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CONTENTS

The Phi Chi Club presents this publication in the hope that the articles it contains will be of scientific interest to the students, faculty, alumni and friends of Providence College.

The articles contained in this issue have been condensed from physics theses and chemistry seminars presented during the past year. Future issues will also include reports of the undergraduate research program recently initiated. Papers for publication are earnestly solicited from Phi Chi Alumni and others interested in this project.

With the acquisition of publishing experience, the staff believes that the JOURNAL will improve both in content and form.

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PHI CHI ALUMNI

With this first issue of the Journal we begin a listing of our graduates in Chemistry and Physics which will be continued, as space permits, in future issues. The list is published to check our files - we take great pride in the accomplishments of our alumni - and for the benefit of classmates and friends who may have lost contact with each other.

Advanced degrees, home addresses, and present positions are given to the best of our knowledge, admitting that our information may be out of date. We shall sincerely appreciate the forwarding of the latest news by other alumni if we are in error, since very probably a copy of this Journal will not reach alumni who are incorrectly listed.

Any suggestions you may care to make as to content of the publication will be appreciated.

. . . .

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TECHNETIUM, THE FIRST SYNTHETIC ELEMENT[1]

Edward A. Healy, B. S. '53

The number of chemical elements now total ninety-eight. Their discovery began in prehistoric times and continues up to the present, sometimes by lucky accident, but more often as the result of long, tedious investigations. By 1937, of the ninety two elements comprising the classical periodic table, only the elements of atomic number 43, 61, 85, and 87 were unknown. These "missing" elements were the subject of extensive research.

Several rules governing the existence of isotopes and isobars had been postulated by Mattauch in the mid-1930's. One of these rules states that stable isotopes of elements of odd atomic numbers have odd mass numbers, e.g., stable isotopes of element number 43 would have the mass numbers 95, 97, or 99. Another rule states that stable isobars of neighboring elements do not exist. Since it was known that the elements of atomic numbers 42 (molybdenum) and 44 (ruthenium) included among their stable isotopes those of mass numbers 95, 97, and 99, it was concluded that any existing isobars of element 43 would be radioactive. Whatever quantities of these isotopes may have existed at one time on earth would most probably have decayed. Thus, attempts to discover element 43 and the other "missing" elements seemed limited to synthetic methods.

Element 43 was artificially produced in 1937 by two Italian scientists, C. Perrier and E. Segré, who later gave it the name technetium. These men found that when molybdenum was irradiated with 8 Mev deuterons, two of the induced radioactive products were chemically separable from all of the other known elements. These had half-lives of 62 days and 90 days. From the method of production, Perrier and Segré concluded that they were isotopes of element 43.

As a result of mass spectrograph measurements it was found that the radioactive material with the 90 day half-life had a mass number of 97 and the material with the 62 day half-life had a mass number of 95. Isotope 43^{97} decayed by isomeric transition to a very long-lived ground state, while isotope 43^{95} decayed by orbital electron capture. The latter decay process, also known as K-capture, consists in the nucleus absorbing a K-orbital electron which causes the neutralization of a nuclear positive charge. This effect transforms the nucleus into one of lower atomic number but does not change the mass number of the new nucleus. It might be noted that K-capture has the same effect as positron emission.

The decay schemes of the isotopes 43^{97} and 43^{95} are represented by the following equations:

(1) $43^{97}(90d) = 43^{97} + \gamma$

(2) $43^{95}(62d) + {}_{-1}e^{0} = 42Mo^{95}$
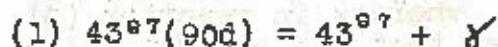
Before Perrier and Segré could study the chemical properties of technetium, they had to devise a method for separating the technetium from the molybdenum target. They succeeded in this by dissolving the target in 8-hydroxy-quinoline.

Because they had only minute samples of the isotopes of element 43, Perrier and Segré encountered considerable difficulty in determining the properties of technetium. They accomplished the task of studying the chemistry of the element by the tracer carrier technic. The upper and lower homologues of technetium, manganese and rhenium were tried as possible carriers. It was found that rhenium is a better carrier of technetium than is manganese. Thus, it was concluded that technetium is closely related to its heavier homologue, rhenium. The following reactions, which have been carried out on the tracer scale, will serve to illustrate this fact.

$$(3) \quad 2Re^{+7}(Tc^{+7}) + 7H_2S =$$

$$Re_2(Tc_2)S_7 + 14H^+$$

$$(4) \quad Mn^{++}(Tc^{++}) + 2OH^- =$$

$$Mn(OH)_2 + (Tc)^{++}$$
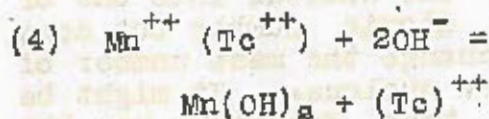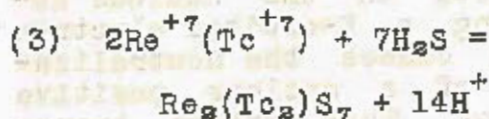
The symbol (Tc) is used in these equations to represent tracer amounts of technetium ions. Reaction (3) indicates that the rhenium sulfide successfully carries the technetium, whereas in reaction (4) we see that the $Mn(OH)_2$ fails to do so.

It has also been found that the $KReO_4$ (potassium perrhenate) and $CsReO_4$ (cesium perrhenate) have successfully

carried the Tc tracer but the MnO_2 has failed to do so. Nitron perrhenate has been established as a quantitative carrier of technetium.

Methods of separating the technetium from the rhenium carriers have also been developed. One of these methods involves a difference in solubility of the heptasulfides of rhenium and technetium Tc_2S_7 is soluble in HCl solutions of concentrations greater than 6 normal, while Re_2S_7 remains insoluble. Thus by dissolving the Tc_2S_7 in concentrated HCl, one can bring about an effective separation of the two substances. Two other methods of separation have been developed: the volatilization of the rhenium compound at 180°C. in the presence of HCl gas, and the fractional crystalization of the perrhenate carriers.

In 1938, another isotope of technetium was discovered by Segré and G. J. Seaborg of the University of California. This isotope, $_{43}Tc^{99}$, was produced by the deuteron and neutron bombardment of molybdenum in the cyclotron of E. O. Lawrence, and was observed to have a half life of 6.6 hours. Segré and Seaborg found that the new isotope also decayed by isomeric transition to a lower energy state with a half-life of more than 40 years.

$$(5) \quad 43(Tc)^{99}(6.6 \ hrs.) =$$

$$43 \ Tc^{99} + \gamma$$
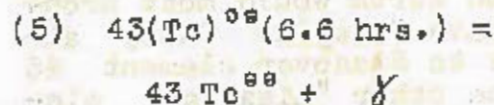
Since its discovery, both isomeric states of the Tc⁹⁹ isotope have been observed

PENICILLIN CHEMISTRY[1]

John L. Morico, A.B. '52

In 1929 Professor Fleming, working at Oxford, accidentally discovered penicillin. He happened to notice that on an agar plate on which he was cultivating staphylcocci there grew a green mold, and around this mold the staphylcocci colonies were dissolving. To this mold he gave the name Penicillium notatum.

The unique chemo-therapeutic properties of this mold were not discovered until 1940. The long interim between the discovery of the mold and its therapeutic properties can be traced to the instability of penicillin and the difficulty of producing it in abundance. Even that produced up until 1940, about two and one-half grams, was only 30-40% pure.

Many groups of English chemists, both academic and industrial, began to take part in the chemical investigations of penicillin. Professor Fleming and his associates came to the United States to formulate a program whereby the scientists of both countries might work together in investigating and producing penicillin which now was needed for casualties of war. This visit turned out favorably and work was begun immediately by American chemical firms. Large scale production was soon in progress.

It was found that there were a number of penicillins having similar properties but differing in composition. These possessed a common nucleus but differed in the nature of the side chain. As accepted today there are two possible basic structures:

$(CH_3)_2C$ — CHCOOH and $(CH_3)_2C$ — CHCOOH

(structures)
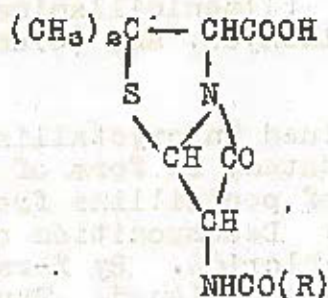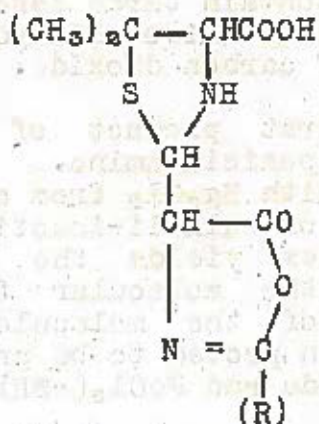
The penicillins are strong monoprotic acids without basic groups. The significant penicillin activity is in the $C_8H_{11}O_4SN_2$-portion of the molecule; thus all penicillins show the same qualitative action against microorganisms. However, quantitative differences in potency depend upon the nature of the radical. The nomenclature depends also upon these side chain formulae, e.g. -

(1) This article was edited from a seminar delivered May 13, 1953.

(Penicillin F)	Δ^2 Pentenyl Penicillin.......$CH_3CH_2CH=CHCH_2-$
(Favididin)	Δ^3 Pentenyl Penicillin......$CH_3CH=CHCH_2CH_2-$
(dihydro Pen. F)	n-Amyl Penicillin............$CH_3CH_2CH_2CH_2CH_2-$
(Penicillin K)	n-Heptyl Penicillin..........$CH_3(CH_2)_5CH_2-$
(Penicillin G)	Benzyl Penicillin............$C_6H_5CH_2-$
(Penicillin X)	p-Hydroxybenzyl Penicillin..$HOC_6H_5CH_2-$

Attempts to extract penicillin from the mold culture with water, acids, bases, and divers organic solvents showed that inactivation of various degrees occurred in most cases. It was shortly realized that the stability of penicillin in aqueous solution was a function of pH. The velocity of inactivation was inversely proportional to the hydrogen ion concentration at constant salt concentration and constant temperature. So by regulating pH, the yield of penicillin could be increased.

Various methods have been used to produce penicillin, and at the present time three methods are widely used. The first method is surface culture whereby the mold is grown on the surface. The second is by a submerged culture in which penicillin is developed within the medium itself. In this case it has been shown that amino acids increase the yield. The third utilizes sterile bran as the culture medium.

Penicillin is obtained in the form of a highly purified barium salt by repeated fractional extraction from amyl acetate into water. After this it is separated chromatographically on an alumina column. Even though many attempts have been made to synthesize penicillin on a commercial basis, all have failed.

In the determination of the structure, one of the first discoveries was that all the penicillins, upon degradation, were found to contain three essential components: (1)penicillamine, (2)an acylated amino aldehyde termed penilloaldehyde, and (3)one molecule of carbon dioxide.

The first product of degradation obtained in crystalline form was penicillamine. It can be precipitated, in form of a complex, with Hg_2Cl_2 from acid hydrolysates of penicillins from solutions of alkali-inactivated penicillins. Decomposition of this complex yields the crystalline hydrochloride. By X-ray analysis, the molecular formula $C_5H_{11}O_2NS$ was assigned. Thus this part of the molecule contained the sulfur which had previously been proved to be present by color reactions with sodium nitroprusside and $FeCl_3$(-SH) reactions.

The Van Slyke method for determining amino-nitrogen showed that the nitrogen was present in this form. The hydrochloride of penicillamine when dissolved in acetone and evaporated to dryness yields a crystalline derivative which contains neither the -SH nor -NH_2 groups, but still had the empirical formula, $C_8H_{15}ONS$. When this substance was heated with dilute acid, acetone was liberated and the original compound was regenerated. This suggested that the sulfur and nitrogen were on adjacent carbon atoms. There are two possible structures for this compound:

HIGH ENERGY PARTICLE ACCELERATORS

Robert M. McLaughlin B. S. '53

Why should science strive to produce higher and higher energies? The answer to this question lies in the desire to uncover the secrets of the microcosm. We cannot look at atoms with conventional optical instruments for the simple reason that the dimensions of atoms, and even large molecules, are many times smaller than the wave lengths of visible light. To "see" them we must resort to the use of high speed beams of particles which, according to the de Broglie principle, will have the desired wave properties. The higher the particle's momentum, (or energy) the shorter will be the wave length.

With the discovery and explanation of natural radioactivity around the beginning of this century, a source of high energy particles became available. With these and the previously discovered cathode rays, many of the secrets of molecular structures were disclosed. In 1919 Rutherford observed the first nuclear transformation, and others soon became interested in finding what existed within the atomic core.

Natural radioactivity gives particles of an energy range of about 4 to 10 mev. This energy produces wave lengths comparable to the diameter of the atomic nucleus. In order to examine the forces active within the nucleus itself, it was necessary to produce particles of higher energies. Even where natural energies were adequate, the supply of particles was meager and it was very difficult to obtain knowledge of their exact energy values. Better sources were needed.

The growth of nuclear research has closely paralleled the production of more and more energetic particle accelerators. Each jump in energy has given impetus to new explorations. Today we can reach over two billion electron volts. In order to explore atomic binding forces, the nature of mesons, the force fields of the elementary particles etc., still higher energies are needed. We know they are somehow attainable for they have been observed in cosmic radiation. Yet this is not a very practical source.

The first successful attempt at fashioning a machine which would give high energy particles of known value was made by Cockcroft and Walton in 1930. They developed a direct voltage source which consisted of an ingenious system for charging a number of condensers in parallel and discharging them in series, the switching being done by vacuum tube rectifiers. The high voltage thereby produced was then applied between the electrodes of an evacuated accelerating tube. The practical limit of such devices is a little over one million volts.

Of the other devices of this direct voltage type that were tried, the most successful was, and still is, the Van De Graaff generator developed in 1931 at M.I.T. It makes use of the principle which states that when a charge is brought into internal contact with a hollow conductor, it is completely transferred to it no matter how high the potential. If it were not for insulation difficulties no

limit would exist for the potential attainable. However the conductor cap must be supported somehow, and the insulating ability of the supports is a limiting factor. A charging belt receives a negative charge from a transformer-rectifier source by a corona discharge spray. The charge is carried up the high speed belt and is transferred through a similar arrangement to the spherical cap. This builds up the potential through the mechanical work done in carrying the charge to the cap against the electrostatic repulsion of the charges already there. More recently the whole unit has been reduced from its original tremendous size by placing it within a pressurized tank, thereby reducing losses through the breakdown of the surrounding air. A maximum of twelve mev. has been reached by this machine. The Van de Graaff generator can perform a greater variety of jobs than any other accelerator.

The simple methods used by the machines described above suffice to produce potentials up to several mev only. To go higher a new principle of operation was needed. In 1931 Lawrence and Sloan built a linear accelerator which used a moderate potential difference to give charged particles a series of successive kicks, thereby accelerating them. Ions are shot into a high vacuum down the axis of a long row of coaxial metal tubes. The tubes are connected alternately with one or the other terminal of a high frequency A.C. generator. When an ion arrives at the first gap between two tubes, the potential difference between them produces a maximum acceleration for the ion. A certain time is required to reach the second gap. Meanwhile the polarity is reversed and, with

the proper tube lengths, the ion will always reach a gap at optimum accelerating voltage. The tube lengths must increase along the ion path, and modern high energy machines of this type using microwave techniques are limited, by the impracticality of tremendous tube lengths, to several hundred mev's.

A more practical approach to the problem was the cyclotron of Lawrence and Livingston, developed in 1932. This apparatus gave the particles energy boosts while held in a curved path by a magnetic field. Despite the complexity of the actual machine, its operating principles are rather simple. The heart of the cyclotron is pair of hollow metal pillbox halves called "dees." They are supported in an evacuated metal envelope with their diametric edges parallel and slightly separated. These dees are connected to the terminals of an R.F. alternating voltage supply. Inside the shielding dees there is no electric field, but in the gap between them the field is directed first toward one and then the other. This whole unit is placed between the poles of a huge electromagnet whose uniform field is directed perpendicular to the plane of the dees. An ion emitted from the source into the gap is accelerated until it enters the electric field-free dee with a velocity v. Once within the dee the magnetic field will cause the charged particle to move in a circular path whose radius is directly proportional to the velocity of the particle.

Suppose that the alternating voltage is applied across the gap in such phase

AUTOMOTIVE ANTIFREEZES[1]

William E. Flynn '54

The combustion of the fuel used in automobile engines is accompanied by the generation of large amounts of heat, approximately 45 million calories per gallon. If this heat were not rapidly dissipated, few known materials could withstand it, and therefore a cooling system has been introduced into the engine. Such a system generally circulates a fluid which cools the engine and is itself cooled in the radiator.

Because of its low viscosity, high heat conductivity and low cost, water is commonly used as a coolant. However, its high freezing point is a severe disadvantage. Since no better low-cost coolant has been found, substances known as antifreezes are added to water to lower its freezing point and enable it to function as a coolant at low temperatures.

The perfect antifreeze, if it did exist, would be a truly remarkable substance. It would be a water-soluble compound of low molecular weight and as such would provide protection in all climates. It would be a chemically stable, non-corrosive, solid non-electrolyte which would not foam when agitated in the presence of small amounts of air, and hence would not cause damage to the cooling system nor cause excessive losses of coolant during operation. Solutions would have low viscosity and high specific heat and heat conductivity so that the operation of the coolant would not be impaired.

The suitability of an actual antifreeze is determined not only by the properties of its principal component but also by the properties imparted to it by the addition of certain modifying agents. The corrosive properties of antifreeze solutions, for example, are reduced by the addition of suitable inhibitors.

In the cooling system of most automobiles an ideal situation for electrochemical corrosion exists. Four or more metals, composed of at least five elements are in contact with each other and with a liquid coolant. According to Speller, appreciable corrosion takes place only if the polarizing film of hydrogen atoms produced by the reaction of the metal with the hydrogen ions of the solution is removed by some means. Large amounts of dissolved oxygen and entrapped air are present in almost every cooling system, due to minute air leaks and the agitation of the coolant in the air space at the top of the radiator. Under the neutral or slightly alkaline conditions normally found in antifreeze solutions, the atomic hydrogen is oxidized to water and corrosion proceeds at a rapid rate.

Chromates have been found useful as corrosion inhibitors. It is believed that a gelatinous complex hydrated oxide, containing both iron and trivalent chromium provides protection for the surfaces of certain metals. However, chromates do not effect-

[1] This article has been edited from a seminar given on March 12, 1953.

ively protect aluminum. Some substances that protect one or more metals may attack other metals found in the cooling system, therefore, it is often necessary to add "an inhibitor to inhibit an inhibitor." Complete information on anti-freeze inhibitors is not available because these inhibitors are the main points of commercial competition.

Most commercial anti-freezes are either alcohol or glycol solutions. The alcohols commonly used as bases for antifreezes are methyl, ethyl, and isopropyl, the higher alcohols being unsatisfactory due to their higher molecular weights.

The advantages of alcohols as antifreezes are their low molecular weights, complete solubility and reasonable price. In addition, they can be easily inhibited so that no corrosion to metals or damage to the radiator hose results from their use. Their main disadvantage is their high volatility and flamability. Methanol is the most satisfactory alcohol for use as an antifreeze, but it has the disadvantage of being highly toxic.

The two main glycols on the market as antifreezes are ethylene glycol and propylene glycol. The glycols are high-boiling or permanent anti-freezes. The principal reason for the extreme permanence of glycol antifreeze solutions is their low vapor pressure in dilute aqueous solutions. The high boiling point of the glycols causes the vapor pressure ratio to be low at $100-105°C$. The vapors from these solutions contain water with practically no glycol. As a result of this, the solution becomes more concentrated with respect to glycol and possess-

es a lower freezing point after extended heating. Addition of water practically restores the solution to its original strength. On the other hand, the vapors from the boiling solution of the lower alcohols contain large percentages of alcohol and as a result the concentration of the boiling solution with respect to alcohol quickly drops. This means that anti-freeze solutions of alcohol become weaker through use with a resulting rise in the freezing point.

The main disadvantage of glycols other than their higher cost is slight shrinkage of radiator hoses which causes serious damage if leakage into cylinder or crank case occurs.

Many other materials besides those already mentioned have been tried as anti-freezes. Honey and sugars were found unsatisfactory because of poor freezing point depressions, instability to heat, and the high viscosity of their solutions. Glycerine solutions were once very popular as coolants but they were found to be corrosive in actual service, incapable of being inhibited, and rather viscous. Inorganic salts have been tried as antifreezes but their corrosive properties cannot readily be inhibited.

Recently ternary systems have appeared on the market. Since methanol and ethylene glycol are two of the most widely used antifreezes it would seem that an antifreeze of superior qualities might be developed by combining the two. The use of methanol would lower the cost and the glycol would lower the volatility of the methanol. Both methanol and glycol produce only small increases in vis-

# KINETIC OF THE IODINE - IODATE EXCHANGE REACTIONS

A. W. Petrocelli '54

With the advent of radio-active tracer methods it has become relatively easy to study isotopic exchange reactions. Such reactions may be defined as processes in which isotopes of an element interchange between atoms of the element as they are found in various molecular states or ionic associations. e.g.

1) $RCl + \overset{*}{Cl}^- = R\overset{*}{Cl} + Cl^-$
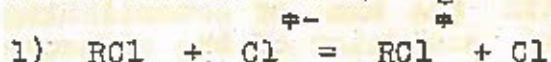
Three possible mechanisms for isotopic exchange have been proposed -- a dissociation mechanism, an electron transfer mechanism and an atom transfer mechanism.

The first of these, the dissociation mechanism, was offered by Cooley and Yost[1] as an explanation of the exchange between S_8 and S_2Cl_2. They postulated a reversible dissociation of one reactant to give a product which rapidly exchanges with the second reactant. Since reaction (2)

2) $\overset{*}{S_8} = S_6 + \overset{*}{S_2}$

3) $\overset{*}{S_6} + S_2Cl_2 = S_2\overset{*}{Cl_2} + S_6$
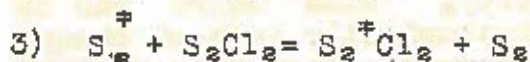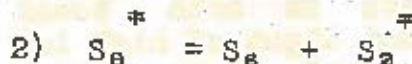
is the slow step, and thus the rate determining step, the rate of the reaction follows a first order rate law:

4) $r = k(S_8)$

The electron transfer mechanism is more involved. It assumes that the transition state which is formed decomposes, and one or more electrons are transferred from one reactant to another effecting the exchange. Evidence for this type of mechanism was offered by Dodson in his work on the ferrous-ferric exchange[2].

There are a number of factors which affect the rate of an exchange reaction involving electron transfer. The more important of these factors are the binding energy, the electrostatic charge on the species, and the similarity in structure of the reactants. One would expect a substance with low binding energy, low potential barrier and large angular momentum to have the electrons far removed from the nucleus and thus be prone to electron transfer.

The factor affecting the rate of electron transfer which affords the most interesting study is that concerned with the similarity in structure of the species. This involves the Frank-Condon principle, which assumes that electron transitions are very rapid compared to the motion of the nuclei. Therefore, it is more probable that a transition will result if no change in the position of the nuclei occurs. It is assumed that in an electron transition in a molecule, the nuclei do not appreciably alter their relative positions. Thus one might expect the probability of electron transfer to be small if the structures of the reacting species differ appreciably from one another. In the case of simple ions hydrated to different degrees, or of complex ions of the same composition but of different bond type, one would not expect electron transfer to occur.

Atom transfer is the most common type of exchange mechanism. It is believed that a transition state is formed, the decomposition of which

results in the transferring of one or more atoms from one species to another. The exchanges between the halide ion and organic halides as well as the exchange between the halide ion and molecular halogen are of the atom transfer type.

The use of radioactive isotopes facilitates the study of the kinetics of exchange reactions. The rate of reaction is calculated from the "half-time", the time necessary for one half the amount of radioactive material originally present as a reactant to appear as a product of the reaction. It has been shown that the appearance of the radioactive atoms in the initially untagged reactant follows a simple exponential law:

5) $r = k(A)^a(B)^b \cdots (J)^j$

where (A), (B)....(J) are the concentrations of the reacting species. This law is obeyed regardless of the mechanism of reaction by which the exchange occurs.

The value of $\underline{a}$ can be determined by holding (A)....(J) constant and plotting log (A) against log r. Once this procedure has been repeated with each reactant the order of the reaction (the number of atoms or molecules whose concentrations determine the rate of the reactions) will be known. Since the order of a reaction is determined by the slowest step in the mechanism of the reaction, it is possible to custom-build a mechanism which will fit the order obtained from experiment. The steps in this procedure will be clarified by the consideration of a special case, the iodine-iodate exchange reaction.

6) $I\,I^* + IO_3^- = I\,I + I^*O_3^-$
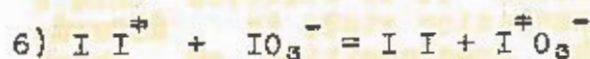
The earliest work on this reaction was performed by Hull Shiflett and Lind using mass isotopes. They found that a partial exchange was produced in 20 N H_2SO_4 but offered no possible mechanism for the reaction, merely suggesting that the exchange occured by way of an oxidation-reduction reaction.

In 1949, Meyers and Kennedy conducted experiments using radioactive iodine (I^{131}) with the aim of establishing the mechanism of the exchange by determining the dependence of the rate of exchange on the concentrations of iodine, iodate ion and hydrogen ion.

Meyers and Kennedy used high and low specific activities of radioactivity to verify the assumption that the exchange is not affected by radioactivity. They demonstrated, by varying the ratio of surface to volume that there was no heterogeneous exchange at glass surfaces for hydrogen ion concentrations as high as one normal. They also demonstrated, by obtaining duplicate results in both total darkness and light of high intensity, that there was no photochemically induced change. Furthermore, they proved that there was no net chemical reaction during exchange.

The expression of the mass action law with regard to the concentrations of iodine, iodate ion and hydrogen ion is:

7) $r = k(I_2)^m (IO_3^-)^n (H^+)^p$

By maintaining (IO_3^-) and (H^+) constant, the dependence of the rate of reaction on (I_2) was studied and the value of $\underline{m}$ was found to be 0.60 ± 0.04. Meyers and Kennedy proceeded to apply the

Technetium -
(Continued from page 4)

among the fission products of uranium, and the half-life of the more stable isomer has an accepted value of 9.4×10^5 years.

M. G. Inghram and co-workers have recently reported a mass spectrometric study of isotope Tc^{99}, using mercuric compounds as standards. Samples of NH_4TcO_4 were distilled into a Nier-type spectrometer and the resolved ion currents were recorded by means of a vibrating reed electrometer. The curve representing the resolved ion currents of Hg^{++} and Tc^{++} showed an increase at mass number 99 over the value obtained from Hg^{++} alone. This evidence confirmed the mass assignment of 99 given to the technetium isotope by Segré and Seaborg. The lower energy isomer of $43Tc^{99}$ has recently been found to exist in macroscopic amounts among the products of the slow neutron induced fission of uranium. It has been determined that a uranium pile operating at a power level of 10^6 kilowatts would produce four grams of Tc^{99} per day.

In 1948 S. Fried reported that he had successfully isolated pure technetium metal. One of the advantages derived from the macroscopic isolation of technetium was the fact that it enabled the physical properties of the element to be studied. Tc_2S_7, when precipitated from $4M$ H_2SO_4 is dark brown and very insoluble. The pertechnetate ion, TcO_4^-, as well as technetium oxide have been found to be pink, the latter being volatile at $200^\circ C$.

X-ray diffraction studies of technetium metal by R. Mooney have shown it to have close-packed hexagonal arrangement. The density of the metal, based on the Tc^{99} isotope, was found to be 11.49.

It is well to note that the results of macroscopic studies of technetium have not contradicted any of the earlier work of Perrier and Segré although they have furnished additional information regarding the element. These studies have definitely established the fact that technetium has multiple oxidation states. These include the +2, +4, +5, +6, +7, and probably the -1 states.
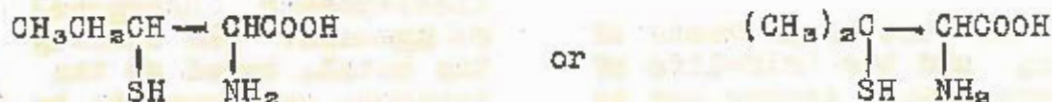
The discovery of technetium by synthetic methods opened a new field of investigation for research. Since 1938, nine other elements have been artificially produced. Included among these are the elements of atomic numbers 61 (promethium), 85 (astatine), and 87 (francium), as well as the six transuranium elements. There is good reason to believe that other elements will be discovered by artificial means in the near future. Glenn J. Seaborg of the University of California has recently predicted that elements of atomic numbers 99-103 and 105 will be of the rare-earth type and that number 104 will be similar in chemical properties to hafnium.

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Penicillin-

$$CH_3CH_2CH \longrightarrow CHCOOH \qquad \text{or} \qquad (CH_3)_2C \longrightarrow CHCOOH$$
$$\quad | \qquad | \qquad\qquad\qquad\qquad\qquad | \qquad |$$
$$\quad SH \quad NH_2 \qquad\qquad\qquad\qquad\qquad SH \quad NH_2$$

It was proven to be the latter through the synthesis of penicillamine by Abraham, Baker, Chain, Cornforth and Robinson.

The determination of the rest of the structure was more complicated, since the penicillins gave different penilloaldehydes. In England the first penilloaldehyde to be isolated was derived from Δ^2pentenyl penicillin. Elementary analysis and determination of molecular weight by crystallographic x-ray measurements indicated the molecular formula to be $C_8H_{13}O_2N$. By the Van Slyke method, nitrogen was found to be present as α-nitrogen. Meanwhile, American chemists had also been able to obtain a penilloaldehyde with a molecular formula $C_{10}H_{11}O_2N$. By oxidation with silver oxide the corresponding acid was obtained, $C_{10}H_{11}O_3N$. Assuming that this acid contained phenylacetic acid and a peptide linkage, it was deduced that its structure could only be phenylacetylglycine, and the penilloaldehyde would therefore be phenyl acetylaminoacetaldehyde. In a corresponding way the acid deriving from the British penilloaldehyde was found to be hexenoyl aminoacetaldehyde. Later the other penilloaldehydes were isolated from natural penicillins and their empirical formulas suggested the two structures now commonly used.

Despite the fact that a commercially practicable synthetic process has not yet been developed, the supply of penicillin has been adequate - more than enough to satisfy both the military and the civilian demand throughout the world. Now that World War II is over, we can look back objectively and thank God for penicillin, the saver of countless lives during the time of war, which now continues to benefit mankind in peace time.

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THIS HAPPENED AT YALE

Asked on an examination to discuss the sources of error, an undergraduate student in a course in volumetric analysis began: "The sources of error in volumetric analysis are of two kinds. Ones that can't be helped (accidental) and ones that can be helped (deliberate)."

High Energy Particle Accelerators
(Continued from page 8)

that it has reversed when the ion reenters it. It will then be accelerated in to the opposite dee, where it will travel at a higher velocity and therefore in a larger radius. If the voltage is kept in phase with the arrival of the spiraling ions, large energies are produced by a series of such kicks. It is found that the necessary phase reversal frequency is independent of the velocity and the energy of the particle and therefore is constant. This is the key to the successful operation of the cyclotron. A typical operating frequency is of the order of 10 megacycles.

The energy of a particle in a given orbit is dependent only on its mass. Alpha particles or deuterons are usually used. A cyclotron cannot be used to accelerate electrons or even protons to sizeable energies because of the relativistic increase in mass involved. This increase would cause them to fall out of step with the alternating voltage. The highest energy reached with the simple cyclotron to date is about 100 Mev.

Above this value even the heaviest particles show relativistic mass effects, and several attempts have been made to overcome this impasse. A non-uniform field has been tried along with higher dee voltages. The best solution, however, was reached by varying the frequency in proportion to the change in mass. This frequency modulation produced what is known as the synchro-cyclotron, a device which has reached ion energies of 400 mev.

The first accelerator which made possible high speed electrons, the betatron, was developed in 1941 by Kerst. A large variable electromagnet serves a double purpose. While holding electrons circulating in a uniform orbit in a doughnut shaped vacuum tube, it also induces an accelerating emf. by means of the change in flux through the doughnut tube. By maintaining the proper relationship between the magnitude of the field and its change rate, the increase in electronic mass is compensated for. The velocity acquired is so great than an electron may make 250,000 revolutions while the field is increasing from zero to its maximum value. During each revolution a potential acceleration, equivalent to that which would be produced by the same flux change in a one turn coil the same diameter as the orbit, is applied to the moving particles (about 400 volts). Since the total gain of the multiple revolutions is acquired by the electrons in less than one cycle of the varying magnetic field, no phase difficulties develop. Near the end of the cycle the magnet becomes saturated at its center, and the electrons spiral inward striking the target which is placed at the inner wall of the doughnut tube. Employing the betatron, a maximum of 250 mev has been reached for electrons.

The synchrotron combines the principles of both the cyclotron and the betatron. Stable orbits are produced by varying the magnetic field properly, while the accelerations are produced by alternating voltage pulses as employed in the synchro-cyclotron. Because the huge total flux requirements are no

longer necessary the whole mass of the magnet can be concentrated at the orbit. With a comparable total mass of magnetic material, much larger orbits, hence higher velocities, are possible. Examples of this type machine are the 2.3 bev. Cosmotron at Brookhaven National Laboratory and the Bevatron at the University of California which is expected to reach the 6 bev. level.

What of still higher energies? The problem would seem to be one of reducing still further the mass of magnetic material per unit length of orbit. We have mentioned the Cosmotron orbit as being constant. Actually, to allow for the straying produced by gas molecule collisions or fluctuations in voltage or frequency, the Cosmotron pipe is seven by thirty-six inches in cross section. Vertical

straying is reduced by the shape of the poles, but horizontal balance is delicate. A tentative design to control this undesirable characteristic consists of a series of C-shaped, strong-focusing magnets around the loop rather than one large single magnet. With such a set up, a much smaller channel and magnet could be employed. Also, a kick could be given to the particles at each of 300 gaps in the circle rather than just one. The Cosmotron's diameter is 75 feet, while the strong focus synchrotron would have a fantastic 2300 foot ring. Many problems such as uniform temperature controls, frequency synchronization, power economy etc. must be first solved, but the one hundred bev. energy level is already in sight.

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THE CHEMIST'S WIFE SPEAKS

My husband's lab work trains him right;
His housework's to my wishes.
From all the training at his job,
He's good at washing dishes

Sidney B. Orman.
C. and E. News

Antifreezes

cosity when added to water and hence permit nearly normal radiator circulation and heat transfer. Unfortunately, when these two compounds are combined, their disadvantages as well as advantages are also imparted to the resultant solution and the ternary systems tried do not appear superior to the better binary systems.

Methanol-water and ethylene glycol-water systems seem to be the best, although neither possesses all the properties of an "ideal antifreeze." In selecting between the two, one should take into consideration the conditions under which the automobile is to be used. For average passenger car service, it is possible to use either. For heavier duty, prolonged idling, or operation at high altitudes a high boiling antifreeze, ethylene glycol, is usually considered preferable. In a locality where high temperatures as well as low temperatures are to be expected the high boiling glycol is preferred. In older automobiles where there may be danger of leaks into the crankcase an alcohol is preferred. In older automobiles equipped with hot air heaters and where there are possibilities of leaks, methyl alcohol should be avoided.

An important source of guidance in the selection of the proper antifreeze is the "owner's manual" provided by automobile manufactures, for it takes into account the specific requirements of a particular cooling system. Complete information concerning the properties and use of vairous commercial antifreezes can be found in National Bureau of Standards Circular 506.

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IT MAKES SCENTS

Why reeks the goat
On yonder hill
Who seems to dote
On chlorophyll?

Richard Armour
C. and E. ,News

Kinetic of the Iodine

same method to determine the dependence of the reaction rate on the hydrogen ion concentration. The value of p was found to be 1.83 ± 0.05.

Meyers and Kennedy reasoned that the iodate ion dependence could be determined by obtaining the iodic acid (HIO_3) dependence using the same procedure and subtracting the known hydrogen ion dependence (1.83) from the iodic acid value obtained. It was found necessary, however, to take into account the mean activity coefficient and the degree of ionization of the iodic acid so that the quantity actually plotted against $\log r$ was $\log \gamma \propto (HIO_3)$. The value obtained for n was 1.80 ± 0.09 so that the expression of the rate law becomes:

8) $r = k(I_2)^{0.6}(IO_3^-)^{1.8}(H^+)^{1.8}$

In order to interpret this result, it was assumed that the exchange occurs by way of the iodide-iodate reaction.

9) $5I^- + I^*O_3^- + 6H^+ \rightleftharpoons II^* + 3H_2O$
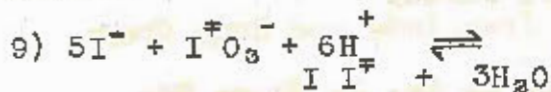
The equation for the equilibrium constant of this reaction was set up and solved for the iodine concentration.

10) $K_{eq.} = \dfrac{(I_2)^3}{(I^-)^5 \, (IO_3^-) \, (H^+)^6}$

11) $(I_2) = K(I^-)^{\frac{5}{3}}(IO_3^-)^{\frac{1}{3}} (H^+)^2$
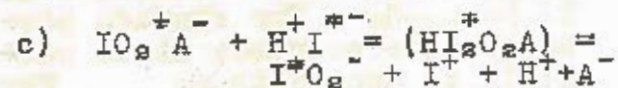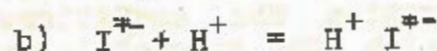
12) $(I_2)^{.6} = K(I^-)(IO_3^-)^{0.2}(H^+)^{1.2}$

By substituting equation (12) into that of the rate law (8), we obtain:

13) $r = k(I^-) \, (IO_3^-)^2 \, (H^+)^3$

This indicates a sixth order reaction with respect to I^-, IO_3^-, and H^+. It was found that if any negative ion (A^-) other than IO_3^- were present the iodate dependence was reduced and the rate of reaction was dependent on the concentration of A^- in such a manner that the following relation held:

14) $r = k(I^-)(IO_3^-)(A^-)(H^+)^3$

The overall reaction mechanism offered by Meyers and Kennedy to fit this result was

a) $IO_3^- + 2H^+ + A^- = IO_2^+A^- + H_2O$

b) $I^* + H^+ = H^+I^{*-}$

c) $IO_2^+A^- + H^+I^{*-} = (HI_2O_2A) = I^*O_2^- + I^+ + H^+ + A^-$

d) $IO_2^- + 4H^+ + 3I^- = 2I_2 + 2H_2O$

e) $I^+ + I^- = I_2$
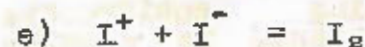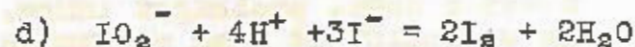
Meyers and Kennedy were able to postulate the formation of the IO_2^+ ion by comparing iodic acid to nitric acid which had been shown to form the NO_2^+ ion in the presence of strong acids.

Reactions a and b are rapid, reversible, equilibrium reactions. Equation c represents the rate determining step while equations d and e indicate rapid follow up reactions. It will be noted that the reactants of equations a and b are the substances represented in equation 9, while the products of these reactions are the reactants of equation c. Therefore, since equation c regulates the overall exchange, the suggested mechanism is in agreement with the experimentally determined, rate expression (14).

It may be observed that equation c represents the transfer of two electrons from the I^- ion to the IO_3^+ ion. This transfer occurs while both of these ions are in the form of ion-pairs.

The work of Meyers and Kennedy does not end the need for study of the iodine-iodate exchange reaction for there are many challenging questions yet to be answered.

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The chemist is a risky man
Explosions are within his span

Of many odors does he reek
The strangest language does he speak

Test tubes, beakers, flasks, and funnels
Liquids flowing through tubes and tunnels

Potions boiling on the bench
Christopher Columbus! What a stench

A flask emitting clouds of smoke
Yet there he stands and does not choke

His B.S., M.S., and Ph.D.
Are proof of his insanity

Yet show no scorn whatever you do
'Cause he can make an ash of you

And if you should a chemist bo
Dear sir, you have my sympathy

                    Richard Beaudet '53

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