate: temperature differences and heat transfer within the reacting mass, viscosity effects and those created by streamline versus turbulent streaming of fluids, relations of surface to volume of particles and droplets in heterogeneous systems, effects of surface film resistances in such systems, dynamic similarity among the several systems as represented by the various physical forces operating in them, and chemical similarity based on concentrations, temperatures, pH, and other such factors. All of these create unfortunate confusion for anyone not habitually thinking in pilot plant terms and a clarification of the whole matter is very much needed.

The most useful discussion of this subject that this writer has been able to find is that of R. Edgeworth-Jonstone in the *Transactions of the Institution of Chemical Engineers* [17, 128 (1939)]. Papers by

Wolford [*News Edition of Ind. Eng. Chem.*, 3 #22, page 1 (November 20, 1925)] and by Damkohler [*Z. f. Elektrochem.*, 42, 846 (1936)] also bear on the subject, but much still remains to be done to arrive at a satisfactory method of transferring from one scale to the other meaningfully.

Chapter 12

Reports are Essential

"Whenever, on account of its vagueness, I am dissatisfied with a conception of the brain, I resort forthwith to the pen, for the purpose of obtaining, through its aid, the necessary form, consequence and precision." —Edgar Allan Poe

Even the most penetrating and successful research amounts to nothing until some use has been made of it. The researcher may complete his job by reporting his results to his superiors or to his co-workers, or by preparing a paper to be read before an interested group or published in the appropriate journal, or both, or by filing a patent application to cover its novel points, or otherwise. But the fact remains that the research cannot be considered complete until it has been reported in some manner. Industrial research commonly partakes of a secret or semi-secret nature and seldom receives general publication except through the patent office. For that reason, industrial researchers usually neglect their reports on the basis that the other interested persons in the company keep adequately familiar with progress by word of mouth and by day-to-day contact with the work.

That attitude is silly in the extreme and may seriously impede or even totally stop a man's progress in a promising career. While careful reports cannot substitute for the research itself, they can and do go a long way to place the work, and by the same token the worker, in the most favorable light. This is important when promotions are in order. We have already pointed out at some length the value to the research itself of adequate interim reports as guiding lights to further progress. That phase of reporting cannot be overemphasized in any discussion of research methods. As Francis Bacon once put it, "Writing maketh an exact man," and nowhere is exactness so necessary as in research. Obviously the most important results can be completely buried in excess verbiage. The point is wonderfully illustrated by this clipping from the New York *Herald Tribune* in which a scientist (presumably) required three successive tries before he was able to make clear a statement of what he originally intended to say:

"A New York City plumber wrote to the Bureau of Standards in Washington saying he had found hydrochloric acid good for cleaning out clogged drains.

"The Bureau wrote him: 'The efficacy of hydrochloric acid is indisputable, but the corrosive residue is incompatible with metallic permanence.'

"The plumber replied he was glad the Bureau agreed.

"The Bureau tried again, writing: 'We cannot assume responsibility for the production of toxic and noxious residue with hydrochloric acid and suggest you use an alternative procedure.'

"The plumber again said he was pleased the Bureau agreed with him.

"Finally the Bureau wrote to the plumber: 'Don't use hydrochloric acid. It eats hell out of the pipes.' "

That man's trouble—and it is by no means characteristic of or confined to the Bureau—arose because he attempted to pussyfoot, to avoid a direct statement, for fear that he might be making an error. Of course in so doing he fell into the far more egregious blunder of failing twice to accomplish any purpose or to convey any meaning at all. No one can reasonably sympathize with this writer, for his trouble was entirely of his own making. He was willing to make a direct statement only when forced to it. It is doubtful if he had even thought out his answer to his correspondent until the third communication forced him to do so.

Therein lies the weakness in the writing of most scientifically trained persons: they do not think out what they wish to say in advance. Obviously an idea must be clear in one's own mind before he can convey it clearly to someone else. Long and intimate contact with a great many research workers has taught me that they express themselves clearly and pointedly in informal conversation, but are overcome by diffidence (or is it buck fever?) when faced with a blank sheet of paper or an audience. They forget under such circumstances that their readers or auditors are intent upon learning from them and have no desire or wish to criticize. They also overlook the basic fact that the most effective protection against criticism is to state ideas clearly and forcefully with only those qualifications necessary to fit the facts. Superfluous qualifications only becloud the meaning intended and at the same time they fail to provide loopholes for the writer or speaker to escape the consequences of his own faulty reasoning.

At the root of the matter lies the reluctance of most research workers to face the fact that they often do not know what they mean and intend to say when they come to write a report. Their unwillingness to go back to their experiments or to the library to clarify their thinking requires that they pussyfoot in making any statements about their work. That leads to the conditions most often complained of in scientific writing: that meaning is hidden or lost entirely among useless words.

This failing of scientists as writers was attacked by A. J. Riker of Wisconsin College of Agriculture in an article in "Phytopathology." Said he:

"The preparation of a manuscript which accurately conveys readable ideas is an essential phase of research. It is just as valuable as doing more experiments. And it is fully as worthy of our best efforts.

"When significant results are actually ready, nothing should delay a prompt and adequate release. Probably as many writers commit sins of omission as sins of commission. Scientists in publicly supported institutions have a special responsibility to give promptly to the public the benefit of their verified investigations. . . .

"One of the basic differences between technical and news writing is that a reporter tells the important thing first; he gives various details later. In contrast to this, the standard arrangement of technical writing begins with the title, introduction, statement of materials and methods used, then the observations, experiments and results, and on through discussion, summary, and citations of other literature. But an investigator should keep his readers in mind and show them the consideration and courtesy of simple and clear exposition—not string together ponderous phrases like wash on a back-alley line.

"Clichés and platitudes, verbosity and circumlocution, obscurity, and long pretentious words in stilted phrases are all to be condemned. Among the diseases of manuscripts, a diarrhea of words is perhaps the most common. In one representative case, I tabulated these deplorable expressions, substituting for their shorter, meaningful equivalents:

"It will be seen from the foregoing figures . . . these figures show.
"It would thus appear that . . . seemingly, or apparently.
"It is true that . . . admittedly.
"It is this that . . . this.
"The fact that the cultures grew shows . . . the growth shows.
"The question as to whether . . . whether.
"During the time that . . . while.
"At an earlier date . . . previously.
"With reference to . . . about, or concerning.
"The treatment having been performed . . . after treatment.
"Under greenhouse conditions . . . in the greenhouse.
"Goes under the name of . . . is called.
"Plants exhibited good growth . . . plants grew well.
"Conducted inoculation experiments on . . . inoculated.

"And if you think the paragraph which contained all those expressions was exaggerated, you should see some examples collected from papers actually submitted for publication.

"Even experienced and skillful writers seldom produce an excellent manuscript without going over it many times."

A similar thought is expressed by Frederick Bodner in his book "The Loom of Language."

The temptation is strong at this point to abandon the subject of research and to convert this book into a dissertation on the use of forceful and exact English. That is a thing much to be desired and it could have important consequences. If it were done in anything like the usual manner of such dissertations, its effect would be no more than those of other courses in English composition that research men universally have suffered. Few human activities are so futile. Actually, the usual course in English composition devotes itself to methods of obtaining rhetorical effects quite outside the area of interest of the student of science and hence it fails to arouse him. The professor of English seldom has any contact with, or sympathy for, the scientific point of view and the hopeful young scientist considers anything an unmitigated bore which attempts to draw his interest away from the subject of his specialty. No wonder scientific training seems in all but the rarest exceptions to be totally incompatible with the use of the best English!

No one seems concerned to teach students the basic fact that language is important and valuable to human beings as the sole and fundamental tool of thinking. Without words, thoughts are mere sensations and impossible to transmit except in the most inexact forms to another person. As soon as words are available to the individual, he acquires the important ability both to experience sensations recognizably differing one from another in ways otherwise indistinguishable and to express not only these gradually shaded sensations but also an increasing range of relationships which he could not even think until he knew words to represent them. As one's thoughts develop to embrace the many concepts of science, special vocabularies are essential, but the basic concepts of language itself do not change simply by the addition of more words to the stock one uses daily.

Clearly, then, the student of science must look upon language as a tool of his calling in just the same way that he does a balance, a microscope or a buret. He spends a great deal of time learning to use each of these patently specialized tools of his craft, but because the English language is not a characteristic nor a monopoly of science (it cannot be requisitioned from the store room), he neglects that as something of little or no possible interest or value to him. If he would devote himself to learning to use language as a tool with something like the enthusiasm he does to learning to use each of the other tools of his profession, not only would he himself benefit, but all others who might have or acquire interest in some part of his original work would be aided to clearer understanding of just what he had added to the store of knowledge. As we have been at some pains to point out in the preceding chapters of this book, the characteristic of original thinking is expressed in new and original relations between two or more concepts, and relations can only be thought in the terms of language. Exact, or what we commonly call scientific, thinking can only be accomplished by the use of words selected for their exactness and related to one another with equal accuracy.

Unfortunately many students of science content themselves with learning new vocabularies to designate the unfamiliar things and ideas encountered in their new pursuit, and forget that grammar and rhetoric are equally important as new words in making clear the specialized relations between new ideas. It is as if, upon learning something of trigonometry, a student should suddenly decide that arithmetic is no longer of any use to him; or learning to drive an automobile, he should forget how to walk.

The most satisfying and scientifically practical discussion of language as a tool which I have seen is "The Art of Plain Talk" by Rudolf Flesch, published by Harper & Brothers. This little book will bountifully reward any scientist who studies it by giving him a surer command of this vital tool of his calling.

Viewed, as a scientist must, as a tool, language ceases to be a bore and takes on new and exciting aspects of supreme importance to everyone, even to scientists.

Chapter 13

Evaluating Research

"*Research is the one function of business which, far more than any other, deals with the future . . . . Only one reliable method of forecasting the future has ever been developed, and that method consists in projecting the continuing trends of the past.*"

—Roland P. Soule

Perhaps no other phase of research is more important and at the same time more neglected than its evaluation. Usual practice is to guess in the beginning that a certain result will be worth-while on the basis of possible return at some future date; and then at the time a result is achieved and there is some possibility of selling the process or the product, the whole thing is examined again and an effort made to establish some reasonable value for the product of the research. Actually, the evaluation of every research must be a practically continuous process. Each time some new phase of the investigation is undertaken, the researcher must establish in some manner that the probable value to be realized will be greater than probable cost.

Academic research yields returns in satisfaction for the investigator, and requires only that his interest be kept alive by the possibilities that can be envisioned. Without continuing interest the research stops.

In industry the situation is obviously different. No investigation or development can long be allowed to proceed unless those responsible can see some reasonable probability of an adequate return on accumulating costs. And no problem is more vexing than that of deciding when to abandon a project and write it off to the profit and loss account. William B. Bell, president of American Cyanamid Co. in discussing the executive's view of research, pointed out that one of the greatest needs of executives is a test that will surely indicate whether a particular research should be continued or dropped. He feared to drop an expensive project lest he lose legitimate return or to continue financing a dead issue. He wished for an indicator that would show green so long as the probabilities favor continuing a project, but that would turn red as soon as the expectation points to loss instead of profit. How convenient! But lacking that, one must seek to establish value by indirection. That requires first an understanding of the nature of such ventures and then an analysis of the specific problem against that background.

The peculiar qualities of research-based enterprises require what John E. Teeple has called "patient money." Investors who seek the high returns that can be realized through successful ventures of the kind must be fully prepared: (1) to see their investment melt away during the early developmental stages of the operation, to watch the tangible assets of their company dwindle and almost if not quite disappear; (2) to realize that a substantial part of the investment has been transformed into the intangible assets of experience, "know-how," processes, patents and like attributes valuable only (or largely) to a going business that has not yet come into being; and (3) to learn that first estimates of capital needed usually fall short of reality and that growing intangible assets are accompanied by troubles equally strange and intangible, not at all the kinds of things that trouble ordinary businesses. Furthermore, the optimistic creators of the venture's intangibles are one day astounded to find that the world has not been waiting with baited breath for their product, but that the result of their ardent and arduous labors has suddenly become a sales problem. Strange, too, is the awakening to the fact that this sales problem is like every other sales problem, only more so.

Charles F. Burgess speaks from long experience on this point:

> "Even when a process or product has been approved in the laboratory, it is not an accomplished success, for it must then share in the hazards which all new commercial ventures experience. It must answer the question, 'Does the public want it?' Our experience is that telling the people about it is a far more expensive operation than is the cost of research leading to the development of a new product or process. It is a common experience to find that the cost of impressing upon the public even the name of a new product may be ten times that involved in the experimental and development work leading to its production."

But that is a little ahead of the story. The economic background of research-based ènterprises drew the earnest consideration of L. V. Redman and he made a significant analysis of this important aspect of research. His paper on the subject appeared in 1928:

"The last half-century has brought greater material progress than have all the centuries gone before, while the quarter-century just past has outdone the hundred years that preceded. This 'endless chain' of accelerated progress is coming about through the growing, widespread substitution of planned experiment for haphazard experience, through making things happen under controlled conditions instead of observing simply what happens by chance.

"In order that this modern method of acquiring knowledge, which has proved so fruitful, may be employed with full advantage in industry, certain economic factors must be properly understood and applied.

"The rank and file of men in business, and not a few in the halls of learning, appear to have the impression that knowledge gained in research, if of potential value in industry, is ordinarily capable of immediate practical application. They have heard it said that research is a gamble, but in this they fail to distinguish between research proper, which is relatively inexpensive, and the industrial exploitation of research, commonly called 'development,' which may be a costly procedure. They are surprised when told that it is not unsuccessful research that gives most cause for concern, but it is the successful research that is to be exploited in terms of a workable process.

"There is much wisdom in the oft-quoted admonition of Baekeland: 'Commit your blunders on a small scale and make your profits on a large scale.' Research, even if negative in its immediate results, generally pays for itself in useful knowledge gained. In its early stages development also may be worth all it costs, but advanced development—the 'semi-works' plant—highly profitable though it be as a means of avoiding failure in full-scale production, is a very unprofitable source of the information that research or earlier development should easily provide.

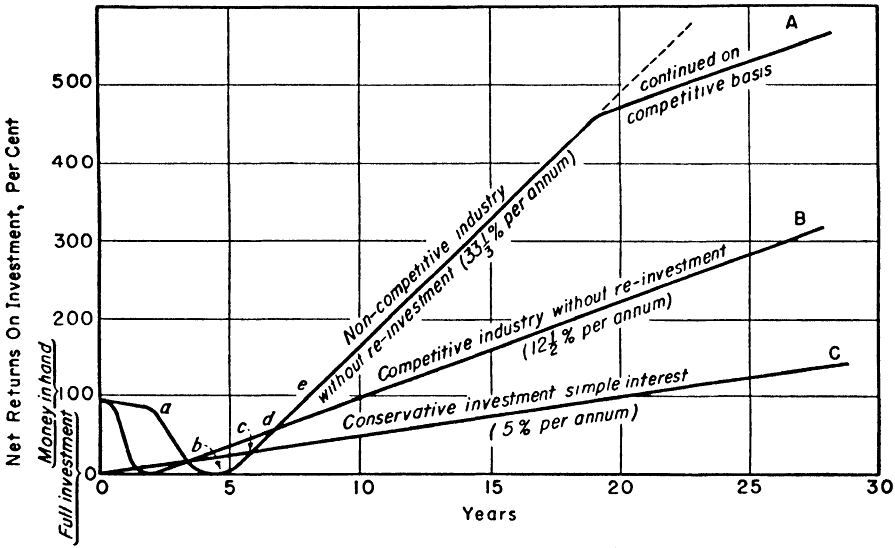
"It may thus be profitable to discuss the hazards that attend the exploitation of research; the rewards which capital must receive if it is to be induced to assume the hazards of industrial development; and the approved means of keeping down the losses and of keeping up the spirits while seeing a development project out of that valley of the shadow of failure through which every major project must pass before coming into the full light of industrial success.

"Let us assume that a given project provides good prospects of successful development—*i.e.*, that it is scientifically sound, presents no apparent, insurmountable difficulties of manufacture, and that the product involved meets a public need, or a demand that can be created. If success in development is to be attained, how much must be invested? How long will it take? What is the reward of success? What is the penalty of failure?

"First let it be observed that the chance of being led into an unprofitable venture is considerably lessened if the project chosen for development is the most promising of a number of interesting research successes arising from intensive study of the industry such as progressive concerns carry on today.

"We shall assume that first-stage development has been completed, and the product, which has been repeatedly prepared in pound lots, and later in hundred-pound lots, has found a reasonable measure of favor with prospective consumers; that a couple of years have been spent by one man and one or more helpers in research and such first-stage development, anticipating optimum conditions of manufacture as nearly as is possible in the small way with disconnected production units; that the precaution has been taken of employing experimentally materials of construction that are feasible in full-scale production; and that, under the conditions of time, temperature, and what not, all of which appear equally practicable, quality and yields have been found satisfactory. If no radical departure from the industry's established conditions of manufacture are to be made, we may proceed with reasonable expectation of success. If, on the other hand, we are considering the production of a new product for which no previous manufacturing experience exists or is available, we then have a very different problem. We must introduce one or more steps to provide gradual transition from the small development scale to the factory scale. We must hook up our experimental production units in manufacturing sequence, in short, construct an experimental plant, in order that we may the better study costs and the whole range of changed conditions imposed by large-scale production.

"All this takes time, calls for faith on the part of everybody, and requires many times as much money as was spent in research and earlier development. Furthermore, financial support must be obtained, not for a few months only, but for a year or several years, if need be, during which time expenses will be increasing rapidly; capital will be melting away without return.



From *Ind. & Eng. Chem.* 20, 1242 (1928)

FIGURE 1. Redman's curves of investment values.

"There certainly is no need to dwell on the necessity of feeling one's way into manufacture. Still the long road to success in new manufacture is strewn with the wreckage of attempted short cuts from small-way experiment, or none at all, into large-scale production.

"Graphically represented, the course of a new project from the initial research through development into successful production is something like that shown in Figure 1, in which *A* is the curve of research, development, and successful production. By way of direct comparison *B* depicts about what may be expected through investment of a like sum in successful extension of established competitive manufacture and *C* shows the return from equal investment in 'gilt-edge' securities.

"If we follow curve *A*, we will see that expenditure starts off rather modestly—let us say with $10,000 the first year—and increases gradually with small-scale development until advanced development is undertaken (*a* on the curve).

"Right here is the time for taking stock, and taking it most carefully, employing the combined wisdom gained in research, in small-way development, in related manufacture, and in the market; for here the die is to be cast that will determine whether a period of rapidly growing expenditure is to lead to gratifying achievement and adequate return or to disheartening failure and consuming loss. In some measure, at least, the reputation of the research man and the future confidence of his backers are at stake. If the project is to be abandoned, do it now; in another year the loss through failure will be manyfold. On the other hand if, after thorough examination from every angle, the venture appears warranted, there will now be in order investment in an experimental plant, one by which the cost of equipment and of raw materials may be kept to a minimum consistent with gaining a reasonably safe knowledge of future manufacturing requirements, yet a plant capable of turning out salable product.

"From now on expenditure may be expected to increase rapidly but, if all goes well, in a couple of years from the beginning of such development the sales, which should be made as early as possible for the added benefit of customer criticism, should begin to provide profits in sufficient amount to offset expenses (*b* on curve) and start the venture on the up-grade. While there is no regularity about this, of course, let us assume that the profits are those that later manufacture should be expected to realize, or, say, 33 1/3 per cent. At this rate, by about the end of the eighth year from the beginning of research, the investment should have been recovered (*e* on curve).

"Such an adventure into new fields of manufacture may involve something like three years of uncertainty and doubt both for the financial man, who sees his capital being rapidly used up, with everything going out and nothing coming in; and for the research man, who must have reason for assuring and reassuring first himself, and in turn his backers, that everything is taking its normal course and in due time will amply justify the venture. The duration of this period of suspense, the total cost of development, and the chance of ultimate success will depend probably more on the thoroughness of the initial research and development than on present resourcefulness.

"If all goes well, the enterprise should pass conservative investment in its returns by perhaps the end of the fifth year (*c* on curve), and by the end of another year (*d*) catch up with investment in established, competitive manufacture. We have now a going business which, as indicated by the curve, should continue on a highly profitable basis as long as the industry remains non-competitive or, we will say, during the life of such basic patents as may have been granted covering process or product. From then on the industry may be expected to take the regular course dictated by competition, and be followed, let us hope, by successful development projects still in their periods of major earnings, so separated in point of time that each has been able to support the next following during its unproductive years.

"Plainly, there is wisdom in avoiding too many of the drops, from *a* to *b*, at one time or in rapid succession, since the length of these periods of large expense without return cannot be definitely foretold and the increasing demand for capital might prove embarrassing if not disastrous. Capital is not easily obtained for development projects. The banker as custodian of the people's money must be guided by last year's statement rather than next year's hope. In fact, the vision and the faith that make successful development possible may be difficult enough to communicate to a board of directors who know their industry's needs and possibilities. In our opinion, the conditions are unusual that would warrant investment in development projects beyond that amount which would permit moderate annual returns to the stockholder.

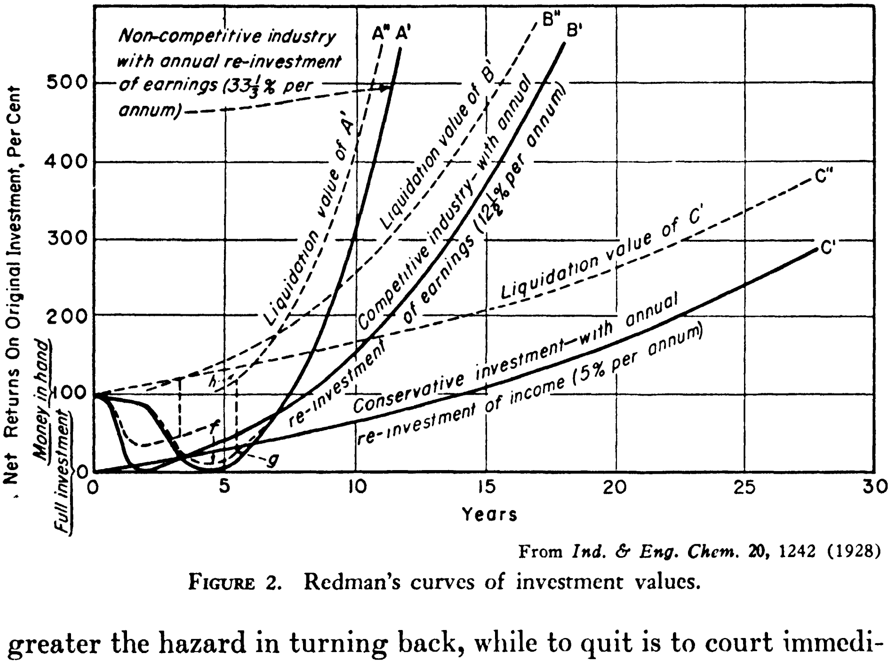
"It must not be forgotten that when one is not observing but experiencing this drop in the curve, the future upward trend is neither so certain nor so apparent as it is on paper. But the period of large expense must not be permitted to become a period of depression; it may be difficult enough to keep up one's courage without the burden of financial worries. Worry can be avoided by keeping within one's means. Desire for early realization of the large returns promised must not lead to indulgence in a more ambitious development program than income or surplus warrants.

"But there is a brighter picture. It is that of the research director who, working within his means, sees his first development project well into its earning stage before he starts another and who, employing sequence with proper interval, comes to see successful manufacture that has grown out of development amply justify, if not directly support, an expanding program of research and development. It may not show on the books as they are kept, but a successful major development project should be able eventually to support one or more new projects through the unproductive period, and in addition satisfy the stockholders' legitimate demand for regular dividends. Here let us step aside to observe that if the funds now going into extra dividends only were invested in research and development our country's industrial progress would leave little to be desired.

"The financial possibilities of successful research and development are not fully indicated in curve *A*, Figure 1, nor are they in curve *A′*, Figure 2, in which annual reinvestment of earnings is shown, since it is evident that to an extent limited only by demand and available capital larger sums may find opportunity for such profitable investment. Here for the benefit of comparison are shown *B′*, reinvestment curve for competitive industry, and *C′*, 'compound interest' curve of highly conservative investment.

"We have followed the curve of successful development into profitable manufacture. We have endeavored to answer the questions: How much must be invested? How long will it take? and What is the reward of success? We have yet to consider—What is the penalty of failure? Or, let us put it more broadly and optimistically, and ask instead—What may one hope to realize on withdrawal at any given time?

"Obviously, the auspicious time to withdraw from an unpromising project is before advanced development is started, and from a promising one not until after profitable industry has been established. It is a bit like flying the Atlantic in that the nearer the goal, the greater the hazard in turning back, while to quit is to court immediate disaster. The probable extent of such disaster may be seen by consulting the dotted curve *A″*, which we may call the curve of liquidation values. It was plotted on the assumption that the salvage from an experimental plant is small—let us say 15 per cent of the first cost—and that there will have been twice as much spent for salaries, labor, and materials as for equipment; that salaries, labor, and materials may be considered as lost; and that, therefore, the liquidation value may be taken as only 5 per cent of the investment until the project becomes an assured success. When it does, valuation becomes that of a going business instead of unprofitable knowl-



From *Ind. & Eng. Chem.* **20**, 1242 (1928)

FIGURE 2. Redman's curves of investment values.

edge and equipment. We have assumed in curve A'' that about a year after the new industry has begun to make money it should represent an alluring investment and that liquidation value should then be not less than the capital represented in the venture plus the profits earned. The transition from a low to a high liquidation value (g to h on the curve) is indicated as being abrupt, because if the enterprise is to be liquidated it will be either as an abandoned plant of junk value only or as a profitable business. However, at any time after rounding the curve (at f) profitable sale becomes a possibility. This is indicated by extension of both the low-value and the high-value portions of the curve on either side of the line of transition.

"The corresponding curve of investment in established industry (B'') is based on the assumption that abandoned equipment is salable at half original cost and that only one-third of the whole sum expended to get into profitable production has been for salaries, wages, and materials and two-thirds for equipment. Curve C'' is drawn to indicate the possibility of complete withdrawal from highly conservative investment at any time without loss.

"The adage 'Nothing fails like a failure nor succeeds like success' finds nowhere greater justification than in the development of new industrial projects. If development can be carried through to successful production, capitalization should be possible at a figure well above the whole cost of research and development. In fact, expansion will be limited only by the commercial possibilities of the field, and may reach an order of magnitude in comparison with which the original investment will look small. Curve A'', like curve A', considerably understates the possibilities of successful development and is chiefly of interest in that part which indicates the losses that may result from failure or abandonment for any cause."

This provides a background against which to examine any part of a research enterprise in order to approximate its value and importance. The situation is the same whether one must evaluate a complete and self-contained going business or merely decide to continue or to abandon a laboratory research. Although the pace of research has been greatly accelerated since Redman's analysis was made, and development is usually completed much more quickly than he assumes, the same factors operate today as then and in much the same way. The only important differences in applying this analysis today lie in the average time required for the various steps. Modern research organizations, together with the engineering and developmental divisions co-operating with them in today's research-based corporations, are able to function effectively at nearly double the speeds of 1928. Instead of requiring an average of seven or eight years to return investment, like enterprises now often reach the same point in four to five years. Naturally, the time scale for investments and for the more orthodox competitive business has undergone no such foreshortening.

The important individual factors to be considered in evaluating any research project look forward and not backward. The cost of successful research can only in the rarest instances bear any close relation to its value. An estimate of the cost of carrying the research from its present state to profitable application on a substantial scale, the probable working space the project will have without interference from or with competitors, both in territory and time, and the potential earning power in terms of net profit that may reasonably be expected within the limitations inherent in the project, these are the prime factors from which one must guess at value. Essentially they are based on the service that may be realized from the project, process or product and on the closeness of competition to this result in terms of the degree or value of the service performed, of originality of the kind protected by patents, and of the time that may be reasonably needed for competition to duplicate the result or provide a reasonable facsimile thereof. This last may or may not be the life of any patent or patents that may be secured covering the project, since a result of striking originality and substantial value always attracts others to assail the monopoly of the originator in the hope of finding a way around his patent protection or of discovering some new and nearly equivalent product that will escape the patent monopoly.

In what we have designated as research-based industries the variations in values of successful projects are staggeringly huge and emphasize the need for extraordinary care in attempting to evaluate them. In the two year period from 1924 to 1926 the production of nitrocellulose lacquers increased nearly sevenfold (from less than 1.5 million gallons in the first half of 1924 to more than 10 million gallons in the first half of 1926). Also in the five years from 1922 to 1927, production of ethylene glycol skyrocketed from 10,000 pounds per annum to 12 million pounds. Obviously a rare second sight would have been necessary to foresee any such growth of either. Occurrences like these have baffled every attempt yet made to reduce the evaluation of research projects to mathematical formulae, and hence the evaluator must depend primarily on the best judgment that he can reach on the basis of experience and ascertainable facts.

Arthur D. Little was particularly successful in this field and that makes his views highly pertinent. His Perkin Medal address was devoted to "The Evaluation of Chemical Projects." In it, he said:

"Since earning power implies operation on the commercial scale, an essential qualification of the person making the type of study under consideration is a sufficient acquaintance with the industry to enable him to formulate the project at that stage.

"Every investment made in revenue-producing property, whether real estate, securities, or a business enterprise, is essentially a capitalization of earning power. That is, the earning power in dollars per year is multiplied by some factor. The factor used depends both on the risk involved and on the credence given to the prospect that earnings will increase. It was this latter element which led to the acceptance of the absurdly high factors generally in use in the late '20s.

"If the industry is unstable, as, for example, that of wood distillation; if the enterprise is new, like the production of alcohols from petroleum; if obsolescence is rapid, as in the early days of the sulfite pulp manufacture, the risk is high and the factor low. The general rule is clearly illustrated in case of bonds. Where there is no doubt of the security of the principal, the factor is high, and conversely, as with United States Government bonds, the yield is low. Doubt lowers the factor and increases the yield required to attract, as with bonds of companies in precarious or waning industries. The evaluation of a chemical project, therefore, requires, first, an authoritative estimate of its earning power, and second, a comparison of the risks involved with the risks of any other investment promising equal returns. . . .

"The best possible outline of what is coming is essential to any industrial evaluation, and one may usually be drawn with reasonable accuracy by those who are sufficiently familiar with the industry to enable them to sense trends and who are alive to incipient developments. Since, therefore, one may be called upon to appraise a chemical project at any stage of its development from the initial inspiration or idea to a plant in operation for a long period, the closer the project is to being a going concern the more one has of past history to base his judgment. The same questions arise at every stage, but guesswork decreases as the basis for opinion broadens.

"When the concern has been in operation for a considerable number of years, the record of the company will be available as an aid to judgment. From this record the weaknesses and the strong characteristics of the business can be picked out, the general trend of the company's affairs determined, and an estimate formed of the ability of the management. Whether, during the period, profits have expanded, contracted, or remain stationary will be apparent.

"The individual chemical industry is apt to be highly specialized. It commonly involves greater risk, and when successful, returns greater profit than industry as a whole. It is peculiarly dependent upon rigid scientific control; highly sensitive to changes in its situation resulting from research by others; and must largely rely, for the continuance of its prosperity, upon the effectiveness of its own research. It is, however, little subject to changes in styles and fashions, though more dependent than many industries upon patent protection.

"There is also in chemical industry a greater gap than in most others between paper work and practice. One cannot go out and rent a building and lease machines and begin manufacture as one can start making shoes.

"While it is frequently possible to use standard equipment, chemical processes often require that which is specially designed and which, if the process is a new one, must be developed, sometimes at great expense, as was the case with the high-pressure cracking processes and ammonia synthesis. Moreover, in the initial stages of process development so many undetermined factors are invariably present that the development must, of necessity, proceed by steps. Even under the most favorable circumstances the bringing into operation of a chemical plant is a much slower and far more complicated matter than that of starting up a cotton mill or a paper mill or a shoe factory, where the performance and capacity of every machine is already known. In a chemical plant, even though it be one in which standard equipment is used throughout, one must still reckon with many variables as time, temperature, pressure, and the disconcerting idiosyncracies of the reacting materials.

"Important as the yield of a process is for the estimation of its economic value, high yields are sometimes secured at disproportionate cost. A German technician once visited an American electrochemical plant and, during his inspection, asked what the current efficiency of the process was. When told it was only 47 per cent he foresaw bankruptcy for the company and said, 'We get 85 per cent in Germany and are still losing money.' 'Of course you are,' the manager replied, 'you have wiped out your profits by adding too many refinements.'

"Many chemical industries are distinguished by the number and importance of their by-products, others by the necessity they are under of making collateral products, as when the electrolysis of salt for chlorine involves a proportionate production of caustic soda. It is as though a cotton mill to make 35 yards of cloth was forced also to turn out forty shoes. The demands for cloth and shoes may not always be in this proportion, and there may also be some difficulty in satisfactorily allocating costs between them. . . .

"Consideration of any chemical project must proceed in stages. There is first an examination of the obvious facts in the situation, and these are often sufficient to cause the immediate rejection of the proposition. One would not undertake the manufacture of alcohol from waste sulfite liquor when molasses could be had for 4 cents a gallon, nor that of synthetic rubber with plantation rubber selling at 8 cents a pound.

"Thus the relation of a process to contemporaneous developments is of the first importance in estimating its value. In 1851 Charles Watt described, in a remarkably comprehensive British patent, methods for the production of hypochlorites, chlorine, and alkali, and chlorates by the electrolysis of common salt. Had this patent appeared thirty years later, it would have had great value. In 1851 it was of no industrial interest because the only current then available was that from expensive primary batteries.

"If the preliminary review fails to disclose anything seriously adverse to its prospects, one may make the tentative assumption that the project is sound and proceed directly to the study of the economics of the situation. This will either reveal such unfavorable conditions as to make further consideration unnecessary or it will indicate that there is a real place for the enterprise if the process concerned is sound in fact. Not until then need one undertake the final rigid examination of the process itself.

"In case, then, that the process appears attractive upon its face, one of the first things to be considered is, of course, its relation to the state of the art. This can only be determined and even then not always conclusively, by a thorough literature and patent search. By way of example, it will be recalled that the apparently impregnable patents of Willson for crystalline calcium carbide were finally found to have been anticipated by a patent in the seemingly remote art of incandescent lighting—namely, the Bohm patent for a filament of calcium carbide.

"Where the product itself is new, the protection afforded by the patent covering it may greatly enhance the value of the opportunity created by the manufacturing process, since it prevents others from marketing the product, even though they should discover an alternative process for making it. By way of illustration one may cite celluloid, vulcanized rubber, and many synthetic dyes.

"Provided the search has reasonably established the novelty of the process and indicated that adequate patent protection may be expected, one has still to consider its relative importance in the art: Is it so fundamentally new that it promises to ensure a broad monopoly, as was the case with the viscose process of Cross, Bevan, and Beadle, or is it supplementary to an existing process, as the Frank process for converting the already patented calcium carbide into calcium cyanamide? In the latter event the value of the process is obviously indeterminate until one has reached an understanding with the owners of the patent controlling the raw material.

"A supplementary process may indeed sometimes have a large measure of control over an important primary process. In the early days of Tilghman's sulfite process for wood pulp the lead linings of the digesters were a source of endless trouble and delay, so that digester repairs alone were fifteen dollars per ton of product. Russell's method of lining the digesters with Portland cement and brick brought this down to a negligible amount and permitted a great expansion of the industry.

"The Bessemer process, in its original form, would never have come into broad general use, because the steel produced was so contaminated with dissolved iron oxide as to be unsuitable for many purposes. Furthermore, the process could not be applied successfully to the treatment of iron rich in phosphorus. The importance and field of the process were, however, soon vastly extended by two supplementary inventions. Robert Mushet eliminated the iron oxide by adding manganese, as spiegeleisen, at the end of the blow, while S. G. Thomas, by demonstrating that phosphorus could readily be removed in the presence of a slag rich in lime, made the process, as thus modified, available for the treatment of the high-phosphorus iron from the vast ore deposits of Lorraine, which thus became the basis of the German iron and steel industry.

"The process of mercerizing cotton yarns and fabrics greatly increased their strength and their capacity for taking dyes. Unfortunately, it involved a 20 per cent shrinkage, and as a result its initial popularity soon waned. The process was practically forgotten until, years afterward, Thomas and Provost devised means of preventing this shrinkage and found to their surprise that they had thereby conferred upon the yarn a brilliant silky luster, which led to its widely extended use.

"Secret processes should rarely have a place even in a speculator's program, and never unless those who sponsor them permit thorough investigation by competent and hardboiled experts. Like Jernegan's seawater gold, the Hickman sugar process, the Lamoine diamond swindle, and many others, they are too often the device of charlatans. Moreover, the secrecy can seldom be long maintained, even in case of an honestly promoted and thoroughly sound process. Nevertheless, Sir Henry Bessemer, who was a prolific inventor, operated secretly for years the process for making bronze powder which brought him his initial fortune, and we ourselves similarly operated on the large scale for more than a decade a process of exceptionally high efficiency for the production of chlorate of potash. In each instance, however, the course was justified and possible only because of the extreme simplicity of the essential feature of the process, this being, in our own case, merely the suppression of reduction at the cathode by the addition of one per cent of calcium chloride to the bath of muriate of potash. . . .

"In evaluating a new process nothing is more important than the stage of development in which it is presented. If still in the laboratory stage it is in effect a liability rather than an asset, for much time, effort, and money must be spent before a return from earnings can be expected. At best the process is no more than an opportunity to develop presumably potential values, and for that development technical skill, a long purse, courage, and staying power are essential. The price of a process at this stage should seldom be other than a reasonable proportion of the equity and the underwriting of the estimated expense of carrying the development through the semi-works stage. All the parties at interest are speculating, not investing.

"When the semi-works stage has been reached by several successive steps and operation has continued for several months, both the possibilities and the limitations of the process should be fairly well defined, and the speculative feature correspondingly reduced. The character and balance of equipment have been determined, conditions for control established, yields and costs approximately ascertained, and markets tested. Although still speculative, the process has now become a project which may be evaluated provisionally on the basis of the showing made. The controlling factors in this evaluation may now well be the estimated time and cost of further development, the cost of the commercial plant, the estimated annual earnings, and their capitalized value.

"When, however, a process has been in operation in a commercial plant for a reasonable length of time, which may be a year or more, we have to deal with a going concern, the evaluation of which will be governed by the considerations involved in the appraisal of any manufacturing business, except as these may be modified or extended to meet the specialized requirements of the chemical industry.

"The relation of a chemical process to its raw material supply is often of even more vital consequence than at first sight appears. The raw material selected by Baeyer for his initial synthesis of indigo was toluene, but when the process was perfected it was found that toluene was not procurable in amount sufficient to make possible the displacement of natural indigo. Baeyer and his associates were thus forced to travel the long road again, starting from the cheaper and abundant naphthalene, but when they finally arrived Germany controlled the indigo market of the world.

"If beryl were as common as bauxite, the beautiful metal beryllium would undoubtedly usurp much of the market for aluminum. Fortunately, the supply of the basic raw materials for chemical industry—salt, sulfur, the atmosphere, coal, oil, natural gas, lime, and cellulose—are available in amounts altogether adequate for any possible development.

"Energy is a raw material in a very definite sense, and its form value is often important, as shown by the advantages of natural gas for firing boilers or for heating the tanks of glass works. In the electrochemical industries the cost of power may determine success or failure.

"It is always perilous when a chemical company depends solely for its raw material upon another enterprise over which it exercises no control. I recall the case of the Standard Alcohol Company, which built a 5,000-gallon plant to make grain alcohol from wood waste. It did this by a process which yielded 10.5 gallons of Cologne spirit per ton of waste. Elihu Thomson said he was not surprised, the alcohol obviously coming from the grain of the wood. Unfortunately the company, which had a choice of sites where the waste from many sawmills was available, chose one where it depended upon a single mill, the waste from which was just sufficient to permit the plant to operate at capacity. Unfortunately, when the plant was ready to begin operations the price of yellow pine lumber had so declined that the sawmill operated at only about one-quarter capacity, with the inevitable consequence that the alcohol company went into liquidation.

"In another instance the unfortunate selection of a site, coupled with a flagrant disregard of ordinary precaution, resulted still more disastrously. The White Mountain Paper Company built at Portsmouth, N. H., what was to be the largest newsprint mill in the world. In the process they proposed to use sea water from the harbor. When the mill was built and the machinery installed, the president, during an interview with me, inquired casually if I thought the salt water would involve them in any difficulties. I told him he would never be able to make paper with it. He never was, and the idle plant stood for years a monument to ignorance of the first principles of evaluation of a chemical project.

"The possibility that a chemical process may create a nuisance must always be kept in mind and has an important bearing on the selection of a location. There are processes which can only be operated with a minimum of friction 'far from the madding crowd.' Damage suits, and injunctions which are sometimes permanent, play havoc with dividends. . . .

"There are other risks, in addition to those involved in operation, which should be carefully weighed in considering a chemical proposition. There is, for example, great danger of underestimating the time and capital required for reducing a laboratory process to commercial practice. One does not always go 'from test tube to tank car in three years.' Many have lost great opportunities in chemical industry simply through lack of staying power, and, as Doctor Baekeland said in his own Perkin Medal address, 'remember that starting a chemical enterprise with insufficient capital is one of the most effective ways of ensuring failure.'

"Generous allowance must also be made for the rapid obsolescence of many types of chemical equipment. Furthermore, management must be of a quality competent to make the rapid adjustments necessitated by the frequency with which new processes and products appear. Doctor Haber attributes the success of German chemical industry to the fact that, from its commencement, the Germans realized the need for close cooperation of the chemist, the technician, and the selling department. It is easier and more profitable to adjust sales to the developments of one's own research department than to those resulting from the research of a competitor.

"Major changes in the industry are apt to cast their shadow far ahead and thus to give more time to meet them than the style changes in some other industries allow. There is, nevertheless, always the possibility that the process in use may be displaced by a new one, as occurred when viscose rayon usurped the place of Chardonnet artificial silk. The encroachment of chlorine upon bleaching powder, the substitution of butanol for amyl alcohol, and of synthetic ammonia for Chile nitrate are examples of the similar replacement of established products.

"A corresponding curtailment of market may be brought about by changes in other industries. Shingle stains are not needed for asbestos shingles; stainless steel competes with chromium plating; and the incandescent lamp replaced acetylene in automobile headlights.

"Fortunately, the converse is even more often true. A great new market for chromium compounds was created by the shift to chrome tanning. Mercerized cotton increased the demand for caustic soda, and it was further increased by the viscose process, which also opened a great new outlet for carbon disulfide. A change in the method of finishing automobiles brought spectacular prosperity to a company loaded down with by-product butanol.

"Adverse laws, tariff changes, the uncertainties of patent litigation, and the prospect of domestic and foreign competition must all be reckoned with. The Volstead Act imposed great burdens on the distillers of grain alcohol, but benefitted methanol. The Pure Food Law restricts the use of saccharin. . . .

"All these considerations emphasize the great advantage of diversification of products as an assurance of stability, and add much weight to the importance of the capacity for tree-like expansion inherent in the chemical industries.

"The relation of a proposed product to the established distribution system of the company is a matter of primary importance. The sale of a household disinfectant would involve altogether disproportionate expense to a company which had previously sold its customary products only to the textile industry. It is similarly important to ascertain whether the product is one for which a broad market already exists or one for which, however promising, the market must be created. Either possibility obviously calls for a careful market survey.

"The final criterion of the value of any chemical enterprise is, of course, its earning power, but the full significance of the item of net earnings is not disclosed in its sum total on the balance sheet. It is especially important that this total be broken down into its major constituents and that the proportion contributed by each of them be considered not only as to its amount in dollars, but more particularly as to the probability of maintaining or increasing this proportion in the future. There is an obsolescence of products as there is of machines and, again, the company making a reasonably diversified line has the larger factor of safety.

"There is in every new project, whether chemical or otherwise, a final element of uncertainty against which provision can rarely be made. We were once called upon to develop, from sulfite pulp, a paper binder-twine for use in harvesting machines. We found that the pulp as then made would not make a paper of sufficient strength. By spending some time at the mill we were at last enabled to produce a pulp which gave a paper of the required tensile test. The twine was made, but it was found necessary to waterproof it, so a method of doing that was worked out. Then it was discovered that, in spite of its strength, the twine broke in the knotter of the machine. The trouble proved to be due to the too sharp curvature of the usual knotter, so a new one was designed. Finally, our client got into production. The twine worked perfectly and every one was happy until the sheaves began to fall apart because the crickets ate the twine.

"The story should, of course, end here, but there is another chapter. We added an entomologist to our staff and aided by his knowledge of the dietary aversions of crickets, we finally were enabled to treat the twine so that it went off their menu.

"While giving due weight to all the foregoing, one must not forget that, however promising a chemical industry may seem to be, its conduct is, after all, only a form of human activity and its success or failure will finally be determined by the human element. The quality and character of the management, its business ability and experience, its attitude toward research, and the strength of its financial connections are primary and often decisive factors in the evaluation of a chemical project. This was summarized by one large investor in the phrase, 'I put my money on men.' "

Clearly all the facts that one can muster plus every bit of experience, whether his own or someone's else, that can be brought to bear upon the problem of evaluation are seldom quite enough to take all the gamble out of the future, even the future of a research-based project.

Chapter 14

Something About Patents

"The Congress shall have power . . . to promote the progress of science and the useful arts by securing for limited times to authors and inventors the exclusive rights to their respective writings and inventions." —The Constitution of the United States

"Our patent system was not created to enrich inventors but to benefit the public by encouraging the invention and the development of new and useful processes and products. . . . Lincoln well summarized the whole situation in his laconic statement that 'the patent system added the fuel of interest to the fire of genius.'"

—Robert E. Wilson

The temptation at this point is well nigh overwhelming to launch into a learned discussion of the patent law as if my own experiences with patents and patent attorneys had made me an expert on the subject. To do so might very well give me and my ego great satisfaction but it would hardly be likely to give the readers of this book the thing that they need on the subject. A more satisfactory procedure might be to quote from an eminent patent attorney who has only a secondhand knowledge of research or from an equally eminent research director whose acquaintance with patent law is similarly hand-me-down. That would, however, hardly meet the need of the research worker himself, for whose particular benefit this book is being written, since he is concerned with patent law only as an adjunct to his work and by no means as an activity of his own. Better far will it be to single out the particular and special aspects of patent law that must concern the research man himself and to discuss them for his guidance.

Only two aspects of patents need become the personal concern of the research man: (1) since his employment is primarily concerned with the creation of new things for the benefit of his employer, he will normally be required to enter an agreement with his employer to surrender certain rights to him covering inventions and patents for them, which agreement is affected by patent law; and (2) in carrying out the provisions of such an agreement, the research man must take certain precautions in his daily labors to insure that his employer obtains these benefits as easily and as fully as possible.

While all the whole field of patent law and the ponderous working of its processes possess inherent lively interest for the research worker, yet only these two phases are vital for the researcher himself to know. For all other phases of patent law, he would be much better advised to depend upon the knowledge and experience of a specialist in the subject than upon any scant knowledge he himself might acquire through secondary study. Obviously his employer's interest requires that capable attorneys handle all such matters and furthermore that the employer provide the needed skill to protect his own interests. If the researcher is working on his own responsibility hoping to benefit himelf by his inventions and discoveries, then it is supremely important to himself that he procure the services of the best patent solicitor he can find to assist him. Not only is the matter of soliciting patents one requiring specialized skill and experience, but many other phases of handling matters concerned with patents under the circumstances can be better placed in the hands of some one both expert and dependably friendly to represent the researcher in the probable subsequent negotiations for the sale or licensing of any such patents to others. These, no less than the solicitation of patents itself, are matters in which researchers are unlikely to be skilled, experienced, or even, in the final analysis, interested.

The question of employment contracts often emerges unexpectedly to confront the prospective researcher when he is intent upon something quite different, and under the usual circumstances this unexpected and strange subject creates in his mind an immediate reaction of fear that something is about to be put over on him, and of antipathy toward the whole matter, including his employer. But the entire procedure is entirely orthodox. The employer, assuming of course that he is honest, is merely seeking to avoid possible future misunderstandings by agreeing on certain crucial points with his employee in advance of trouble. By expressing these conditions of employment in a contract, the conduct of both parties can be calculated in advance to avoid trouble through inadvertance (and lawsuits arising from inadvertance can create just as much expense and ill will as any other kind).

A few basic principles govern employment contracts, and once these are clearly understood by the researcher, he is unlikely to have any more trouble with the subject. Fundamentally, the employee agrees in such a contract: (1) to do certain types of work for his employer and for his employer's benefit; (2) to preserve the employer's confidence in all matters affecting the business; (3) to make and to assign to his employer any patent applications arising out of his employment; and (4) to avoid giving the employer's competitors the benefit of his specialized knowledge and experience gained in the employer's activities. These are, of course, reasonable conditions without which an employer would scarcely be willing to hire a man.

On his side, the employer also agrees to certain reasonable and basic conditions benefitting the employee: (1) to pay the employee wages at stated intervals and in specified amounts; (2) to provide facilities for the employee's use in doing his work; and (3) otherwise to provide for the employee's welfare during, and for some specified period following the end of, his employment.

Those broad principles are in no wise likely to cause any misunderstanding or unpleasantness between the parties so long as they are understood in advance. Only when either party attempts to go beyond such reasonable provisions and to make a contract extend to minute details of conduct is trouble likely to arise. Such reasonable conditions of employment can be enforced without a contract, although it is better to have the conditions in writing. On the other hand unreasonable conditions can only be maintained with the greatest difficulty should either party undertake to break the contract. The courts will not uphold a contract as valid and binding if its provisions transgress certain established principles of "public policy." These necessary requirements for the validity of a contract of any kind, and especially of this particular kind, are worth recounting.

A contract of any kind to be binding on the parties must: benefit both, be specific and be limited in its operation. In an employment contract, the work of the employee is the benefit which the employer expects and that necessarily includes, when research is involved, patent rights and inventions. The return consideration is the wages to be paid. Necessarily, there is no sense in writing out an agreement unless the writing is specific and by the same token, vague contracts or conditions can be enforced only with the greatest difficulty, if in fact at all. Finally, a contract cannot be made to cover an unlimited scope of activity or an unlimited time, nor can any of the provisions of an otherwise valid contract hold if they themselves attempt to impose conditions without limit. The employer, for example, can only obtain by contract ownership in his employee's patent applications that relate to the employer's business as specified in the contract. If an employee of a chemical manufacturer should, quite aside from his contracted employment, invent and patent a safety pin, that would fall outside of the limitations of the contract. In some cases, where the invention of the employee lies outside the scope of the employer's business, the employer may acquire "shop rights" to the invention which permit him to use in his business, but not to sell, the patented article. An example might be of a special type of valve useful to the employer's business of chemical manufacture but which he would have no reasonable interest in marketing. "Shop rights" might be acquired by the employer because the employee's invention grew out of his employment or because the employer's materials or contracted time were used in arriving at the result. These questions can seldom be answered entirely and completely in advance, but the more specific a contract can be in specifying the employer's field of interest the better.

By the same token the contract should recite any fields in which the employee has interests that he wishes to except from the provisions of the contract.

The requirement that the contract be limited both in subject matter and in time is a matter of public policy stemming from the Magna Carta of King John in England in 1215. The basic idea is that no man shall be deprived of his tools or of his means of livelihood. That applies equally well to the experience of a modern research worker as it did to the axe, hammer and saw of the medieval journeyman carpenter. Thus, it is impossible under our law for a research worker, or anyone else, to enter a contract which may subsequently operate to deprive him of his usual means of livelihood. If a contract undertook to do that, the courts would without hesitance declare it void.

Operation of these considerations nullifies a contract of employment which seeks to impose conditions which could not be maintained if there were no contract. Obviously it is better to have these matters written out so that each party has a record of the understanding, but it is quite futile on either side to attempt to impose conditions which the courts have heretofore held invalid when contracts have contained them.

Obviously the simpler a contract can be made the better. There is no inducement on either side to break a contract which is reasonable and which represents an exchange of values satisfactory to both parties. The fewer conditions a contract seeks to impose the less likely it is to become onerous.

Based on these ideas, the contract of employment used by the Kilmar Corporation some years ago seemed to me to possess highly desirable brevity and conciseness, and at the same time to cover the ground adequately. Certainly it encouraged compliance instead of inviting dispute as many other such contracts do when their writers attempt to be legalistic and excessively detailed in the provisions included. This contract took the form of a letter sent in duplicate to each new employee at the time he was hired. One copy was to be acknowledged by the employee and returned for the company's records, and the other retained by the employee. Here it is:

"Inasmuch as the Kilmar Corporation is engaged in the development of various processes, apparatus and devices for use in refrigeration and in the manufacture and use of carbon dioxide in gaseous, solid and liquid forms, it is essential that the following conditions of your employment be understood and observed.

"You agree that at no time during or after the term of your employment will you disclose to anyone not in the employ of this corporation any secret methods, processes or trade secrets which you may learn as a result of your employment unless authorized in writing by its president so to do.

"You agree to communicate with reasonable promptness to the president of this corporation, or to a person designated by him for such purpose, all inventions made or conceived by you relating to the corporation's business from the time of entering its employ and until three months after the termination thereof.

"You agree to assist the corporation in every proper way, at its expense, in the preparation and execution of any and all patent applications and other instruments necessary to secure for its benefit, or that of its nominees, patents for any of said inventions in any and all countries, said inventions to be and remain the exclusive property of this corporation or its nominees whether patented or not. The corporation agrees to compensate you for any time actually spent by you at its request in this connection after the termination of your employment at the same rate as that paid you at the time of such termination, and further agrees not to call upon you for any extended or continuous time after such termination to the detriment of any employment in which you may then be engaged.

"You are employed on your express representation that there are no inventions (patented or not) made or conceived by you before entering this corporation's employ related in any way to its business except those listed on the back hereof, which inventions are specifically excepted from this agreement.

Truly yours,
Kilmar Corporation
By
President

Accepted:
Date:"

Having thus formed an attachment for the express purpose—among other things—of making inventions and discoveries for the benefit of his employer,—and of himself through his earnings,—the researcher is ready to tackle the job. His first care must be to concentrate and direct his thinking into channels that are likely to be fruitful. But equally important is the necessity to keep an accurate, concise and continuous record of what he does. Unrecorded thoughts might as well never have been.

The provision of the contract of employment that the employee assist his employer in every way to secure for the business the exclusive benefit of the employee's inventions places a responsibility on the employee that begins immediately. He must be ready at any future time to testify, in court if necessary, to the exact times and circumstances that certain experiments were performed, certain ideas conceived and certain actions taken.

This requires records, for no active human mind can maintain a continuous memory of all the events of a busy life over a long stretch of years. Furthermore, the records most effective in refreshing the memory and possessing the greatest weight in a subsequent inquiry are written out in long hand at the time by the person whose memory is being refreshed and take the form of a continuing diary in a bound book.

Several reasons for the importance of these characteristics of the written record appear on close examination. Most important is the fact that the record itself can call to the mind of the person who wrote it many other circumstances extending and amplifying the written words. Associations of ideas that may have been forgotten in the meantime are readily recalled by rereading something one set down on paper even many years before. This cannot operate to aid a second person in quite the same way, and even the witnesses who sign a paper at the time it is originally written can seldom recall more than the most obvious circumstances surrounding the act. Certainly a person seeing an account of a past action for the first time is more likely to recall later the circumstances under which he first saw it rather than those of its original composition, even if he was present at that event.

The second characteristic of a good record for patent purposes is that it be more or less continuous over a period of time. No event in our lives or our thinking can ever be wholly detached from events preceding and following it. The "flash of genius" concept of original thinking has already been examined in an earlier chapter. There we noted that whatever may be the flash-like characteristics of the final synthesis, no one can achieve such without serious and often prolonged prior preparation. The well of our thinking must be charged with material from which the mind finally synthesizes the inspiration. Clearly, then, the circumstances preceding and following the "flash" form vital parts of the record needed to prove the various aspects of an invention or discovery and the vital time element.

For the grant of a patent is effective in conferring a monopoly on only the *original* inventor. Contests on this point are so frequent as to be the rule. Repeatedly several persons have reached the same or similar results at very nearly the same time and the courts must decide which of several claimants is in truth the *first* inventor in point of time and hence entitled to the protection of the patent. This stresses the value as evidence of continuing records covering the period before and after the actual invention not only as a means to refresh the memory of the person who made the record but also to assist others in reaching important conclusions regarding the elements of time and of the nature and extent of the invention, discovery and inspiration at the various times in question.

Records made in one's own handwriting are more valuable than any others primarily because alterations of any kind by some one else are usually obvious. Each of us can readily recognize his own handwriting and similarly any departure from it or changes made by another. This grows out of extreme familiarity with relatively large amounts of material one writes in the course of time. In addition, the circumstances surrounding any act of writing can frequently be recalled more completely and easily than can the mere signing of a paper produced mechanically or otherwise.

Obviously, these little aids to memory gather weight with the passage of time. While it is readily possible to recall major events over long periods, the details, which are often vital in patent matters, gradually fade out and may be completely lost unless some steps are taken in advance to save them. It is quite possible to recall some of the major events of V-E Day ending World War II in Europe, for example, and just what one did in general to celebrate that event. However, within a few days, or at most a few weeks, our precise memories of what clothes we put on or what foods we ate for breakfast on that day had completely faded. An exception is the extent that we did exactly as we always had done, but that is undependable. Yet details roughly equivalent can often prove crucial in the testimony a researcher may be required to give in a patent case. It might, for instance, be crucial to remember whether the melting point of a particular compound was determined on a particular day, using a thermometer that had been checked by the researcher on that day or whether he had employed an unidentified and unchecked thermometer direct from the store room stock. Such details, even though they may have seemed inconsequential at the time, can sometimes be recalled by the aid of one's own handwritten record, *even though the record does not state the specific detail.*

The final requisite of the research man's record is that it should be kept in a permanently bound book. The first effect of this is that the entries are likely to be made in the order of the pages and are more difficult to lose or to disarrange than are loose sheets. A bound book by its very nature encourages orderly records and orderly records simplify the task of the memory to recall some distant and seemingly unimportant detail. Furthermore, a minimum amount of orderliness and attention on the part of the individual conveys the greatest impression of order when it has been expended on keeping a record in a book, in contrast to attempts to put together fragmentary notes on loose sheets. The form of a diary approaches the ideal for a running account of one's research activities, since the provision of a page, or other specific space for recording each day's actions in a sense requires the diarist to find an excuse *not* to make an entry each day. That helps to establish the continuing relations between one's thoughts and the calendar.

The question of what should be included in the researcher's record of each day is a matter that only he can determine. The objective is to be able to recall at some future time *all* of one's thoughts and actions on that particular day. The extent of the record needed for this purpose must necessarily be determined both by the activities of the person involved and by his need of reminders.

Finally the researcher should so order his own schedule that entries in his diary become matters of routine to be made regularly each day at a convenient time, whatever may be the other events of the day. No one can surely foretell whether one's actions on this day will be important a decade hence or not, but if a record is made of them at the time, any future significance they may acquire can be easily handled then. Without a record the emergence of an idea into significance in the future can only be accompanied by futile "wailing and gnashing of teeth." Whether one makes and keeps his diary in the laboratory or at home, it should be given a specific time each day and this should be faithfully observed.

All of this has been set down without reference to the kinds of things involved in patents and their relative weights. It is not necessary for the researcher to burden himself unduly with such ideas. They are better entrusted to someone else in any case; the firm's patent attorney or its director of research is better equipped to evaluate a man's work than he himself and is far better able to utilize it in the next and subsequent steps toward an issued patent. Usually it is far better to trust to experts in this as in other activities than to attempt to become expert oneself in an alien field. Nothing can substitute in patent matters for close cooperation with a capable patent attorney.

Chapter 15

Loose Ends Gathered Here

"The method which our race has found most effective in acquiring knowledge is by this time familiar to all men. It is the method of modern science—that process which consists in an interrogation of Nature entirely dispassionate, patient, systematic; such careful experiment and cumulative record as can often elicit from her slightest indications her deepest truths. That method is now dominant throughout the civilized world; and although in many directions experiments may be difficult and dubious, facts rare and elusive, science works slowly on and bides her time—refusing to fall back upon tradition or to launch into speculation merely because strait is the gate which leads to valid discovery, indisputable truth. —F. W. H. Myers

This discussion of the methods of industrial research must necessarily remain incomplete. Because research is a living, growing thing, its many ramifications can have no end, and certainly no end is reasonably possible to the number and variety of the problems research will be called upon to solve for industry. So, from a great diversity of problems must come an equally great diversity of solutions, and the available variety of methods of attack must be equal to these demands. That, of course, leads inevitably to the conclusion that the prime objective of this book, to set forth the pattern of industrial research, is quite impossible to attain.

Even at that, some help may have been extended to the worker in research and new paths of exploration opened to him by following as we have through many works of masters in this art. We have brought together stimulating thoughts of successful industrial researchers for the guidance they may afford to those who follow after them. But all around the selections quoted in the foregoing pages are others quite as fascinating and quite as instructive, which the mere physical limitations of a single volume must necessarily exclude here. Any bibliography of this subject approaching completeness would compare with the catalog of a quite respectable library. Obviously, too, an extension of the subject by even a little to include the direction and management of research would tremendously expand that beyond reasonable limits.

Clearly, the reader will look for something more. And that, he can find for himself better than anyone else can find it for him by continuing to study material published about this important art. That is the reason the index to this volume takes a peculiar form; it is presented as part of the last chapter and not in a separate section as an afterthought. Furthermore, the needs and desires of the reader will be more likely met by reference to the sources of the material quoted rather than simply to those pages in this book where it appears. That is apparently sufficient reason for the strange form of author index following.

Even with that, the reader's needs may still be incompletely satisfied. Therefore, the author at this point suggests that not all these references are equally valuable and offers further comment on certain of them.

The first important comment refers the unsatiated reader to three sources containing a great many useful thoughts quoted from original sources. These are principally valuable as savers of time and labor.

Writings of Bacon, Darwin, and Hobbes appear at length in The Harvard Classics, published by P. F. Collier, and this set of books provides a convenient source for this material.

Numerous other authors quoted in this book have also been quoted before. In several instances, it is easier to find the material pertinent to this discussion in the quoted than in the original works. Wherever possible the original references have been given. However, the reader may be able to satisfy his needs with a saving of much labor by referring to: Sir Richard Gregory's "Discovery," published by The Macmillan Company; and to Curtis & Greenslet's "The Practical Cogitator," published by Houghton Mifflin Company.

Beyond that, it seems desirable to place greater emphasis for purposes of supplementary reading on certain works than has been done in the foregoing pages. This, primarily, because the nature of some of the material does not lend itself well to quotation here. Furthermore, there seems to this writer to be much more value in some of these articles and books than even skillful abstracting can realize.

The psychological processes of research are investigated in detail and to an extent impractical here by Graham Wallas in his "Art of Thought," published by Harcourt Brace & Co. Anyone interested in this art should by all means spend the effort to find and study this book, which unfortunately is now out of print, but which is likely to be found on the shelves of good public libraries. James W. Young deals with the same subject from the point of view of an advertising man in his "Technique for Producing Ideas," published by Advertising Publications, Inc. This is a brief book that can be read in an hour or so but which merits much longer study. Both of these books are written from points of view quite outside of scientific research, but they provide invaluable guidance to anyone who must think creatively, scientist as well as layman. A final discussion of this subject which every research man should know is contained in the survey made by Platt and Baker among research workers and published by them under the title, "Relation of the Scientific 'Hunch' to Research," in the *Journal of Chemical Education* for October, 1931. This study investigated the "hunches" (or as we might now call them, "flashes of genius") forming vital parts of the work of research workers. In addition to the helpful information gathered directly, this article contains an excellent bibliography of books and papers on the same general subject. Each of these three works will repay careful study by any researcher, neophyte or adept.

One serious omission from the foregoing pages must be made good by special mention here. Wilder D. Bancroft in 1928 delivered a series of three important lectures on the "Methods of Research" at the Rice Institute in Houston, Texas. In due time, these lectures were published as number 4 of volume XV of the Rice Institute Pamphlet. Let no one be misled by the word pamphlet applied to this work; actually, the single number containing the three Bancroft lectures comprises a volume of 186 pages. Because Bancroft devotes himself heartily to the promotion and promulgation of the Aristotelian or deductive method of research and to the damnation and confusion of the experimental, inductive method of Bacon, much of his valuable material is in no form to be quoted directly in a discussion like this one which straddles that issue. Even though our views may differ from those of Dr. Bancroft, nevertheless his analysis of the functioning of the research mind is too valuable to be omitted from the training of anyone who seeks to perfect himself in this art. The Rice Institute Pamphlet is likely to be found in most large, general libraries, but not so frequently in technical libraries, since its subject matter covers the broadest fields of interest and only occasionally touches upon science and technology.

Anyone interested in the several aspects of the researches described will find not only further information in the articles noted in the following author index, but he will also find in each of them further references to still other material that can be traced down with profit.

Finally it seems fitting to conclude this dissertation with a valedictory quotation. This emphasizes in words slightly paraphrased from those of a highly successful researcher, Thomas Midgley, Jr., the tremendous value of what has become the *sine qua non* of attainment in this art, cooperation:

"*And the moral . . . is simply this: You must be lucky as well as have good associates and assistants to succeed in this world of applied research.*"

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