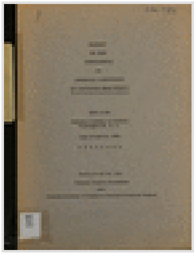

Report on the Conference on Chemical Compounds of Certified High Purity (1959)

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REPORT

ON THE

CONFERENCE

ON

CHEMICAL COMPOUNDS

OF CERTIFIED HIGH PURITY

Held at the

National Academy of Sciences
Washington 25, D. C.

June 22 and 23, 1959

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Sponsored by the

National Science Foundation

and

National Academy of Sciences-National Research Council

Report on the Conference
on Chemical Compounds
of High Purity

CONTENTS

INTRODUCTORY STATEMENT

For some years, many scientists have been concerned about the problem of chemical compounds of certified high purity. Apart from nearly 300 hydrocarbons, and a few compounds of other kinds, many of the simplest chemical compounds most used in science and industry are nowhere available as samples of certified high purity. The lack of such samples leads to duplication of effort in many laboratories in preparing samples just good enough for their respective needs. Were samples of certified high purity available for these compounds, experts could make on them definitive measurements of physical, thermodynamic, and spectral properties, which are so much needed by science and industry. Accurate data of this kind on basic compounds constitute necessary fodder for projects engaged in preparing critical tables of physicochemical properties, and such data provide a framework for the creation, without experimental measurement, of data on related compounds by appropriate analysis and correlation.

These matters were discussed in 1956 and 1957 at meetings of the Advisory Committee for the Manufacturing Chemists Association Research Project at the Carnegie Institute of Technology. On July 9, 1958, a meeting was held at the National Research Council in Washington, D. C., to discuss the problem more fully. In attendance at this meeting were the following persons: Allen V. Astin, Chairman of the Executive Committee, and Guy Waddington, Director, of the Office of Critical Tables of the National Research Council; Edward F. Hillenbrand, Jr., Chairman, and Robert R. Dreisbach, Member, of the Advisory Committee for the Manufacturing Chemists Association Research Project; Walter R. Kirner, Program Director for Chemistry, of the National Science Foundation; Clem O. Miller, Executive Secretary of the Division of Chemistry and Chemical Technology of the National Research Council; and Frederick D. Rossini, Director, and Bruno J. Zwolinski, Assistant Director, of the American Petroleum Institute Research Project 44 and the Manufacturing Chemists Association Research Project at the Carnegie Institute of Technology. This group felt that the problem was sufficiently important to merit formal discussion by a selected group of scientists of the country in a Conference on Chemical Compounds of Certified High Purity sponsored jointly by the National Science Foundation and the National Academy of Sciences-National Research Council. Acting on this recommendation and that of Ernest H. Volwiler, Chairman of the Division of Chemistry and Chemical Technology of the National Research Council, President Bronk of the National Academy of Sciences appointed an Organizing Committee for the Conference. Financial support was provided by the National Science Foundation. The Conference on Chemical Compounds of Certified High Purity was held on June 22 and 23, 1959, at the National Academy of Sciences in Washington, D. C., with Guy Waddington as Secretary and the undersigned as Chairman. These proceedings constitute our report on that Conference.

Frederick D. Rossini
Chairman

AGENDA OF THE CONFERENCE

Monday, June 22

	9:15 AM	Registration
A.	9:40	Introductions, by Chariman, Frederick D. Rossini
B.	9:45	Welcoming remarks, by S. D. Cornell, Executive Officer, National Academy of Sciences - National Research Council
C.	10:00	Preliminary remarks, by the Chairman
D.	10:05	Report on the current live program of the National Bureau of Standards on chemical compounds of certified high purity, by Edward Wichers
E.	10:45	Report on the current live program of the American Petroleum Institute on chemical compounds of certified high purity, by Charles L. Thomas
F.	11:05	Coffee break
G.	11:25	Discussion of the reports presented and contribution of information from the floor on similar work known to be in progress
H.	12:10 PM	Recess
I.	12:30	Luncheon
J.	1:30	General discussion, I, of the philosophical and intellectual aspects of the problem
K.	2:15	General discussion, II, of the scope of the Conference
L.	3:00	General discussion, III, of specific classes of chemical compounds of certified high purity needed
M.	3:40	Coffee break
N.	4:00	General discussion, IV, of the financial resources available for supporting work on the preparation and distribution of chemical compounds of certified high purity
O.	4:40	General discussion, V, of the places to perform the work and the organization to manage the operation
P.	5:10	Recess
Q.	5:30	Social hour
R.	6:00	Dinner

AGENDA OF THE CONFERENCE

(continued)

Monday, June 22

S.	7:30 PM	Separation into five groups, for the preparation of summary reports, on I. The philosophical and intellectual aspects of the problem II. The scope of the Conference III. The specific classes of chemical compounds needed IV. The financial resources available for supporting the work V. The places to perform the work and the organization to manage the operation
T.	(9:00 to 10:00)	Adjournment, by each group separately

Tuesday, June 23

U.	9:05 AM	Remarks by the Chairman
V.	9:15	Report of Group I
W.	9:25	Report of Group II
X.	9:35	Report of Group III
Y.	9:45	Report of Group IV
Z.	9:55	Report of Group V
AA.	10:05	Discussion
AB.	10:25	Adjournment.

LIST OF PARTICIPANTS AND OBSERVERS, WITH THEIR REPRESENTATION

Representatives for Industrial Associations

American Petroleum Institute: Charles L. Thomas; Charles W. Montgomery
Manufacturing Chemists Association: Frank H. Carman; Edward F. Hillenbrand[1]
American Society for Testing Materials: Jesse W. Stillman
Industrial Research Institute: Beverly L. Clarke

Representatives for Government Research

National Bureau of Standards: Allen V. Astin[1]; Edward Wichers
U. S. Department of Agriculture: Herbert L. Haller
U. S. Bureau of Mines: Earl T. Hayes
U. S. Department of Defense: Donald B. Brooks
National Science Foundation: Randall Robertson; Walter R. Kirner[2]
Office of Naval Research: Paul H. Egli
Atomic Energy Commission: Alexander R. Van Dyken
Army Office of Ordnance Research: John W. Dawson
Air Research and Development: Amos G. Horney

Representative for AEC National Laboratories

Winston Manning (of Argonne National Laboratory)

Representative for Non-Profit Research Institutes

Harold P. Klug (of Mellon Institute)

Representatives for University Research

Farrington Daniels[3] (of the University of Wisconsin)
Lyman C. Craig (of Rockefeller Institute)
Frank H. Spedding (of Iowa State College)
I. M. Kolthoff (of the University of Minnesota)
Frederick C. Brown (of the University of Illinois)
John R. Bowman (of Northwestern University)
Charles P. Smyth (of Princeton University)
Robert C. Elderfield (of the University of Michigan)
Bruno J. Zwolinski[1] (of Carnegie Institute of Technology)

Representatives for Independent Research Agencies

American Chemical Society Petroleum Research Fund: Robert L. Burwell, Jr.; Karl Dittmer
Welch Foundation: W. O. Milligan

Members of the Organizing Committee

Frederick D. Rossini (Chairman)
Allen V. Astin
Robert R. Dreisbach
Edward F. Hillenbrand, Jr.
Bruno J. Zwolinski

Advisors to the Organizing Committee

Ernest H. Volwiler[4], Chairman, NRC Division of Chemistry and Chemical Technology
Clem O. Miller, Executive Secretary, NRC Division of Chemistry and Chemical Technology
Guy Waddington, Director, NRC Office of Critical Tables
W. R. Kirner, Program Director for Chemistry, National Science Foundation

Observers

National Research Council Committee Advisory to the National Bureau of Standards: Oswald F. Schuette, Executive Secretary; Hans H. Jaffe, John R. Ruhoff, and Norman A. Shepard, Chemistry Panel
National Research Council Office of Critical Tables: Richard Wiebe, James Watters, and M. Joan Callanan

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1 Also on the Conference Organizing Committee
2 Also an Advisor to the Conference Organizing Committee
3 Also Chairman of the National Research Council Committee Advisory to the National Bureau of Standards
4 Not present at the Conference

COMPOSITION OF THE FIVE GROUP MEETINGS

Group I: Philosophical and Intellectual Aspects of the Problem

Burwell (1)
Dawson
Milligan
Robertson
Schuette
Zwolinski (1, 2)

Group II: Scope of the Conference

Craig (1)
Hayes
Montgomery
Smyth
Waddington (1, 2)
Wiebe

Group III: Specific Classes of Chemical Compounds Needed

Brown (1)
Clarke
Dreisbach
Elderfield (1)
Haller
Hillenbrand (1, 2)
Kolthoff
Manning (1)
Ruhoff
Stillman

Group IV: Financial Resources Available for Supporting the Work

Astin (2)
Brooks (1)
Carman (1)
Horney
Kirner (1)
Shepard
Van Dyken

Group V: Places to Perform the Work and the Organization to Manage the Operation

Bowman
Daniels (1, 2)
Klug
Spedding
Wichers (1)
Egli

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(1) Presented oral report of about 5 minutes on Monday afternoon on this subject before all participants.

(2) Chairman for the Monday evening session for this group.

Summary of the Proceedings

of the

Conference

on

Chemical Compounds of Certified High Purity

O. Opening of the Conference by Chairman Rossini:

I am very happy to welcome you to this Conference on "Chemical Compounds of Certified High Purity," sponsored by the National Science Foundation and the National Academy of Sciences - National Research Council.

A. Introductions, by Chairman Rossini:

I would like first to introduce each of the persons present and to identify his representation. (This was done substantially as given in the "List of Participants and Observers, with their Representation.")

B. Welcoming remarks, by S. D. Cornell, Executive Officer:

Dr. Rossini: I am very happy to introduce to you, Dr. S. D. Cornell, the Executive Officer of the National Academy of Sciences - National Research Council, who will extend an official welcome to our Conference.

Dr. Cornell: Thank you very much.

I am always happy to speak to groups meeting in this building for purposes such as yours today. But I am particularly glad on this occasion with this particular group because your purpose in meeting is so close to what I feel to be our most significant scientific purpose. Your chairman has asked me to enlarge a little on that subject.

As most of you know the National Academy of Sciences was established as a non-governmental agency at the time of the Civil War for two purposes, to further science in the national interest and to assist and advise the government in scientific matters.

The National Research Council is a part of the Academy. It was established some fifty-five years later at the request of President Wilson for the purpose of establishing a close association of effort between the Academy and the scientists across the country generally. This was done through the medium of the scientific and engineering societies, which nominate representatives to the Research Council who are then appointed by the President of the Academy. Governmental representatives and members-at-large are also appointed to the Research Council by the President of the Academy. Together these two bodies, which form a single organization, have since 1916 performed the services provided in the charter of the Academy on behalf of science and on behalf of the Government of the United States.

A unique combination of features characterizes the Academy - Research Council. No one of these is unique by itself, but the combination gives the Academy - Research Council its peculiar capabilities and its peculiar strength.

The first of these is that it is non-governmental and yet enjoys the very closest relationships with the Federal Government through a variety of governmental agencies.

Second, it covers all fields of the natural sciences so that it is able to bring together interdisciplinary interests among mathematics, physics, chemistry, engineering, biology, medicine, anthropology, psychology, geology, and so on.

Third, it covers the whole range of scientific and technical endeavor from basic research to the most applied research. We have six divisions that may be called basic divisions, in mathematics, physics and astronomy, chemistry, earth sciences, biology and agriculture, and anthropology and psychology. We also have two divisions in the two great areas of applied science, namely engineering and medicine. These two are the largest divisions; in general, scientific work of interest to the other six divisions leads ultimately to applications either in engineering or in medicine. Thus we cover the whole spectrum from basic research to its ultimate applications.

The fourth important feature of the Academy - Research Council is that, in a very real sense, it is led and guided by the scientists and engineers themselves. Very many of the things we undertake, we undertake because individual scientists or groups of scientists have said, "Here is something that we believe needs to be done in the interests of science. Can this be done through the mechanisms of the Academy - Research Council?" I believe that our most significant activities are those that arise out of the conviction of people like yourselves who see the needs of science and are able to find here, to the extent that we are able to provide it, an effective mechanism for the furthering of those aims and for carrying out the things that you feel need to be done.

It is on this last count that the significance of your meeting today especially impresses me. A need has been detected. You are exploring it. We are confident that by coming together here you will find the most effective way to meet it.

The total scope of the Academy - Research Council today is considerable. We have more than four hundred committees in various areas of science carrying out functions related to the two great purposes of the Academy which I have described. Some four thousand scientists from all over the country are associated together in these undertakings.

Our total budget is about ten million dollars a year. Most of this is expended for advisory services, but we do operate a few sizable research projects, for example, the Atomic Bomb Casualty Commission in Japan. This is a medical research project which has been in progress for thirteen years to study the consequences of the atomic bombs on the populations of Hiroshima and Nagasaki. Another example is the National Road Test in Ottawa, Illinois, where we are responsible for a 20-million-dollar test of the effects of heavy traffic on specially constructed test sections. This is supported by the Federal Government, the State Highway Departments, and the motor vehicle industry, and has the interest and participation of the concrete and asphalt industries and others as well.

But whether we are providing advice on behalf of science or on behalf of the government, or whether we are, as a public service, conducting or coordinating research programs requiring the cooperation of many interests, our strength lies mostly in the tremendous response of the scientists of this country to the needs of science through this organization, as evidenced today.

I would not close without expressing the gratitude of the Academy - Research Council to the National Science Foundation for its support of this conference and for the generous and effective way in which the Foundation has aided in its planning and its sponsorship. And, finally, I would say a word not of greeting but of gratitude to all of you for coming together. I wish you a most profitable and fruitful meeting.

Dr. Rossini: Thank you very much for your remarks which continue to be inspiring to us all.

C. Preliminary remarks by Chairman Rossini:

To start off our Conference, I would like to quote several passages from the report of President Eisenhower's Science Advisory Committee on "Strengthening American Science":

> "The secrets and treasures of Nature are hidden in the most obscure and unexpected places. ---- The strongest scientific program is the one with the greatest breadth and scope. It is impossible to predict from which quarter the next scientific advance will come; but we can try to make sure that the Nation has able people at work across the whole frontier."

> "The job of strengthening U.S. science is so broad that there is ample room for Government, industry, universities, foundations,

and individuals to find a challenging and rewarding role to play. It is vital to the future growth of American science that all these components participate in the support and encouragement of research."

We all know how frequently research investigations in university, government, and industrial laboratories are seriously hampered by lack of reliable data on the physical, thermodynamic, and spectral properties of simple chemical compounds, -- the kinds of data that provide fingerprints and characterization of the behavior of matter.

To obtain missing basic data, investigators make expeditious, short-cut measurements, on nearly pure compounds, with an accuracy barely adequate for the particular investigation at hand. Such data generally remain in the files because they fall short of the quality meriting publication. This procedure is repeated many times in the same and other laboratories.

By having such data obtained systematically on compounds of high purity, with apparatus of high accuracy, followed by prompt publication of the results, all laboratories are benefited, much scientific manpower over-all is saved, and our stockpile of basic data on chemical compounds can be built to levels of high quality as well as adequate quantity.

In addition to these basic needs for really pure chemical compounds, there are numerous requirements of such compounds for purposes of calibration and reference, in the analyses of materials in university, government, and industrial laboratories, and in the control of processes for manufacturing.

Many of us have been concerned about this problem. We realize that one of the principal impediments to the acquisition of our stockpile of accurate, basic physicochemical data is the lack of chemical compounds of certified high purity. Once such compounds are available, the problem of getting the accurate data on them can be tackled and solved.

The purpose of this Conference, therefore, is to define the problem of chemical compounds of certified high purity, and to make recommendations for such action as seems appropriate.

May I say here, as did Dr. Cornell, that we are grateful to each of you for giving of your time and talents to the consideration of this important problem.

The outline of our Conference is as follows:

This morning we will receive background information on the problem by way of two prepared reports on current live programs on chemical compounds of certified high purity, one from the National Bureau of Standards and the other from the American Petroleum Institute.

The presentation of these reports will be followed by discussion of the reported work and the contribution by the Conference Participants from the floor of information on similar other work known to be in progress.

Following luncheon, our afternoon program will consist in a general discussion, by all Conference Participants, of the following five topics:

I. The Philosophical and Intellectual Aspects of the Problem.

II. The Scope of the Conference.

III. The Specific Classes of Chemical Compounds Needed.

IV. The Financial Resources Available for Supporting the Work.

V. The Places to Perform the Work and the Organization to Manage the Operation.

After dinner this evening, we will divide into five groups, for the preparation of summary reports on the five topics discussed at the afternoon session. Assignments to these groups have been made on a more or less arbitrary basis. Please inform me if any changes in assignments are desired. I have asked the following persons to serve as Chairmen of the groups for our sessions this evening: I. Dr. Zwolinski; II. Dr. Waddington; III. Dr. Hillenbrand; IV. Dr. Astin; V. Dr. Daniels. These gentlemen will also report to us tomorrow morning on the summary reports and recommendations of their respective groups.

This evening each group will adjourn separately as soon as its work is completed.

Tomorrow morning at 9 o'clock, we will reconvene here in one body to receive the reports of the five groups.

We hope to end our Conference before 11 o'clock tomorrow morning.

Before proceeding with our program, I wish to take the liberty of making several general statements, as follows:

In the United States today, our over-all work in science has a breadth of scope and a depth of inquiry that is unequalled in any country of the world.

This has been made possible through the urge of free inquiry and competitive effort, nurtured to the degree appropriate, in our universities, in our government laboratories, and in our industrial laboratories. The continued cooperation of these partner components can lead us to new heights in our national advance in science.

Solution of any problem, such as the one facing us today, requires cognizance of all our resources of manpower, experience, and facilities, whether they be in universities, in government laboratories, or in industrial laboratories.

Our biggest need may be for an improved mechanism for coordinating our scientific efforts without significantly lessening the freedom of the investigator and the dignity of his person.

D. We come now to the first of our two prepared reports for this morning. I am very happy to call on Dr. Edward Wichers who will present from the podium a report on the current live program of the National Bureau of Standards dealing with chemical compounds of certified high purity.

Dr. Wichers: Thank you, Dr. Rossini.

Chemical compounds of certified high purity have a natural and inherent interest to the National Bureau of Standards because of the Bureau's mission to prepare standards, to develop standard methods of measurement, and to promote uniformity of such methods of measurement throughout the technical community. The preparation of standards frequently involves the observation of a characteristic property of a substance or system of substances that will serve as a guide in making the standard reproducible. We call the substance pure when further use of the purification method has no measurable effect on the property of interest.

There is a tendency to define purity in some sort of absolute descriptive terms. Years ago "chemically pure" was a familiar phrase. When spectroscopy developed as an analytical tool we began to hear about spectroscopic purity. Neither of these is justified unless it is defined, and the term "absolute purity" which we hear so frequently is without any justification whatsoever. If one considers that a gram of water contains about 3×10^{22} molecules it is hard to believe that in this gram of water there are not a few atoms of most, if not all, elements in the periodic system.

Purity ought to be defined numerically and this can be done in one of two ways. It can be done in terms of the major component which is actually a difference determination. The percentages of individual minor components are determined and subtracted from 100 per cent; the difference is, by definition, the major component. Or one may define purity numerically in detail in terms of the individual components. It is necessary to point out that purity differs markedly with respect to substances when so numerically defined. The jargon familiar to most of us is to use the number of 9's (five 9's, six 9's, etc.) indicating either the mole fraction or weight fraction of the major component.

The Bureau's interests in pure compounds can be classified in three categories. Our first interest in pure substances is connected with the preparation of standards for special purposes. These are used mainly in the Bureau or in a few instances are made available for limited distribution to national laboratories or investigators of special competence. Our second interest lies in those materials made available for general issue to promote uniformity of physical measurement. Our third interest covers certain classes of compounds which are provided for research on their properties. This topic, I am sure, is of very direct interest to this conference.

An example of the first category is the Bureau's concern with establishing the international temperature scale and with maintaining the scale to be consistent with that used in other countries. The so-called normal range of the international scale covers the temperature interval from the boiling point of oxygen up to about 600 degrees. It is defined by the boiling point of oxygen, the triple point of water, the boiling point of water, and the boiling point of sulfur. These points define the platinum thermometer scale. At temperatures above the platinum thermometer scale the platinum-rhodium thermocouple is used and this scale is defined in terms of certain melting points, in particular that of gold. It is therefore necessary to know a great deal about the preparation of pure water, pure oxygen, pure sulfur, pure gold, etc. Much time has been spent on these problems with occasional surprising results.

Sulfur, which should be well known, is an instance of this. Evidence showed the presence of impurities in the supposedly pure sulfur used for the sulfur boiling bath. Investigation showed that all sulfur, formerly considered pure, contained heavy hydrocarbons. When sulfur was prepared free of these compounds we found, to our surprise, that the freezing point of sulfur was now 0.7° higher than any value reported in the literature. Gold is no problem to purify and we purify it regularly for use in maintaining the temperature scale.

There now are available for limited issue to qualified calorimetrists samples of n-heptane, benzoic acid, and aluminum oxide as heat capacity standards. The first two are purified at the Bureau; the pure aluminum oxide is available commercially.

Luminous flux is an example of a physical standard defined in terms of a property of a pure substance. Originally defined in terms of a candle of specified composition and dimensions, it is now defined in terms of radiation from a black body at the temperature of freezing platinum. This standard was not realized until a method of preparing platinum of high purity was developed. It is now an international standard.

Another example is the pressure standard. Pressure is commonly defined in terms of a column of mercury of specified density under specified conditions and, of course, a specified height, 760 millimeters. The density of this mercury is the problem. Although mercury is rather easily purified chemically, it has 8 or 9 isotopes and the isotopic composition is subject to small variations. Unfortunately present isotopic abundance measurements are not of sufficient accuracy to specify accurately the isotopic composition of any specimen of mercury that may be used for such a density measurement. As a result of some very beautiful work on the density of mercury by the National Physical Laboratory in England, NBS has sent to the NPL a supply of purified mercury the density of which is now being measured at Teddington. This mercury will hereafter be available for issue to highly qualified laboratories. The differences with which we are concerned are of the order of parts in a million, and only a few laboratories will be very concerned.

Standard samples of many kinds are prepared and issued by the Bureau. Our catalog now lists some 600 types of standard materials which are certified either with respect to composition or to some particular physical property. About 40,000 units are issued a year. I will confine my talk to the ones classed as pure substances.

Some of these are certified with respect to a particular physical property and are used to promote uniform measurement of that property in all laboratories. For melting point standards we have aluminum, copper, lead, tin, and zinc. For a more precise fixing of the temperature measurement we issue benzoic acid of specially refined quality in a sealed cell which enables one to reproduce a temperature in the vicinity of the boiling point of water with a reproducibility of better than a thousandth of a degree. It is a much simpler device for calibrating a platinum thermometer than a boiling water bath because the measurement is independent of barometric pressure.

I will refer later to the long list of hydrocarbons which are issued as pure substances with a definition of purity only. Glucose with a certified optical rotatory power is issued for the standardization of polarimeters. Then there are several standards for oxidation and reduction measurements. For acidimetric standardization benzoic acid and potassium biphthalate are the most common ones and I suspect these are universally used throughout industry. There is a set of six indicators for pH standardization. Each indicator provides a fixed point on the pH scale.

We have, as most of you know, 184 hydrocarbons which were produced under the leadership of Dr. Rossini in the period 1943 to 1950. These have been available since then for issue. Each sample is certified as to its purity. This program was carried out under the joint sponsorship of the Bureau and the American Petroleum Institute during the war and for some years thereafter. When Dr. Rossini and the API project transferred to the Carnegie Institute of Technology, the decision was made that both the Bureau and the American Petroleum Institute would continue to issue these materials as pure substances, the Petroleum Institute to petroleum laboratories and our Bureau to others. However, in the interests of efficiency, the Bureau has proposed to the American Petroleum Institute that they take over the sole issue of certified hydrocarbons. This proposal has not yet been fully studied by the American Petroleum Institute.

The class of substances prepared for research on their properties may either be used in the Bureau's own research program or issued for research in other laboratories. Examples of the latter group are the titanium halides prepared a few years ago, under the auspices of the Office of Naval Research, for a general research program on fundamental properties of titanium halides important in the extractive metallurgy of titanium. The Bureau has prepared and made available to laboratories titanium tetrachloride of purity better than five 9's, tetrabromide of about the same purity, and trichloride of slightly lower purity.

As a result of the 1957 Amsterdam Symposium on Purity, the Committee on Physico-Chemical Data and Standards of IUPAC requested the Bureau to prepare a large sample of highly purified benzene (between five and six 9's), to permit a careful study of the reproducibility of freezing point methods for the evaluation of purity. It was thought that this industrially important technique could not be advanced rapidly without a cooperative study of several known systems. The Bureau prepared about ten liters of the extremely pure benzene and then added known amounts of appropriate known impurities. A total of 170 preparations was made for issue to cooperative laboratories.

A preparation of immediate interest to us and of significance in the issue of standard material is single crystals of potassium biphthalate, important as an acidimetric standard. A few years ago we were not quite sure of the certification of potassium biphthalate and undertook to compare its acid strength with that of single crystals of potassium biphthalate. It turned out that the granular material contained mother liquor occlusions. Single crystals of benzoic acid were prepared at the same time in order to have two substances for comparison. The purity of benzoic acid was also evaluated by an independent method. The two substances agreed in acid strength, conforming to their nominal composition to within one part in a hundred thousand. We are now growing single crystals of potassium dichromate to make a more precise certification of its oxidizing power. We are also growing single crystals of uranyl nitrate because the present assay method for uranium, which is very important in the atomic energy business, leaves something to be desired. We hope by producing single crystals, to have a single primary standard for the chemical assay of uranium compounds.

Our policy is never to prepare a substance if it can be bought in pure form from commercial sources. Many years ago benzoic acid adequately pure for heat of combustion calibration could not be obtained commercially. Industry caught up and soon was able to supply benzoic acid of acceptable purity. Now, unfortunately, the requirements are increasing and we may again have to prepare benzoic acid in the purity needed. Whereas the Bureau originally had to prepare the platinum used for the standard of luminous flux, platinum of that purity, or perhaps of even greater purity, is now available from commercial sources. This is, of course, very gratifying and I hope that this Conference may stimulate industry members to seek ways of serving the total technical community by providing these materials with their plant facilities. The big obstacle, of course, is that these samples are seldom wanted in large quantities. There is little profit in making pure substances in small quantities.

Many different laboratories of the Bureau participate in the work. The Metallurgy Division has done all of the work on pure iron except for some advice from the Chemistry Division on methods of purification and the analytical services necessary to determine the purity of the final product. The Electrical Division has done a good deal of work on the preparation of pure silver for a redetermination of the Faraday. But the principal work on preparation is concentrated in two sections of the Chemistry Division, the Inorganic Chemistry Section and the Pure Substances Section. These two sections have a combined staff of about twenty people and operate on an annual budget of over $250,000. The Inorganic Chemistry Section is concerned usually with the preparation of inorganic materials by the conventional techniques of crystallization, precipitation, and distillation. This is the Section in which the previously mentioned sulfur was prepared. They have also prepared barium salts free of detectable amounts of strontium, strontium salts free of detectable amounts of barium and sodium similarly free of potassium. Nickel is thoroughly freed of cobalt by a process which shows that one can reach a limit almost equal to the contamination of cobalt that would result from the persistent recontamination of any pure substance by its environment. The titanium compounds were also prepared in this group. The Mineral Products Division is interested in the electrical properties of barium titanate, a substance of great current interest in the electronic industries. A preparation of very high purity was needed that could then be modified with known additions to study their effect on its electrical properties. It was found that barium titanate could be prepared from the extremely pure titanium tetrachloride and barium chloride available at the Bureau.

The Pure Substances Section studies methods of purification and purity evaluation. Its distillation laboratory has eight stills with capacities from five milliliters to two liters with rates of distillation from 1 to 150 ml per hr., operating from pressures of about two hundredths of a millimeter of mercury up to atmospheric pressure with efficiencies varying from 10 to 300 theoretical plates. Most of these stills are designed for automatic takeoff so that they can be operated for weeks with little or no attention. These facilities have been extremely useful to research activities throughout the Bureau. A wide variety of substances has been prepared. Research on the design of stills and on a better means of evaluating their efficiency is also being carried on.

Another part of the Section is concerned with crystallization as a purification technique. Here the emphasis is on the growing of single crystals. It is known that growing crystalline material in the form of single crystals may result in a purification factor in one step of as great as 1000. This method provides extraordinarily high leverage on the problem of purification. The facilities used in this laboratory are of two kinds, one for the growing of crystals from aqueous solutions or other solvents and the other for crystallization from melts. While the latter is preferable because the occlusion of mother liquor is minimized, there are many substances, unstable at their melting points, for which one must choose a suitable solvent. A major part of the effort has gone into finding out under what conditions a growing crystal rejects or accepts impurities. Interesting results have been obtained.

One other current task at the Bureau is the redetermination of the Faraday based on the anodic solution of silver which is a better method than the cathodic deposition of silver. Before this work on silver was undertaken there were high hopes of using the anodic oxidation of sodium oxalate to obtain a good value of the Faraday constant. This is a very clean chemical reaction but its usefulness is limited now by the uncertainties of the composition of sodium oxalate. So the Pure Substances Section is endeavoring to grow crystals from which mother liquor impurities can be excluded. While the oxalates are most reluctant to grow in the form of single crystals there is some hope that that can be accomplished.

The third part of this section is concerned with the physical means of evaluating purity. I shall not mention the conventional chemical means of analysis. Radioactive analysis and partition chromatography promise to be useful as means of evaluating purity.

One important physical means is the observation of the freezing curve of a system composed of a major component and impurities which are soluble in the liquid phase but not soluble in the solid phase. Dr. Rossini played an important part in the development of this very sensitive tool in his work on hydrocarbon reference standard materials. It has come into very extensive use industrially. The freezing curve can be determined calorimetrically and thermometrically. In the latter method freezing curves are now automatically recorded. Temperature differences as small as one thousandth of a degree can be followed. Although the thermometric method is, in some respects, less sensitive for the estimation of impurities than the calorimetric one, it is nevertheless capable of determining impurities to one part in a million or perhaps one part in a billion.

The Bureau's appropriation bill, passed by the Senate last week, provides a gratifying increase in our research funds, part of which will be directed toward a strengthening of our work in pure materials and the measurement of their properties. Among other things it is hoped to provide a bank of substances in single crystal form which is of great interest to solid state physicists.

E. Dr. Rossini: Thank you very much, Dr. Wichers, for this very comprehensive report of the work being done by the Bureau of Standards on this program.

Now I am happy to present to you Dr. Charles Thomas who will present a report on the current live program of the American Petroleum Institute on chemical compounds of certified high purity.

Dr. Thomas: Dr. Wichers has already mentioned how the pure hydrocarbon sample program of the API was started at the Bureau of Standards under Dr. Rossini. I would like to expand this story, indicate the extent of the present program, and disclose our future plans.

In 1943, the National Bureau of Standards began to provide standard samples of selected hydrocarbons of known high purity for calibration. Later that same year the American Petroleum Institute, after an extensive survey, recommended that a fundamental research project be initiated to prepare hydrocarbons for spectrometric calibration. This recommendation was approved and on July 1, 1944, API Research Project 46, "Hydrocarbons for Spectrometer Calibration," under the direction of Dr. F. D. Rossini was initiated at the National Bureau of Standards. The first year's budget of $40,000 was contributed by various petroleum companies.

The purpose of API Research Project 46 was to make available, as analytical standards, a specific list of hydrocarbons representing the important constituents of petroleum, particularly for the calibration of spectrometric equipment used in the manufacturing of, or research on, aviation gasoline or synthetic rubber. The National Bureau of Standards offered to cooperate in this program by accepting samples of adequate purity provided through the API, certifying them as to purity, packaging them as NBS Standard Samples, and acting as distributing agent. The synthesis work was carried on at the Ohio State University under the auspices of API Research Project 45, "Synthesis, Purification and Properties of Hydrocarbons of Low Molecular Weight," and at the Pennsylvania State University under API Research Project 42, "Synthesis and Properties of High Molecular Weight Hydrocarbons," directed by the late Prof. Frank Whitmore.

Hydrocarbons were also purchased from independent companies and further purified by the API Research Project 6. The first list contained 102 hydrocarbons scheduled to be made. The samples were distributed in containers with internal breakoff tips so that they could be used in high vacuum systems with a minimum of contamination. The purity of the samples furnished is generally more than 99.8 percent, although there was, and still is, great interest in purity of 95-98 percent. The API Research Project 46 was terminated July 1, 1946, when a total of 93 compounds had been made available. Research Project 6, then in operation, continued the work of Research Project 46 devoting essentially one-half of its effort to the issuing of hydrocarbon samples.

Present operation. The annual contract drawn up between the American Petroleum Institute and the Ohio State University Research Foundation (Project 45) contains a list of hydrocarbons desired for the Standard Sample program. This list is made after consultation with the Advisory Committees of API Research Project 6 and API Research Project 45 and the coordinating committee which provides liaison between these two groups. API Research Project 45 then attempts to synthesize the hydrocarbons desired. It is understood, of course, that is is not always possible to adhere strictly to the list, particularly if a new synthesis has to be developed. Frequently other hydrocarbons of interest are produced in developing such a method of synthesis. After synthesis, the compounds are shipped to API Research Project 6 at Carnegie Institute of Technology for further purification to bring them to the desired 99.8+ percent purity for certification. The material is then bottled in 5 ml ampoules for distribution.

An announcement is made at the time of the issuance of a new hydrocarbon as a Standard Sample. Sales are handled directly by the API Samples and Data Office, located at Carnegie Institute of Technology. Income from sales helps to defray costs but has never been sufficient to meet the total expenses of research and sample handling. This emphasizes Dr. Wichers' statement, that there can be little profit in preparing and selling pure substances. Hydrocarbons in the lubricating oil range, synthesized by API Project 42, are loaned to laboratories for research or instrument calibration but are not sold. The only requirement is that the American Petroleum Institute be furnished with the information obtained on the sample.

Extent of operation. In addition to 270 standard hydrocarbon samples there are also available 38 standard samples of organic sulfur compounds and 6 of organic nitrogen compounds. These are provided by API Research Project 48, "Synthesis, Properties and Identification of Sulfur Compounds in Petroleum," and by API Research Project 52, "Nitrogen Constituents in Petroleum," both of which are located at the U. S. Bureau of Mines, Laramie, Wyoming. Synthesis, as well as the purification and bottling of the organic sulfur and the organic nitrogen standard samples, is handled by the two Projects at the U. S. Bureau of Mines. After that the samples are shipped to the API Samples and Data Office at Pittsburgh for distribution. In order to make these programs more nearly self-sustaining the price will be raised to $65 per unit effective July 1, 1959.

Future plans. An expansion of this program is planned which will include the molecular weight range, C_{14} to C_{18}. This is necessitated by the advent of jet fuels and other important distillates.

I think you may be interested in statistics on the sale of these units (5 ml ampoules) of certified hydrocarbons.

1944-1950	NBS	2,394 units
	API	4,171 units
1950-1958	API	11,161 units

In closing I would like to say that the scientific community owes a tremendous debt of gratitude to Prof. Rossini for his leadership in the preparation and distribution of certified pure hydrocarbons. Undoubtedly the API bank of certified substances is unique in the world today.

Dr. Rossini: Thank you very much, Dr. Thomas.

F. Coffee break.

G. Dr. Rossini: We are ready to discuss the reports which were presented this morning as background information and also to hear of any similar work going on in other places. We are ready for questions, comments, or other reports from the floor.

Dr. Clarke: For many years the U. S. Pharmacopoeia has been supplying what are called reference samples of important drugs. Seventy such compounds are now available to anyone on payment of a small fee. These compounds are primarily for use in differential spectrophotometric assay programs. In addition there are about 24 standard steroids primarily for use in chromatographic analysis. A new edition, to appear next year, will show an expansion of this program. Samples may be obtained from the U. S. Pharmacopoeia headquarters in New York.

Dr. Elderfield: A new National Research Council Committee on biochemical standards was started several years ago. It was originally under the chairmanship of Prof. H. C. Carter but is now under Dr. G. B. Brown. The Committee has a list of 40 to 60 samples tentatively selected for procurement on a certified purity standard basis. I don't know how far this program has developed. Working with relatively unstable compounds creates a dual problem. The first problem is how to get the compound pure and the second one is how to keep it pure.

At the Lilly Laboratories in Indianapolis a selected group of about 50 naturally occurring indole-alkaloids has been collected. Ultraviolet, infrared, and X-ray data for these compounds are recorded and the information is published and distributed at intervals in the form of loose-leaf sheets.

Dr. Craig: The collection of steroids at the Sloan-Kettering Institute formerly under Dr. Dobriner is, I believe, now under Dr. T. F. Gallagher.

Dr. Stillman: ASTM publishes a report "Standard Samples and Related Materials for Spectrochemical Analysis," STP 58-C. This report shows not only what is available from the Bureau of Standards but also from several industrial concerns.

Dr. Rossini: Does anyone know of other high purity compounds or groups of compounds available from industry?

Dr. Burwell: The Phillips Petroleum Company has a list of 40 to 50 useful hydrocarbons.

Dr. Brown: The photographic industry has long been in need of pure silver halides. Silver nitrate having a purity of a few parts in 10^7 of heavy metals is available from Eastman Kodak Company. Very pure optical crystals are available from the Harshaw Chemical Company. The purity of these is not specified.

Dr. Van Dyken: The Solid State Physics Division of the AEC has recently embarked on a program of producing single crystals by contract through some of the laboratories of the Commission. Work is being done on pure metals, alkali halides, and silver chloride. New criteria are needed for determining purity, and research on such criteria should be encouraged.

Dr. Spedding: Dr. Harley A. Wilhelm has made a survey of all companies claiming to issue the highest purity metals. A report of the survey is available. We have been supplying a standard spectrographic kit of rare earth metals to anyone wanting to compare their purity with ours. The charge is $50.00 for the kit which contains five grams of the common, one gram of intermediate, and 200 milligrams of the rare ones.

Dr. Klug: Are those rare earths the same ones that the Nuclear Corporation of America is providing in kits?

Dr. Spedding: No. But industry is starting to make rare earths and is selling them at reasonable prices.

Dr. Klug: A pamphlet of the Nuclear Corporation of America lists rare earths of about 99.8 percent purity. Also there is an AEC Bulletin "Availability and Sources of the 96 Elements in High Purity Forms" (1949) which lists not only the pure metals but also compounds.

The Johnson, Matthey Company of London has for many years provided high purity materials to spectroscopists. The Jarrell Ash Company is their agent in this country. Each sample describes the analysis and reports all detectable elements in parts per million. Their best grade of copper is five 9's and contains traces of lead, nickel and silver. Some of their elements are of six 9's purity. If they have prepared the material themselves they say so. The metal may be obtained in the form of rods, as a 10 percent solution of the anhydrous salt, or as a one percent solution of anhydrous salt in water. All elements and quite a few salts of each element are available.

Dr. Craig: We once obtained four or five fatty acids of supposedly high purity with melting points given to hundredths of a degree from the Armour Co. Strenuous efforts to purify them further were not very successful. Certain amino acids of high purity can now be bought from several companies. The California Biochemical Foundation furnishes a carbon-hydrogen analysis and optical rotation values with each. These standards are being constantly improved because of the influence of chromatography and better ways of measuring optical activity.

There is a great demand for pure polypeptides. We have been sending out small samples of a number of antibiotic polypeptides from time to time but we don't have facilities for expanding this service.

At a meeting of the Commission on Protein Standards at the 1957 IUPAC Conference in Paris the importance of having available several samples of pure proteins was discussed. There would be a great demand for such samples if they could be obtained in sufficient quantity and purity. Insulin was selected as being the most promising at that time and a rather large sample of insulin was prepared by an English drug firm. Although supposedly pure, this sample didn't stand up very well in our laboratory. It can be obtained in gram lots by anybody. We don't know what its impurity is.

Dr. Horney: The Orlando Research Laboratories (Dr. Glenn A. Greathouse) are issuing high purity tagged organic compounds with C^{14} in specified positions in the molecules. They are sold in terms of micro-curies depending on the amount of C^{14} they contain. I think any consideration of this problem might very well include that class of compounds. Their catalog lists a diversity of simple organic compounds including some sugars. The position of the carbon can be specified when ordering. If the particular compound is not available they will synthesize it. Nothing is sent out unless it has a very high degree of purity.

Dr. Dawson: Does the National Institutes of Health or similar organization have a list of materials? What are their standards?

Dr. Rossini: From what has been said it seems that a large number of fairly pure substances are available, but we do not know exactly what the purity is and where the substances may be obtained.

Dr. Kolthoff: I just would like to ask whether any other countries are producing chemicals of known purity. I understand that a very high grade of Na_2SO_4 is available in Holland for calibration of thermometers.

Dr. Wichers: A supposedly very pure benzoic acid sample from Holland contained 0.15% of water and the manufacturer did not know it. Except for a few materials listed by the National Physical Laboratory there is very little available from European sources.

Dr. Daniels: Transistor research has led to very high purity silicon (six or seven 9's) and germanium of similar quality. It is reported that duPont is now making pure anthracene.

Dr. Hayes: Samarium is now commercially available.

Dr. Smyth: Would it be possible to prepare annually a list of all sources of pure compounds, the specific compounds available from each, and the criteria of purity used in their certification? Even if published only every two or three years it would be very useful to people all over the country.

Dr. Rossini: The suggestion of an annual list of sources of pure materials might very well be covered by one of the recommendations.

Dr. Wichers: A tabulation of sources of supply would be an extremely useful thing but the claims might be unreliable unless the purity were stated in some systematic way. It would be a tremendous task for a central laboratory to check the purity.

Dr. Shepard: Speaking of foreign sources, is Kahlbaum still in existence?

Dr. Kolthoff: Thirty years or so ago Kahlbaum was an important source of pure chemicals but I don't know whether it exists today.

Dr. Smyth: It would be of great help to graduate students and others if methods of purification such as have been developed by the Bureau of Standards were published in a book which would be revised frequently. Weissberger's "Organic Solvents," Vol. VII is not complete but it has gone through two editions and has proved quite useful.

Dr. Klug: It would be preferable to have large scale purification carried out elsewhere and simply pay for the purified material instead of relying on graduate students or laboratory assistants.

Dr. Clarke: The work of the ACS Committee on Analytical Reagents should be mentioned. It does not provide chemicals, but merely writes specifications, and makes these available to manufacturers.

Dr. Bowman: I would like to enter a strong plea for a study of stability. We believe that ethyl alcohol is a pretty stable compound, but there seems to be some doubt about it. Hiram Walker had prepared an exceptionally pure alcohol (vodka) which in vapor liquid chromatography showed just two peaks. After storage in sealed glass in the absence of air for six months several small peaks appeared and their expert tasters could detect a difference. Do cosmic rays cause ordinary ethyl alcohol to break down? I would also like to call attention to the registry of rare chemicals maintained by the Armour Institute.

Dr. Elderfield: This is often true for organic chemicals, storage is a difficult problem.

Dr. Craig: I might mention the difficulty we have in protein chemistry. Moore and Stein of our Institute embarked on a long study of the purification and structural study of a ribonuclease preparation from Armour. At first it seemed to be about 93% pure. By countercurrent distribution we also had a hand in the study of its purity and the major component finally appeared to be present in approximately 70%. There were six minor components present in about equal amounts. This protein had been kept in a cold room.

Dr. Rossini: Dr. Bowman has brought up a very important point. A number of years ago Prof. Boord sent us a pure sample of 2, 5-dimethylhexane in a screw-cap bottle. It was put on the shelf in the same condition after its purity was determined. About a month later white crystals of a peroxide had formed in the bottom indicating an intake of oxygen through the closure.

Dr. Wichers: For organic compounds storage at very low temperatures is imperative. Modern refrigerants make low temperature storage quite possible.

Dr. Brown: In connection with the problem of storage I would like to point out that organic materials are subject to a damage by radiation, very often similar to that resulting from chemical change. For pure inorganic materials, damage produced by cosmic rays would be very small indeed.

H. Noon Recess

I. Luncheon

G. (cont.) The afternoon session was convened at 1:30 P.M. by Dr. Rossini who first called on Dr. Paul Egli for a brief report on crystal research going on at the Naval Research Laboratory.

Dr. Egli: We have been engaged for 15 or 16 years in growing a wide variety of crystalline materials and making high quality ceramic glasses. Our program, which is usually motivated by a search for a particular physical property, was started in a search for piezo-electric properties and materials. In that search we grew crystals of many of the substances listed in the Chemical Rubber Handbook. The next search was for crystals possessing special optical properties, optical elements for infrared and ultraviolet prisms, lenses, and so on. The metal halides were studied intensively.

In both of these programs we learned much about purification. We learned that most crystals grow more perfectly, and frequently with a higher degree of purity, from systems which contain deliberately introduced impurities. In many cases impurities which helped the growth are not included in the crystal. We learned that sodium chloride grown from a melt almost always contains detectible amounts of hydroxyl while that grown from water solution does not. So we are more conscious of the questions raised than of our achievements.

In our more recent research on various electrical properties such as of transistor and rectifier materials, ferro-electric materials, and luminous materials we have ranged over most of the periodic chart. The transistor and rectifier research involves primarily the elements and simple binary compounds. The ferro-magnetic electric materials are generally the complex oxides. We have made some reasonably high quality materials but are again more impressed with problems raised than with problems solved. In all of this work the detection of stoichiometry and homogeneity is a limiting factor. I would like to suggest that this group do whatever it can to stimulate research in this area.

Dr. Rossini: Thank you very much, Dr. Egli.

Dr. Horney: Our Cambridge Research Center has a large and growing program on single crystals research in the same general area described by Dr. Egli.

J. Dr. Rossini: We will now proceed to our General Discussion I which is a consideration of the philosophical and intellectual aspects of our problem, the advantages and disadvantages of having certified pure chemical compounds available to the research laboratories of industry, government, universities, and non-profit research institutes. Two of our conference participants, Dr. Burwell and Dr. Zwolinski, will make opening statements on this topic.

Dr. Burwell: We will delve into the philosophical and metaphysical aspects of purity and ask the questions, "what is purity" and "purity for what." Certainly, entirely too much research has been done on substances of unspecified purity. It seems to me that there are three general types of application for certified pure compounds. These are: (1) As standards for calibration and identification; (2) for physico-chemical measurements; and (3) for research on chemical reactions.

I can report from recent personal experience that, in switching from isotopic exchange studies on certified hydrocarbons to uncertified ethers, esters, and ketones, the difference in ease of procedure is startling. I am convinced of the advantages of having certified standards.

The API has not stressed production of samples for chemical conversion reactions. In any future program one ought to consider whether samples for this purpose should be made available. Since the average physical chemist is not too willing or qualified to prepare unusual compounds, important physico-chemical research is frequently not done.

We should not lose sight of the cost problem. On the one hand, if the university must pay full price for samples, it will prevent waste. On the other hand, in many university laboratories, full cost will mean that the pure compounds will not be used to fullest advantage.

I would like to touch on one philosophical problem -- the matter of user responsibility. If there is a great increase in the availability of pure compounds, then inevitably the responsibility for the purity will become diffuse even though it ought to rest with the scientist who uses the compounds. This I think will be particularly critical with graduate students. Many will obtain a Ph.D. degree without ever facing the problem of purity. We will have to balance improved and faster research against this pedagogical loss.

Dr. Rossini: Thank you, Dr. Burwell. You have given us several important points to think about.

I would like to call on Dr. Zwolinski for a statement on this problem.

Dr. Zwolinski: A cursory examination of the open literature reveals a dearth of published material on the philosophical aspects of the problem of the purity and identification of chemical compounds. The most recent discussions of certain aspects of the purity problem were the subject of an ACS symposium entitled "Symposium on Purity and Identity of Organic Compounds" held in New York City in 1947. Some of the papers appeared in the February 1948 issue of the Journal of Analytical Chemistry. One paper is actually entitled the "Philosophy of the Purity and Identity of Organic Compounds." In these papers are mentioned some of the problems that we are concerned with today. It was difficult then as it is now to find an absolute definition of purity.

Purity is intimately associated with the universal or total set of all physical, molecular, and thermodynamic properties which identify any single substance. Perhaps the only absolute definition of purity stems from the third law of thermodynamics when we assign zero entropy to a pure crystalline solid at the absolute zero of temperature which requires identical molecules to be in identically the same state of energy. For the purpose of our discussion, we should consider more practical standards or definitions of purity by regarding this concept as a function of variables and conditions in five separate categories. Some of these points were brought up in the presentations and discussions of this morning session of the conference. Perhaps five categories can be delineated:

1. Advances in experimental techniques of measurement with respect to sensitivity and precision and development of new methods and procedures such as NMR, EPR, and chromatography.

2. Thermodynamic variables, particularly temperature and pressure.

3. Kinetic variables, particularly with respect to stability or metastability of a substance.

4. Particular uses of material with respect to the research interests and requirements of a specific discipline.

5. The kinds of materials, i.e., the number and different kinds of compounds to serve as representative purity standards for groups of compounds now known or to be known by man in the future.

The problem of stability of compounds plays a crucial role in the separation, identification, and storage of pure or certified samples of organic compounds in particular. The thermodynamic aspects of stability were pointed out by Professors Elderfield and Bowman, and Dr. Wichers. The problem of stability or perhaps metastability can be more advantageously discussed from the point of view of kinetics. If the potential barriers for certain kinds of transformation are sufficiently high for the reaction path leading out of the valley for a particular molecule, stability is assured at a specific temperature no matter what thermodynamics tells us about the stability of this substance. I do not believe that the maintenance of purity for a large group of organic molecules is a completely hopeless problem. Inhibitors exist which when added to a sample of an isolated organic compound will maintain the purity of the compound for an indefinite period. In many cases such inhibitors will not affect certain physical and thermodynamic properties of the certified sample within specified ranges of sensitivity. In addition to temperature and defined inhibitors, the phase of a substance is of great importance in the problem of stability. It is a well known fact how solidification imparts an additional degree of stability. While stability is a formidable problem, it certainly can be adequately handled in the setting up of a chemical depository.

The last two points that came into our discussion of the purity concept are its relation to the uses of the certified compounds and the kinds of samples. The former point was discussed by Dr. Wichers this morning in his presentation. The problem of the number of different kinds of molecules in our planetary system at present and in the future has not been adequately discussed or even defined. There is probably a steady state concentration of different kinds of molecules in our universe which is steadily evolving with changing physical conditions. The metaphysical aspects of this problem need not concern us at the present time, while a practical or empirical classification of needed classes and kinds of compounds for purity and certification needs can readily be set up.

Professor Smyth's comments on the need of a report listing current sources of available compounds of defined purity which is to be continually revised should be seriously considered even though, as Dr. Wichers pointed out, the scientific public may have to be educated to exercise caution in its use.

Dr. Rossini: Thank you very much, Dr. Zwolinski. You have raised important points for discussion. Topic I is now open for general discussion.

Topic I

To start the discussion, I would like to stress the importance of the question raised by Dr. Burwell, namely, how do we make pure compounds available without losing the educational value of having graduate students face the problem of purity and its determination.

Dr. Milligan: From experience I have concluded that there is little use in trying to get an absolutely pure compound. The thing to do is to seek to eliminate harmful impurities. In working with catalysts, it is hard to know whether one should remove or add impurities. Our materials are not pure enough to permit an answer to that question.

Dr. Dreisbach: It is absolutely necessary in the modern industrial analytical laboratory to have pure compounds for calibration of spectroscopic instruments. With the aid of modern instruments and calibration standards you can analyze a sample in a few minutes. Old methods were much more time consuming.

Dr. Dawson: For a given procedure or experiment it may be more important to maintain a constant level of impurity than to strive for perfection. That is, in some cases reproducibility may be of dominant importance.

Dr. Wichers: I would like to comment on one of Dr. Burwell's points. I have felt that in the graduate student's education there ought to be some time devoted to the question of purity, its definition, how we get it, and what it means. We should not have chemists who are dependent on labels alone.

Dr. Egli: Recently part of the responsibility of purifying materials has passed from the chemist to the physicist who knows even less than the chemist about purity. With between 10 and 20 million dollars a year beging spent on purifying conductor materials, it is important to improve understanding of purity and its control.

Dr. Brown: As a physicist, I would like to ask if there is a real interest by chemists in preparing materials for physicists. What does a physicist do when he wants some good material? I see this as a difficult problem involving both fields.

Dr. Egli: The physicist must learn more chemistry. He should be able to do the purification himself.

Dr. Spedding: There is another problem, the maintenance of purity. An individual given a pure compound can very quickly make it very impure by improper handling.

Dr. Dreisbach: From the standpoint of time, it is a tremendous saving if a physical property is determined once and for all on a very pure compound.

Dr. Wichers: In certain areas of solid state physics and in the study of ceramic aggregates purity means more than chemical purity. It includes characterization of the physical state. The presence of dislocations and defects may be just as important in those areas as what we call chemical impurities. This should be included in our thinking.

Dr. Hayes: The national stockpile has literally hundreds of millions of dollars worth of materials which originally met certain specifications. They may not meet present day specifications. I think this means that purity should be considered only as it relates to a specific problem.

Dr. Burwell: I disagree with that slightly. In research one simply can't anticipate what a sample will be used for. It is desirable to have it pure enough to meet unforeseen demands of purity.

Dr. Hayes: I am attempting to compromise between cost and quality.

Dr. Burwell: There is a practical limit, but even so I think that it is advantageous to have a sample in which you know the amount and nature of the impurities. It makes for more flexible research applications.

Dr. Spedding: The small amount of purest materials should be reserved for special purposes. The less pure material may be used for less exacting purposes.

Dr. Elderfield: My feeling is that it is a saving of time and money not to purify the compound any more than necessary for a given purpose. A 95% sample may be good enough in many cases.

Dr. Dreisbach: On the other hand, in plastics research, the starting materials must be of the very highest purity for the first polymerization. Later you may wish to add impurities to improve the product.

Dr. Rossini: I would like to ask my university friends if they wish to comment on the educational problem that is being posed here.

Dr. Smyth: I would offer the suggestion that while it is extremely useful to make a graduate student purify material -- and he certainly ought to know how to do it -- it is also very useful to have a pure sample of material on which he can determine properties that later he can use as standards of comparison.

Dr. Daniels: Fifty years ago a physical chemist spent two years building his apparatus, a year purifying his compounds, a few months making his measurements, and a few weeks on their interpretation. Now he buys his apparatus for a few thousand dollars, his pure compounds at $65.00 for 5 ml, and he has three years for measurements and interpretation. He ought to go a lot faster and he is going a lot faster. A loss of training in experimental methods has resulted. I don't know how to supply this needed training and the appreciation for the techniques of building apparatus and purifying compounds. We must recognize the change and the gains and seek ways to compensate for the losses.

Dr. Brown: There is a change in the nature of graduate research. The difficulty of mastering complex apparatus and methods does not leave time for glass blowing and preparation of pure materials.

Dr. Burwell: Today's graduate student simply cannot master the theory and operation of all the marvellous instruments now available nor can he master all there is to know about purity.

Dr. Craig: In my work with graduate students at the Rockefeller Institute, I was dismayed to find that they were not interested in purity. They appeared to adopt the view that this is old fashioned. They can't seem to get the idea that if one wants to work on really interesting things in biochemistry one must know how to purify his own compounds. I think that getting this idea across is important.

Dr. Waddington: I would like to speak on the advantages of a pure compounds program to a governmental laboratory. For ten or twelve years I was associated with a program of thermodynamic research on the fundamental properties of hydrocarbons. Careful measurements were carried out on more than a hundred certified hydrocarbons, nitrogen compounds, and sulfur compounds such as were described by Dr. Thomas this morning. The measurements were made on loaned samples having a value of the order of $100,000. The amount of work done would have been cut to half or one quarter if our own scientists had had to make the pure material. Then, too, the NBS provided other kinds of certified materials, namely those used in establishing the reliability of the means of measurement of variables such as temperature and energy. So we see that certified material and calibration standards are cornerstones supporting programs of physico-chemical research.

Dr. Astin: Dr. Waddington's comments bring to mind another important point. It is the problem which faces the compiler of critical data. There are instances, with some of which the Office of Critical Tables is familiar, where the compiler of critical data is faced with discrepancies probably attributable to the fact that original data from different laboratories were based on materials actually different in characteristics although presumed to be the same. There is a need for the investigator to have available sources of certified or highly characterized material. In this way only can the composition variable be eliminated from experimental results. If the compiler of critical data is forced to resolve discrepancies between observations by different investigators, the elimination of purity of sample as a variable would simplify his problem. The reliability of all new data will be enhanced by the extension of sources of pure materials for research. And this, of course, was one of the basic reasons which led Dr. Rossini and other members of the Academy's Committee on Critical Tables to initiate the setting up of a conference of this sort.

Dr. Rossini: Thank you very much Dr. Astin. Dr. Zwolinski, Dr. Waddington and I from our own experience can testify to the importance of this point. Does anyone wish to say a final word on this topic?

Dr. Thomas: In a recent API survey, industrial purchasers of certified pure hydrocarbons were asked if they were interested in more compounds of 95 per cent purity or fewer compounds of 99.8+ per cent purity. The greater interest was in more rapid production of compounds 95% pure.

K. Dr. Rossini: We will now start General Discussion II pertaining to the scope of the program, classes and kinds of compounds to be considered, ranges of purity to be considered, and criteria of purity to be considered.

The introductory statements on this subject will be made by two or three of our conference participants. I am going to call first on Dr. Waddington.

Dr. Waddington: The morning session enjoyed several informative statements about existing programs for the preparation and certification of pure compounds. The areas that are well covered are known to us. The API program with its several classes of substances and the activities going on at the Bureau of Standards are excellent as far as they go. The immediate problem is to look at these existing programs, decide if they are doing all that needs to be done in their areas, and look also at other territories not now receiving the benefits of similar services.

In estimating the need for pure compound programs, a distinction may be made between large groups of related chemical substances, e.g., hydrocarbons prepared by systematic procedures, and the production of one or a few special substances of unique properties. The first group lends itself to systematization. The second will involve more research and higher costs per compound.

We may speculate as to classes of pure substances needed by science today. Obviously in the field of organic chemistry there will be gaps. Hydrocarbons, nitrogen compounds, and sulfur compounds are being made available by the API program. Alcohols, ethers, ketones, aldehydes, halogenated compounds, and many other groups are not available.

In the inorganic field, substances meeting the specifications of the American Chemical Society are available for analytical purposes but such samples are limited in number and will not meet the exacting requirements of some research areas. It is obvious that highly purified metals will be of interest. Many substances of interest to solid state physicists should be listed. Single crystals of many substances are to be considered. The biologists undoubtedly would be happy to have many compounds. It is clear that needed and desired compounds will exceed the capacity to produce them. A selection will have to be made.

We have used the terms "pure" and "certified" in our discussion. It is necessary to refine these concepts, and to discuss ranges of purity and criteria of purity.

Dr. Wichers stated this morning that one should attempt to attain a purity of sample that will suffice for the most exacting application. The sample should be pure enough so that whatever impurities are present will not have an adverse effect on the measurements to be made.

Economic considerations will influence the establishment of purity ranges. As pointed out earlier, one may be forced to decide between a single high purity grade and several different grades for different purposes. For example, Dr. Paul Emmett of The Johns Hopkins University in a letter to Dr. Rossini asked that this Conference consider the idea of a large bank of hydrocarbons having a purity of 95 to 98 percent to be used in gas chromatography calibration. Such samples should be cheap. Obviously the less pure materials should not supplant the highest grades essential in determination of fundamental properties.

In the fields of semi-conductors and pure metals, purity requirements may be in the range of five to ten 9's. So we see that a very wide range of purities must be considered. Fortunately, the means for attaining purity are constantly improving. Old fashioned distillation becomes less old fashioned. Gas liquid partition chromatography promises to be a powerful preparative tool. Zone melting is a phenomenal development. The single crystal technique in use at NBS is another powerful tool. With the aid of such developments, we are able to make better and better samples as time goes on.

Compounds cannot be certified unless we have acceptable criteria of purity. The criteria used in designating purity should be uniformly applicable to specific classes of compounds. Methods based on a study of the melting or freezing behavior of a compound have been intensively studied and are widely used. They are good but not applicable to all situations. Obviously the method or methods best suited to a particular class of substances will be determined by experts in the field. Any method of purity determination to be used in a large scale program should be studied carefully, formalized somewhat, and described in the literature so that it is available for all to use.

Dr. Rossini: Thank you very much, Dr. Waddington. That is a very good starting point for us.

I would like next to call on Dr. Craig.

Dr. Craig: I will restrict my remarks to fields that have not been touched on thus far. We all know of the excellent work that is done on the purification of hydrocarbons and so forth. Existing in the world about us are countless numbers of substances about which we know very little in terms of structure. We know the structure of a good many alkaloids and plant dyes. Phosphorus compounds, about which we know relatively little, are of great interest because of their high energy bonds. Molecules of still higher molecular weight, such as the proteins, the polysaccharides, and the nucleic acids are interrelated and particularly important for biosynthesis. All of these substances are in areas in which we have great need for better standards and methods of purification.

We have been giving a lot of thought to this general over-all problem and have been thinking of it primarily in terms of molecular size. As molecular weights increase, the difficulty of purification becomes greater. When molecular weights are in the thousands, we have quite a different problem. Some of the large molecules crystallize. This property provides a valuable approach. Other techniques in use include sedimentation, adsorption, chromatography, counter-current distribution, and membrane diffusion which we have been using recently with considerable success.

The problem of working with large molecules is confounded by association. A large molecule with polyfunctional groups tends to associate with other molecules, either like or unlike. In this field information from the sedimentation technique can be supplemented with that from membrane diffusion. Also, when an organic molecule reaches a certain size, it assumes a definite configuration. This configuration is largely due to hydrogen bonding or to interaction between various parts of the molecule which, in many cases, can take place only in solution. If the water is removed, the molecule, which is stable in aqueous solution, assumes another configuration and is no longer stable. We are lacking in specific information about the structural details of these larger molecules. If we had structural models we would understand better how to handle the substances. But first we must have pure preparations and much research on fractionation methods.

The insulin from a pig is slightly different from the insulin from a cow. They are barely separable by counter-current distribution. The separability may be related to structural differences. We can compare the results of this separation with the results of separations obtained by other methods. There is a constant competition between the various separation methods. The separation method itself becomes a criterion of purity which can be combined with the measurement of physical constants and biological assay.

The latter should not be overlooked in determination of purity because the purest large molecules we have available are those which have a definite biological response.

We cannot be very definite about the desired range of purity. At the present state of development a protein that is 95 percent pure is a very good one. It is clear that the biochemist is faced with tremendous difficulties in the realm of pure materials.

Dr. Rossini: Thank you very much, Dr. Craig. Your remarks have been very helpful.

I will now call on Dr. Wichers to elaborate on his morning remarks on the general subject of purity.

Dr. Wichers: *In any discussion of pure substances, it is desirable to consider first whether the adjective "pure" can be defined unambiguously. The word is often misused. Of the faulty uses the worst is the one that conveys the sense of absoluteness. Frequently we read or hear that some substance is "absolutely pure." A moment's consideration will show that no experimentally obtainable quantity of a substance can be prepared so as to contain no single atom or molecule of a foreign species. For example, a gram of water containing only one in 10^9 mole fraction of impurities would still have in it some 10^{13} molecules of one or more foreign species.

Thus one sees that the notion of absolute purity is experimentally meaningless. However, this does not mean that the term "pure" should never be used. There are two kinds of situations in which its use is proper. One of these involves the relation of the composition of the "pure" substance to its use. For example, we speak correctly of "pure" drinking water, even though such water may contain concentrations of mineral matter that would make it entirely unsuitable for most uses in the chemical laboratory. On the other hand, the permissible content of pathogenic organisms, if expressed on the basis of percentage by weight, would be very small indeed. Similarly, experience may show that a given bottle of a reagent chemical yields analytical results indistinguishable from those obtained with a purer lot of the same reagent. Under these circumstances it is not unreasonable to call this substance "pure." That is, the impurities it contains have no detectable effect on the suitability of the substance for a particular use. One could wish, however, that the qualified term "pure enough" might come into use for such situations.

The second situation in which "pure" can be used properly occurs as follows: In studying progressive approach of a substance to ideal purity, a stage may be reached when further purification cannot be shown to have

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* At Dr. Wichers' request, this statement, prepared after the Conference, is substituted for his extemporaneous answers to questions.

occurred, by the available means of inspection or measurement. It is reasonable to call such a substance "pure" even though it may later be judged impure when new or more sensitive means are found for evaluating its purity. This situation has occurred repeatedly throughout the history of chemistry.

It is obviously desirable, whenever possible, to define the purity of a substance in numerical terms. There are two ways of doing this, depending upon the means of examination used. One is to state the composition of the substance in detail, that is to give the concentrations, in weight or mole fraction, of individual impurities. A common example of this practice is the list of impurities on the label of a bottle of an analytical reagent. Such a statement of composition may be made either in terms of the actual concentrations or of the upper limit of the concentrations. If all foreign species present in the substance are included in the statement, the difference between unity and the sum of their concentrations yields the degree of purity of the substance. An inescapable limitation on the accuracy of such a numerical definition of purity is imposed by the adequacy of the means used for detecting all the foreign species present and determining their concentrations.

The second way of defining purity in numerical terms is to make a collective determination of the concentration of the foreign species present, or of all such species susceptible of determination by the method of measurement that is used. A common example is provided by the cryometric evaluation of purity, in which one measures either the freezing temperature of a substance or the variation of this temperature as a function of the ratio of liquid and solid phases. This measurement yields the total mole fraction of impurities which are soluble in the liquid phase but not in the solid, with the further proviso that the system is assumed to behave "ideally." The purity of the substance is expressed as the difference between unity and the mole fraction of impurities.

The principle of collective determination of impurities is applicable to many other types of measurement of a selected physical property of a substance. The usefulness of such methods is very great, but it depends in each case on the adequacy of the knowledge concerning the behavior of the substance under study.

In conclusion it should be noted that no numerical expression of the purity of a substance is really complete without a description of the means of measurement that have been used. A generalization of the measuring process is that the nature of the measuring device or technique affects the results of the measurement. In considering pure substances, it is especially important to note that no single technique of evaluating purity is inherently superior to all others.

Dr. Rossini: Thank you, Dr. Wichers.

The floor is now open for general discussion of this topic.

Dr. Daniels: We have three or four separate problems. The first is how pure samples are to be made available, certified, and distributed. The second is how to stimulate research on obtaining better purity. The third is how to stimulate research to find new and improved criteria for determining the purity.

Concerning physical criteria, melting points, visual, ultraviolet, and infrared spectroscopy, X-ray measurements, and so on are well known. A new type of criterion such as thermo-luminescence is the sort of thing that ought to be explored further. We should constantly develop new types of measurements which can be used as criteria of purity.

Dr. Dreisbach: Anything more accurate than a freezing point would be very valuable in industry where a few hundredths of a percent impurity may influence the molding characteristics of a plastic. Does anyone know of anything better?

Dr. Egli: The number of free electrons available to carry current is a very sensitive measure of purity useful in solid state studies. It would be helpful, however, to be able to generalize the characteristics of materials in terms of two more basic properties, phase and texture. These have widespread import for characterizing physical defects, grain boundaries, dislocations, and electronic defects.

Dr. Craig: I would like to return to Dr. Dreisbach's question. Hydrocarbons have been studied very carefully by the freezing point method. Has the gas or liquid-vapor chromatographic method in any of these cases revealed impurity where the freezing point method did not?

Dr. Rossini: So far as I know, not in any significant way. We have always been careful to express the quantity of impurity in a realistic way. Although gas-liquid chromatographic studies have been able to disclose the existence of perhaps small quantities of several impurities, presumably their total amount will fall within the limits expressed on the label.

Dr. Spedding: We are talking about several different things. The freezing point method is fine for organic compounds but not applicable to solid state physics. Methods for high molecular weight compounds are quite different from those suitable for metals or phosphors. We should have separate groups considering these several problems.

L. Dr. Rossini: I think we should now pass on to our General Discussion III dealing with specific classes of chemical compounds of certified high purity, not now available at reasonable cost, needed by industrial laboratories, government laboratories, non-profit research institutes, and university laboratories.

We have four statements on this subject and I would like first to call on Dr. Hillenbrand.

Dr. Hillenbrand: The organic chemicals industry has a great need for specific compounds for calibration of analytical instruments, for the measurement of physical property data, for synthesis (studies), and as reference standards to establish the purity of commercial products.

The API and MCA projects have been very helpful to us and we are very pleased to hear that the range of compounds will be extended. There is a great need for data on many classes of oxygenated compounds, such as: aldehydes, ketones, esters, acetals, alcohols, and ethers. We need amines, particularly primary, secondary, and tertiary amines free from isomers. These compounds have been difficult to obtain in a fairly high state of purity, that is, in the range of 99.5 to 99.9 percent.

In the field of polymer chemistry we require pure monomers to determine the effect of impurities on the course of reactions. We manufacture tons of polyethylene daily but we do not have adequate thermodynamic data for ethylene at pressures from 30,000 to 50,000 pounds. We need a source of pure ethylene for such studies. Other useful monomers would be the acroleins, ethylene oxide, styrene, ethylene imine, and so forth. Then there are other fields of organic chemistry that are important in the industrial picture. There are very few physical data on the silicon, phosphorus, and boron compounds. Standards are needed in the fields of rocket fuels, synthetic lubricants, detergents, and many others.

The foregoing are some of the specific compounds that we would like to have available in our research and development laboratories, but undoubtedly there are others which could be added to this list.

Dr. Rossini: Thank you. That is going to be a lot of work for somebody.

I would like next to call on Dr. Elderfield for a statement on this phase of our problem.

Dr. Elderfield: Detergents have just been mentioned. If a supply of the pure isomers of dodecyl benzene had been available a couple of years ago it would have saved a tremendous number of man-hours of work in making a comparison of these compounds. Some of you may know about the frightening problems in England and in certain localities in this country brought about by benzene-type detergent. Certain dodecyl benzenes apparently resist action of the bacteria and are a problem in sewage disposal plants. It would be of great help if the effects of structure on the problem could be studied.

From a university point of view the problem of pure compounds is difficult. For instance one of my colleagues is interested in the properties of extremely weak Lewis bases, such as ethers and alcohols. He needs exceedingly pure compounds to establish the basic properties of coordination compounds on substances such as chloroform. We have been helping out in the preparation of these compounds. It would be very helpful if more compounds were readily available at a reasonable price.

Availability of hydrogenation catalysts of good uniformity, platinum oxide for instance, would be of great help. We have found too much variation in platinum oxide from commercial sources. Dr. Wichers may know how completely ruthenium can be separated from platinum. I don't know how the presence of a few parts per million of ruthenium or rhodium might influence the activity of a platinum catalyst.

The biochemist is getting down into the lower molecular weight region too. That is becoming more and more important because of our increasing knowledge that relatively small quantities of lower molecular weight substances may antagonize a given action of a biochemically active compound.

The synthetic organic chemist may not need ultra high-purity compounds for his routine work. On the other hand, a physical chemist needs them for his accurate measurements. Dr. Westrum, a physical chemist in our laboratories, has been studying thermodynamic properties, particularly heat contents of substances at very low temperatures. Over the past few years we have prepared what we think are pure organic compounds for his measurements. His particular interest is in organic compounds of high symmetry.

Another group of compounds of potential use is pure, optically active, organic acids. Only a few of these of reasonable purity are available. The supply of other compounds for resolution of optically active compounds should be increased. That shouldn't be too expensive a job. Most of them are natural compounds which may require only two or three extra steps in purification.

Dr. Rossini: Thank you very much. That was indeed a good rundown on many needs in this area.

I would like next to call on Dr. Frederick Brown who will give us something of the point of view of the solid state physicists.

Dr. Brown: In pure materials for solid state applications, the limits of allowable purity are generally much lower than for most chemicals. Transistor grade germanium now produced contains of the order of 1 part in 10^{10} (10^{12} atoms/cc) of electrically active impurities. While it is true that other foreign substances are present at higher concentration, the best germanium and silicon are still extremely pure on a chemical basis. Many substances not electrically active in the sense of being donor or acceptor impurities may trap carriers and must be eliminated. Electron or hole trapping due to trace impurities is particularly important in PbS and CdS, examples of substances which have undergone a high state of development for photoconductor devices.

Luminescent solids are another class of materials which have undergone extensive purification. This is because of the extreme sensitivity of luminescence, including thermoluminescence, to trace impurities. The preparation of many luminescent materials is still in the cook-book stage.

Regarding electrical properties, crystalline solids may be classified as (1) semi-conductors, (2) metals, and (3) insulators. Some specific needs for high purity materials under these three categories follow.

Many compound semi-conducting materials are in need of improvement. Whereas much of the difficulty with intermetallic compounds has to do with deviation from stoichiometry, purity is also an important factor. The development of more thermoelectric devices is primarily a materials research problem. Although useful solids for this purpose may be highly doped compounds, the starting point is usually pure and stoichiometric raw material. The study of carrier mobility as a function of temperature and the electron-lattice interaction is best carried out in highly pure crystals. A similar statement can be made about thermal conductivity over certain temperature ranges. The electrical properties of wide-band gap semi-conductors such as ZnO are still controlled by unknown trace impurities. High temperature refractories such as SiC are of intense interest but are far from pure. The trouble with many of these semi-conductors lies in the difficulty of preparation of crystals.

Metals such as copper, silver, and gold are now available in very high purity (six 9's) adequate for most solid state measurements. However, the list of very high purity metals needs to be expanded. The mechanical properties of solids, in particular metals, are of great interest. As techniques for observing the motion of single dislocations become available, additional concepts of purity will be required.

Insulating crystals such as the alkali and silver halides are of great interest in connection with point imperfections in solids. Color centers may be mentioned as examples of electronic defects which are widely studied. It is becoming increasingly clear that the purity of the alkali halide crystals currently employed is not always adequate. This is particularly true of studies of the rate of production and bleaching of color centers. The electron properties of ionic crystals are just beginning to be understood. At high temperatures carriers are scattering primarily by lattice vibration but below 20°K. impurity scattering predominates as in atomic semiconductors. Concentrations of multi-valent impurity ions of the order of 10^{14} to 10^{15} per cm^2 are important. It appears so far that the silver halides, AgCl and AgBr, have yielded to purification by both chemical and physical methods more rapidly than the alkali halides. Single crystals of AgCl have been prepared containing no more than 1 in 10^7 of total heavy metal impurities. Similar purities may soon be achieved in the case of alkali halides.

New analytical techniques for detecting trace impurities must be found. Spectrochemical techniques, though laborious, are adequate for some impurities but inadequate for others. One possibility would be to extend the measurements of ionic conductivity vs. temperature into the low-temperature, structure-sensitive range for ionic compounds containing known amounts of trace impurities ($1:10^5$). The valence state of added impurities will have to be controlled. Some impurities such as Mn^{++} and Cu^{++} have yielded to investigation by spin techniques.

Dr. Rossini: Thank you, Dr. Brown, very much for this comprehensive statement of the needs of solid state science.

I would like next to call on Dr. Winston Manning for a statement on this problem.

Dr. Manning: I shall assume that the scope of the meeting includes questions of isotopic contamination and purity since that is one of the major problems of the Atomic Energy Commission.

The research people in our laboratories have profited quite frequently from material procured for production purposes. Examples are the pure reactor grade natural uranium, zirconium, enriched 235, and 99+ % D_2O for reactor moderator purposes. More recent examples are lithium, boron, and quite a few of the stable isotopes which have come as by-products from the earlier U-235 enrichment program.

There are at least two pure isotopic preparations, not now in existence, which would be very valuable. One is 99+ % carbon-13 which would be particularly useful in biosynthesis studies and certain kinds of nuclear bombardment work. The best now available, so far as I know, is around 50 to 60 percent isotopic purity. I would strongly recommend that somebody start producing 99+ % C^{13}. It would be much in demand.

Oxygen-17 is available only in five percent enrichment. This isotope is of interest in nuclear-magnetic-resonance studies because it is the only oxygen isotope which has a nuclear spin. The enrichment is a difficult task because its isotopic abundance is only a few hundredths percent. It might be very expensive to produce but is highly desirable.

The identification and segregation of isotopically altered material is another important field. So far as I know there is no krypton available which does not contain krypton-85 which has a half life of ten years. The best krypton has a thousand disintegrations per liter per minute. While unfortunate, this is a special case since it occurs only in the atmosphere. But because we are increasing the possibilities for contamination by fallout I would urge that this sort of problem be given close attention.

Because most of the lithium on the market now has had a large fraction of lithium-6 removed, it is very important for precise work to know whether the lithium sample is normal or not. Similar problems will arise with the large stockpiles of uranium which sooner or later will go on the market. Zirconium, which has been used for fuel elements, will be contaminated with radioactivity. We want to be sure that such zirconium does not get back into normal channels for research.

Production of radioactive-free reagents for research in Atomic Energy laboratories is important for nuclear research, especially low-level activity studies. For instance, radioactivity specifications are very important in the shielding of low-level counters with kilogram quantities of lead or of iron. If this lead contains a tenth of a part per million of uranium one does not have much protection because a microgram of uranium will give about five or six counts per minute. Similarly defective materials for low-level counting materials are plastics, copper, and brass.

Another very practical problem is the desirability of having containers and backing materials free of impurities which will become radioactive when exposed to nuclear bombardment. This is a very serious problem. Aluminum, which is commonly used for packaging materials for radiation, contains iron, copper, manganese, zinc, and chromium, all of which have a very high neutron absorption. So a one-ton shipping container may be needed for a sample which would require little or no shielding if it were not for these impurities. Reduction of copper, manganese, chromium, and so forth to well below one part per million would be advantageous. Platinum used as supporting material should be thoroughly free of radium. It is desirable to establish a category of uranium and thorium free chemicals or reagents for the types of investigations going on in the Atomic Energy laboratories and in many universities.

To generalize there is a need for ultra-pure reagents for extremely low-level work, for example, with trans-uranium elements of which only small amounts are available. Working among low levels, specifications that formerly were satisfactory for substances like iron, for example, are no longer so. In this work the spectrometer has become a very sensitive tool for research and analysis, and one is able to characterize 10^{-15} grams of material. But to utilize fully these astounding sensitivities one needs to have correspondingly purer chemical reagents. Otherwise the contaminants may hopelessly confuse the picture.

Dr. Rossini: Thank you very much. You have given us a number of very interesting points to consider, and I am sure something will have to be done about several of them. I am quite sure your point about the krypton-85 is news to a lot of people here.

We now have reached the point where this topic is open for general discussion. Do any of you want to contribute items from the viewpoint of industry, university, government, or non-profit research institute laboratories?

Dr. Thomas: The advent of the liquid-vapor chromatography has given us a new dimension for investigating composition and processes. We in the petroleum industry need samples of almost every hydrocarbon that boils below about 300 degrees Centigrade.

Dr. Elderfield: I would like to emphasize that the universities are interested in pure compounds for purposes of standardization, for spectroscopic research, and many other purposes.

Dr. Klug: Independent research foundations have the same type of problems as industry and university laboratories. We need pure compounds for use as thermometric standards, spectrographic standards, and so forth. We are called upon to analyze materials for smaller and smaller amounts of impurity. As time goes on we will need reagents of greater and greater purity for determining smaller and smaller amounts of impurity.

M. Coffee break

N. Dr. Rossini: We will now start our General Discussion IV dealing with the resources available for supporting work on the preparation and distribution of chemical compounds of certified high purity by whatever groups or organizations are available to do that. We have starting statements on this topic to be made by several of our conference participants. I would like first to call on Donald Brooks.

Dr. Brooks: I am in the Office of the Director (Dr. York), Defense Research and Engineering. Our mission is to see that the many service programs are well-rounded and do not overlap to an unnecessary degree, recognizing that in new fields some duplication may be desired. It is also part of the mission of the staff to advise the Director as needed.

In general, support for programs of the type we are discussing would come from the services rather than from the Office of Secretary of Defense of which we are a part. However, under some circumstances it is possible for the Director to take action through the emergency fund which is set up to provide for unforeseen contingencies. This fund amounts to $150 million at present or roughly 10 percent of the direct and earmarked R & D funds. As an example, the emergency funds were used about three years ago in connection with the program on the possibility of getting propellants from free radicals. This work was being carried out at the Bureau of Standards. It was agreed that the Army would undertake the administration of this program for a period of three years. Emergency funds were provided to start it and some additional emergency funds were furnished later to keep it going. If for any reason an area of the Services needs additional support we can request action or, if necessary, provide the funds.

Dr. Rossini: Thank you very much, Dr. Brooks.

I would like next to ask the representative from the National Science Foundation, Dr. Kirner, if he will make a statement on this general subject.

Dr. Kirner: I think it is obvious in an undertaking such as this that the combined support of a number of groups will be needed. The Bureau of Standards, as a government agency, is making important contributions to the program. Industry, through the API, has contributed extensively. If there are certain areas that concern a specific industry, it would seem that this particular industry should contribute to the support of the appropriate program. For example, monomers and certain other types of compounds were mentioned which are of greater interest to a given industry than to anybody else. The same would apply to the various government agencies. If a branch of DOD has a specific interest in a certain type of compound presumably it would be the one which would support the preparation of those particular compounds.

Other agencies such as the National Science Foundation have no specific objective as far as the ultimate applications of any of the compounds are concerned. However, cooperative group efforts such as this will certainly advance research which is one of the purposes of the Foundation.

During the afternoon discussion mention was made of the fact that graduate students are not being adequately trained in purification procedures. Steps to remedy this situation might be included in our program. Many improvements in analytical methods have occurred since I was a student. Micro-analysis has replaced macro procedures and is more tedious and tricky and for this reason has almost been dropped from the curriculum. Professional micro-analysts are now doing this work.

Perhaps the same thing is true for purification. It is time-consuming as Dr. Daniels pointed out, and if the purification can be done in other ways, well and good. One possible aid to this problem is through one type of support in which the National Science Foundation is interested. Our division is concerned primarily with the support of research, but another division provides funds for fellowships, summer institutes, the training of undergraduates, summer research for faculty, and so forth. It might be possible for them to provide a grant to a liberal arts college where a faculty member is interested in this general problem of purification of compounds. While it is not pioneering research, nevertheless it could serve a very useful purpose. If we had a number of these grants in liberal arts colleges throughout the country, we would get some of this work done and at the same time we would be training the undergraduate students primarily in the whole process of purification.

I can summarize by saying that NSF might be able to contribute to this general problem through our normal programs in addition to any special effort that might be necessary to support the general idea.

Dr. Rossini: Thank you very much, Dr. Kirner.

I would like now to call on Frank Carman for a statement on this general subject.

Dr. Carman: Most of the people here know that for four years the Manufacturing Chemists Association has been supporting an activity at Carnegie similar to API Project 44 which compiles and publishes critical data. In this project no compounds of high purity are made nor do we have plans to undertake such a program. The MCA is now in its fifth year of sponsoring the publication of critical data. These data are the result of a very critical analysis of published information. For some time the MCA has recognized that the large amount of experimental work necessary for the determination of needed new data would probably involve synthesis of pure compounds not now available. We have been searching for a way to do this, but have found none within the limits of the funds presently available. We can not double our expenditure at the present time which would probably be required if we were to undertake the experimental work. Ten percent of our total budget is now going for research of some type and the data project takes by far the largest portion. Perhaps a way can be found whereby industry would supply pure compounds to some agency, such as NBS, for characterization. This possibility is being explored.

Dr. Hillenbrand mentioned that some groups would like to have pure monomers, but others are not interested in pure monomers. There are differences in the interests of industry groups but certainly the chemical industry in general and our program at Carnegie Tech in particular would benefit from pure compound programs.

Dr. Rossini: Thank you very much, Dr. Carman.

We appreciate these statements from Don Brooks, Walter Kirner, and Frank Carman.

The subject is now open for general discussion from the floor.

Dr. Astin: I might comment on the general fiscal status of the National Bureau of Standards in this area. Our method of financing the Standard Samples program has been changed in the past three years. The program is now to a large extent self-supporting. We are now authorized to charge fees to cover the cost of producing Standard Samples. These fees should include not only the cost of preparation and purification of the materials involved in the Standard Sample but the cost of any testing necessary to obtain a proper characterization of the material. For our Standard Samples composition or properties are certified on the basis of cooperation with four or five other laboratories with competence in measuring the particular properties involved. All such costs can now be recovered in terms of the fees collected for the Standard Samples. However, cost of developing new techniques, new purification techniques, and new measurement techniques necessary in preparing Standard Samples or other highly characterized materials must be borne by our own appropriations or by funds obtained from other sources. But our ability to put the program on a self-supporting basis is a very fortunate one, I think, since it permits us to put these services more nearly in line with the demand for them.

There are some limits to the amount of work we can do. Working capital must be invested in producing Standard Samples and this investment may not be recovered for five to ten years. So we are limited by the size of the working capital fund available for investment. A question also arises as to how the universities or other non-profit organizations will react to the rather sizeable cost increase for research materials.

Dr. Dreisbach: There is another possibility of support. Chemical companies should be able to supply a good many pure compounds for certification. The Dow Company has assured me that they will do their share in making pure compounds available if other companies would also cooperate. Dr. Hillenbrand has sent a circular to the member companies, but not all the results are in. Chemical companies could do such things more cheaply than the Bureau of Standards because the equipment is already available. For instance, from one available experimental setup a whole series of pure compounds can be made by one purification procedure at very little cost. I think this cooperation by industry will be helpful provided the Bureau of Standards and other groups will perform the property characterizations.

Industry could also cooperate in the determination of physical properties. Our chemists are measuring density, refractive index, and surface tension very accurately. We have equipment for solubility measurements in water. A lot of work of this kind has been done and we would like to continue it provided other companies would cooperate in such a program.

Dr. Rossini: Thank you very much, Bob. Gentlemen, I want to correct one statement I made this morning. I referred to Dr. Dreisbach as having been retired from the Dow Company. You can see very well he is not. Are there any other comments or contributions to this part of the discussion?

Dr. Elderfield: As a corollary to Dr. Dreisbach's remarks, the universities are going to be a rather poor source of materials of the type he mentions. With the rise of micro-methods, the average graduate student is satisfied when he has made enough of the compound to determine a melting point. It is hard enough to get a few grams of a drug for pharmacological screening. When talking about the amounts of compounds needed for this kind of work, it is going to be hopeless as far as the average graduate student is concerned.

Dr. Carman: What quantity of hydrocarbons is supplied, for example, in the API project?

Dr. Thomas: API Research Project 45 normally supplies two gallons to Project 6. It is then further purified. We may obtain 50, 75, or 90% of final pure product depending on the efficiency of the distillation.

Dr. Hillenbrand: The MCA has supported the project on physical property data for the past four or five years at Carnegie Tech at a rate of about $40,000 a year. The resulting tables are published and made available free to universities, government agencies, and other groups in this country and abroad. The MCA and others in the chemical industry are rather disappointed that so little support has been forthcoming from universities and government. If other groups would be willing to provide funds either for physical property determinations or to develop pure compounds, I am sure that industry would be encouraged sufficiently to increase their own contributions.

Dr. Rossini: Thank you. Are there any other comments?

Dr. Elderfield: Perhaps Dr. Brown knows whether companies dealing with semi-conductors, pure single crystals, and related products have an organization similar to the MCA. The Sylvania Company two or three years ago had a very big program going. Last fall I visited the Hughes plant in Culver City where a huge program was going on in the field of solid state physics. There must be others in that field.

Dr. Brown: I don't know of any specific agency. In fact, the work on germanium and silicon has been done in separate organizations. The Bell Telephone laboratories and Hughes all make their own material. I understand that DuPont is now supplying transistor grade material on a commercial basis.

Dr. Egli: In this area the closest thing to a coordinating body, outside of various defense committees, is the solid state advisory committee which is a semi-official body at least. It has considered various ways of coordinating and stimulating this problem. There have been various proposals considered, for new laboratories for example, one of which was aimed precisely at this problem. As a start they rather warmly indorse a proposal from the Bureau of Standards for an information exchange and possibly a materials exchange. When somebody makes a good crystal sample, one or two out of the batch would be submitted to the central location where it can be made available to others for experimental purposes. That is the closest thing to coordination that we have at the present time.

Dr. Rossini: I would like to ask Dr. Kirner one question that pertains to Dr. Astin's report regarding increased cost of Standard Samples and its possible effect on university research. Since in a large majority of cases university costs are borne by research grants or government contracts, would the National Science Foundation have any objection if the increased cost of the materials could be included in or added to their grants? Suppose the investigator needed ten samples from the Bureau of Standards each of which costs $100.

Dr. Kirner: No, there would be no objection to that. If the samples are necessary to do the research they ought to be included in the budget and the Foundation ought to pay for it.

Dr. Rossini: I assume that Dr. Dawson and Dr. Horney have the same answer on this?

Dr. Horney: Yes.

O. Dr. Rossini: I think we should halt this discussion and proceed to the General Discussion V of the appropriate places for performing the work and the organization to manage the operation.

I have asked two of our conference participants to present starting statements on this. First, I would like to call on Dr. Daniels.

Dr. Daniels: First I would like to discuss appropriate places for performing the work. The Eastman Kodak Company and the duPont Company are examples of industrial organizations which supply materials. Years ago the University of Illinois started a program of making organic compounds. Carnegie Tech is preparing pure compounds now. The use of college professors for summer research is another possible source of facilities and manpower. Furthermore, a program like this would make it unnecessary for them to do non-technical work during the summer. The Bureau of Standards, of course, is an example of a government agency where this work could be done. In addition, research institutions might use government contract funds for work on pure compounds.

My second point of discussion concerns the choice between private enterprise and public tax support, a subject about which people become quite emotional. But since there is no profit in making pure compounds, private organizations may have to be subsidized. What controls can be imposed to insure that purity standards will be established and maintained? This is a difficult problem but we do have a precedent in the development of radiation measuring instruments by private enterprise.

This brings to focus the problem of centralization versus decentralization. In the United States we tend to avoid centralization but perhaps it would be well if a central authority would take the responsibility for pointing out fields of research which ought to be explored and areas where new materials of high purity should be manufactured and dispensed.

There have been rumors that the establishment of a central agency for the control of production of pure materials is under consideration. Should there be an entirely new agency or should the experience and long and distinguished record of the Bureau of Standards be utilized? Personally, with the facts at hand, I favor allowing the Bureau of Standards to take responsibility for any such expanded program.

What are some of the sources of manpower to prepare pure materials? University people could be given grants; private enterprise could be subsidized. Foreign workers represent another source of manpower. There are many individuals trained in America who return to India, other parts of Asia, and even to Europe, who find it difficult to get technical jobs commensurate with their training. The foreign aid programs of the United States leave accumulated credits in some countries which can't easily be recovered in dollars but could be used to pay for services. If there is a demand for routine but exacting work in the preparation of pure compounds we might look into the possibility of using foreign aid funds under Public Law 480 for personnel who are not being used adequately in foreign countries.

The distribution problem seems to me quite as important as the preparation problem. Looking ahead to a time when we have available thousands of compounds, many more than are now available from API, would it not be desirable to devise a larger-scale distribution system? Should not the chemical supply houses be retail agents for pure compounds as they are for many other things?

Another problem is that of publication. Results of research on purification and pure compounds are now scattered in various journals. One or two books were mentioned that have been written on this subject, but, in general, I think the literature is rather deficient in this area. In my own experience, I would have been very pleased to be able to refer my students to standard books on purification and preparation of pure compounds. We need books on purification for organic chemistry, inorganic chemistry, semi-conductors and related subjects, and for biological chemistry. A symposium on pure compounds also would be of great interest. Perhaps there should be a division of a society and a journal devoted to the pure-compounds field.

One of the biggest problems of all, the competition between service and research, is one which has been faced already by government laboratories such as the Bureau of Standards. While no creative scientist wants to do routine service jobs only, these laboratories have been able to combine the functions of service and research in a rather successful way. Research minded people who are creative are allowed to do their research, and the people who are less creative gradually drift into production and service work. But we ought to find a way to attach more prestige to the job of preparing pure compounds.

One of the three phases which I mentioned before is the preparation and dispensing of these samples. Because this is largely service it requires some increased prestige or an incentive, such as a higher salary. The development of new methods of preparation and new methods of physical measurement should come under the category of research. No particular incentive is needed here because the creative scientists are glad to do this kind of work.

Dr. Rossini: Thank you very much. Your statement provides a very comprehensive picture for us.

I would like next to call on Dr. Wichers for a report on this subject.

Dr. Wichers: The magnitude and complexity of the problem we have been discussing today is now clearly apparent to all. The use of impure substances has resulted in economic and scientific loss. This situation must be corrected by all possible means.

Competence and interest must be utilized wherever they exist. There have been comments today about many diversified and specialized areas where this competence exists. There are groups, such as the American Petroleum Institute, where preparation of pure substances constitutes proper background research for the problems of the industry. A real coordination of effort and more cross-fertilization of ideas are needed. This coordination should be done by a group that also has a technical understanding of the problems involved, otherwise it will not be an effective coordination. Our Bureau, because of its mission, is bound to continue in this field. Its level of activity will depend on money, on facilities, and so on.

If a new administrative agency is formed, its greatest need will be for a diversity of skills and facilities. This is especially true when one deals with criteria of purity because we haven't begun to utilize all physical properties. Today thermal properties are used quite extensively and optical properties are beginning to be used. Electrical properties have not been exploited and the utilization of mechanical properties for characterization of substances is not understood at all. It is not hard to outline the kind of broad diversified skills and the spirit of cooperation that would be essential to make a successful new coordinating institution. Such an institution, to be operative, must be staffed by people who have the proper knowledge and interest.

Dr. Daniels spoke of incentives. The best incentive for really productive creative work in the purification field is a general interest in the problem. It may be incredible to the majority of people working in chemistry, but there are chemists who get starry-eyed when talking about purifying substances. They don't need much more incentive than the opportunity to go at it.

Now I would like to say a word about the future. The interest in, and the need for, pure substances has grown tremendously during my lifetime and there is no reason to think this growth will stop. This means that more people must be trained to work in this field. Just how this is to be done I don't know, but I believe the universities must take some responsibility for this.

Dr. Rossini: Thank you. That has been a very helpful report supporting that of Dr. Daniels.

Dr. Craig: A very interesting Gordon Research Conference on separation and purification was held last week. A good many of the subjects about which we have been talking were discussed. It meets every year and is a very illuminating conference to attend.

Dr. Dreisbach: I am sure industry would furnish the raw materials without cost to college programs for preparation of pure compounds.

Dr. Kolthoff: I would like to mention the obligation of universities in educating students in the field of purification. There is much waste of time because there is no central agency to collect information, past and present, on purification. An editor of a scientific journal normally publishes one or two lines on a chemical purification, but there may be two chapters in a thesis about a student's research on the several purification processes he has attempted to use. Somewhere there should be an agency to collect the existing information from all sources.

Dr. Burwell: Professor Kolthoff has referred to the more effective use of available information. Professor Smyth made a second suggestion this morning regarding the use of existing resources. I would like to make still another. A relatively small sum of money, as a sort of an underwriting grant, might encourage a few companies with large stocks of pure compounds to identify and dispense them. Nobody would have any distribution problems. I think a fairly small sum of money might do quite a lot. The problem, of course, is that one can not always rely on the claims to purity.

Dr. Rossini: Yes. The problem is one that involves selecting and collecting starting materials (whether they be already in existence or whether they need to be synthesized), the purification of these materials to the proper degree, the evaluation of the purity, and most importantly their certification. All of these things must in some way be coordinated and brought together. I am very hopeful that our report will make a statement concerning the coordination of these problems.

Are there further comments or questions on this part of our discussion?

Dr. Egli: What is the role of the General Services Administration in this area? They are spending substantial funds of money on materials.

Dr. Hayes: GSA has financed development projects aimed at producing metals above the general commercial purity, but I don't think that they support research of the type being considered today.

Dr. Wichers: It is my impression that they are not in the field.

Dr. Rossini: Any other comments or questions?

If not, we will recess until this evening.

P. Recess

Q. Social hour

R. Dinner

S. In the evening the participants separated into five groups, with membership as specified on page vii, for the preparation of summary reports, on

I. The philosophical and intellectual aspects of the problem
II. The scope of the Conference
III. The specific classes of chemical compounds needed
IV. The financial resources available for supporting the work
V. The places to perform the work and the organization to manage the operation

The reports were duly prepared to be presented the next morning by the chairmen of the respective groups.

T. Adjournment, by each group separately

U. Dr. Rossini: Gentlemen, I would like to call the final session of the Conference to order.

The report of the conference will be transmitted to Dr. Bronk, President of the National Academy of Sciences, and will consist of the following parts:

(1) Copies of the agenda, list of participants, observers, etc., which were given to you yesterday but which will be corrected in some details;

(2) An introductory statement concerning the Conference by the Chairman;

(3) A condensed summary of yesterday's proceedings as reported by the stenotypist and the reporters and prepared by the Secretary of the Conference, Dr. Waddington, assisted by his staff;

(4) A copy of the summary reports and recommendations from the five groups;

(5) A concluding statement by the Chairman in which I will try to reflect the views of the Conference regarding the importance of this problem to science and industry in the country.

<u>Note inserted by the Secretary.</u> At this point Dr. Rossini called on the Chairmen of Groups I to V in turn to present the summary reports and recommendations prepared by the five groups on the previous evening. The reports were presented and discussed. Minor suggestions for clarification were accepted by the Chairmen. The reports, modified in accordance with accepted suggestions, are presented in the following pages.

V. Summary Statement and Recommendations of Group I on the Philosophical and Intellectual Aspects of the Problem

Mr. Chairman, with your permission I would like to comment briefly on the guide lines adhered to by the Group I members in the preparation of the report dealing with the philosophical and intellectual aspects of the problem of the availability of chemical compounds of certified high purity. There was unanimous agreement that the diversity and complexity of the problem dictated against a comprehensive treatment of the matter in a brief report. It was decided to condense some of the more relevent ideas or concepts into a few preliminary statements with an associated group of specific recommendations, nine in number. Furthermore, in view of the overlapping interests of some of the groups, it was agreed that it was unavoidable and in view of the preliminary nature of this report, even proper to make specific recommendations on topics rightfully delegated to other groups. The report is presented for your consideration:

1. The need for chemical compounds of established purity is universally admitted in all areas of scientific endeavor, whether they be the physical sciences, the engineering sciences or the biological sciences. The general availability of compounds of defined purity through some proper official agency would assure many and varied benefits to science and technology such as the acceleration and augmentation of research on the basic and the applied or developmental level; the elimination of wastefulness and duplication in research expenditures; the release of professional manpower for more direct research effort; and finally the broadening of the scope of research in all areas. This has been decisively demonstrated by existing activities in a few fields such as the National Bureau of Standards program in the fields of primary standards, and the American Petroleum Institute program in research hydrocarbons and related substances, which has stimulated research in the petroleum field and proved most effective in the preparation of the most complete set of selected values of physical and thermodynamic properties available on any known class of compounds.

Recommendation (1) The recommendation is made for the establishment of a permanent central technical agency with assigned responsibility for the identification, certification and distribution of substances of established purity. This organization should be primarily self-supporting with a minimum amount of permanent funds. Furthermore, this agency should have a coordinating function and be empowered to approach competent individuals and groups in government, industrial and educational laboratories for necessary work dealing with the preparation, purification and identification of substances.

2. In consideration of the concept of purity, it was agreed that a more practical approach was to deal with the problem of certification defined in terms of what is known about the particular chemical compound. A group of four recommendations is made with respect to the certification of chemical compounds:

Recommendation (2) (i) Two kinds of certified standards to be recognized.

(a) General - primarily to be defined as standards of identity and as standards for the measurement of physical thermodynamic and spectral properties. The group will consist of highly useful compounds representative of the important chemical classes.

(b) Specific Standards - as defined for purposes of calibration and standardization.

Recommendation (3) (ii) It is recommended that the list of compounds be dictated by apparent demands with some appropriate balance.

Recommendation (4) (iii) It is recommended that certification be based on defined equilibrium properties.

Recommendation (5) (iv) It is recommended that the certification of the general standards, particularly the organic compounds, be based on the major component by difference, however, with qualitative identification given of the minor constituents whenever possible; that the specific standards and the inorganic compounds be certified by a complete quantitative identification of all the minor constituents.

3. In the implementation of a program dealing with the certification of chemical substances:

Recommendation (6) It is recommended that some existing organization such as the National Academy of Sciences or the National Bureau of Standards take the initial steps in such a program by establishment of an information center for the purpose of compilation and dissemination of maximum current information on existing sources of compounds of established purity in all categories on a continuing basis.

4. With respect to the costs of certified samples, the unique problems of investigators in educational institutions are recognized and a firm recommendation is made that:

Recommendation (7) Certified standards be made available to educational institutions on a reduced cost basis.

5. There is a recognized need for extension of present analytical procedures and development of new methods for analysis, characterization and identification of a variety of substances.

Recommendation (8) It is thus recommended that research in the area of extending current procedures and the development of new methods in the general area of chemical analysis be encouraged and supported.

Recommendation (9) 6. The final recommendation is made that the Analytical Division of the American Chemical Society be contacted about sponsorship in the immediate future of a major joint divisional symposium on the Purity and Identification of Chemical Compounds.

Respectfully submitted by

B. J. Zwolinski, Chairman
R. L. Burwell, Jr.
J. W. Dawson
W. O. Milligan
R. Robertson
Oswald F. Schuette

W. Summary Statement and Recommendations of Group II on the Scope of the Conference under the Headings

(a) Classes and Kinds of Compounds to be Considered
(b) Ranges of Purity to be Considered
(c) Criteria of Purity to be Considered

Subcommittee II reviewed the discussions of the Monday, June 22 session under the three indicated headings.

The group recognized that:

(1) a broad interest exists in certified pure substances ranging from isotopically pure elements to organic molecules of the most complex nature;

(2) the purity range set as a goal for a given category of substance will be governed in varying degrees by the joint considerations of the efficacy of existing modes of purification and the end use of the pure product;

(3) the assignment of a meaningful purity value to a sample tends to become difficult as molecular size or required purity increases.

Classes of Compounds. The subcommittee made no effort to assign priorities to particular classes of compounds. It went no further than outlining groups of substances in which there is an expressed interest. The following table may be used as a basis for study and selection:

A. Elements (including selected isotopes)

B. Inorganic Compounds (including selected isotopically pure substances)

(a) semi-conductors
(b) phosphors
(c) halides, oxides, hydrides, sulfates and other salts
(d) other groups of inorganic compounds of current interest not specifically included in the above.

C. Organic Compounds

(a) hydrocarbons and simple derivatives such as halogenated compounds, alcohols, aldehydes, ketones, amines and other groups important to science and industry

(b) biologically important classes of compounds such as carbohydrates, lipids, amino acids, proteins, alkaloids, nucleic acid derivatives, organophophorus compounds and so forth.

D. Organometallic Compounds

E. Selected single crystals of both organic and inorganic substances

Recommendation (1) It is recommended that selection of classes of compounds for preparation should be made only after a survey of the opinions of competent authorities.

Ranges of Purity

The level of attainable purity will differ for each class of compound. It may be as low as 90% for proteins and as high as "nine 9's" or better for certain components in semiconducting materials. It is obvious that no general statement can be made concerning "ranges of purity." However, for each class of compounds the goal will be a purity sufficiently high to satisfy the requirements of the most exacting application of the sample.

Full use should be made, as appropriate, of purification techniques such as the following: distillation, fractional crystallization, extraction, ion exchange, absorption, counter-current distribution, zone melting, electrophoresis, sublimation, electrolysis, precipitation, sedimentation, single-crystal growth, gas-liquid partition chromatography, other chromatographic methods, and chemical analysis.

Recommendation (2) It is recommended that research on new purification techniques and the improvement of existing methods should be encouraged.

Criteria of Purity

The subcommittee recognizes that no one criterion of purity will suffice for all classes of compounds. Available for use in the determination of purity are: cryoscopic methods, various spectroscopic techniques, ebulliometric methods, optical properties, viscosity determinations, electrical and magnetic properties, bio-assay and other methods. New concepts of purity such as texture, stoichiometry, and others pertaining to the physical state of the substance are to be considered.

It is recognized that in cases where the method of purification serves as a purity criterion, e.g., the purification of a protein by a repetitive operation, the method of purification and the labile nature of the molecule being purified will need to be specified in a statement of purity. In others the purification and the determination of purity are independent operations. It will be desirable to indicate when possible not only the total amount of impurity but also the chemical nature of the individual contaminants.

Recommendation (3) It is recommended that for each category of compounds, appropriate criteria be selected by experts in the pertinent fields and that standardized methods of purity determination be applied in so far as possible. These specific criteria and the standardized methods for their use should be described and published.

Existing Sources of Pure Compounds

A large amount of information was revealed during the meeting about existing sources of "pure" compounds.

Recommendation (4) It is recommended that a survey be made of all available sources of pure compounds by the National Bureau of Standards or other appropriate body. The results of such a study would be useful in delineating the scope of activities directed toward the production of certified pure compounds.

Submitted by

Guy Waddington, Chairman
Lyman C. Craig
Earl T. Hayes
C. W. Montgomery
C. P. Smyth
Richard Wiebe

X. Summary Statement and Recommendations of Group III on Specific Classes of Chemical Compounds of Certified High Purity, Not Now Available at Reasonable Cost Needed by Scientific Laboratories

In arriving at a list of needed compounds of specified high purity, it is necessary to classify compounds according to intended uses since the required degree of purity is determined by the ultimate use of the material. For example, the measurement of the classical physical constants of organic compounds would not be influenced to any considerable extent by the presence of 0.001 mole % of impurity while on the other hand the physicist and the chemist interested in properties dependent on structure can be extremely concerned about very much smaller quantities. Biochemical compounds are specifically omitted as they are discussed in sufficient detail in the report of Group II.

Certified samples of organic compounds of moderately high purity are needed for:

1. Determination of physical property data
2. Reaction studies
3. Solvents suitable for study of physical-chemical phenomena in non-aqueous solutions
4. Optical standards
5. Cryoscopic standards
6. Analytical standards for gas chromatography, mass spectroscopy, nuclear magnetic resonance, X-ray diffraction, paramagnetic resonance, and rotary dispersion.

Hydrocarbon samples available from the API Project have proved highly useful as evidenced by the increasing demand for these materials. It is reasonable to conclude that the availability of other organic compounds (e.g., alcohols) of similar quality would also be desirable. However, the group does not feel that priorities for specific classes of compounds can be made without further study.

In the area of inorganic and physical chemistry where there is a general interest in the use of chemical compounds as reagents, the development of new sensitive techniques, such as nuclear magnetic resonance, mass spectrometry, and radio-chemical analysis, together with the general development of ultra micro chemical techniques and especially with the interest in rare chemical elements which are available only in trace or micro amounts, there is a great need for compounds free from specified impurities to a much greater extent than the older specifications for reagent chemicals; expecially, freedom from radioactive elements, such as uranium, thorium, etc., and also from some of the more common elements -- especially iron.

In the field of Pure Materials for solid state applications, the limits of allowable impurity are generally much lower than for most chemicals; i.e., transistor grade germanium is now being produced which contains less than one part in 10^9 electrically active impurities. While it is true that other foreign substances are present in orders of magnitude higher concentrations, the best germanium and silicon is still high-purity on a chemical basis.

Some specific needs for high-purity materials are as follows:

1. Intermetallic compounds for thermoelectric applications (improved stoichiometry as well as purity)
2. Certain wide-band gap semiconductors, such as ZnO, high temperature refractories, such as SiC and many others
3. Extension of the list of very high purity ($1:10^6$) metals. The study of single dislocations and their motion may be particularly sensitive to impurity
4. Insulating ionic crystals, such as the alkali halides, are needed in high-purity form -- particularly for the study of color centers and other point imperfections. The development of new analytical techniques will be required as these materials become available.

Recommendation While it is recognized that there is increasing demand for compounds of certified high purity, it is thought that a further study should be made to establish priorities for specific classes of compounds. This study should include the field of pure materials for solid state applications.

Submitted by

E. F. Hillenbrand, Jr., Chairman
Frederick C. Brown
Beverly L. Clarke
R. R. Dreisbach
R. C. Elderfield
Herbert L. Haller
I. M. Kolthoff
Winston Manning
John R. Ruhoff
J. W. Stillman

Y. Summary Statement and Recommendations of Group IV on Resources Available for Supporting the Work

The group on resources available for supporting work on chemical compounds of certified high purity recognizes 3 general areas of work requiring different approaches for their support. These are:

1. Critical information services involving a) data on sources of high purity materials and b) information on techniques for the preparation and characterization of high purity materials.
2. Routine production, characterization and distribution of materials of certified high purity.
3. Research and development leading to new or improved techniques for the purification, synthesis and characterization of very pure chemical compounds.

Recommendation (1) It is recommended that the NSF assure broad support for work in area 1 with the suggestion that the services rendered by the NBS and NIH in this area be covered by their own appropriations. It is further suggested that charges be made for publications covering this information service so that users of the service will pay a reasonable percentage of the cost.

Recommendation (2) In area 2 it is recommended that the fees charged for certified materials of high purity be set to cover the total cost of their preparation, characterization and distribution. It is further recommended that organizations supporting research in universities and other non-profit institutions pay for the cost of certified materials whenever these materials are required.

Recommendation (3) Where the requirements for research and development leading to new or improved materials of certified high purity can be identified with a direct and limited interest of a segment of industry or specific government organization this group recommends that the interested segment or agency finance the needed work.

Recommendation (4) Where the requirements have broad general applicability and at the same time fall within the statutory responsibilities of a particular government agency such as NBS and NIH, the group recommends that the appropriate agency seek support for such work in its own appropriation.

In addition, it is recommended that the NSF, the AEC and general research supporting agencies of the DOD recognize the area of research in purification, synthesis, analysis and characterization of chemical compounds by high purity as one warranting increased support.

Submitted by

A. V. Astin, Chairman
D. B. Brooks
F. H. Carman
A. G. Horney
W. R. Kirner
N. A. Shepard
A. R. Van Dyken

Z. Summary Statement and Recommendations of Group V on Appropriate Places to Perform the Work and the Organization to Manage the Operation

It is the consensus of this group that existing agencies such as the NBS should not only continue but greatly expand their present activities in the field of pure substances. Research on the preparation and characterization of pure compounds should be encouraged and greatly expanded in university, governmental and industrial laboratories. For maximum usefulness the work on pure substances should be coordinated. To accomplish these objectives, the following six recommendations are made:

Recommendation (1) The National Bureau of Standards undertake an expanded service in the certification and issue of substances of high purity or special characteristics.

Recommendation (2) The National Bureau of Standards endeavor to provide information concerning availabilities and sources of chemical compounds of high purity and materials of special characteristics, without underwriting responsibility for them.

Recommendation (3) The National Academy of Sciences -- National Research Council promote participation of university, industrial governmental and private laboratories in an expanded and coordinated program for the preparation of substances of high purity or special characterictics.

Recommendation (4) The National Academy of Sciences -- National Research Council encourage improved communication among laboratories concerned with the preparation of substances of high purity and special characteristics.

Recommendation (5) The National Academy of Sciences -- National Research Council encourage universities and colleges to recognize the needs for research and education directed toward increasing the availability of substances of high purity and special characteristics.

Recommendation (6) The National Bureau of Standards and the National Academy of Sciences -- National Research Council explore the possibility of utilizing qualified scientists and facilities in foreign countries for the preparation of substances of high purity and special characteristics.

Submitted by

F. Daniels, Chairman
J. R. Bowman
H. P. Klug
F. H. Spedding
E. Wichers
P. H. Egli

AA. Dr. Rossini: I am grateful to all those who have participated in the preparation, presentation, and discussion of the five reports we have heard. Is there any further discussion of the reports?

Dr. Astin: I appreciate very much the references to the National Bureau of Standards. We will make every effort to implement recommendations which are in our proper areas of interest. We could not become involved in the preparation of biochemicals that require biological methods for their characterization. Such work is clearly in the area of interest of the National Institutes of Health or the Public Health Service. The recommendation of Group V might be modified to include expansion of their services into the field of pure compounds of biological interest.

Dr. Daniels: Regarding the expansion of the services of the Bureau of Standards, it is implied that a larger congressional appropriation would be needed to implement an expansion of the Standard Sample program.

Dr. Astin: Our increased appropriation this year is in part for the single-crystal research that has been mentioned. Any new large program, of course, would require adequate support.

Dr. Kolthoff: No statement has been made regarding the reliability of certification. It has not been stated who would arbitrate questions regarding the correctness of any claims of purity.

Dr. Rossini: May I ask Dr. Wichers to comment on that question, please?

Dr. Wichers: The difficult problem of certification has to be approached on a cooperative basis and not simply by choosing some one agency to have authority in this field. Every test of purity applied should be subject to cooperative study. In general, an information service would indicate sources of supply, but not guarantee any claims for purity, at least not for the present.

Dr. Burwell: Would the Bureau of Standards in certain cases undertake the certification, by the cryoscopic method, of materials made elsewhere? If the Bureau were to certify the purity, a substantial amount of commercial material of possibly adequate purity would become available. This service would be similar to its certification of thermometers.

Dr. Rossini: Dr. Wichers, we should have an answer to that important question for our record.

Dr. Wichers: I would say that Dr. Burwell's suggestion does not come within the provision "that the Bureau may not only prepare but also procure materials which it subsequently issues after certification."

This suggestion touches on an area where very careful control is needed. When we certify samples we also like to issue them. There is a hazard involved in certification of a sample of material from a large batch of material which is then distributed by some other agency. If we procure a large commercial sample pure enough not to need further treatment, then we can make sure it is uniform, before determination of purity and certification.

Dr. Burwell: Dozens of companies are engaged in the sale of laboratory grades of organic compounds some of which are in the 99+ % purity range. If a reliable method can be found to certify these products for the companies, we would get a large number of compounds on the market more rapidly than if the Bureau had to procure each one individually. First, the company would probably know which compounds are pure enough to warrant this premium.

Dr. Spedding: If an individual wants to know whether his particular sample is good, why couldn't he send it to the NBS for certification as he does with a thermometer? It would be his responsibility to make a pure sample and the certification would cover only that sample.

Dr. Elderfield: I am afraid we are opening up a Pandora's Box. Not all companies are of equal reliability and the Bureau would be faced with an impossible task if it were to undertake certification of samples for individuals and any and all companies.

Dr. Brooks: Could the problem be handled similarly to the present certification of primary standards? The Bureau could make the test at the request of a group such as the American Society for Testing Materials.

Dr. Rossini: That is a possibility and will be included in the record. Are there any other comments or questions?

Dr. Astin: I would agree that this question cannot be settled here. We have been considering a different approach in other areas and have even made a start in applying this method. It is to make an intercomparison, either of instruments or materials, between our measurement techniques and those of an issuing company. We have done this with gauge blocks and are now planning to do it in cement testing. The company is at liberty to make use of these results in its sales program. One would have to depend on the integrity of the company when buying, but at least one would have confidence that the measuring technique of the issuing company was consistent with that used by NBS.

Dr. Rossini: Thank you. Are there any other comments or questions on this particular point?

Dr. Wichers: May I add a word to prevent the impression that the Bureau of Standards wants to have a monopoly on certification. Obviously, this is not consistent even with the API certification of hydrocarbons. As I indicated yesterday, the Bureau would like to see the API take over the whole responsibility in the hydrocarbons field. Similar cases might develop for certification in other areas.

Dr. Rossini: At this point I would like to ask if there are any statements on any of the points that we may have omitted or perhaps not stressed enough in our Conference, either this morning or yesterday.

Dr. Astin: I would like to see included the point that Dr. Spedding made: that research on methods of analysis and characterization should be strongly encouraged throughout the country.

Dr. Dittmer: Research on analytical methods is not very popular; research on the improvement of a method is even less so. If a group like this would endorse more research in the development and refinement of methods, as well as the discovery of completely new ones, research on analytical methods might gain recognition.

Dr. Rossini: Dr. Dittmer refers to the fact that all research proposals made to any agency are subject to the scrutiny of a panel of experts in, for example, the fields of physical or organic chemistry. Thus proposals for research in analysis must compete with those for research in more dramatic and popular areas.

Dr. Spedding: A spectacular new method, like gas chromatography, receives immediate attention. But a proposal to improve the determination of the amount of iron in chromium from a sensitivity of 100 ppm to 0.1 ppm receives no attention. However, it is extremely critical if one wants to produce chromium with one tenth of a ppm iron in it and has no method of analysis.

Dr. Kirner: The National Science Foundation has tried hard to increase support of analytical chemistry and has invited suggestions on how this can be done more effectively. Not many proposals are received but we are anxious to stimulate research in this area.

Dr. Van Dyken: This isn't a problem of just the supporting agency; it is a problem of the whole chemical community. Analytical chemistry is not receiving the recognition it deserves.

AB. Dr. Rossini: If there is no more discussion, we will now bring our meeting to a close. As I remarked earlier, the reports, and the recommendations of this Conference, will be put together in the report for the President of the National Academy of Sciences who will transmit a copy to the co-sponsor of the Conference, the National Science Foundation.

I hope very much that this Conference may be the forerunner of several following conferences that will deal with more specific phases of this problem which we think is so important to science and industry in the country.

As we conclude our Conference here, I can't help but feel that we have been engaged in an activity the principles of which President Abraham Lincoln must have had in mind when in 1863 he signed the bill creating the National Academy of Sciences and of which 55 years later President Woodrow Wilson must have thought when he created the National Research Council as an operating instrument of the National Academy of Sciences.

And finally, I want to express to each of you on behalf of President Bronk the sincere thanks of the National Academy of Sciences -- National Research Council for your contributions to this Conference.

Thank you very much. The meeting is adjourned.

CONCLUDING STATEMENT

There appears to be a general agreement on two points regarding the progress of science in the United States:

1. We must have a strong scientific program, with great breadth and depth, to probe the secrets of Nature and develop its treasures for the good of Mankind.

2. Our scientific program is so broad that government, universities, foundations, and industry must all participate in the support and encouragement of research, each playing its appropriate part.

The discussions and recommendations of this Conference show clearly how important it is to the broad support of pure and applied research to have available chemical compounds of certified high purity. Science and industry have much at stake in the development of a fruitful program in this area of science. The outpouring of constructive ideas by the Participants and Observers of the Conference underscores the urgency of the problem.

As may be seen from the recommendations of the several discussion groups of the Conference, to which the reader is referred for details, suggestions have been made along the following lines:

1. That some existing organization such as the National Academy of Sciences-National Research Council or the National Bureau of Standards, or both jointly, establish a permanent information center for compiling and disseminating complete and up-to-date information on existing sources of chemical compounds of certified purity.

2. That there be established, at an appropriate institution such as the National Bureau of Standards, a permanent central technical organization with responsibility for the identification, preparation (if needed), purification (as necessary), and certification of purity of chemical compounds of certified high purity, and with responsibility to provide for the general distribution of such compounds at appropriate cost.

3. That the program cover, in appropriate ways, the broad spectrum of chemical compounds required by the many branches of science and industry.

4. That the program take cognizance not only of the needs and resources of the United States but also those of our sister countries abroad.

5. That government, industry, and individual research investigators assume their appropriate responsibilities in support of the financial and scientific aspects of the problem.

6. That the National Academy of Sciences-National Research Council on a national and international basis, by collaboration with the Division of Analytical Chemistry of the American Chemical Society, appropriate divisions of other societies in the United States, the Section of Analytical Chemistry of the International Union of Pure and Applied Chemistry, etc., (a) implement improved communication and interchange of ideas and experience among laboratories concerned with the preparation, purification, and purity of chemical compounds, for example, by conferences and symposia, and (b) encourage research on the purification and purity of chemical compounds and on the analytical chemistry pertaining to this work.

It is hoped that the foregoing recommendations and suggestions can soon be appropriately implemented in a way that will provide a solid and sure footing in this area for the fruitful development of science and technology in the United States and our sister countries, with resulting broad benefits to research in universities, government organizations, and industrial laboratories.

Frederick D. Rossini
Chairman

APPENDIX

Alphabetical List of Participants

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