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THE BELL SYSTEM TECHNICAL JOURNAL

A JOURNAL DEVOTED TO THE
SCIENTIFIC AND ENGINEERING
ASPECTS OF ELECTRICAL
COMMUNICATION

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No. 1

The Future of Transoceanic Telephony*

By OLIVER E. BUCKLEY

President, Bell Telephone Laboratories

WHEN Sir William Thomson saw the newly invented telephone of Alexander Graham Bell at the Philadelphia Centennial Exposition in 1876, he stated that "it was the greatest marvel hitherto achieved by the telegraph." Recognizing that the limitations of the first crude instruments would soon be removed, he remarked that "the invention is yet in its infancy and is susceptible of great improvements," and also said "with somewhat more advanced plans and more powerful apparatus, we may confidently expect that Mr. Bell will give us the means of making voice and spoken words audible through the electric wire to an ear hundreds of miles distant." Lord Kelvin lived to see these prophecies rapidly proved true. Had he lived only a few years longer, he would have seen the quality of transmitted speech brought close to perfection, and he would have seen the hundreds of miles extended to thousands.

That Lord Kelvin should have looked upon the telephone as an improvement on the telegraph was natural, for that is the way in which Bell approached it. Bell was experimenting with his harmonic telegraph when he invented the telephone. He was extending the possibilities of the telegraph by making use of a wider band of frequencies than were employed in the systems of Wheatstone and Morse. With its sufficient range of frequencies, Bell's system proved capable of transmitting speech as well as simple signals. Thus, telephony was born from telegraphy by an expansion of the band of frequencies employed in the electrical transmission of intelligence.

More recently, further expansion of the frequency band has been associated both with improvement of quality of transmitted speech and with multiplication of the number of conversations which can be simultaneously transmitted. So far have these developments progressed that today we can transmit speech overland as perfectly as we may desire for any distance we may choose, and we may do so with hundreds of conversations at once over a single coaxial line.

In fact, we have gone further and have so broadened the frequency band

* Thirty-third Kelvin Lecture. Read on April 23, 1942 for Dr. Buckley by Vice President Sir A. Stanley Angwin before the Institution of Electrical Engineers.

that vision as well as speech may be carried long distances overland. It does not require a bold stretch of the imagination to predict that some day we shall have multiple-channel transmission of television as today we have multiple-channel transmission of speech. Conductors consisting of hollow pipes offer promise of such application.

Indeed, frequency band width has become almost a commodity to the communication engineer. Telegraphy takes a certain band width as measured in cycles per second for a particular speed of signaling as measured in words per minute. We may assign about 100 cycles to a printing telegraph machine that prints 60 words per minute. To get intelligible telephone communication requires about 1000 cycles, though Bell's original instrument probably used effectively somewhat less than that, which accounts for Kelvin's difficulty in understanding certain words over it. Commercial telephony has benefited from a gradually widened frequency band, until now we look on 3000 cycles as a reasonable engineering standard. This does not provide, however, for perfect transmission of speech. The frequencies in speech commonly cover about 8000 cycles, though frequencies above 4000 contribute little to either intelligibility or quality. Music requires more band width than speech. The range of the normal human ear is about 15,000 cycles, and perfect transmission of music requires that band width. In practice, however, one loses little of esthetic value if the music is limited to 8000 cycles. In fact, most listeners cannot readily distinguish music transmitted over an 8000-cycle band from that over a 15,000-cycle band. Television requires from 20,000 cycles for a recognizable human face, to 20,000,000 or more for vision as well defined as in standard cinema practice, but in present commercial practice the band width is limited to about 3,000,000 cycles.

With a transmission line of given band width, we can allocate its available frequency range to telegraphy, telephony or television as we will. Twenty printing telegraph channels with adequate separation cost in frequencies about as much as one ordinary telephone channel, but for a television channel we must pay the price, in frequencies, of 1000 telephone or 20,000 printing telegraph channels.

It is of the extension of the range of frequencies and their availability for transoceanic communication and particularly transatlantic telephony that I wish to speak. We shall first review what have been the consequences of the extension of frequencies and then explore some of the future possibilities of further expansion of band width in transoceanic communication. Both radio and wire systems must be included to make the picture complete.

The first messages to cross the transatlantic cable were sent at the rate of two words per minute. In frequencies, this means a band width of less

than one cycle per second. Lord Kelvin with his mirror galvanometer and later with his siphon recorder and other improvements increased the effective band width and raised the speed to three words per minute. He showed also how to design cables to raise the frequency limits further, with the result that ocean cables were soon made to work at much higher speeds.

Other important advances in terminal apparatus and in methods of operation followed. The application of the duplex principle, permitting simultaneous operation of the cable in the two directions, practically doubled its traffic capacity. Improvements in methods of correcting the signals for the distortion introduced by the cable, and the introduction of mechanical means of sending resulted in a further increase of a third in traffic capacity. Another increase of about the same amount was realized when the cable magnifier was introduced in the early part of the present century.

A major advance ensued with the introduction of the permalloy loaded cable in 1924. The advantages of inductive loading for reducing the attenuation in long circuits had been known for some time and some applications of the Krarup or continuous method of loading had been made to short submarine telephone cables. No practical means, however, of applying this principle to ocean cables was available, since for telegraph frequencies loading with iron wire was not advantageous because of its low permeability. The discovery of permalloy, a material with very high permeability at low flux densities, together with the invention of means for protecting the loading material from the severe stresses that it would otherwise encounter at the ocean bottom, made it possible to build a cable with many times the band width of corresponding non-loaded cables. The increase in traffic over the cable was, however, less than proportional to the increase in frequency range, because duplexing the loaded cable involves a greater sacrifice of one-way speed than is the case for the non-loaded cable. The fastest loaded transatlantic cable has an effective frequency band of over 100 cycles per second and can carry four times as much traffic as a non-loaded cable of the same size and length.

Development of permalloy loading for telegraph cables naturally led to consideration of the possibilities of a loaded telephone cable to span the Atlantic. Whether viewed as an extension of frequency from 100 cycles to the 3000 cycles needed for high grade telephony, or as an extension of distance, the step was a formidable one. The longest deep-sea telephone cable reached only 105 nautical miles from Key West to Havana, where three cables continuously loaded with iron wire were laid in 1921. The transatlantic span called for a minimum of 1350 miles via the Azores, or 1800 miles by the more direct route from Newfoundland to Ireland. It

was obvious that such a step could not be accomplished by mere structural changes. New materials were required. For years, a systematic search had been made to improve the properties of electric and dielectric materials for use in submarine cables. By 1928 sufficient progress had been made in the development of materials and in the structure of the cable itself to permit seriously undertaking a transatlantic telephone cable. A decision was then made to embark on a test of a section of such a cable under practical conditions.

In determining the requirements for this cable, it was decided to engineer it for the Newfoundland-Ireland route rather than for the route via the Azores. The longer link made the cable more difficult and its cost per mile higher, but the total cost and considerations of operation and maintenance favored the more direct route.

The structure proposed for the Newfoundland-Ireland telephone cable was of the single-core type with a continuously loaded central conductor and a concentric return conductor similar to that of the Key West-Havana cables, but different in materials and dimensions. Instead of a serving of iron wire or permalloy to provide inductance, there were used four layers of very thin perminvar tape. Perminvar is an alloy which, in the form of loading tape, has a permeability and resistivity suitable for telephone use and at the same time has very low hysteresis, which helps in preventing distortion of speech due to magnetic modulation. The loaded conductor was insulated with paragutta rather than with gutta percha. Paragutta is a mixture of specially purified and deproteinized rubber, desinated balata or gutta percha, and some wax. It has a dielectric constant 15 per cent lower than the gutta percha in the Key West-Havana cables, and leakage at telephone frequencies about one-fifteenth as great.

The cable was designed on the basis of as high attenuation as would be permitted by considerations of noise at the receiving end and usable power at the sending end. Since the attenuation of such a cable increases rapidly with frequency, only the noise at the high-frequency end of the speech band is significant; here the noise is entirely of thermal origin, for static and other external interference are eliminated by shielding. The sending power is limited by magnetic hysteresis and there is little advantage in applying more than about 50 volts. Most of the power can be concentrated in the high frequencies by placing, at the sending end, part of the network which corrects the distortion of the cable. By these means, it is possible to set a permissible overall attenuation as high as 165 db for a top frequency of 3,000 cycles. This far exceeds attenuation permissible in other wire telephone practice. The cable was designed to give this attenuation with the most economical disposition of materials within practical limits. Its core comprised a loaded central conductor of 800 pounds of copper and 95 pounds of perminvar per nautical mile, 720 pounds of paragutta insula-

tion, and a concentric copper return conductor of 1700 pounds, making the cable much heavier than any that had previously been laid in great depths.

A 20-mile section of this cable was made in 1930 under the supervision of Bell Telephone Laboratories engineers by the Norddeutsche Seekabelwerke in Nordenham, Germany. There it was loaded aboard the cable ship *Norderney* and taken to a location in the Bay of Biscay where a depth of 2,500 fathoms was conveniently available. This depth was greater than would be encountered on the proposed cable route. The 20-mile section was paid out on the sea floor and its open-end impedance measured over the telephone range of frequencies. From these measurements, changes in its electrical parameters could readily be deduced. The cable was then pulled in and carried to Frenchport Harbor near Belmullet, County Mayo, Ireland, whence it was laid out to sea to permit measurement of terminal noise. Measurements of impedance both from the ship and from the shore showed the cable to be quite unimpaired both at $2\frac{1}{2}$ miles depth and after recovery and relaying in shallow water. Measurements of noise from shore, however, showed that the location was unsuitable for this type of cable because of the rocky bottom. Such a cable is somewhat microphonic on account of the strain sensitivity of permivar and the terminal sections of the cable must lie quietly on a soft bottom if a low terminal noise level is to be assured.

Simultaneously with the experiments on the cable, experiments were conducted with the terminal apparatus in the laboratory in New York. An artificial line had been built closely simulating the proposed cable in electrical performance, and over this speech was transmitted at the levels intended for the cable. The method of operation was extreme as well as novel. The high attenuation made it impossible to balance the simulated cable for two-way talking, and voice switching had to be used. At both ends the receiving apparatus was normally connected to the line. The speaker's voice currents caused his end of the line to be switched to the transmitting apparatus. Arrangements were devised to avoid loss of speech during the switching interval, and to minimize interference due to the persons at the two ends of the cable speaking almost simultaneously. The time required for speech to travel over such a cable is not negligible. In this case it was about a tenth of a second. This is long enough to be noticed but not serious enough to count as a major disadvantage.

All of the measurements in the laboratory, at sea, and from shore joined in giving assurance of the technical soundness of the proposal to install a cable of this type. Its performance would have been superior to that afforded by radio. The cost, however, would have been much greater than that for a radio circuit. The cable system from Nova Scotia via Newfoundland and Ireland to Great Britain promised to cost about \$15,000,000. When the project was first considered, the radio connection had been

subject to frequent interruption and the cable was regarded as an economically justified supplement to the radio services as they then were.

Postponed temporarily because of general business depression, the cable project was later postponed indefinitely because, in the face of improvements in transatlantic radio communication, so expensive a cable to carry a single conversation could no longer be justified. Today it seems improbable that such a cable will ever be laid across the Atlantic. Fortunately, other cable possibilities have in the meantime been developed which look more attractive. Before going into these, however, let us review the development of transatlantic radio telephony and estimate some of its future possibilities.

The development of radio communication, even more strikingly than that of wire communication, has been characterized by widening of its spectrum. In fact, starting with Marconi's low-frequency transatlantic experiments of 1901, the spectrum has widened until today it provides some thousands of megacycles. Only a small portion of this range is, however, available for transoceanic communication. There are utilized only two isolated ranges each of which, by comparison with the total radio band, is comparatively narrow. The low-frequency or long-wave range is a band some tens of kilocycles wide with a top of about 100 kilocycles. This low-frequency portion of the spectrum was intensely cultivated during the first two decades of the present century and by the close of that period had become rather densely populated with radio transmissions.

In the 1920's the band of frequencies useful for long distances was widened several hundredfold by the discovery that long-distance transmission could be carried on by short waves, that is, by frequencies in the range 3 to 30 megacycles. This discovery put transoceanic radio communication on its present world-wide basis. Short waves not only contributed greatly to the communication band width but contributed as well as to the demand for service by reducing costs, since the apparatus required for short-wave circuits proved to be less expensive than that for long waves.

The transatlantic telephone like its telegraph predecessor started in the relatively cramped long-wave band and then moved into the freer region of the short-wave range. It was in 1915, 14 years after Marconi had spanned the Atlantic by radio telegraph, that speech was first sent across the oceans from Arlington, Virginia to Paris and to Honolulu. This achievement, somewhat beclouded by the events of the first World War, was the result of a plan to talk across the ocean which was definitely undertaken by Bell System engineers after they had successfully established wire telephone communication across the North American continent. For its accomplishment there were evolved the first high-power vacuum tubes and the first master-oscillator, power-amplifier tube transmitter. This experiment was

thus, in a technical sense, the forerunner of modern radio telephony, including broadcasting as well as transoceanic telephony.

It required much study of radio transmission and many further improvements in apparatus technique before speech could be projected across the Atlantic with sufficient clarity and reliability to be truly serviceable. In the long-wave range and for transatlantic distances, radio is seriously limited in two respects: first, the level of noise is high, particularly in summer, due to the frequency of occurrence of thunderstorms in northern latitudes; and second, the received signals become weak during the sunset and sunrise periods. The ionized layers of the upper atmosphere upon which long waves depend for their guidance around the earth are then going through the transition from daylight to nighttime condition. The development of the water-cooled high-power vacuum tube made possible high-power amplifiers to deliver tens of kilowatts needed to lift the signal higher above the level of atmospheric noise. The influence of static was further reduced by the use of directive receiving antennas. Additional improvement was provided by the technique of single-sideband transmission first used on wires. These developments and others assured fairly reliable telephone connections and in 1927 public service was opened jointly by the General Post Office and the American Telephone and Telegraph Company. The carrier frequency was 60 kc corresponding to a wave-length of 5000 meters.

The opening of the first transatlantic short-wave telephone circuit in 1928 followed close on the heels of the long-wave circuit, and was followed in turn by the establishment of additional short-wave circuits in 1929. These were years of increasing disturbance in short-wave transmission and about 1929 preparations were started on both sides of the Atlantic for a second long-wave channel to diversify facilities and thus improve the continuity of the service. This work had not progressed very far, however, before there came in sight opportunities for greatly improving short-wave transmission. Accordingly, the project of the second long-wave circuit was deferred and, upon the actual realization of the short-wave improvements years later, was postponed indefinitely. More recently, experiments have been conducted which have demonstrated the feasibility of transmitting two channels at different frequencies using the same transmitting equipment. This may lead ultimately to more economical provision of an additional long-wave circuit.

Short-wave radio has certain outstanding advantages over long waves for transoceanic service; these are less attenuation, lower noise and a wider frequency band in which to operate. The first two factors together with the ability to obtain readily a high degree of antenna directivity, result in considerable economies. In the case of a radio telephone connection between the United States and England, the cost of short waves under

present practice for an approximately comparable quality of service is about one-half that of long waves. The wider band provides an opportunity for the service to expand, for although the short-wave band is by no means unlimited in extent and within the last few years has become increasingly congested, much can be accomplished by careful and coordinated planning for use, and in any case it is hundreds of times wider than the long-wave band. These advantages have been reflected in the rapid growth of short-wave transoceanic telephony, as indicated by the fact that by the beginning of 1939 there were in service throughout the world about 170 important long-distance short-wave telephone circuits, of which five were in regular use between the United States and Europe. There has grown up also a host of short-wave broadcasting channels, the better coordination of which has yet to be worked out.

Certain disadvantages of short-wave transmission must nevertheless be reckoned with. The greatest by far is its susceptibility to complete or partial interruption at certain times, particularly around the maxima of the 11-year sunspot cycle. This weakness of short-wave transmission is fresh in the minds of many of us because we are only now emerging from one of these maxima. Short waves are also affected adversely by various types of signal distortion which arise from the circumstance that the signal picked up at a receiving site is usually made up of several components which have traveled over different paths. Sometimes these paths all lie along the same great circle but involve different numbers of reflections between the earth and the Heaviside layer. Sometimes signal components arrive over other than the great-circle path. Occasionally components travel along the longer of the two great-circle paths between the transmitter and receiver or even clear around the world, producing a distinctive phenomenon known as "round-the-world-echo." Interference between waves arriving over different paths results at times in "general fading" caused by variations in the level of the whole band and at other times in "selective fading" in which portions of the speech band are affected differently.

These phenomena and their causes have been widely and intensively studied ever since the advent of short waves and as a result much progress has been made in improving short-wave telephone transmission. Single-sideband transmission has been helpful in eliminating a particularly disagreeable type of mutilation common to double-sideband transmission wherein the fading out from time to time of the carrier signal gives rise to a harsh, grating character of received speech. The multiple-unit steerable antenna recently developed in Bell Telephone Laboratories, and known familiarly as "musa," has been found useful in reducing speech distortion accompanying wave-interference effects. The musa reduces selective fading by combining signals arriving over different paths or by eliminating all

signals except those arriving over one path. By providing additional antenna directivity it makes possible operation in periods of reduced signal strength, though it does not eliminate circuit interruptions at times of very severe disturbance. Single-sideband transmission and the *musa* are now in regular use on the New York-London telephone circuits.

The combination of modern short and long-wave technique now provides across the Atlantic a telephone service which is acceptable for general commercial use, though admittedly of somewhat variable quality. Complete interruption of short-wave service with inadequate long-wave service to fall back on, remains the most serious limitation. Neither the reliability nor the quality of transatlantic telephony is yet up to the standards of a well-constructed and well-maintained wire line.

As matters stand today the short-wave bands, carefully used, could be made to handle a very substantially increased load. The long-wave band is much more restricted yet it is on the long waves that we now depend when short waves fail, as they do at times. Marked improvement in reliability of present systems, or some altogether new and independent system, is needed to provide an alternative group of circuits to insure availability of service as users come to rely on it in their business and social intercourse. This is one of the important factors that led to the development of the transatlantic telephone cable.

To predict the future development of transoceanic telephony is presumptuous, to say the least. So rapid has been the advance in the art of communication and so revolutionary have been the discoveries in this field that one is quite unwarranted in setting any limits to the progress that may be achieved. However, there are some developments that have progressed far enough in the laboratory to discuss with reference to their early application; also there are pertinent indications as to the future of transoceanic telephony apparent from consideration of developments which have occurred in long-distance overland telephony.

Perhaps the most significant recent development in land-line telephony is that of broad-band transmission over open wires, cables and coaxial conductors. Broad-band transmission means the transmission by carrier methods of a considerable group of telephone bands on closely spaced channels. Over open-wire lines and over pairs in lead-covered cables, 12 telephone bands spaced at 4000-cycle intervals are commonly transmitted in a group occupying a total band width of 48,000 cycles. With coaxial conductors, the band has been increased to 2,000,000 cycles giving frequency space for some 500 telephone channels and it may be expanded still further when more channels are required.

The application of broad-band methods to transoceanic radio telephony may be anticipated with some confidence. To achieve it requires broad-

band amplifying systems capable of delivering high power without distortion. Commercial success has already been achieved with small numbers of channels in the Holland-East Indies and the United States-England single-sideband systems. More recently, by applying the principles of negative feedback, Bell Laboratories engineers have developed a short-wave transmitting amplifier of 200 kw capable of handling 12 or more closely spaced telephone channels.

One might visualize the broad-band transatlantic radio telephone system of the future as being built up of successive groups of these 12-channel blocks. The number of groups that might be used simultaneously is, of course, limited. Over any path where radio transmission depends upon reflections between the ionosphere and the earth, Nature sets a rather definite limit on the range of frequencies that is usable at any given time. In effect, there is provided a transmission path between transmitter and receiver which is capable of passing a broad but nevertheless limited band of frequencies. Frequencies above this band are not consistently returned to earth from the ionized regions. Frequencies below this range are absorbed. The high-frequency end is marked by a sharp cutoff, while there is a more gradual diminution of effectiveness at the low-frequency end. The position in the spectrum of the useful band shifts with time of day, season of the year and phase of the solar cycle. Its width varies, too, being narrow at night and wider during the day.

Thus, for example, when the sun is over the mid-Atlantic in summer there is available a useful band of frequencies about 4 megacycles wide, extending from about 14 to 18 megacycles. It is not sharply defined on its lower side, and its position in the spectrum varies with the season of the year and the sunspot cycle. But we may say roughly that nature provides at any one time, at least during the most useful hours of the day, a band width of the order of 4 megacycles. If this entire range could be utilized for telephony over this particular path, and were subdivided sharply into telephone bands of 4 kilocycles width, there could be realized 1,000 telephone channels. These might be used in any of the several ways, as to two-way transmission and as to the points at which they terminate.

But public service transatlantic telephony is not the only service requiring these important short waves. There are many other uses of them such as radio telegraphy, ship-to-shore telephony, airplane communication and navigation, and overseas broadcasting. There are also other natural barriers than the Atlantic to be bridged in this manner, and these short waves because of their world-wide effect and despite the directivity that can be imparted to them, cannot be counted upon to be duplicated very often for simultaneous use at different locations throughout the world. So we must allow for the available 4 megacycles to be divided to meet a large

number of requirements, perhaps none more important than the Atlantic route, yet collectively of great consequence. Let us say that, in view of all the other requirements, public service telephony across the Atlantic deserves something like a tenth of the total facilities in this band. This would mean an allotment of 400 kilocycles or 100 one-way telephone channels, yielding 50 or more two-way circuits realizable under the natural limitations of the medium and the other requirements placed upon it.

Of course, the demand for such a number of transatlantic telephone circuits will depend in large measure upon the economy with which they can be realized, but the estimate serves at least the purpose of pointing out that short waves can provide physical facilities for a volume of telephone communication far beyond that now obtaining. Surely we can anticipate with confidence a great growth of transatlantic telephone traffic, but in proportion as the demands for service grow and we come closer to the realization of the ultimate physical possibilities, the more serious becomes the threat of interruption to this service by magnetic storms.

These conclusions lead us to reconsideration of the transatlantic telephone cable as an auxiliary to short-wave systems. It is readily apparent now, however, that a single-channel cable such as we projected in 1929 would be of little value in supplementing a radio telephone service of so many channels as there may be in the future. To be of any real value in this situation, the cable also must be capable of carrying a considerable group of telephone channels. It was toward such a possibility that we turned when the project of a single-channel cable was suspended. We have made considerable progress in that direction, and I would like to tell you about it, if you will excuse my presenting a proposal which has still many elements of speculation in it.

It was obvious at the start that a multi-channel telephone cable to cross the ocean would have to be provided with intermediate repeaters since even a single-channel cable without repeaters required going to practical extremes in structural design. Consideration of mechanical difficulties ruled out locating the repeaters elsewhere than on the ocean bottom. Problems of laying and lifting made it obvious that the repeater housing should, if possible, be incorporated within the cable structure and treated as a part of the cable rather than as an appendage to it. Hence we were led to develop a small-diameter cylindrical housing to be incorporated as a part of the cable underneath its armor. The whole structure had to be flexible so that it could be bent around a cable drum and passed over the bow or stern sheave of a cable ship.

The structure of the repeater housing which was devised comprises first a succession of pressure-resisting steel rings each having a diameter of about $1\frac{1}{2}$ inches and a width of $\frac{3}{4}$ inch. Over these is slid a succession of thinner

steel rings of the same width but so placed as to overlap the joints of the inner rings. So assembled, the rings form an articulated cylinder about seven feet long. To exclude water, there is placed over this cylinder an annealed copper tube with water-tight seals at its ends. The details of the seal are of the greatest importance. It combines a strictly hermetic seal, in which the conductors are brought out through glass, with a plastic seal through which diffusion of water vapor would be extremely slow, should the glass seal fail. Joined to the copper cylinder, and extending over the cable core for several feet, is a tapered copper sheath which serves to distribute bending strain and protect the conductor joint at the seal. Containers of the type described have been tested at pressures considerably higher than would be encountered in a transatlantic cable. They have also been subjected to repeated bending around a six-foot drum without failure.

Within the repeater housing the elements of the repeater are separately contained in plastic cylinders about six inches long, loosely fitting inside the inner steel rings. Connections between these units are made with flexible conductors.

A repeater must, of course, be supplied with power and, as it is impracticable to provide a primary source of power in such a small housing, power must be fed to the repeater over the cable from a direct-current supply. The supply voltage is one of the limiting considerations in the design of such a cable system. It must not be so high as to endanger the insulation of the cable or repeater elements. An operating potential-to-ground of 2000 volts oppositely poled at the ends of the cable was assumed. Power would be supplied on a constant current basis so that fluctuations of earth-potential would not cause variations of current-supply. The repeater elements were designed to withstand the anticipated voltage-to-earth. Tests of cable-core and joints over a long period of time have shown no observable change under this impressed voltage.

The difficulties of lifting a deep-sea cable for repairs are such as practically to prohibit frequent access to the repeaters for maintenance. Hence, the repeater must be provided with elements which will rarely, if ever, require attention. A period of 20 years without replacement of parts was assumed as a reasonable requirement.

The problem of life and maintenance is principally the problem of a rugged long-lived vacuum tube. Ordinary vacuum tubes have limited service-life on account of evaporation of material from thermionic cathodes. By making the level of transmitted signals relatively low, the space current may be kept very small. By making the cathode surface relatively large, this small current can be obtained at a temperature so low that the cathodes of the tubes may be expected to last for a very long time. This is a different approach to the tube problem than has ordinarily been made. New

types of tubes based on these principles were developed and put on life tests more than five years ago. As yet they have shown no evidence of deterioration, and one now may be reasonably sure from their behavior and from physical considerations of a life of at least ten years. There is good reason to think that they should last several times that long, but further observation will be required before a life of as much as 20 years steady operation can be confidently predicted. The tubes must also be more rugged than ordinary vacuum tubes since the cable will be subjected to considerable vibration and perhaps to heavy blows in the course of laying and lifting, though the tubes can be protected to some degree by resilient mountings.

Other elements of the repeater structure such as coils and condensers are also subject to special requirements both electrical and mechanical. These requirements have been met in a preliminary way and the assembled repeater in its housing subjected to mechanical tests in the laboratory.

Although the electrical requirements of such a cable are very severe, there are some respects in which the submarine telephone repeater is simpler than a land-line repeater. The temperature at the bottom of the ocean is nearly constant; consequently, the repeater does not have to be regulated to compensate changes of cable characteristics with temperature. Also, once the cable is laid, it is in a very quiet place, and except in shallow water near shore is not likely to be disturbed. True, the electrical characteristics of the cable may show effects of aging, but over a long period of time changes are not great, and they can be allowed for by providing some margin in the electrical design.

In the circuit of the repeater the heating filaments of the amplifying tubes are placed in series with the central cable conductor. The fall of potential through the heater filaments provides the plate potential for the tubes. Appropriate networks compensate for variation of cable attenuation with frequency. A negative feedback circuit gives a high degree of stability over a wide band of frequencies and minimizes the effect of variations of tube characteristics. It is interesting to note that the amplification provided by a single tube could drop to a tenth its normal value with scarcely appreciable effect on the performance of the repeater.

The number and spacing of repeaters depends of course on the length and design of the cable. For a cable 2000 miles long to connect Newfoundland and Great Britain there was calculated a core comprising 516 pounds of copper per mile insulated with 370 pounds of paragutta, surrounded by a return conductor of 600 pounds. This is like the core of the 1930 Key West-Havana telephone cable but somewhat smaller. Paragutta was assumed as the insulating material because of extensive experience with it. By using for the calculation the characteristics of one of the newer synthetic

insulating materials a somewhat more favorable design would have been obtained. On this cable 47 repeaters spaced 42 miles apart would provide for the transmission of a band 48,000 cycles wide.

¶ The repeater is a one-way device and to provide two-way conversations two cables have been assumed, one directed eastward and the other westward. This is the simplest solution of the two-way problem but it is not inconceivable that the problem could be solved with a single cable. Using two cables, each transmitting 48,000 cycles, the number of telephone circuits will depend on the band assigned per channel. If we adhere to the present best land-line practice, and assign 4000 cycles per channel there would be room for 12 telephone circuits. For a small sacrifice of quality the number could be materially increased. Even as many as 24 fairly satisfactory circuits could be provided by assigning only 2000 cycles per channel.

Although in Bell Laboratories we have gone a considerable distance in the design of a broad-band repeatered submarine telephone cable, and have developed many of the essential parts, I would not wish to give the impression that all the problems of such a cable have been solved, or that the time has come to proceed with its construction and installation. Indeed, it is only by building trial sections of such a cable and subjecting them to repeated punishment more severe than a cable is likely to encounter, that the problems can be fully recognized. Extensive electrical tests will also have to be made on a complete assembly of repeaters with artificial lines simulating sections of cable. These steps have yet to be taken.

A submarine cable requires a degree of care and precaution in engineering such as is required in few other situations. It is usually not possible to provide large factors of safety, and yet failure of a single part such as a break in the conductor or a leak in the insulation completely destroys the operation of the whole system. Experiences of over eighty years since the failure of the first attempt at an Atlantic cable have led to the development of practices which give good assurance of the reliability of cables of simple construction, but when a device such as the proposed repeater is made a part of the structure a new set of hazards is introduced. Whether these hazards can be guarded against well enough to justify the risks of such a cable project remains to be seen, but I am optimistic that by a sufficiently thorough job of cable manufacture and a well planned program of trials, the hazards can be reduced to an acceptable degree. It will take some years to reach this point, and at best it must be expected that some degree of hazard will still remain. Submarine cables, like all things that go to sea, can never be completely dissociated from some chance of disaster.

As to the costs of such a cable project for establishment of broad-band wire telephony to England via Newfoundland, only the roughest sort of

estimates can be made at this time. However, even applying annual charges somewhat higher than have commonly been used for cables, it appears that the total cost per telephone circuit for the system of two cables with associated equipment will be comparable with that of prospective short-wave radio systems. A considerable increment of cost of cable over that of radio would be justified by the better quality of transmitted speech and the very significant advantage of privacy. Added to this is the value of the cable as a supplement to radio systems to provide against their failure. Indeed it is possible that once the cable were in service radio would be looked on as a supplement to it.

The comparison of cable and radio telephony is not easy to make. It is the composite of cable and radio that assures continuity of service since while radio is sensitive to disturbances accompanying magnetic storms, and cable less so, radio service is not so exposed to the possibility of interruption by mechanical accident or malicious intent. An advantage of radio systems is their flexibility, whereby new routes can be established or old routes abandoned without incurring excessive costs. Further, provision can be made for expansion of radio facilities as required without having to install so large a complement of circuits at the outset. The prospect of the combined radio and cable system is a happy one in that it affords the advantage of both types of facility.

In the foregoing discussion I have treated the transoceanic telephone problem principally as the transatlantic problem and more particularly as the problem of connecting North America and Great Britain. Community of language and many interests lend particular emphasis to that connection, but it is, after all, only one of the many transoceanic links required to build the world-wide telephone network of the future.

When we come to look at other situations, the relative advantages of radio and cable weigh differently. Shortwave radio links have a great advantage in affording direct connection between points on the globe far apart, and the tendency has been to establish short-wave connections directly between large centers rather than through extensive land-line links, particularly where political boundaries have been involved. There has thus grown up an extensive network of single-channel short-wave radio connections operated at low power, giving good service part of the time but not to be depended on all of the time. Most of these connections are over routes which would not support broad-band systems such as I have discussed. The introduction of broad-band methods for transoceanic radio telephony will tend to favor centralizing radio traffic at a smaller number of more important radio terminals, but it is hardly to be expected that all transoceanic radio traffic will thus be concentrated. Even with radio systems dispersed rather than centralized, broad-band cable may still

serve as an effective supplement to radio not only between North America and Great Britain but also between North America and all of Europe, with land lines extending the circuits to all important centers of the European continent. It is to be expected, too, that the cable will find important application in other locations than across the north Atlantic. Notably, this type of cable is particularly promising for trans-Mediterranean service. Indeed, the same principles of construction which are proposed for the transatlantic cable may be applied over much shorter distances. With some modification of design, the repeater can be incorporated in lead-covered cables for shallow seas and afford transmission advantages of carrier as well as the economy of broad-band.

If one tries to imagine the world-wide transoceanic network of the future, he may well envisage a net comprising a large number of light linkages and a small number of heavy linkages over the most important routes. The light linkages will represent direct short-wave single-channel or twin-channel connections using relatively small power. The heavy linkages will comprise highly developed powerful broad-band short-wave radio systems making full use of frequency and directional diversity supplemented by broad-band submarine cables and in a few cases by long-wave radio as well.

From purely physical considerations, it appears feasible to provide all of the facilities for telephone connection between all points on the earth that its inhabitants are likely soon to require. To what extent these facilities will actually be developed will depend on demand and that, to a considerable extent, on cost. It will be interesting to survey briefly this question of prospective demand to see whether after all it promises to be great enough to justify the installation of broad-band cable and radio systems such as are here proposed.

There are so many factors that contribute to telephone demand that it is impossible to make any very reliable estimate. In addition to cost, there are factors of differences in time, in language and in telephone habits and also the factors of community of interest and speed of service. Similar factors affect the demand for telegraph service, but the transatlantic telegraph habit has had more time to mature fully and may reflect more accurately than the telephone the demand that exists for rapid communication between Europe and America.

One possible way to estimate what the future may have in store for transatlantic telephony is to compare the flow of telegraph traffic, say between London and New York, with that between New York and some west-coast American city, and then to examine how intensively telephone service has been developed relative to telegraphy over the two routes. Because of its comparative stability over a period of years, New York-

San Francisco traffic provides an interesting basis of comparison. The distance and difference in standard time between these two cities compare fairly well with those between New York and London. Difference in community of interest is compensated to some degree by the difference in size of London and San Francisco.

This comparison may be made on two bases not very different in character, but leading to widely different results. In the first, let us compare the two routes as regards telegraph traffic, using as our measure the total number of words transmitted in a single year. In the second, let us use as our measure the number of public service telegraph messages, excluding such telegraph business as is comprised under the headings of press service, leased-wire service and code and cipher messages. In each case the estimate is based on terminating messages and excludes traffic routed via the cities named. Data for the year 1937 are available and this particular year has some further advantage in that it represents something between the peak of the 1929 era and the trough of the succeeding depression.

On the first basis of comparison we find that the total number of telegraph words transmitted between New York and San Francisco in 1937 was approximately the same as that between New York and London. On the second basis we find that the number of telegraph messages was about seven times as great between New York and London as between New York and San Francisco. The wide discrepancy between the two comparisons is doubtless accounted for partly by rates and partly by the character of business and social intercourse. Of the two the second, which is based on plain-word public-service messages, would seem to be more significant in relation to potential demand for telephone service. The information transmitted in press and coded telegraph messages and over leased wires is presumably business of record. Public message telegraphy, as a somewhat closer approximation to the informal exchange of ideas by telephone, may be a better index of telephone demand.

On the basis of these figures we may speculate that the potential demand for telephone connection between New York and London is somewhere between one and seven times that between New York and San Francisco. Actually, in the year 1937 the telephone traffic between New York and San Francisco was about three times that between New York and London. Thus it would appear that not more than a third, and possibly not more than a twentieth, of the potential telephone demand has been realized.

If we assume, as seems reasonable, that the same ratio of potential to realized demand exists for all European-North American connections as for the New York-London connection, we may estimate that in place of the five pre-war telephone circuits across the North Atlantic there will be needed from fifteen to one hundred circuits. Which of these figures proves to be

the better measure will doubtless depend greatly on costs that can be achieved but I do not think that I can fairly be accused of excessive optimism in predicting a demand for forty or more telephone circuits in the reasonably near future if full advantage is taken of technical possibilities already in view to decrease costs and improve reliability of service.

In estimating the demand for growth it may be a mistake to attach too much importance to cost of service. Speed and reliability are, within limits, just as important. When it becomes possible to pick up a telephone and get a reply within two minutes, which is about the normal time for a long distance connection in the United States, and when the connection provides the clarity and freedom from noise of a local telephone call, then the transoceanic telephone service will, I believe, be used to a degree not even approached at present.

To provide this indicated increase in number of circuits, and to approach land-line standards of reliability and quality of service will demand utilization of all three types of transmission systems: short-wave, long-wave and repeatered cable. Considerations of cost, flexibility and directness of connection suggest that the bulk of the transatlantic business will be handled on the short waves, but any service important enough to justify so large a group of circuits as has been estimated would have to live up to a higher standard of reliability than short-wave circuits alone can provide. A cable between America and Britain would provide this reliability, acting as insurance against serious interruptions of service that would result from a simultaneous failure of all the short-wave facilities during periods of magnetic storm. It would in addition set a high standard of transmission performance in competition with short waves. The cable and short-wave circuit groups plus a few long-wave circuits should provide a high degree of reliability and excellent transmission at a level of cost such as would assure the continued growth of the service.

It may not be necessary to wait until the growth of transatlantic telephone business provides enough traffic to utilize fully a cable of the type described. When once the engineers are ready to give reasonable assurance of the cable, I believe that it will not have to await complete economic justification, because of the tremendous importance which it would have in insuring privacy and continuity of transatlantic telephone service. What the cable really waits on is technical development. To achieve this is fairly straightforward, since there do not appear to be any insurmountable difficulties. There is still much to be done and many difficulties must be overcome before the broad-band repeatered cable can be installed but it does not impress me as a more difficult problem than many that have been solved in the past.

In developing this picture of transoceanic telephony I have endeavored to stay within the realm of engineering fact, and not to count on products

yet to be born from the inventor's fancy. Indeed, I may have been over-conservative for there are already partly developed inventions which might greatly modify the picture. One such is the vocoder, an instrument which, in a sense, compresses speech into a narrow band. More accurately it dissects speech, transmits it in code and recreates it at the other end of the line. With vocoders a hundred or more simultaneous conversations might be carried by a pair of repeatered cables. While the vocoder would transmit the primary elements of conversation it would not provide all of those qualities of speech which words alone do not convey. The vocoder gains in band width at the cost of naturalness of speech, but even so, it may find important application.

Other inventions may extend the band width available for transoceanic communication far beyond the range here discussed. Projects such as repeatered ultra-short wave radio systems and undersea wave-guides, which today appear fantastic, may some day come within the range of practicability.

The electrical channels over which peoples of one continent hold their more urgent communication with those of another have always been of surpassing technical interest. Ever since the first electrical impulses to carry words across the ocean were traced in the wavering beam of Kelvin's mirror galvanometer, the improvement of these channels has been a fruitful field for scientist and inventor. But these paths for the transmission of intelligence have a wider significance than mere technical achievement. They are strands of an ever-growing bond that unites widely separated continents. The newest of these strands, the overseas telephone, has yet to reach its maturity. Not until conversations can be carried on as easily and reliably between continents as between cities within a continent, can we claim that the art of transoceanic telephony has come of age. When this time arrives, we shall probably realize as we look back that the half-dozen telephone circuits of the 1930's formed indeed a slender thread to bind together in speech the people of North America and those of Europe. Some tens of kilocycles of band width may then appear as inadequate as the slowly dispatched words over the first transatlantic cable appear to us today.

Diamond Dies for the High-Speed Drawing of Copper Wire*

By H. N. PADOWICZ

ESSENTIAL to the drawing of copper wire at any speed are the dies to effect the desired reduction steps. It can be readily surmised that this item is one of major importance at drawing speeds of 10,000 and 12,000 feet per minute which are being used in the copper wire drawing plants at the Kearny Works and the Baltimore Works of the Western Electric Company.¹ In these machines diamond dies are used to draft 12 and 14 A.W.G. supply wire to the final sizes of 19, 22, 24 and 26 A.W.G., respectively. As pointed out in the paper¹ describing these machines in the above noted plants, the maximum possible drawing speed is limited by the stresses set up in the take-up reel rims. Drawing dies in themselves should not place any limitations on the wire drawing speeds if the factors of heat generated and the rapid movement of lineal wire surfaces are logically considered and provided for.

In 1924 the manufacture of copper wire at a drawing speed of 2500 feet per minute in a new type of wire drawing machinery, developed and designed by the Western Electric Company, was started in its Chicago plant.² At that time copper wire was being generally produced at speeds ranging from 800 to 1200 feet per minute. A study of the manufacture of diamond dies for use in these machines developed that dies suitable for this work required a differently shaped "approach," a better polish and a shorter "land" than those that were available for low-speed operation. These same factors are still the important items which must be considered for today's drawing speed of 10,000 and 12,000 feet per minute.

The technique of making diamond dies for the drawing machines which operate up to about 5,000 feet per minute is now well established. The specifications covering the dies for this purpose are known and available to the trade which is well qualified to produce them. However, the opportunity and necessity for diamond dies to draw copper wire at the noted high speeds did not exist prior to the recent development of these high-speed machines and for this reason the industry was not familiar with the necessary die requirements.

The Kearny Wire Mill was set up to purchase finished mounted dies from outside suppliers and to recut them when oversize. These dies are usually acquired at the smaller final sizes as governed by production schedule requirements and enlarged to the larger sizes for both finisher and line die use.

* Published in *Wire and Wire Products*, October, 1941.

A large part of the success attained was due to specifications defining the die requirements and the setting up of adequate inspection means to check the new and recut dies for these requirements. Prior experience of this company and the cooperation of our suppliers greatly aided this policy.

The following details of diamond wire drawing dies have been found to be essential to the desired performance of these tools in our drawing operations:

- Shape and Quality of the Diamond Stone
- Stone Size
- Mounting
- Contour of the Die Hole
- Polish and Finish
- Pounds Pull to Draw the Wire through the Die

SHAPE AND QUALITY OF DIAMOND STONES

Round, clear stones of sound structure are selected, and these should be free from cracks, pits, carbon spots, porosity or any flaws and imperfections which would affect the present or recut drawing surfaces of the die. *Round* is the trade term for stones of polyhedral sides, approximating a spherical form as distinguished from flats and irregular, unsymmetrical shapes.

Usually these stones are octahedral in habit with smooth rounded corners. The coloration and clarity of the mounted stone should permit inspection of all drawing surfaces, relief angle, approach angle and bell. A close-grained stone as determined by the crystal growth lines seems best.

STONE SIZE

The size of stone for specified hole sizes, consistent with the quality of stone previously noted, has been well standardized for the copper wire industry by the American wire die manufacturers. Good die performance has been obtained from these sizes. The average stone size of these manufacturers has been specified for our requirements.

MOUNTING

The mounting encasing the stone is a vital factor in the life of diamond wire drawing dies. Diamonds when used for drawing dies ultimately fail by breakage (i.e. cracks, spalling, chipping out) and not by erosion of the wearing surfaces. Diamonds due to their formation and crystalline structure and to the physical properties resulting therefrom, are particularly prone to breakage when subjected to fatigue, impact and disrupting tensile stresses such as those commonly met in wire drawing operations. To compensate for this weakness it is necessary to effectively encase the stone in a mounting which adequately supports it on all sides. The methods of mountings are many and varied. Mountings which are made by hot

pressing, forging or upsetting to obtain definite bonding of the component parts were found to be superior to those made by brazing, puddling, or casting. High-strength metals processed with the proper technique to effect good metal flow and alloying bonding are preferable. The interface of the stone and metal should be free from porosity and crevices. Figure 2 depicts a defective mounting due to poor metal flow which caused the early breakage of the stone.

CONTOUR OF THE DIE HOLE

The contour of the die hole is shown in Fig. 1. It is the familiar radial or parabolic type which is commonly used in the copper wire industry with

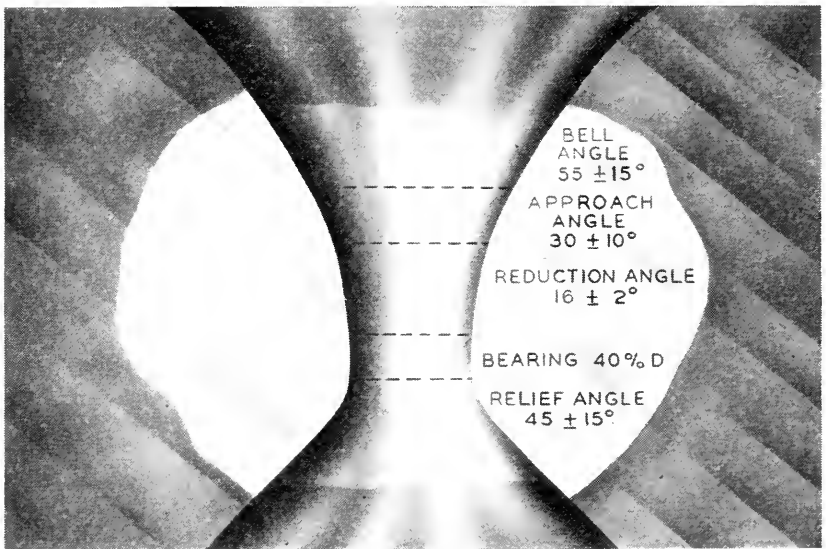


Fig. 1—Contour of the die hole

good results. The straight angles associated with cemented carbide dies do not exist in the present day commercial diamond dies. The noted angles are arcs and the values cited refer to the average chords subtending these arcs. In agreement with the findings of comparatively recent English investigations³ of the theoretical factors affecting wire die performance, it was found that small changes of angle do not appreciably influence the die pull. Whatever differences do exist are blanketed out by changes in the die frictional forces. The permissible variations in angle are consistent with the average found in today's best commercial dies. In recutting dies ob-

tained from different sources the variations narrow after one or two recuts. This is to be expected when standardized recutting practises are followed.

BELL ANGLE

The bell angle should permit ready ingress of the compound solution to wash out those materials (dust, slivers, sludge, dirt, etc.) which tend to accumulate here and have an abrasive action when pulled through the die

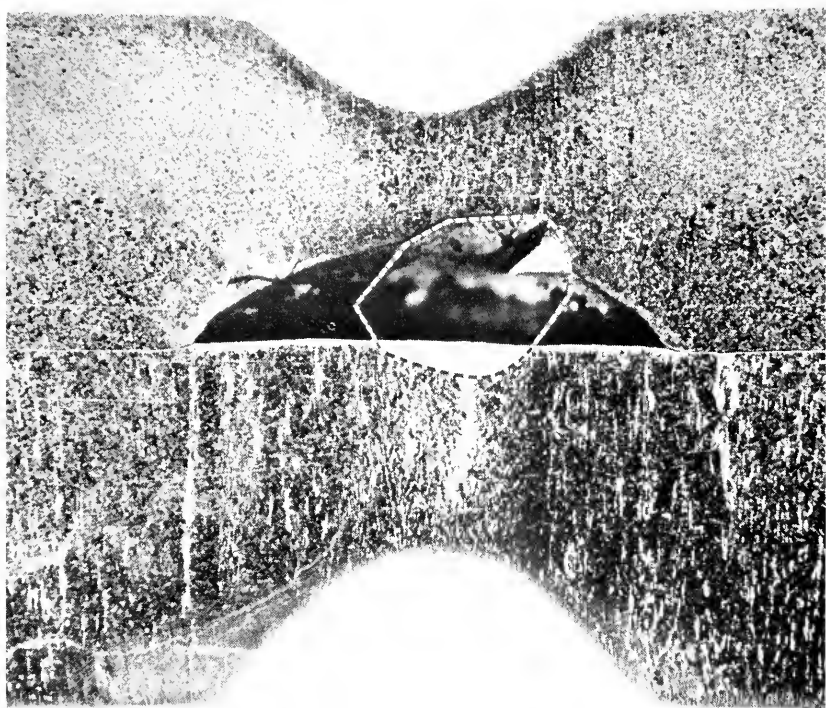


Fig. 2—Defective diamond die mounting due to poor metal flow

by the wire. The bell angle is highly polished to minimize the packing of the noted materials. This polish can be more easily achieved in a smooth tapering angle than in one of a wide flare.

APPROACH ANGLE

At high drawing speeds, appreciable wire whip and vibration are present. Also, the higher centrifugal forces tend to “throw out” the wire in relation to the normal axis of the die. An approach angle not too wide in relation

to the reduction angle is necessary to guide the wire concentric to the drawing cone.

REDUCTION ANGLE

In this angle, the most important sector of the die, the reduction of diameter, except for the sizing accomplished in the bearing, is carried out. Following the practice of the trade a 16° angle is used. The depth of this area is designed to have the entering wire hit well within it to prevent excessive chipping and undercutting in the pressure ring and to maintain the desired die pull values. The line of contact of the entering wire and the reduction area is located at 65-70% of the vertical height of the reduction angle.

In general, the ratios of the vertical heights of the reduction, approach and bell angles are as follows: 1:0.7:1.5 for dies of 20-26 A.W.G. inclusive and 1:0.5:1 for the larger sizes. The dimensions of the approach and bell angles are of course dependent on the stone size and the number of previous recuts. The heights of the two latter angles may vary appreciably from the above noted values provided that adequate lubrication and "washing out" of the die can take place.

BEARING

A bearing length of about 40% diameter is formed. It is checked by the die pull requirements. The bearing is purposely drilled to obtain a slight front taper of about 2° . The slight taper aids the metal flow and reduces "sucking".

RELIEF ANGLE

Here again, the wire vibration necessitates a smooth angle which will not tear the wire leaving the die. Recutting for good reproduction of contour and die pull also requires a smooth angle. Proper care should be taken to prevent a cup shaped depression which is commonly formed by jamming a diamond chip in the back of the die as a fast intermediate step to final sizing.

POLISH AND FINISH

The degree of polish of the die drawing surfaces is a most important factor in determining satisfactory die performance. In wire drawing there is encountered a vicious repetitive cycle consisting of (1) the wire abrades due to the condition of the wire and die surfaces, (2) the resultant abraded metal particles pack in the die throat and gall the incoming wire, and (3) the heat and the conditions created by this action again adversely affect the wire and the die surfaces to repeat the cycle. There have been cases

noticed where the fine copper particles have been compacted by the heat and pressure to form a solid conical mass which has welded to the wire. Deep grooves in the reduction angle and bearing invariably follow back to the pressure ring or irregularities in the die surfaces in which the metal particles, dirt, etc. have lodged.

Characteristic of copper and other non-ferrous metals is its ready flow under pressure such as is present in the die reduction angle. This condition causes die packing, metal galling and the resultant wire scoring to take place at surprisingly slight irregularities in the die drawing surfaces. This is particularly true at high drawing speeds due to the rapid lineal movement of the wire surfaces. Again this emphasizes the necessity for a high polish. The harder ferrous metals tend to bridge across these small irregularities rather than to flow into them.

Highly polished surfaces free from scores, traces of ripping rings and scratches are desired. All the die surfaces with the exception of the relief

TABLE I

Diamond Die Diameter	Max. Pounds Pull	Diamond Die Diameter	Max. Pounds Pull
13 A.W.G.	113	20 A.W.G.	25
14 "	92	21 "	21
15 "	75	22 "	17
16 "	60	23 "	13.5
17 "	49	24 "	11
18 "	39.5	25 "	9
19 "	32	26 "	7

angle and top flare of the bell should be so finished. The polished surfaces should be a smooth curve as undulating surfaces are undesirable.

Dies after full use to oversize will retain their original high polish if no breaks in the stone, i.e. chips, cracks, etc. have occurred. This polish will also be present in the wear eroded areas.

POUNDS PULL TO DRAW THE WIRE THROUGH THE DIE

Die pull has long been known to the trade as a factor which greatly influences wire drawing operations. However, it has not been customary to recognize its relation to the drawing die itself and it has not been applied as an everyday simple means of checking a die's possible performance. The Western Electric Company has considered for a long time this die characteristic in its wire drawing developments¹ and practical values for use in the present high-speed drawing machines have been established. Listed in Table 1 are the values used for these dies. It should be added that, while die pulls are important, these are not critical and a deviation of +10% can be used but this would result in greater power consumption and more

frequent wire breaks. The noted figures are 45–50% of the wire breaking strength based on A.W.G. reduction steps. Die pull is a cumulative check of the following die characteristics: contour as correlated to the reduction angle and bearing length, and the polish of the drawing surfaces. In conjunction with the die diameter, it affords a means of grouping the dies in matched balanced sets and obviates actual try out of these dies in the machines.

INSPECTION METHODS

Suitable inspection methods and equipment to check the die requirements contribute much to good die performance. Microscopes have been used with good results by some manufacturers of fine wires and by several of the more progressive die manufacturers for some time for this purpose. The Western Electric Company has adopted this practice. The binocular wide field microscope has proved to be an indispensable tool for inspection. It is used to the complete exclusion of loupes. The stereoscopic effect, the wide field and the long focal distance features of this instrument make satisfactory examination possible. We have found a magnification of 30× to be most practical for the previously noted die sizes. Good agreement to observations by different persons can be had by the use of this apparatus. This is a rare occurrence in the case of loupes. It is surprising that this inexpensive tool which removes much of the guessing and so-called art in diamond die manufacture has not been universally utilized by wire drawers and die manufacturers.

Frequent examination of finished dies and dies in the various stages of recutting is expediently accomplished by microscopic observation. Routine die contour checks are visually made in this manner. Periodic checks of die angles and die contour are accurately made with a contour projector. Shadowgraphs of 100× magnification are made of die impressions formed of a soft metal.

When polished to the proper degree, it is possible to examine a mounted die under a microscope with a suitable light source and discern the internal flaws in the stone. The examination of stones removed intact from the mounting will also check this point. Mountings of metals having a low reflectivity will require a light source from above to illuminate the stone.

The die pull is checked on a commercial instrument shown in Fig. 3. Auxiliary equipment and gauges have been added to it to make it more versatile for this use. The device consists of a piston which fits snugly into a hydraulic chamber filled with a suitable liquid. The piston is recessed at the outer end to hold the die. The die pull causes the movement of the piston which builds up the registered pressure. The wire is reduced one A.W.G. step and the pressure against the die holder is noted as indicated on

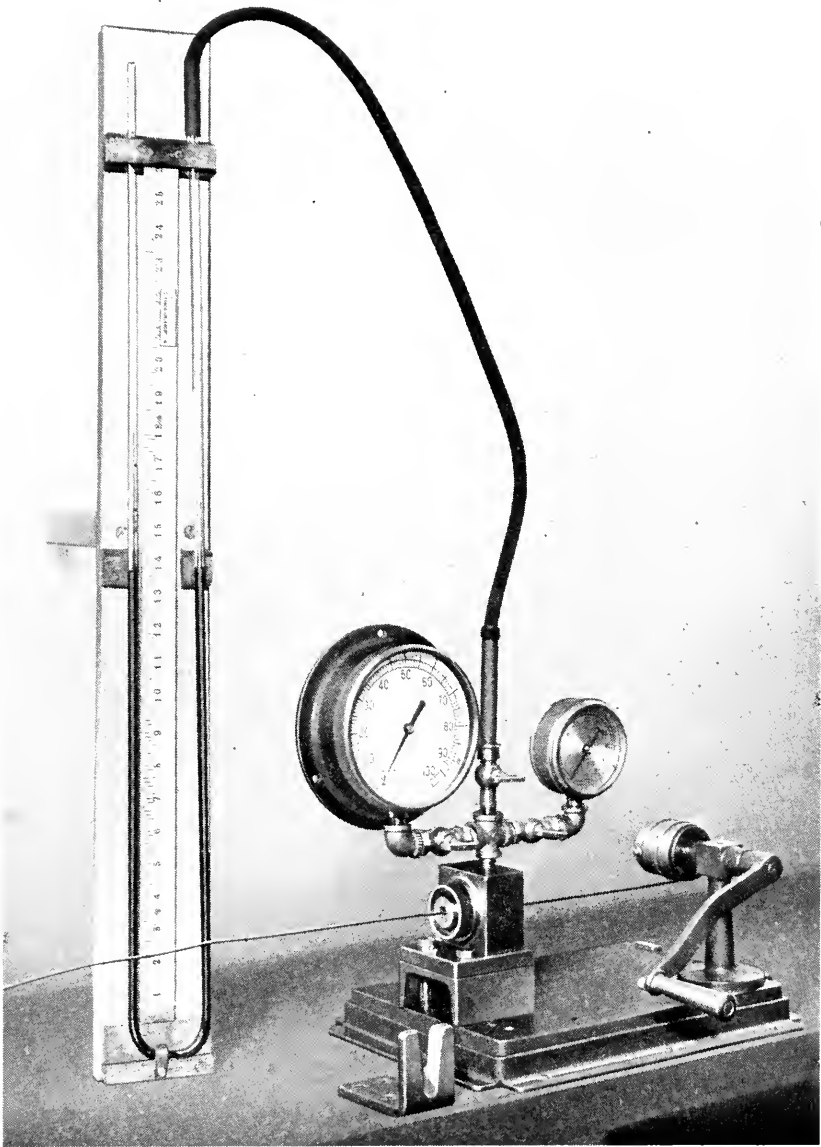


Fig. 3—Die pull indicator

the adjoining gauge. Small die sizes having die pulls below five pounds are checked by means of a manometer filled with an appropriate liquid. When measuring die pulls of low magnitude, the device should be calibrated for the frictional drag of its moving parts.

DIE RECORDS

Die control is greatly enhanced by comprehensive records. All dies are logged on individual record cards. A facsimile of each side of this card is shown in Fig. 4. As noted, the individual die characteristics as received, at oversize, and after recutting to final disposition are recorded. These

EL 2954-J (6-41)
 DIE NO. - , DATE REC'D. 8-31-39 , P.O. NO. EM 500 , SUPPLIER -

A.W.G. 24
 Type FINISHED
 Size Stone .50 CT
 Mount BRASS

Size:-	Mean	Max.	Min.	Shape	PARABOLIC CURVE	Polish	O.K.
Supplier .020				Bell	O.K.		O.K.
Dept. 2181 .01995	.020	.0199		Approach	O.K.	Flaws	NONE
Lbs. Pull 11.5				Bearing	O.K.		
				Relief	O.K.	Remarks	NONE

Recuts:-

Date	A.W.G.	Mean	Max.	Min.	Lbs. Pull	Shape	Polish	Remarks & Reason for Completion of Gage Size
10-17-39	24	.0203	.0205	.0201				OVERSIZE
	23	.02233	.02235	.02230	14.0	O.K.	FAIR	OVERSIZE
4-10-40	23	.02322	.0236	.02285				OVERSIZE
	22	.02525	.02528	.02522	18.0	O.K.	O.K.	OVERSIZE
7-9-40	22	.02575	.0262	.0253				OVERSIZE
	21	.02825	.0283	.0282	21.0	O.K.		
11-26-40	21	.02905	.0294	.0287				CIRCULAR CRACK



Date	Finish or Line Die	A.W.G.	By Gage	M ² .C.F. Drawn
DEC. 1939	FINISH	24	55.0	55.0
DEC. 1939	LINE	23	48.0	103.4
APR. 1940	"	23	190.2	293.2
AUG. 1940	"	22	138.9	432.1

Fig. 4—Facsimile of a die record card

cards are periodically correlated to the daily machine performance sheets by mechanical tabulation to obtain the die life.

SHOP DIE CONTROL

All drawing dies are grouped in sets for use and matched for balance in relation to their diameters. This is necessary because of the minimum slip characteristics of the drawing machines. It is also a convenient means to reduce machine down time. The sets are used in the drawing machines as units. Replacements and rematchings are made in the Die Shop. Definite

oversize diameter limits consistent with best enlargement practice and overall operating efficiency have been set for each finisher and line die size. The die sets are removed from the machine when any one die, with the exception of the finisher, has reached the specified limit. Usually two finishers are used for each set of 26 A.W.G. and one plus for the other final gauge sets before returning these units to the Die Shop. This procedure has greatly enhanced the economics of die costs, operating efficiency and wire quality. It has also made possible the issuance of dies by the Die Shop for shop use without the necessity for preliminary "tryout" in the drawing machines.

RECUTTING PRACTICE

Diamond die recutting is a series of lapping operations in which the abrasive is diamond dust for obvious reasons and the lap or carrier is a suitable pin or wire, usually steel, depending upon the specific operation. The theory and practice of lapping tool gauges to a fine finish is applicable here. The diamond dust imbeds in the lap, is held there temporarily stationary and cuts the die stone when it is forced in contact with it. As its position is fixed relative to the lap, but moving with respect to the stone, it cuts the die surface. However, due to the great hardness of diamond, appreciable wear of the lap takes place and its shape is rapidly changed. In ripping where the shaping of the die contour is done, the pin must be frequently reground. It is necessary to have a hard material for the lap to keep the diamond dust working in contact with the die surface and to retain its shape for an appreciable time. Also, some diamond dust would imbed deeply in a soft material and be removed in the grind.

Successful recutting and reproduction of die characteristics require definite procedures and controls. Specific hole size enlargement, surface requirements, frequency of lapping pin grinds, diamond dust additions, etc. are essential for each operation to achieve the desired results.

Standard commercial machines are used for the various enlarging and refinishing operations. In general, recommended trade practices are followed.

Ripping (the roughing operation which removes the pressure rings, chips, etc. and reshapes the die contour) is most important as it determines the die contour and the subsequent degree of polish. We have found the RPM of the drilling pin spindles to be a determining factor. Spindle RPM's from 4,000 to 12,000 have been tried, and 5,000 RPM has been found to be most satisfactory. Other important elements are the diamond dust size, frequency of pin grinds, speed and kick of the reciprocating vertical motion. A definite sequence of these factors is necessary to achieve the desired results. A gradual breakdown of the diamond dust effecting a cutting and lapping action as controlled by the centrifugal forces dispersing it in the liquid

medium takes place. The steel lapping pins are accurately ground to a definite straight included angle and circular arc on a special grinder. The ripped die surface should be a smooth, dull matte surface free of deep rings and scores.

In polishing, the die contour has already been established and it is expedient to have the lap of a material which will rapidly shape itself to the contour to be polished to obtain maximum contact. Here the loading of the lap will hold the diamond dust in contact with the work. A viscous medium for the dust will also help. On the wire polishing machines, the springback of the wire on flexing is important. It was found that a wire resiliency tester will aid to evaluate the desired wire properties. Diamond dust of a uniform and fine grain size is vital to the polishing operation. High RPM in the case of revolving die mounts is beneficial provided it does not "throw out" the diamond dust from the working area.

Sizing of the bearing requires a spindle RPM about 100% higher than that used in ripping. Other factors in this operation are the diamond dust, frequency of its addition and the frequency of the pin grinds.

All die recutting machines should be periodically checked and maintained to minimize vibration.

DIAMOND DUST

Another important factor in the recutting operations is the diamond dust abrasive. This is especially true in the finishing operations of polishing and sizing where no appreciable breakdown of the original dust takes place. Uniformity of particle size range and grain size determine the efficacy of the abrasive. Diamond dust graded by air flotation is now being used with good results. It was found that this material was more satisfactory for our use than that obtained by sedimentation in liquid media. Recent investigations in the separation of microscopic size dry powdered material have been actively carried out in the ceramics and powdered metal industries. The *Journal of the American Ceramic Society* and the *Bureau of Mines publications* contain noteworthy papers describing practices which could be applicable to diamond dust grading. Stokes⁵ law of fall for microscopic size particles will also hold true for the separation of diamond dust by means of air.

DIE LIFE

In theory and practice, die life resolves itself into a problem of wear. The wear is due to the movement of the wire surface over the drawing die area in contact with the wire. In turn the wear is proportional to the forces acting on these surfaces, their area, the condition of these surfaces and the coefficient of friction. This is dependent on the nature of the wire, the die

materials and the lubrication of the contacting surfaces which in turn is affected by their condition. Considered on this general basis, the die life is proportional to the wire lineal footage. A good criterion for determining the overall diamond die performance is the total useful life in million conductor feet. This in turn will be proportional to the number of recuts obtainable before breakage renders the die non-usable.

Although diamond die life is theoretically a function of wear, actually it is limited by the failure of the die stone by breakage and "chipping out." Due to the peculiar physical properties of diamonds some breakage will always occur. This condition is also affected by fatigue caused by vibra-

TABLE II

B & S Ga.	Kearny Wire Mill 1/39-8/40					
	Finishers		Line Dies		Average*	
	M Lbs.	M. ² C.F.	M Lbs.	M. ² C.F.	M Lbs.	M. ² C.F.
26	35	45	—	—	35	45
25	—	—	90	93	90	93
24	92	75	105	86	97	79
23	—	—	162	108	162	108
22	136	70	159	82	148	76
21	—	—	226	92	226	92
20	—	—	250	81	250	81
19	250	64	284	73	277	71
18	—	—	368	75	368	75
17	—	—	595	96	595	96
16	—	—	740	95	740	95
15	—	—	1040	106	1040	106
Average M. ² C.F. per die gauge step.....						85

NOTE: Some of the results listed above appear to be inconsistent with the expected trends. This is attributed to the many variables which exist in normal Wire Mill Operations.

* Based on Kearny's distribution of gauges.

tion, impact, thermal stresses and other factors. An important element influencing die breakage which is often overlooked is the detrimental effect produced by improper maintenance of the drawing machine parts. An appreciable reduction in die breakage was obtained by proper periodic maintenance checks.

Kearny's Wire Mill diamond die life data are listed in million conductor feet per die per gauge step in Table II. The finisher and line die life is tabulated separately to account for the allowable oversize diameter limits for each type. No data are available at the present time to permit listing of the total useful life in million conductor feet.

STRAINS IN DIAMOND STONES

Rough diamond stones as well as those removed after use in drawing dies have been examined in polarized light to determine the presence of internal strains. In general, the clear flawless stones of alluvial origin were free of strains. Mined stones of South African origin which are commonly found in dies of French manufacture did show in several cases very definite strains. These latter stones were of poor quality. Due to the high index of refraction of the diamond which is much higher than available high refractive liquids, and to local surface strains which distort the interference figures, it was impractical to establish a satisfactory procedure to investigate this subject.

CRYSTALLOGRAPHIC STUDIES

In several cases exceptional die performance was noted, three to four times the average, which could not be accounted for by our regular inspection methods. Also, several dies which chipped initially in use, consistently chipped at subsequent recut sizes after enlargement had completely removed the visible defect. Again and most important is that the majority of our dies are rendered non-usable by the breakage of the die stone, which occurs in a characteristically peculiar manner. These discrepancies are attributed to the crystallographic structure of diamonds. It is well known that the reticular density (atom spacing), hardness and cleavage are greater along certain crystallographic planes.

Investigations as to whether or not the relation of the planes of cleavage to the direction in which the hole is drilled has any practical bearing on die life were made by the Western Electric Company in 1929⁴. The x-ray was used to determine the orientation of the crystal planes. The results of a limited test at that date, in which nineteen dies were drilled at right angles and nine parallel to the plane of cleavage, showed no superiority of these positions. The diamond stones used for dies then were of different origin and quality than those now commonly employed for this purpose. Further studies, with particular reference to the relation of crystal structure to die breakage, are now under way for reasons noted previously, and some of our results to date are cited here having a bearing on die performance.

It is well known that hardness in a diamond varies with the crystal planes. However, since the contour of the die hole consists of cylindrical and conical surfaces, it is questionable if this plane property could be effectively utilized in drawing dies.

An x-ray method⁶ on a shop production basis is now being used to orient quartz plates preparatory to their cutting along certain crystallographic planes incident to their manufacture into radio and carrier frequency control filters. A similar technique was applied to determine the location of the axis of the die drawing hole with relation to the diamond structure. The

orientation of the drilled hole was determined by means of a back reflection Laue photograph.

Diamond stones which meet our drawing die requirements are mostly octahedral in shape, a common crystal form of this material. These are usually alluvial in character and predominantly of Brazilian origin with the exception of a few Southwest African stones.

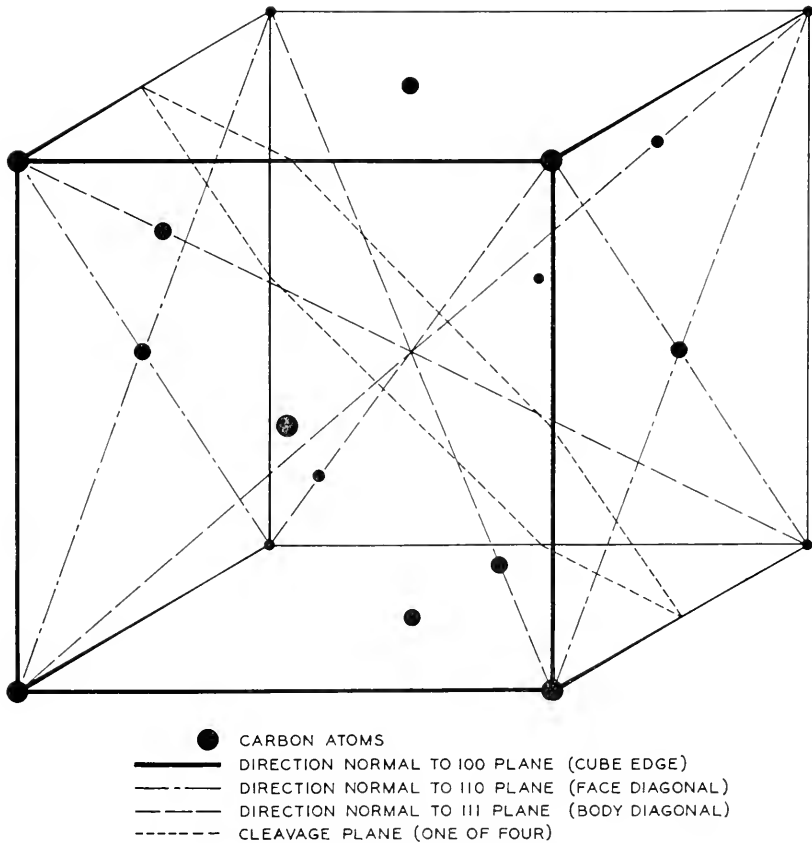


Fig. 5—Diamond structure and the directions of drawing hole axis to the crystallographic planes

Our examinations of numerous die stones have shown that the positioning of these is random with regard to a predetermined drilling axis. About 75% of those studied were drilled normal to the 111 orientation. The axis of the drawing hole in these cases was in the direction of a body diagonal of the cube representing the crystal structure of the diamond. The 111 planes, the cleavage planes for the diamond, are those which appear most

frequently as the natural faces of the most common form of the diamond crystal, the octahedron. The disposition of the stone in the above manner would be logically expected to take place in the mounting methods generally used by the American die manufacturers since the stone would probably rest on a flat side, an octahedral face. This placement for very obvious reasons also facilitates cutting true the starting cone for the drilling operations.

A few stones had been drilled normal to the 110 and 100 planes or at an angle to the 111 plane. Holes normal to the 110 plane, which is the face of the rhombic dodecahedron, another diamond crystal form, are along a face diagonal of the cube. Holes normal to the 100 plane, which is the cube face,

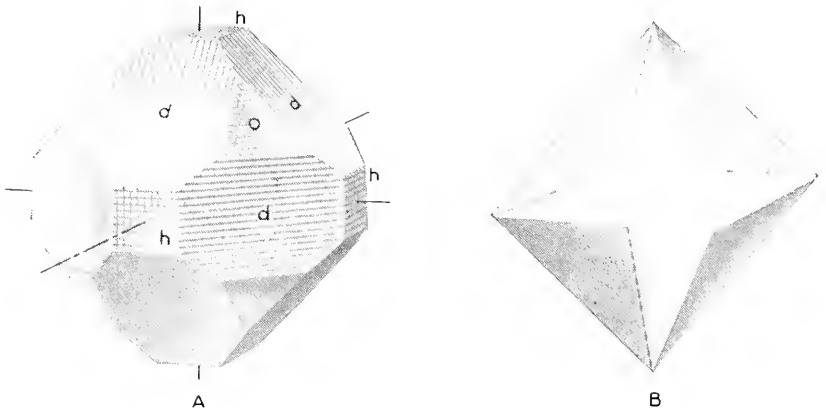


Fig. 67

- A—Diamond crystal showing grain and faces (crystallographic planes)
 - h. Cube face. 100 plane
 - d. Rhombic dodecahedron. 110 plane
 - o. Octahedron 111 plane
- B—Diamond octahedron

are along a cube edge. Very few of these were found. This is as expected since natural crystals with faces parallel to the 100 plane are rare. This face is usually produced by sawing or “bruting.”

As previously noted, diamond die life is restricted by the breakage and “chipping out” of the stone. The manufacture of the dies with due consideration of the peculiar crystallographic structure of the diamond to minimize this condition should greatly enhance its performance. Findings to date substantiate this conclusion. Seventy per cent of the dies which were drilled normal or at a small angle to the 111 plane failed due to cracks parallel to this plane and normal to the drawing axis. The crack usually occurred at the pressure ring and its plane coincided with the cleavage plane, the weakest one in the diamond crystal. The stone in many cases on re-

removal from the metal mounting separated into two sections. The majority of the dies failed in this manner.

Examination of worn oversize dies invariably shows that the erosion and the effect of the forces incident to wire drawing are concentrated at the pressure ring where the entering wire contacts the reduction area. Here, the abrasive action of the wire and die contacting surfaces, and the disrupting stresses are most evident. An analysis of the forces present in a wire drawing die indicates that secondary stresses normal to the drawing axis are set up in this sector. In dies drilled normal to the 111 plane these stresses, coupled with the thermal, impact and fatigue forces converging in this area, would tend to shear the diamond stone parallel to this plane. Overdrawing and poor operating conditions would of course accentuate this effect and bring it about prematurely.

The previously mentioned dies drilled normal to 110 and 100 planes did not crack in the manner noted above. These failed due to chipping and spalling. Cracks, when present, were small and inclined to the drawing axis. Dies drilled normal to 110 plane have cleavage planes parallel to the die hole axis. In one case a stone drilled in this manner cracked along this plane. Data to date indicate that better die life was obtained from these dies than from those drilled normal to the 111 plane.

The noted studies indicate that the orientation of the drawing hole is of practical importance with regard to stone breakage, the limiting factor of die life. A better understanding of its relation to die performance should achieve appreciable economies. No conclusions have been made as yet with regard to the exact desired orientation of the drawing axis. In Fig. 5 is depicted a unit cube of a diamond structure. Here is shown the possible directions of drilling and the location of the cleavage plane. Figure 6 shows the diamond crystal faces and planes.

Whether or not the aforementioned die breakage characteristics are local to our drawing operations and die sizes is not known. We invite comments from other wire manufacturers whose equipment and practices vary significantly from those used at the Kearny Wire Mill.

ACKNOWLEDGMENT

The author wishes to acknowledge and thank Mr. F. E. Haworth, of the Bell Laboratories, for his x-ray determinations and Mr. W. W. Broughton, of the Quartz Crystal Development Group of this Company, for his many suggestions with reference to the crystallographic studies.

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Using Double Sampling Inspection in a Manufacturing Plant

By D. B. KEELING and L. E. CISNE

THE necessity for quality control in a manufacturing plant arises from the fact that all units of product cannot be made identical. To limit variations and attain controlled uniformity some sort of inspection must be established. It has been the experience of the Western Electric Company that quality control may be attained most economically by the use of a sampling inspection wherein only a portion of the entire output is examined for desired quality characteristics.

Advantages which have been gained through the use of sampling inspection, and with no adverse effect on previously existing quality levels, are: a reduction in the cost of inspection by economies in inspection time; a reduction in the amount of scrap produced by making available for supervisory action useful records of the results of inspection; and as an end result, the attainment of uniform quality of a satisfactory level.

It is the purpose of this paper to provide a detailed method of procedure that has proved successful in establishing and maintaining one type of sampling—the “Average Outgoing Quality Limit” Double Sampling Plan. Statistically determined tables of lot sizes and corresponding sample sizes which guarantee a certain degree of protection have been used by the Western Electric Company for approximately fifteen years. They were furnished by the Bell Telephone Laboratories and have recently been made generally available in an article published in the January 1941 issue of the Bell System Technical Journal.¹ A typical sampling table, reproduced from the preceding article, is shown in Fig. 1.

Briefly stated, the AOQL Double Sampling Plan involves the examination on a “go—no go” basis of a specified number of articles taken at random from a large group. The acceptance or rejection of this group is usually made on the basis of results obtained from the first sample alone. How-

¹ The AOQL Double Sampling Tables specifically referred to in the present article are Tables DA-0.1 to DA-10.0 shown on pages 49-61, inclusive, of a preceding article: H. F. Dodge and H. G. Romig, “Single Sampling and Double Sampling Inspection Tables”, *Bell Sys. Tech. Jour.*, pp. 1-61, Jan. 1941. These tables give sample sizes and allowable numbers of defectives for a variety of AOQL values, lot sizes, and process average values. The sampling table reproduced in Fig. 1 is based on an AOQL value of 1.5 per cent defective. In tables prepared for shop use, it has been found preferable to use a notation slightly different from that shown in Fig. 1, specifically to use AN instead of c to represent “allowable number of defectives” and to use SS instead of n to represent “sample size”. The shop notation is used in the present article. It should be noted that, in the original article, C was generally referred to as an allowable number of “defects”, since primary attention was given to inspection of a single characteristic. See footnote 2 for explanation of the terms “defective” and “defect”.

TABLE IV CONT'D: DOUBLE SAMPLING LOT INSPECTION TABLES—BASED ON STATED VALUES OF "AVERAGE OUTGOING QUALITY LIMIT"

TABLE DA-1.5

AVERAGE OUTGOING QUALITY LIMIT = 1.5%

Process Average $c\%$.04- .30				.31- .60				.61- .90				.91-1.20				1.21-1.50							
	Trial 1		Trial 2		Trial 1		Trial 2		Trial 1		Trial 2		Trial 1		Trial 2		Trial 1		Trial 2					
	n	c1	n2	m1+n2	c2	Pd %	n	c1	n2	m1+n2	c2	Pd %	n	c1	n2	m1+n2	c2	Pd %	n	c1	n2	m1+n2	c2	Pd %
1-15	All 0	--	--	--	--	11.6	All 0	--	--	--	11.6	All 0	--	--	--	--	11.6	All 0	--	--	--	--	11.6	
16-50	16 0	--	--	--	--	11.6	16 0	--	--	--	11.6	16 0	--	--	--	--	11.6	16 0	--	--	--	--	11.6	
51-75	23 0	11	34	10.5	23 0	10.5	23 0	11	34	10.5	23 0	10.5	23 0	11	34	10.5	23 0	11	34	10.5	23 0	10.5	23 0	
76-100	26 0	14	40	9.4	26 0	9.4	26 0	14	40	9.4	26 0	9.4	26 0	14	40	9.4	26 0	14	40	9.4	26 0	9.4	26 0	
101-200	31 0	18	49	8.4	31 0	8.4	31 0	18	49	8.4	31 0	8.4	31 0	18	49	8.4	31 0	18	49	8.4	31 0	8.4	31 0	
201-300	33 0	22	55	8.0	33 0	8.0	33 0	22	55	8.0	33 0	8.0	33 0	22	55	8.0	33 0	22	55	8.0	33 0	8.0	33 0	
301-400	34 0	21	55	7.9	34 0	7.9	34 0	21	55	7.9	34 0	7.9	34 0	21	55	7.9	34 0	21	55	7.9	34 0	7.9	34 0	
401-500	35 0	20	55	7.8	35 0	7.8	35 0	20	55	7.8	35 0	7.8	35 0	20	55	7.8	35 0	20	55	7.8	35 0	7.8	35 0	
501-600	35 0	20	55	7.8	40 0	6.8	40 0	45	85	2	6.8	44 0	44 0	45	85	2	6.8	44 0	44 0	44 0	44 0	44 0	6.1	47 0
601-800	35 0	20	55	7.8	41 0	6.7	46 0	74	120	3	6.6	49 0	49 0	74	120	3	6.6	49 0	101	150	4	5.6	85 1	85 1
801-1000	36 0	19	55	7.8	42 0	6.5	47 0	78	125	3	5.9	50 0	50 0	78	125	3	5.9	50 0	105	155	4	5.5	90 1	90 1
1001-2000	44 0	51	95	6.3	44 0	6.3	49 0	81	130	5	5.7	55 0	55 0	81	130	5	5.7	55 0	175	270	7	4.6	100 1	100 1
2001-3000	45 0	50	95	6.2	45 0	6.2	55 0	110	165	5	5.4	106 1	106 1	115	245	6	4.6	110 1	255	365	9	4.1	155 2	155 2
3001-4000	45 0	50	95	6.2	50 0	5.5	55 0	115	170	4	5.2	105 1	105 1	190	295	7	4.3	160 2	300	460	11	3.8	205 3	205 3
4001-5000	45 0	50	95	6.2	50 0	5.5	55 0	120	175	4	5.1	105 1	105 1	190	295	7	4.3	165 2	340	505	12	3.7	250 4	250 4
5001-7000	46 0	54	100	6.1	50 0	5.4	60 0	155	245	5	4.7	110 1	110 1	225	335	8	4.2	165 2	375	540	13	3.7	310 5	310 5
7001-10,000	46 0	54	100	6.1	50 0	5.4	60 0	160	220	5	4.6	115 1	115 1	280	395	9	3.9	170 2	420	590	14	3.6	360 6	360 6
10,001-20,000	46 0	54	100	6.1	50 0	5.4	60 0	165	225	5	4.5	120 1	120 1	315	435	10	3.8	210 3	420	630	15	3.6	415 7	415 7
20,001-50,000	47 0	53	100	6.1	55 0	5.0	65 0	195	260	6	4.3	165 2	165 2	350	515	12	3.7	225 4	640	865	20	3.3	510 9	510 9
50,001-100,000	47 0	53	100	6.1	55 0	4.9	115 1	235	350	8	4.0	175 2	175 2	440	615	14	3.5	275 4	725	1000	23	3.2	570 10	570 10

Fig. 1—Typical sampling table for the AOQL double sampling plan; AOQL = 1.5 per cent defective (Reproduced from article referred to in footnote on page 37)

ever, if the results from the first sample are not conclusive, an additional sample is examined before disposition of the lot is made.

The particular type of articles to which this plan has been applied are products consisting of individual parts, sub-assemblies, or completed apparatus, which, at the various stages of production where control is necessary, are the result of repetitive operations capable of considerable uniformity. The plan has also been applied to some extent on completed products and purchased materials where there is evidence that the product is of reasonable uniformity even though the quality history is meager or unavailable.

1. STEPS IN SETTING UP A DOUBLE SAMPLING LOT INSPECTION PLAN

1.1 *Analysis of the Production Process*

In order to determine the applicability of the Double Sampling Plan to existing inspection operations it is necessary to examine the manufacturing and inspection processes and all data available regarding past quality performance, such as records of per cent defective, consumers' complaints, etc. The following outline should serve not only as a measuring stick to determine the applicability of Double Sampling but also as an index of the conditions to be met for the successful use of Double Sampling with any inspection operation.

1.11 The *lot*, or group of articles to be examined, should consist of product which is available in its entirety for acceptance or rejection at one time. For sampling purposes, the lot should have characteristics which are the result of a common system of causes. By this it is meant that the lot should, as far as possible, consist of articles made from relatively uniform raw material by operators of equivalent skill and by machines or methods of equivalent precision. If there is evidence of appreciable variation between corresponding machines, operators, or materials, it is desirable to confine a lot to the output of one machine, one operator, or one batch of material, in order to isolate a uniform group of product suitable for sampling inspection.

In brief, Double Sampling may be applied to the output of any repetitive unit operation capable of sufficient uniformity. However, unless immediately essential for economic reasons, it need not be applied at the particular time such an operation is completed, provided succeeding operations do not modify the inspection item under consideration.

1.12 In order to gain the maximum advantage from the use of Double Sampling, it is necessary that lots be as large as the limitation of uniformity will allow so that protection and control may be achieved with

a minimum sample size relative to the number of units in the lot. The fact that proportionately smaller sample sizes are used with the larger lot sizes may be seen by reference to the Sampling Table of Fig. 1.

In sampling from larger lots it becomes *increasingly important* in practice to observe certain precautions in order to take care of instances where the lot may not be homogeneous; specifically, each sample should be a group of articles *taken at random from different locations throughout the lot* so that it will represent an impartial cross section of the lot.

1.13 It is necessary for the successful operation of any sampling inspection that at all times there be a known standard of acceptability for the individual article, that is, a definite description of the requirement for each inspection item and reliable measuring equipment against which product may be conclusively checked. Practically, this condition will be realized when the characteristic is defined in such a manner that different observers will obtain consistent results.

1.14 The theoretical background of the plan assumes the repair or elimination of all defectives² in samples of accepted lots, as well as all defectives in rejected lots before such lots are passed.

In order to accomplish this, close cooperation between production and inspection personnel is required in assuring that rejected lots are thoroughly cleared of all defectives, since failure to comply with this fundamental part of the procedure destroys the very foundation of the plan.

1.2 Selection of Proper Double Sampling Table

Tables are provided for a variety of Average Outgoing Quality Limit (AOQL) values and Process Average classes. The AOQL value is the maximum value of average per cent defective in the product after inspection, which the sampling plan will assure over a long period of time, no matter how defective the product submitted for inspection may be. The process average is the normal per cent defective which is to be expected from the process.

To determine what AOQL value should be adopted, it is necessary to decide upon a maximum average per cent defective which may be permitted in the product without serious consequences to the user. Product which is of such a nature that defects will be eliminated in subsequent operations may be assigned a rather generous AOQL, and conversely, product which by its relation to the entire assembly may cause considerable inconvenience

² A *defective* is defined as an individual article that fails to meet the requirements for one or more inspection items. A *defect*, however, is defined as a failure to meet a requirement for a single quality characteristic for which inspection is made. It follows that when several characteristics are inspected, an individual article may have several *defects*, yet be only a single *defective*.

if it fails to meet requirements, usually warrants a strict AOQL. A rather generous AOQL may be assigned to inspection features which are considered relatively unimportant. In other cases the use of sampling may be definitely inadvisable due to the importance of the requirement from a functional standpoint or from the standpoint of the possible effect of a failure upon the safety or health of an individual.

As a guide in the selection of the AOQL, the following table is given, showing values that have been found to be satisfactory for the product listed. These percentage values of AOQL represent per cent of articles defective; if more than one defect is found on an article, the article is counted as one defective. Here, as elsewhere throughout the paper, all figures relate to number of defectives and per cent of articles defective rather than number of defects.

<i>Description</i>	<i>Requirements</i>	<i>AOQL</i>
Machine Screws	5 Dimensions	2.0%
Hexagon Nuts	Visual Inspection after Zinc Plating	2.0%
Twin Eyelets	6 Dimensions and 4 Visual Requirements	3.0%
Relay Coils*	Inductance and Electrical Breakdown	1.0%
Misc. Completed Electrical Apparatus	Resistance	.5%

The process average is commonly determined by summarizing the results of the first samples inspected during a representative period and may usually be obtained if there has been a previous inspection with associated records. In case suitable records are not available, an approximation may be made on the basis of an examination of a number of random samples selected from product of current manufacture. This will be a tentative figure and may require revision when data accumulated from the operation of the Double Sampling Plan are available.

1.3 Issuance of the Inspection Layout—Fig. 2

After the AOQL value has been established, definite instructions in the form of a Sampling Layout (See Fig. 2) should be provided for the use of the inspector. The layout should contain a list of the inspection items for which inspection is required. It should also contain a copy of the sampling table selected, a description of the material to be inspected, AOQL value, process average and other information which is of importance either in using or in maintaining the Double Sampling Plan.

* This is a process check for these requirements which is supplemented by another sampling inspection after assembly.

HL 3346-R (5-40)

LAYOUT FOR STATISTICAL SAMPLING INSPECTION LAYOUT NO. X

ISSUE NO. X DATE X

MATERIAL INSPECTED LAMPS CODE OR P.P. NO. X

MATERIAL FROM OPERATING DEPT. NO. XX PROCESS AVERAGE CLASS. .31-.60% A.O.L. 1.5

OPERATING DEPT. OPERATIONS Assembly

FOR USE BY INSP. SECT. X AUTHORIZED AND APPROVED BY X APPROVAL DATE X

Sampling Table					INSPECTION OPERATIONS
Lot Size	1st Sample	2nd Sample			
	SS	AN	Add	SS	AN
1-15	All 0	-	-	-	-
16-50	16 0	-	-	-	-
51-75	23 0	11	34	1	1
76-100	26 0	14	40	1	1
101-200	31 0	18	49	1	1
201-300	38 0	27	75	2	2
301-400	36 0	41	80	2	2
401-500	39 0	46	85	2	2
501-600	40 0	49	89	2	2
601-800	46 0	74	120	3	3
801-1000	47 0	78	125	3	3
1001-2000	49 0	91	130	3	3
2001-3000	55 0	110	165	4	4
3001-4000	55 0	115	170	4	4
4001-5000	55 0	120	175	4	4
5001-7000	60 0	155	215	5	5
7001-10000	60 0	160	220	5	5
10001-20000	65 0	165	225	5	5

Gage for overall length and distance from end of terminal to end of bulb.

MATERIAL TO BE USED ON X

PROCESS AVERAGE ACTUAL RECORDS DATED

FROM .557 TO 7-6-40 FROM 12-28-40 FROM TO FROM TO

LAYOUT ISSUED BY X

APPROX. ANNUAL OUTPUT X USUAL LOT SIZE 4000 EST. HRS. PER YEAR 300

DELIVERY CONTINUOUS INTERMITTENT IRREGULAR NON-ACCEPTABLE LOTS DETAILED REJECTED EITHER

O.L.O. SAMPLING SCHEME USUAL LOT SIZE 2500 SAMPLE SIZE 100 A.O.L. 1.5 PROCESS AVERAGE .709

REMARKS Reissued to place in proper process average class.

NOTES BY STATISTICAL DEPT. CHECKED BY X DATE X

Fig. 2

1.4 Records

This section contains a description of the running records and clerical operations which are used for supervisory control. The records are "Lot by Lot Record of Statistical Sampling Inspection", and "Summary of Results of Inspection", shown in Figs. 3 and 4, respectively.

MD 870-H
(6-39)

LOT BY LOT RECORD OF STATISTICAL SAMPLING INSPECTION LAYOUT X

INSPECTION SECTION X

MATERIAL INSPECTED LAMPS

INSPECTION GAGE FOR OVERALL LENGTH AND DISTANCE OPERATIONS FROM END OF TERMINAL TO END OF BULB.

OPERATING DEPT. OPERATIONS ASSEM. SPER DEPT. NO. X

LIST OF DEFECTS IN 1ST SAMPLE

NO. CHANGE PLACES

LENGTH UNDERSIZE
LENGTH OVERSIZE
BULB UNDER MIN.

AOQL 1.5
SUMMARY PERIOD WEEKLY

OTHER WORKING CHECK NUMBER INSPECTOR'S INSPECTION OF LOT PARTS, REJECTS, ETC. GROUP NUMBER

1944	YEAR	DATE	CODE OR P. NO.	LOT SIZE	1ST SAMPLE		2ND SAMPLE		TOTAL DETAILED		LENGTH UNDERSIZE	LENGTH OVERSIZE	BULB UNDER MIN.	P
					SS	DEF	TOTAL	DEF.	PARTS	DEF.				
1	5-5	C-2	4615	55	1	175	3				1			P
2	"	2-F	1750	49	0									P
3	"	E-1	1425	49	0									P
4	"	2-Y	4440	55	0									P
5	"	2-F	1975	49	0									P
6	5-6	E-1	2225	55	1	165	4				1			P
7	"	C-2	3570	55	0									P
8	"	K-1	3280	55	0									P
9	"	2-U	1275	49	0									P
10	"	2-Y	7140	60	2	220	2				1	1		P
11	5-7	2-Y	11865	60	0									P
12	"	E-1	2250	55	0									P
13	"	K-1	2110	55	0									P
14	"	2-F	1400	49	0									P
15	5-8	2-Y	5400	55	1	215	3				1			P
16	"	K-1	2340	55	0									P
17	"	E-1	5860	60	0									P
18	"	2-U	7155	60	1	220	2				1			P
19	"	2-Y	980	49	0									P
20	5-9	K-1	1740	49	0									P
21	"	2-Y	2645	55	0									P
22	"	E-1	5645	60	0									P
23	"	B-2	2495	55	0									P
24	"	2-U	4575	55	2	175	5				2			P
25	"	2-F	1160	49	0									P
26	"	2-U	1020	49	0									P
27	5-10	E-1	6695	60	0									P
28	"	2-F	1525	49	1	130	1				1			P
29	"	B-2	4020	55	0									P
30	"	2-U	6240	60	1	215	3				1			P
31	"	K-1	2915	55	0									P
32	"	2-Y	1275	49	0									P
33	"	2-U	4575	55	0									P
34	TOTAL		114225	1725	10	2789	33				4	2	4	P(U)
35														
36														
37														
38	REMARKS:													
39	(1) LOT REJECTED - SUBMITTED FOR REINSPECTION AFTER REPAIR													
40														

Fig. 3

The Lot by Lot Record of Statistical Sampling Inspection—Fig. 3

On this form the inspector records the results of his inspection at the time of his observation. An examination of Fig. 3 will indicate how the form is filled out.

M.D. 870-J (7-37) Weekly SUMMARY OF RESULTS OF INSPECTION INSPECTION SECTION X

MATERIAL INSPECTED LAmps FREQ. OF DEF. X

OPERATING OPERATIONS Assemble AQL 1.5 %

INSPECTION OPERATIONS Gage for Length and Dist. from Term. to End of Bulb UPPER LIMIT LINE .93 %

PA .557 ? LIMIT LINES BASED ON 1640 PARTS LOWER LIMIT LINE .59 %

SS = SAMPLE SIZE SS + D = TOTAL SAMPLED PLUS AMT. DETAILED PER CENT DEFECTIVE

DATE	LOT	TOT. IN LOTS	1ST SAMPLE	TOTAL INSP.	%	%	%	%	%	%	%	%	%	%	%	%	%	%	
16	11	18	25	2-1	7	15	22	3-1	9	16	23	30	37	44	51	58	65	72	
SS	DEF.	SS	DEF.	SS	DEF.	SS	DEF.	SS	DEF.	SS	DEF.	SS	DEF.	SS	DEF.	SS	DEF.	SS	DEF.
16	11	57345	266	12	4447	114	3.2	4.5	7.7	0	1.4								
11	17	81430	947	21	2173	53	2.7	0	3.7	8.7	2.1								
18	13	90295	975	13	3402	141	2.2	1.7	3.9	0	1.3								
25	24	82455	1262	20	2502	44	2.3	0	3.9	9.4	1.6								
2-1	15	82915	811	8	2649	41	1.6	7	2.5	0	1.0								
7	26	96710	1434	9	3227	52	2.4	9.3	3.3	0	1.2								
15	27	96175	1477	20	3049	247	2.1	5.1	2.9	0	1.4								
22	28	107371	1565	23	3462	48	3.2	0	3.2	0	1.5								
3-1	19	102095	1700	24	3235	55	3.2	0	3.2	1.3	1.4								
9	24	102693	2115	25	4450	118	3.5	8	4.3	7.8	1.2								
15	28	104741	2277	13	3552	15	2.7	0	2.7	0	1.5								
22	26	104140	2319	16	2778	15	2.7	0	2.7	0	1.4								
29	26	105916	2226	16	2727	15	2.5	0	2.5	0	1.5								
4	24	105725	2193	16	2452	16	2.2	0	2.2	0	1.5								
12	21	97425	2520	12	3252	20	3.2	0	3.2	0	1.4								
19	29	96205	2314	11	2632	12	2.7	0	2.7	0	1.7								
26	23	112975	2166	26	3317	32	2.6	3	2.9	0	1.9								
5-2	21	87150	2274	9	2704	10	3.1	0	3.1	0	1.3								
16	22	114225	1725	11	3240	34	3.2	0	2.8	4.0	1.4								
17	21	132950	2741	12	2072	18	2.2	0	2.2	0	1.7								
24	41	127070	3253	4			3.4	0	3.4	0	1.2								
31	20	82385	1557	6	1723	7	2.1	0	2.1	0	1.9								
6	21	27525	1799	4	1265	5	2.1	0	2.1	0	1.2								
14	28	12525	2222	9	2492	9	2.0	0	2.0	0	1.1								
21	25	152225	2622	13	3223	13	2.1	0	2.1	0	1.2								
28	24	104830	2020	11	3225	12	2.2	0	2.2	0	1.4								
TOTAL																			

Fig. 4

The Summary of Results of Inspection—Fig. 4

This form is kept with the inspection layout and the Lot by Lot Records. Entries are made as indicated on Fig. 4. Clerical operations involved in making the necessary computations are explained in the following paragraphs.

1.41 PA (Process Average)

The Process Average should be computed at least once every six months, and more frequently when conditions warrant. Only data

accumulated since the last computation should be used. When it is known that the quality of the product has changed significantly during the period, use only the data collected since the change.

Record the results of all process average computations and the periods covered by them in the space provided on the sampling layout.

1.42 Periodic Totaling of Lot by Lot Record and Posting on Summary of Results Form, Fig. 4

The following columns on the Lot by Lot Record should be totaled at intervals, and may, for contrast, be marked in red:

<i>No. of Lots</i>	<i>Lot Size</i>	<i>1st Sample SS</i>	<i>1st Sample Def.</i>	<i>2nd Sample Total</i>	<i>List of Defects in 1st Sample Total by Columns</i>
X	X	X	X	X	XXXX etc.

Totals after approximately 20 entries are generally considered satisfactory. The required totals are then posted to the Summary Form, Fig. 4.

1.43 Per Cent Defective

The purpose of this figure is to show the average quality of the product as received by the inspector during the period covered and is obtained by dividing the total number of defectives found in first samples by the total number of articles inspected in first samples, and multiplying by 100. Only the results of the first samples are used, in order to accord equitable treatment to all lots.

1.44 Control Chart

The per cent defective is plotted on the graph at the right of the summary form (Fig. 4). Control Limit Lines are drawn around the process average to indicate the variation that may be expected due to random sampling. These control limits are determined by the following formulae³:

$$\left. \begin{array}{l} \text{Upper Control Limit} \\ \text{for fraction defective} \end{array} \right\} = \bar{p} + 2 \sqrt{\frac{\bar{p}(1-\bar{p})}{n}}$$

$$\left. \begin{array}{l} \text{Lower Control Limit}^4 \\ \text{for fraction defective} \end{array} \right\} = \bar{p} - 2 \sqrt{\frac{\bar{p}(1-\bar{p})}{n}}$$

³ The considerations involved in the establishment of control chart limits are discussed in ASA Standards Z1.1-1941 and Z1.2-1941, "Guide for Quality Control and Control Chart Method of Analyzing Data". In this case, 2-sigma limits have been chosen. For this particular application within the manufacturing plant over a period of years, this choice has appeared to strike an economic balance with respect to the net consequences of two kinds of "errors" that may occur in practice; namely, looking for trouble that does not exist and not looking for trouble that does exist.

⁴ If this result is negative, the lower control limit is to be taken as zero.

Where \bar{p} = Process average fraction defective

n = Average number of articles in first samples inspected during the summary period.

For example, the records for a typical period of 10 weeks might show the following:

Total number of articles inspected in first samples = 16,400

Process average fraction defective = \bar{p} = .00557 or .56%

Thus, $n = \frac{16,400}{10} = 1640$ articles

Hence:

$$\text{Upper Control Limit} = .00557 + 2 \sqrt{\frac{.00557(1 - .00557)}{1640}}$$

$$\text{“ “ “} = .00557 + .00368$$

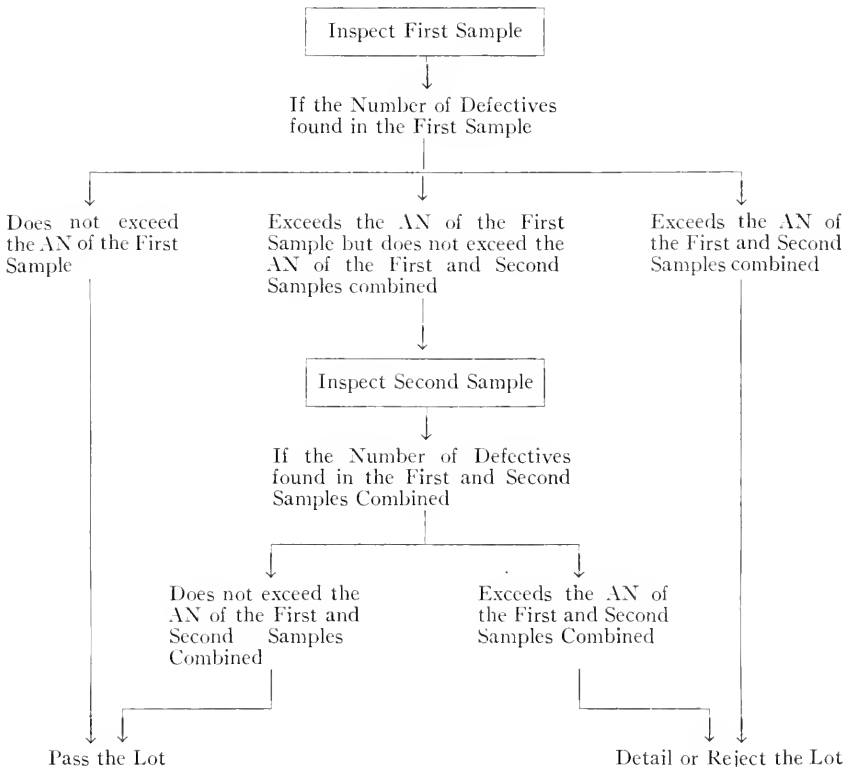
$$\text{“ “ “} = .00925 = .93\%$$

$$\text{Lower Control Limit} = .00557 - .00368$$

$$\text{“ “ “} = .00189 = .19\%$$

2. APPLICATION OF THE DOUBLE SAMPLING PLAN BY THE INSPECTOR

The following flow chart illustrates in sequence the basic steps involved in the inspection of a lot.



An example of the operation of this chart is shown below:

<i>Example:</i>	
AOQL	= 1.5%
Process Average	= .56%
Lot Size	= 4615

On consulting the sampling table on the layout, which is information obtained from the table for AOQL = 1.5%, Process Average Column .31—.60% (see Fig. 1), it will be found that for a lot of 4001-5000 parts the following sample sizes (SS) and allowable numbers of defectives (AN) are shown:

<i>Lot Size</i>	<i>First Sample</i>			<i>Total Sample</i>	
	<i>SS</i>	<i>AN</i>	<i>Add.</i>	<i>Total</i>	<i>AN</i>
4001-5000	55	0	120	175	4

This means that for the first sample 55 parts should be selected and completely inspected for all items covered by the Sampling Layout. In order that the per cent defective may be accurately determined for control purposes, a *complete inspection* of the first sample must be made regardless of how defective it may be. If five or more defectives are found in the sample of 55 parts, the lot should be rejected or detail inspected, or otherwise disposed of as shown on the layout.

If no defectives are found in the 55 parts, the lot should be passed.

If one, two, three, or four defectives are found in the 55 parts, the second sample of 120 additional parts should be selected.

In the combined sample of 175 parts, a total of four defectives is allowed. if a total of five defectives is found before all of the 175 parts are inspected, sampling should be discontinued and the lot disposed of as indicated on the layout.

If less than five defectives are found in the combined sample of 175 parts, the lot should be passed.

2.1 *Counting the Lot Size*

The determination of the lot size may be made by weighing methods or careful estimates. It has been found in practice that an estimate which is within 20% of the true value of lot size is satisfactory for sampling purposes.

2.2 *Counting the Sample Size*

Since the relation between corresponding Lot Sizes and Sample Sizes for a particular AOQL is not linear the same order of accuracy of count does not prevail. If, in using a given sampling table, a sample smaller than that prescribed is taken, the result is to increase the AOQL, and if a sample larger than that prescribed is taken, the result is to decrease the AOQL and increase the cost of inspection.

Counting becomes a simple matter when articles are handled in compart-

ment boxes or when the gage or testing device provides for automatic count. Regardless of what method of counting is used there should be agreement between the size of sample selected and sample size indicated in the sampling table.

2.3 *Reinspection of Rejected Lots*

In order to guarantee the protection promised by a particular Double Sampling Plan it is required that a rejected lot be completely cleared of all defects. The rejected material should be repaired and returned for reinspection as one lot. It should then be reinspected for all inspection items using the sample size that would normally apply to a new lot of the same size. If a defect is found during reinspection it is evident that proper repair or sorting has not been accomplished. Such a lot should, of course, not be considered acceptable until all defects are removed.

In the Lot-by-Lot Record, the results of resampling of rejected lots are recorded on a separate line and the entry circled or otherwise identified so that it will not be included with the results of first samples on the Summary Form.

3. SUPERVISION OF THE DOUBLE SAMPLING PLAN

In order that maximum advantage may be gained from the use of Double Sampling Lot Inspection it is necessary that attention be given to the topics listed below. Upon proper attention to these factors depends the effectiveness of the Plan.

3.1 *Changes in AOQL*

There is no assurance that the value originally selected for an AOQL will continue to be the most satisfactory in view of changing factors relating to the product, such as:

3.11 Changes in design of the product or changes in the requirements for inspection items may increase or decrease the trouble caused by the acceptance of defective parts and therefore will occasion a review of the AOQL value.

3.12 New methods of manufacture that change the difficulty and therefore the cost of making a product will necessitate a reconsideration of the AOQL value.

3.13 An excessive number of complaints or other reports of difficulty from succeeding stages of manufacture or from customers may indicate too large an AOQL.

3.14 If no significant changes such as those mentioned above exist and there are repeated lot rejections, it would appear that quality is unsatis-

factory. However, it should be determined whether or not succeeding operations can possibly tolerate more defectives than they are actually receiving and, if this is the case, the AOQL may profitably be increased.

3.2 *Changes in Process Average*

The economy of the sampling plan tends to decrease when the level of quality of the product shifts outside the range of process average on which the layout was based. The sampling table on the layout should ordinarily be changed whenever the process average shifts from one range to another. However, before reissuing the layout, the reason for the shift should be determined. If the process average has been reduced, an attempt should be made to make the change permanent; or if it has been increased, the cause should be eliminated.

3.3 *Interpretation of the Control Chart on "Summary of Results of Inspection" Form*

It is very important to review the Control Chart of per cent defective (Fig. 4) frequently as it is an index of the success of the sampling plan. Not all fluctuations of the per cent defective are significant. Even though the quality of the product is controlled, the results of sampling inspection may produce fluctuations in the indicated per cent defective. These variations are measured by a simple control chart on the "Summary" form which employs control limits for values of per cent defective. As long as the plotted points of the per cent defective remain within control limits the fluctuations are no greater than may reasonably be expected from a uniform manufacturing process. However, if a point goes above the upper control limit, the cause may be defective workmanship, defective raw materials, or even a change in the severity of inspection. If a point goes below the lower control limit, the cause may be an improvement in quality or a change in the definition of a defect through misinterpretation or changes in inspection equipment or method of check. If the curve of the plotted points hugs either limit line or shows a definite trend toward one side or the other, a significant change in the quality of the product is indicated.

In order to achieve control of the quality of a manufactured product, direct and immediate action must be taken in order to stem unfavorable trends. The presence or absence of a satisfactory quality level may be detected by means of inspection, but such a level can only be originated and maintained by adequate manufacturing methods and equipment in the hands of a quality-minded producing personnel.

3.4 *Changes in the Definition of a Defect*

Either laxity or severity of inspection may cause the "reported" per cent defective to show significant changes even though the actual per cent defec-

tive is unchanged. This may result from a change in the definition of a defect; that is, the same condition may at times be considered defective and at other times acceptable. This happens most frequently in border-line cases. To avoid such variations it is necessary that the condition that constitutes a defect be clearly defined and strictly followed in all inspections.

3.5 *The Abnormal Existence of One Kind of Defect*

When the sampling scheme includes the inspection for several different requirements, the Allowable Number may at times be exceeded because of one kind of defect only. In other words, the lot would be satisfactory if this one kind of defect did not exist. If the same defect persists for several lots, it should receive definite supervisory attention. If substantial improvement is not feasible, it may be convenient to remove the inspection item to a separate sampling layout.

3.6 *Abnormal Distribution of Defectives*

Occasionally there may be reason to believe that a group of parts submitted for inspection is not uniform in quality throughout, that is, not a true lot as defined in the early part of the paper. Such a group should be divided into homogeneous sections and each section sampled separately. However, when this happens, subsequent lots for sampling purposes should be similarly subdivided, that is, they should be confined to the output of one source at a time; for example, one machine, one operator, or one batch of material, etc., based on one system of causes, so that control of quality at each source may be applied, and the consumer protected from receiving spotty product.

In addition to the specific steps followed in establishing and operating a sampling plan it must always be remembered that, since relatively important decisions concerning the acceptance of product hinge upon the results of an examination of a small group of parts, inspection must be conscientious and accurate. In order to guarantee the order of protection promised by the sampling plan, the results of inspection and the prescribed procedure for disposing of individual lots must be regarded with thorough respect.

Entropy

By KARL K. DARROW

MANY of the important ideas of physics are of such recent birth that if they still seem hard to grasp, it may be contended that the world has not yet had the time to assimilate them. Of entropy this cannot be said; with its centenary almost upon us, entropy is ancient compared with most of the concepts which baffle the student today. Yet an aura of mystery seems to envelop it still, and two other things inseparably joined to it: the scale of temperature called absolute, and the Second Law of Thermodynamics. One is driven to wonder why the three of them resist the understanding so tenaciously, and certain reasons are not hard to find. Thus, to speak of the three as "joined together" is too weak, for it implies that they can at least be taken in a certain order for didactic purposes, the student ascending from the one to the next and finally to the last. Actually they are much too tightly interlocked for this, a sort of trinity one and indivisible, which must be apprehended as a whole if ever to be properly grasped at all. Again, the Second Law has been expressed in many different ways, and it is one of the oddest things in science to see how various authorities can claim that the law is obeyed absolutely without exception, while they themselves cannot agree how to state it. A further cause of trouble lies in the unlucky boundary between chemistry and physics, which nowhere harms these sciences more than in the study of entropy. Like the worst of the old-fashioned boundaries of Europe, it wanders capriciously across the natural lines of intercourse and trade, cutting off the traditional chemist from the origin and development of some of his most valuable ideas, cutting off the traditional physicist from some of the finest verifications of the thought of his fore-runners. It will be the principal object of this paper to dwell on these verifications, abolishing the barrier so far as may be feasible.

First to illustrate how the three ideas are tangled up together, I give one of the most useful of the definitions of entropy: *when a system passes in a reversible way from one to another state, at a constant absolute temperature T , its change of entropy ΔS is equal to the heat Q which it absorbs, divided by T .* That both the entropy and the absolute temperature have slipped into this definition is all too obvious; as for the Second Law, it lurks underneath the phrase "in a reversible way." Quite evidently we are invited to master all the three in a single mental operation, but quite as evidently this is impossible. A breach must somehow be made in this hard and unified surface,

and the best of scaling-ladders appears to be the ideal gas, as everybody has used it for the purpose.

We therefore receive the definition of the "ideal gas": a substance whereof (a) the temperature remains unchanged when the gas is given and seizes the chance of expanding without any hindrance into a vacuous space; and (b) the pressure varies inversely as the volume, so long as the temperature remains unchanged. Now rather than being an aid to enter the citadel, this definition appears to presume that we are in the citadel already, since the word of "temperature" is all too prominent in it. But the word comes up only in the phrase "... temperature remains unchanged ..."; so nothing more is implied, than that the onlooker knows how to recognize whether temperature is changing or staying the same. This ability can be his, whether or not he knows about the scale called absolute; and so the definition implies nothing about the scale.

The definition would be an idle collection of words, were there not actual gases conforming to it so nearly, that at least for a time they may safely be taken to conform to it exactly. All gases in fact approach conformity, as the density lessens; and with helium and hydrogen especially, the approach is already close while the density is still so high that there is no trouble at all in using them as thermometers. Now, to use an ideal gas as a thermometer means simply this: P being the pressure of the gas and V its volume and n the quantity of the gas measured in moles, there is the equation,

$$PV = nRT \quad (1)$$

which is a mixture of a new definition and a theorem. The part which is definition is, that the temperature called absolute is taken to be proportional to the product PV . The part which is theorem is, that if at the same temperature we compare the product PV for equal numbers of moles of various gases, its value is the same. What is denoted by R in equation (1) is a universal constant. Its value is 1.985 in the customary units, which are calories per degree per mole. Since now the degree of temperature has appeared in this discourse, I recall that its value is fixed by the convention that there are one hundred degrees from the freezing to the boiling point of water; but on this I need not dwell.

It is tacitly assumed that nothing in this definition will ever clash with the threefold simultaneous definition of temperature and entropy and Second Law, should we ever arrive at it. Taking this for granted, and taking advantage of the breach which has thus been made in the formerly impenetrable surface of our definition of entropy, we now attack the concepts of "state" and "reversible way."

The usual way of dealing with "state" is to say that it is determined completely by any two of the three variables P , V , and T , which are inter-

connected among themselves by what is called an "equation of state." This takes for granted that one knows what kind of substance one is speaking of, how many moles there are of it, and which phase it is in; for the statement is valid not only for gases but also for liquids, and even (under certain restrictions) for solids. If two or three phases are coexisting, precautions must be taken. The statement is not valid for mixtures of substances which differ; but there is doubt as to just how much it takes to constitute a difference, and isotopes of a single element are usually considered to be the same.

Now let us envisage two states which differ in temperature but are the same in pressure. P is to stand for the common value of pressure, T_0 for the lower and T_1 for the higher of the temperatures. For the utmost in simplicity at the beginning, the substance shall be an ideal gas, and moreover a gas of which the specific heats do not depend upon the temperature; any noble gas under ordinary conditions approaches very closely to these stipulations.

One may operate the transition from (P, T_0) to (P, T_1) in the manner which follows: Let the gas be heated from T_0 to T_1 while the volume of its container remains the same. Its pressure will have gone up meanwhile; let this situation be remedied by piercing a hole through the container wall, into an evacuated chamber prepared in advance of just the right dimensions, so that after the "free expansion" the pressure of the gas will be down again to P . The temperature will still be T_1 , for that is one of the qualities of the ideal gas.

Or one may operate the transition in the manner which follows: Let the container be made in advance with a movable wall, say a piston-head against which an outer pressure P —it might be that of the atmosphere—is steadily pressing. Let the gas be gradually heated: as its temperature rises, the piston-head glides gradually outward, increasing the volume of the container at such a rate that the pressure of the gas always remains the same and equal to P . The process is to be stopped when the temperature reaches T_1 .

These, then, are two very different ways of carrying through the transition; and the reason for bringing them in is to elucidate the words "in a reversible way" which occur in the phrase defining entropy. The former way includes a process which is spontaneous, rapid, turbulent, explosive; nothing can inhibit it when the piercing of the hole creates the opportunity. The latter way is gradual, languid, crawling, always on the verge of stopping, would instantly stop if the inflow of heat should cease, would reverse its trend if the inflow should be turned into outflow. The former way includes a process during which the pressure of the gas is ill-defined or not defined at all, for the gas is spurting through the hole and reverberating in the chamber

formerly empty. During the entire latter process, if it be gradual enough, the pressure of the gas is definite, and related to V and T by the equation (1). The former is an irreversible way of effecting the transition. The latter is *the reversible way* of effecting the transition.

As the heat flows into the gas, its entropy mounts up. Since the temperature is meanwhile changing, we must mentally subdivide the incoming heat into dribblets dQ , during the inflow of each of which T remains about the same. The corresponding dribblets of energy are given by dQ/T , the total change in entropy due to inflow of heat is given by $\int dQ/T$ integrated from beginning to end of the inflow.¹ By the former way the integral is $\int (C_v/T)dT$ or $C_v \ln(T_1/T_0)$, by the latter way the integral is $\int (C_p/T)dT$ or $C_p \ln(T_1/T_0)$. The two are not the same. Now we see why the phrase "in a reversible way" was necessary in the definition of change-of-entropy. But for that phrase or something similar, we should now have no definition. But having accepted the phrase, we are invited and required to write,

$$\Delta S = \int (C_p/T) dT \quad (2)$$

for all transitions of a single substance within a single phase; ΔS signifying the change of entropy, and the use of C_p implying that the conditions are those under which specific heat at constant pressure is properly measured: the pressure of the substance being definite, nothing turbulent or gusty or explosive happening within the substance, and an equal pressure bearing down upon it from the outer world.

We have now the necessary and complete statement for the variation of entropy with temperature, pressure remaining the same; but it has to be supplemented with a statement for the dependence of entropy on pressure, T remaining the same. For this and other purposes, let us return to the irreversible passage between (P, T_0) and (P, T_1) —the passage, rather, of which one stage is reversible but the other not. During the reversible stage, the gain of entropy is $\int (C_v/T)dT$. This falls short of the gain of entropy incurred along the other route as given by (2). However the other route leads reversibly all the way to the goal, while the reversible part of this one brings us only a part of the way, leaving us with the irreversible expansion still before us. By assuming that the remainder of the total gain of entropy demanded by (2) is made up during the irreversible expansion, we rescue the concept of entropy. Now to save and establish the concept

¹ It is often said or implied that this formula should not be used unless the process is fully reversible, in the sense that the inflow of heat occurs from a reservoir of temperature identical with that of the gas. As no such precaution is taken when specific heats are measured, and as measurements of specific heat are commonly used for establishing values of entropy, I assume that the limitation is needless.

of entropy, to make it a definite property of the state of a substance, is one of the offices of the Second Law.

It is therefore a part and a consequence of the Second Law to affirm that when an ideal gas undergoes a free expansion, it experiences a gain of entropy despite the fact that it receives no heat from the world without! Nor is the affirmation confined to ideal gases; it would be true of any substance, though in general a free expansion would be attended with a change in temperature. Nothing, therefore, could be more wrong than to repeat our first definition of change-of-entropy with the words "in a reversible way" left out.

One now begins to see why the concept of entropy is so much harder to receive than that of energy. Every scientist is accustomed by now to the "conservation" of energy: whereby it is meant that if the energy of a system rises or falls by any amount, it is because there has been an inflow or an efflux of just that amount from or into the outer world. Nothing of the sort can be said of entropy, of which we have just seen that it may vary even within a system which is having no transactions at all with the outer world. One may not speak of the conservation of entropy excepting under the sharp and severe restriction that all of the processes in the system *and* in the outside world are reversible: and "reversible" must be used in the full sense adumbrated in a previous footnote, whereby no transfer of heat is reversible unless the body whence it comes and the body to which it goes are of identical temperature. Yet nothing of all this contradicts the assertion that entropy and energy are, both of them, uniquely determined functions of the state of a system—functions, therefore, of any two of the three variables P and V and T , for substances of a single kind in a single phase.

Since the equating of entropy-change to inflow of heat divided by temperature is something that positively must not be done for an irreversible process, we must seek other ways to assess it.

One such way has already been stated. If it is possible to start from a particular state, and thence to arrive by reversible ways at both the beginning and the end of the irreversible process in question, all the necessary knowledge is at hand; for now by integrating dQ/T along the two ways we find two quantities, of which the difference is the entropy-change desired.

Applied in the special case which we have been considering, this method has given

$$\Delta S = (C_p - C_v) \ln (T_1/T_0) \quad (3)$$

not, however, a useful expression as yet, since it contains a quantity (T_0) which does not figure at all in the irreversible process in question—a process which, I recall, is the free expansion of one mole of ideal gas, at a constant temperature T_1 , from a higher pressure and lower volume which we will denote by P' and V' , to a lower pressure and a higher volume which we will

denote by P and V . Remembering (1) the equation of state of the ideal gas, and applying it to the reversible heating at constant volume which preceded this expansion, we find

$$T_1/T_0 = P'/P \quad (4)$$

and so,

$$\Delta S = (C_p - C_v) \ln (P'/P) \quad (5)$$

for the entropy-change incurred when one mole of ideal gas expands at uniform temperature so that its pressure falls from P' to P . I do not have to state the temperature, since it has vanished from the equation. I do not have to say that the expansion is irreversible, for if there be such a thing as entropy at all, its alteration depends only upon its values in the initial and in the final state, and not on the manner in which the system has made the passage from initial to final. I ought, however, to recall that we are still supposing a gas of which the specific heats do not depend upon temperature, nor in fact upon any variable whatsoever.

Now we have an expression—equation (5)—for the way in which entropy changes with pressure at constant temperature, and another—equation (2)—for the way in which entropy changes with temperature at constant pressure. We may combine them to get the change of entropy occurring when the gas proceeds, by whatever route, from an initial state (P_1, T_1) to a final state (P_2, T_2). This is,

$$S_2 - S_1 = C_p \ln(T_2/T_1) - (C_p - C_v) \ln(P_2/P_1) \quad (6)$$

which, by stripping off the subscripts 2, and gathering into one term I all of the terms containing the subscripts 1, may be written,

$$S = C_p \ln T - (C_p - C_v) \ln P + I \quad (7)$$

the expression, for a gas of the special type stated, of entropy as a function of absolute temperature and of pressure. The quantity I is an "additive constant" which will turn out to be one of the major topics of this paper.

All this way we have come without invoking the First Law of thermodynamics, and we might even go further without its aid! But there is no point in deferring it longer, and I wish to be able to convert (7) into a more familiar form by replacing $(C_p - C_v)$ with the constant R of the equation-of-state of the ideal gas. To do this I return to the irreversible process which has so long engaged our attention; the free expansion of the gas from the higher pressure P' to the lower pressure P , its temperature remaining the same. I seek a reversible way of conducting the expansion from the same beginning to the same ending under the same condition of steady temperature. A reversible way of going between the extremes we have

indeed already found, but it involves a retracing of our steps: the cooling of the gas to a lower temperature at a constant volume, followed by the heating of the gas to the original temperature at the constant pressure. We wish a forward-going reversible way, and such a one can be found. It is necessary to have the container built with a frictionless piston-head for one wall, and to bear down upon this from without with a pressure always nicely calculated to be equal to the internal pressure of the gas. If under this condition the piston-head is gliding slowly outward it will continue so to glide, and the gas will expand in the gradual, languid, crawling manner, with its internal pressure always definite—the manner which we call “reversible.” All that is now required is to know the amount of heat which enters the gas during this process, so that we may divide it by T and so assess the entropy-change. It is from the First Law that we get this information.

The First Law is to be spoken in the form

$$\text{energy-gain} = \text{“heat in”} \text{ less “work out”}$$

and written in the form

$$\Delta U = \Delta Q - \Delta W \tag{8}$$

the symbols fitting the words in the way which is obvious.

For an ideal gas, the energy U is independent of pressure or volume, depending on the temperature alone. The reader may or may not take this as a matter of course, but it will be proved later on. We are considering an isothermal expansion, and therefore ΔU is zero, and the problem of evaluating ΔQ is that of evaluating ΔW . Now the “work out”—the work done by the gas upon the outer world—is equal to the pressure bearing down upon the piston-head from the outer world, multiplied by the area of the piston-head and the distance through which it advances. The last two factors multiplied together give the gain in volume of the gas, ΔV ; and without a moment’s hesitation one usually puts for the first factor the symbol P signifying the pressure of the gas. However, it is wise to hesitate just long enough to realize that by so doing one assumes the *reversible* expansion with all the attributes set forth above. For an irreversible expansion ΔW would not be equal to $P\Delta V$, but less. But assuming the reversible expansion, and remembering that P is not independent of volume as in these last few lines I have tacitly assumed, we find

$$\begin{aligned} \Delta W &= \int P dV = RT \int (1/V) dV \\ &= RT \ln (V/V') = RT \ln (P'/P) \end{aligned} \tag{9}$$

the unprimed symbols referring to the final state of the expanding gas and the primed symbols to the initial state. Now identifying ΔW with ΔQ , and dividing it by T to get the change-of-entropy, we have for the very quantity ΔS which figured in equation (5) a second expression, *viz.*

$$\Delta S = R \ln(P'/P) \quad (10)$$

where now R stands in place of $(C_p - C_v)$. We make the substitution into (7), and arrive at our next-to-final form for the entropy of the ideal gas of constant specific heats:

$$S = C_p \ln T - R \ln P + I \text{ (one mole)} \quad (11)$$

I pause to mention that since for any gas PV/T is measurable and so is also $(C_p - C_v)$, the rightness of our assumptions may be tested by ascertaining whether for gases nearly ideal, the one—which for an ideal gas is R —and the other are nearly equal. This is so; and if we wish to pick out a special one among the assumptions for which this shall constitute a special test, then we may set down as having been particularly proved the assertion, that the energy of an ideal gas depends upon its temperature alone and not upon its pressure nor its volume.

For quite some time I have been referring to a single mole of the gas in question; but for an odd and probably an unexpected reason, it is going to be desirable to make an explicit broadening of these equations to the general case of any number n of moles. The broadening required for (11) is so simple and trite as to seem not worth the doing: we have simply to multiply every term of (11) by n , and so obtain

$$S = nC_p \ln T - nR \ln P + nI \text{ (} n \text{ moles)} \quad (12)$$

But now let us translate this into an expression for S as a function of volume and temperature, by use of the fact that P is nRT/V , and the further fact that R is $C_p - C_v$. We come upon the astonishing equation,

$$S = nC_v \ln T + nR \ln V - nR \ln(nR) + nI \quad (13)$$

astonishing because the terms to the right of $nR \ln V$ are not reducible to n multiplied into a constant, but involve a more intricate function of n . Perhaps, after all, we ought not to have taken the simple recourse of broadening (12) by multiplying n into every term of (11) including the last one? Actually it is quite all right; the additive constant in (12) is truly proportionate to the number n of moles; that in (13) is the more intricate function of n which we have just derived.

In Fig. 1 there is shown a "phase-diagram" appropriate to a substance of a single kind, capable of existing as a gas and as a liquid and as a solid. Pressure and temperature are the coordinates along the vertical and hori-

zontal axes, but no coordinate-scales are shown, and no attempt has been made to shape the curves in exactly the manner correct for any particular substance, since all that matters here is the general idea. Envisage any point (P, T) in the area "gas," lying just off the curve which separates that area and the other one marked "solid." This is the point—I will call it the "point of interest"—for which we are to obtain two expressions for entropy S arising from different sources, and find an important result by comparing the two so obtained.

One of the two is of course the right-hand member of (12). It may create surprise that one should be treating the gas as ideal, under conditions where the slightest fall in temperature or rise in pressure would con-

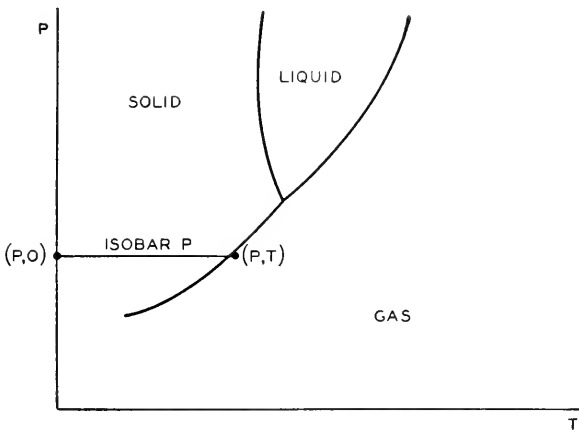


Fig. 1

dense it. The approximation, however, may still be a good one, and if it is not close, the equation of state of the actual gas may be used in place of (1).

To form the other expression, we commence at the point $(P, 0)$ where the isobar P which traverses the point of interest reaches the vertical axis, and call the entropy there by the symbol $S(P, 0)$. We proceed along the isobar toward the point of interest, building up the integral $\int (C_p/T)dT$; since we remain in the area called "solid," it is C_p of the solid which concerns us, and we may mark it so. Just before the isobar passes over the curve dividing solid from gas, the entropy arrives at the value

$$S(P, 0) + \int_0^T (C_p^{sol}/T) dT$$

but this is not yet the value at the point of interest, for the "divide" is yet to be crossed. At the crossing of the divide a certain amount of heat is

absorbed: denote it by L for one mole. If the crossing of the divide is a reversible process, the entropy of the substance goes up by L/T as it turns from solid to gas.

Is the crossing of the divide a reversible process? It is indeed, and that is why phase-diagrams are constructed. Think of the substance enclosed in a container with frictionless piston-head, equal pressures P bearing upon the piston from the world without and from the substance within, and the whole affair at temperature T . If the point defined by P and T lies exactly on one of the curves which partition the diagram off, then the substance within the container may be a mixture of the two adjoining phases in any ratio imaginable. If the piston-head is gliding slowly inward it continues so to glide, P and T remaining steadily the same while all that there is of the phase of greater specific volume² is converted gradually into the other. If the piston-head is gliding slowly outward it continues so to glide, P and T remaining constant while the latter phase is converted into the former. All of the attributes of the reversible process are here: gradualness, lack of turbulence and of explosiveness, willingness to go in either sense, willingness to stand indefinitely still at any partway stage. For ease of formulation it is the prince of reversible processes, since P and T are both unchanging while it is going on.³

Accepting then the crossing of the divide as a reversible process, we have our second expression for the entropy at the point of interest:

$$S(P, T) = S(P, 0) + \int_0^T (C_p^{sol}/T) dT + L/T \quad (14)$$

I pause to quiet the fear that the expression here written down is necessarily infinite, because of T standing in the denominator of the integrand on the right! It is a fact of experience that as T approaches absolute zero, C_p approaches zero for all solids, and with such rapidity that (if extrapolation is safe) the integrand tends to zero and not to infinity. Now comes the climax, which consists in equating the right-hand members of (12) and (14). Referring to a single mole of the substance, and rearranging the terms, we find:

² Volume per unit mass.

³ Irreversible transitions from "supercooled" liquid to solid may occur. In such a case the area called "liquid" may be regarded as spreading somewhat over the divide and overlapping a portion of the area called "solid." The values of P and T for any point in this region of overlapping may characterize either a solid or a liquid, though what is called a "liquid" for this purpose may be so stiff and tough as to deserve and bear the name of "glass." If the solid and the liquid are brought into contact the latter may pass into the former (but never the former into the latter) in a manner so nearly explosive as to be clearly not reversible. I should be less than frank were I to imply that this is always so. With the transition from "supersaturated gas" to liquid, the irreversibility is manifest.

$$I - S(P, 0) = R \ln P - C_p^{gas} \ln T + \int (C_p^{sol}/T) dT + L/T \quad (15)$$

All of the terms on the right are measurable quantities, excepting that C_p^{sol} cannot be followed clear down to the absolute zero, so that the piece of the integral extending from zero up to a few degrees absolute must be guessed. Now at the bottom of the accessible temperature-range C_p is already very small, and in most cases the curve of C_p versus T seems to be heading very smoothly toward zero, so that the uncertainty is probably slight. Surprises in the unreachable range are, however, not inconceivable.

Everyone familiar with entropy will have known in advance, and on reading equations (12) and (14) will have remembered, that the additive constants I and $S(P, 0)$ are beyond the reach of all experiment, be it physical or be it chemical. No way can be devised of measuring them, for in chemistry or in physics it is never the entropy of a system in any one state which is measured, but only the difference of the entropies in two different states, and the additive constant is cancelled in the subtraction. So far as (12) by itself or (14) by itself is concerned, each constant is but a vain appendage, and to develop a theoretical value of either would be reasoning in a void. In spite of all this, the difference between I and $S(P, 0)$ is within the reach of experiment. This permits of one, or two, or even of all three of the following situations:

(a) If there is a plausible theory of entropy which leads to a value for I , experiment will fix a value for $S(P, 0)$ corresponding to that theory.

(b) If there is a plausible theory of entropy which leads to a value for $S(P, 0)$, experiment will fix a value for I corresponding to that theory.

(c) If there is a theory which leads to a value for $S(P, 0)$, and there is another and independent theory which leads to a value for I , then experiment can tell whether the two are compatible.

The actual situation is most nearly like the last of these three; and from this viewpoint I will describe it.

Before going on to the theories of I and of $S(P, 0)$ I point out that (15) is the equation of the vapor-pressure curve; for P and T occur in it as variables, and it refers explicitly to such paired values of P and T as correspond to points lying on the divide between solid and gas, and P for any such point is called the vapor-pressure of the substance for the temperature corresponding. Measurements of vapor-pressure are therefore the ones which are called to decide on these questions—measurements of vapor-pressure and of specific heat, and of the heat of vaporization. The last-named, the quantity L , need be measured at a single temperature only, for there is a formula which gives its value at any temperature in terms of its value at any other temperature and the specific heats over the range between.

This is often incorporated into (15), and alters its aspect; but until page 71 I will pass over this detail. If the point (P, T) lies beside the liquid-gas divide, the isobar to which (14) refers will cut both this and the solid-liquid divide, and traverse the liquid region. Extra terms will then appear in (14) and in (15), but I leave it to the student to divine them.

THE THEORY OF THE CONSTANT S_0

The theory of the constant S_0 is easy to state, provided that no objection is raised to having it stated in a manner rather too drastic at first, and waiting for the necessary reservations to be added later.

The constant S_0 —the entropy at the absolute zero—is taken to be zero for every substance of a single kind.

This is a way of putting, and the strongest possible way of putting, what is known as "Nernst's Law" or "Nernst's Heat Theorem" or even "the Third Law of thermodynamics." Originally expressed in a much milder form nearly forty years ago, it rapidly progressed to the stringent form embodied in these words. As I have suggested already, it is a form too stringent; but the truth lies nearer to it than to the milder phrasings earlier used, and therefore it is justifiable as a commencement.

Notice to begin with that, in the statement as just given, there is no allusion to the pressure or the volume. It is therefore asserted that, at the absolute zero, the entropy of a substance (of a single kind) does not depend on either. This I implied already in the caption to this section, by discarding the symbol $S(P, 0)$ which had previously served for the additive constant in (14), and replacing it by S_0 . From the general thermodynamic equations based on First and Second Laws, it can be shown that if this is true for any substance in particular, then certain measurable features of that substance—notably the coefficient of thermal expansion—must be zero at the absolute zero. Now it does appear to be a general rule that this coefficient, and the other features in question, are trending rapidly to zero at the lower end of the accessible range of temperatures; so this, the mildest form of the "Third Law," is well attested.

Notice then that in the statement as given there is no allusion to phase. Thus, if any substance can exist in both the solid and the liquid phase at the absolute zero, its entropy must be the same in both (if the theorem is true). If we insist on fluidity as a quality of a liquid, there is evidently just one such substance—helium, of course. It appears that for this case the theorem is true.⁴

⁴ At the lowest accessible temperatures, the divide between the "liquid" area and the "solid" area of the phase-diagram is running nearly parallel to the temperature axis, and heading for the ordinate 25 (in atmospheres) on the pressure-axis. Strict parallelism of the divide to the temperature-axis, which is probably realized just before the absolute zero, would imply equality of entropy in the two phases (by one of the thermodynamic equations hinted at above). Another item of evidence is cited on p. 72.

There are substances able to exist in two or more crystalline phases: tin and sulphur are probably the best-known examples. For some of these it is possible to start with one phase at a temperature extremely low; warm the substance up to a temperature of "transition," at which it changes reversibly into the other phase; and cool the new phase down to the temperature at which the experimenter started. Let me denote by S_1 the entropy at the commencement of this process; by S_2 the entropy at its finish; by C_{p1} and C_{p2} the specific heats of the two phases; by T_t the temperature of transition, by L_t the heat absorbed during the transition. We have:

$$S_2 - S_1 = \int_0^{T_t} (C_{p1}/T) dT + L_t/T_t - \int_0^{T_t} (C_{p2}/T) dT \quad (16)$$

According to Nernst's Theorem, S_2 and S_1 and consequently their difference should vanish if the extremely low temperature at start and finish were the absolute zero. We should therefore expect the right-hand member of this equation to be at any rate extremely small, if the temperature in question is at the bottom of the accessible range. Such is indeed the case.

It is very evident that the argument just given proves at the very most that the entropies of the two phases are equal at the absolute zero—not that either of them has the particular value *zero*. The like is true for the other arguments thus far cited; and indeed in the earliest phrasings of the "Third Law," no value was assigned to the entropy at the absolute zero—neither the value *zero*, nor any other. Why then are we to adopt, and presently seek to justify, the particular value *zero*? One part of the answer will be the climax of this paper. The other derives from the speculations as to the nature of entropy, which for half a century have been among the most deeply perpended, the most difficult and the most fruitful of the divisions of theoretical physics.

There are two words which dominate these speculations: "probability" on the one hand, "disorder" on the other. Both of these are very familiar words with very familiar meanings, and some tinge of the familiar meaning is in each case carried over into the technical meaning. The technical meanings, are, however, abstruse; and cynical though it may sound, there is no exaggeration in saying that a large part of the speculation consists in trying to find meanings for the one and the other, which can be fruitfully used in the study of entropy. "Disorder" is the word which we shall examine first.

The familiar meaning of the word "disorder" leads straight to one useful consequence. Of all the possible or conceivable states of matter, the one which anybody would choose as the least disorderly is the crystalline state. But moreover, most people would deem the thermal agitation of the atoms in a crystal as a departure from order; therefore the colder the crystal, the

closer its approach to perfect order. Perfect order would consist in every atom located at rest in exactly its proper place in the crystalline lattice. If such is the state of affairs at the absolute zero, then a crystalline phase at the absolute zero exhibits perfect order. Now as I have implied without precisely saying, entropy is taken to be a measure of disorder. If this is proper, then it is sensible and correct to say that entropy vanishes for the perfect crystal at the absolute zero. This is a reason, it is in fact *the* reason, for assigning the value *zero* to the additive constant S_0 .

If I were to stop my exposition at this point, it would certainly be an impressive conclusion, but hardly a just one. We cannot solve the mysteries of entropy in any so simple a way; in fact they have never been completely solved. Many additions should be made to the foregoing paragraph: some would help out its evident meaning and some would not. Thus, as it stands, it certainly implies that a liquid at the absolute zero—helium offering such a case—must exhibit disorder and therefore have a greater value of entropy than does the crystalline solid. However, it turns out that liquid helium near the absolute zero has the same entropy as solid helium does, and therefore if one value is zero so also must the other be. If instead of liquid helium I had taken the supercooled and toughened liquid which is called a “glass”—glycerol or alcohol in the glassy state, for instance—the result would have been more agreeable. Several of these glasses have been studied with great care, and the right-hand member of equation (16) evaluated for them; it turns out that the entropy near the absolute zero is markedly and indubitably greater for the glass than for the crystal. “Order” must therefore prevail in the glass, but the result with liquid helium impedes the physicist from proclaiming that it is simply the obvious disorder of the irregular placing of the atoms in the glass. A mixture of two substances of a single kind, even when this mixture forms a beautiful crystal, may nevertheless present disorder; for the two kinds of atoms may be sprinkled in a thoroughly chaotic manner over the available points of the crystalline lattice. Such a mixture, it has been found, does have an entropy near the absolute zero which is definitely greater than the sum of the entropies of the two substances when unmixed. But it is also possible for the mixture of two substances to be orderly, in the usual sense of the word! Thus in a mixture—“alloy” is the customary word—of equal numbers of atoms of copper and zinc, the copper atoms may all be found upon one lattice and the zinc atoms upon another, the two lattices interpenetrating and interlocking with each other so as to form the lattice of the crystal of the alloy. This is one of the extreme possibilities: the other is, the entirely chaotic besprinkling of the points of the two lattices with atoms of the two kinds. Both can be realized, the transition between the two being

known as "the order-disorder transition." The entropy goes down as the transition is made from disorder into order.

The conclusion then is, that we may accept entropy as a measure of disorder and disorder as a way of visualizing entropy, provided that we are prepared to define "disorder" in ways which at least in certain striking cases do not depart impossibly far from its traditional meaning. A consequence of this attitude is, that it is plausible and sensible to attach the value *zero* to the constant here called S_0 , the entropy of any substance of a single kind in a crystalline phase at the absolute zero. The words "in a crystalline phase" are a reservation to the original statement. If further reservations become necessary, they will of course have to be made.

THE THEORY OF THE CONSTANT I .

To give even an inkling of the theory of the constant I , it is desirable to take "probability" as the word for which meanings must be found, not too distant from the popular meaning and yet fruitful for the study of entropy. Those who began this process were Gibbs and Boltzmann, working in the closing years of the nineteenth century. Their ideas have since undergone many a transformation, usually in the direction of greater adequacy but also (alas!) in that of greater difficulty. I will follow a route beginning as Boltzmann's did, but carried onward in a manner which became possible about thirty-five years ago, at the time when Nernst's Heat Theorem was being established. It does not lead us quite the whole way to the accepted value of I , so that at the end I shall have to make an extra step without doing more than to indicate whence its justification comes.

We begin by considering a gas in a container of volume V , in equilibrium with itself and with the outer world at a temperature T . "In equilibrium with itself" implies first of all that it is evenly spread throughout the volume of the container—surely one of the earliest of all inbred ideas concerning the behavior of gases. To give a quantitative meaning to this notion of the gas being evenly spread throughout the container, we imagine the volume divided into little compartments or cells of equal volume V_0 . The statement then is that the number of atoms in every cell is the same. Putting N for the total number of atoms and Nf_i for the number in the i th compartment,

$$f_i = \text{constant} = V_0/V \quad (17)$$

The quantity f_i is called the "probability" that an atom chosen at random shall be in the i th cell—the first occurrence of the word "probability" with a definite meaning in this discourse.

The next step is to define the entropy in the manner which follows:

$$S = -kN \sum f_i \ln f_i \quad (18)$$

a definition which in the case of the even distribution of the gas throughout the container reduces to this,

$$S = kN \ln V - kN \ln V_0 \quad (19)$$

This is of course a *tentative* definition, to be eschewed if ever it should lead us into contradiction with the known properties of entropy. As yet it leads us into none, for the term in $\ln V$ corresponds to a similar term in the description of entropy which equation (13) has already supplied. To make the two agree exactly, we have simply to assign a special value to the factor k ; and as will be seen at once, this value is

$$k = R/N_0 \quad (20)$$

N_0 standing for the number of atoms per mole, the Avogadro number. Though k is known as Boltzmann's constant, this evaluation was beyond Boltzmann's powers, for in his time the value of N_0 was not known.

The expression (19) contains no allusion to temperature. It is in fact not the entropy in full which has so far been defined, but only what I may call the "contribution of volume to entropy." We have now to account for the contribution of the kinetic energy of the molecules to the entropy of the gas. Thus far I have been able to come by adducing the deeply-inbred conviction that a gas in equilibrium in a container is evenly spread throughout the container. There is no such widely-held conviction about the distribution-in-energy of the molecules of the gas; but to everyone who has studied physics for more than a year or two there will be nothing surprising in the formula which follows. It must be introduced by asking the reader to imagine a three-dimensional space, in which the variables along the three axes are identified not as coordinates in ordinary space, but as components of momentum p_x, p_y, p_z . The momentum which is meant is the momentum of the individual atom, and the axes x, y, z along which its components are taken are axes of a coordinate frame in ordinary space—they might be along three edges of the container, for instance. A point in the "momentum-space" represents an individual atom in respect of its momentum and therefore in respect of its energy, but not in respect of its position.

The momentum-space is now to be divided into compartments of equal volume H_0 ; but we are not to besprinkle its compartments uniformly with the dots representing the atoms! Instead, when comparing any two of the cells, say the i th and the j th, we are to write

$$f_i/f_j = \exp [-(E_i - E_j)/kT] \quad (21)$$

which reduces to the statement,

$$f_i = Z^{-1} \exp(-E_i/kT) \quad (22)$$

Z being a symbol for the sum,

$$Z = \sum_i \exp(-E_i/kT) \quad (23)$$

which, incidentally, is known as the "partition-function" or "state-sum" of the system—here, of the individual atom of the gas.

In these latest equations, E_i stands for the energy-value corresponding to some point in the i th cell. It is kinetic energy of translatory motion with which we are concerned; therefore E_i is given by the equation

$$E_i = (1/2m)[(p_x^2)_i + (p_y^2)_i + (p_z^2)_i] \quad (24)$$

where now the components of momentum are to be evaluated at some particular point in the i th cell. But at which particular point? And to go further back, just how are the cells of volume H_0 to be designed in the momentum-space? As cubical blocks with their edges parallel to the coordinate-axes, or how? There are problems in which definite answers must be given to these questions, but we shall be able to avoid them. It will be adequate here to conceive of the cells as cubical blocks and the value of E_i as the *average* value of the right-hand member of (24) in the i th cell.

Now we require from (24) the value of Z as defined in (23), to establish the values of f_i as given in (22), to yield finally the value of entropy as given in (18).

Let us form the integral

$$\iiint \exp(-E/kT) dp_x dp_y dp_z, \quad E = (1/2m)(p_x^2 + p_y^2 + p_z^2) \quad (25)$$

the range of integration extending over the whole of momentum-space. This integral may be described as follows. Let the momentum-space be divided into *cells of unit volume*. Each of these cells of unit volume makes a contribution

$$\exp(-\bar{E}/kT)$$

to the integral, \bar{E} standing now for the *average value of E in the cell in question*. The integral is the sum of all of these contributions. Now let us inquire how much of a contribution is made by this same cell of unit volume to the partition-function. This second contribution is made up of $1/H_0$ terms, one for each of the cells of volume H_0 which occupy the cell of unit volume. The values E_i corresponding to these cells will not be exactly equal to the value \bar{E} corresponding to the entire cell of unit volume;

but to the degree of approximation which is now being used, the difference may be neglected. The partition-function is then equal to $1/H_0$ times the integral (25). Now the value of the integral (25) is given in all tables of definite integrals, and in terms of our symbols it amounts to

$$(2\pi mkT)^{3/2}$$

We are now to divide this by H_0 , and proceed along the path which has been indicated.

The procedure is simple and straightforward. As a byproduct one finds the result that the energy of the gas—which I have earlier symbolized by U —is equal to $(3/2)kNT$. It follows that the specific heat at constant volume is equal to $(3/2)kN_0$ for one mole, to n times this value for n moles of gas. Utilizing this result, and putting nR for Nk wherever the latter occurs, one duly arrives at (18) all filled out in the proper way. This represents the contribution of the temperature to the entropy; now adding the contribution of the volume from (19), one arrives at *the entropy of n moles of the gas as function of temperature and of volume, as derived by the statistical method*:

$$S = nR \ln V + nC_v \ln T + nR \ln \frac{(2\pi m)^{3/2} k^{3/2}}{V_0 H_0} + (3/2)nR \quad (26)$$

This is now to be compared with the equation (13) for entropy as function of volume and of temperature, embodying the definition of entropy wherefrom we started.

So far as the dependence on T and on V is concerned, all is well! And there seems even to be a prospect of finding a formula for the additive constant. The prospect, though, is still befogged in two ways: by my lack of precision till now as to the magnitudes of V_0 and H_0 , and by the absence from (26) of any term convertible into the term $nR \ln(nR)$ which stands out so prominently in (13).

As to V_0 and H_0 : no assumption shall be made about either by itself, but it will be assumed that *their product is equal to Planck's constant h raised to the third power* (third power, because of the three dimensions of space):

$$V_0 H_0 = h^3 \quad (27)$$

This I will attempt to justify from a fact not even divined when the formula was made.

To divide the momentum-space into cells of definite size, and to allot to the partition-function just one term from each cell—this comes to the same thing as allowing certain discrete momentum-values to the atoms in question, and denying them all values intermediate to these “permitted”

ones. By using the words "permitted values" I am recalling the quantum-theory, and it is in fact a part of the quantum-theory which we are now employing, as betokened already by the entry of the symbol h . It is one of the oldest parts of the quantum-theory; but the new fact—comparatively new—is this. Atoms, like all other particles, are attended and governed by waves. These waves, when with their atoms they exist in a limited space such as that which the container offers to the gas, are constrained to what in acoustics is known as "resonance." Not every frequency of vibration is allowed to the air within an organ-pipe, to the wire of a piano or to the membrane of a drum, but only such as have wave-lengths fitting neatly into the compass of the cavity, the wire or the drumhead. The dimensions of these acoustical resonators control the permitted wave-lengths, and these in their turn determine the frequencies. In the case which we are now considering of a container filled with a gas, the dimensions of the container control the wave-lengths associated with the atoms, which are the wave-lengths of resonance. These in turn control the momenta of the atoms, because of the relation between the momentum of a particle and the wave-length of its associated waves—the "Rule of Correlation":

$$p = h/\lambda \quad (28)$$

To say that the momenta of the atoms are those and only those corresponding to the resonant wave-lengths, and to say that $V_0 H_0$ in (26) is equal to h^3 —these are equivalent statements. When the former is accepted, so perforce is the latter, and the additive constant in (26) is fully determined. But still it lacks the term $-nR \ln nR$ or $-Nk \ln Nk$ which figures in (13)!

To introduce this term into the theory in a way both logical and simple is not an easy task. The formula at which we are about to arrive is frequently known as the "Sackur-Tetrode formula" after the two physicists of whom (before the first world war) one was the first to approach and the other the first to reach it. Sackur assumed outright that $V_0 H_0$ is inversely proportional to N , while Tetrode subtracted from (26) a term $k \ln N!$ —the exclamation-point here not having its rhetorical meaning, but signifying that $N!$ is " N factorial," the product $1 \cdot 2 \cdot 3 \cdots N$. By Stirling's celebrated formula,

$$\ln N! = N \ln(N/e) \quad (29)$$

an approximation amply valid for such enormous values of N as are normally here considered. Be it noted that e here stands for the exponential base and not for the electron-charge (in the latter sense it is never used in this article).

To make clear the basis for this subtraction of $k \ln N!$ I should have to go far into the roots of the conception of entropy as probability. The best

I can do for the present is to follow Tetrode by saying that he deemed (26) as it stands to be an overstatement of the entropy, arising because in advancing from the underlying theory to equation (18) one assumes the atoms of the gas to be distinguishable, whereas actually for a substance of a single kind they are indistinguishable. In somewhat the same way one might overstate the entropy of a crystal by supposing it to be composed of atoms no two of which were alike, while actually it was a substance of a single kind. The subtraction of $k \ln N!$ was Tetrode's manner of correcting the overstatement. He did better than perhaps he knew, for while his reasons never commanded universal assent, his choice of a term to be subtracted was ratified first by experiment and then by the "new statistics" which made their appearance in physics some fifteen years ago.

Returning to (26): writing the last term of the right-hand member as $nR \ln e^{3/2}$, and consolidating it with the third term; introducing Tetrode's subtractive term; augmenting this last by a term $-nR \ln k$, and compensating by adding $+nR \ln k$ to the third term—doing all this, one finds,

$$S = nR \ln V + nC_v \ln T - nR \ln (nR) + nR \ln \frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3} \quad (30)$$

Now the additive constant is filled out completely, and ready for whatever test experiment may impose.

To prepare it for the test, we turn back first to equations (12) and (13), and note that the constant there denoted by nI is none other than the fourth term in the right-hand member of (30):

$$I = R \ln \frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3} \quad (31)$$

Continuing onward to (15) we are reminded that no theoretical statement about I is worth anything by itself, since all that data can supply is the value of the combination $(I - S_0)$. A hopeless situation, in appearance! But now it is high time to hearken to what the data say. The data say, to begin with:

For many monatomic gases, the right-hand member of equation (15) is equal to the "statistical" value of I .

This may be taken as meaning two things at once: that (a) the statistical theory of the entropy of a gas is right, and (b) the entropy of a solid (crystal-line and of a single kind, for such are these solidified gases) is zero at the absolute zero. It is taken as meaning these things. It might of course also be taken as meaning that both statements are wrong by about the same amount, the errors compensating one another. But so unlikely does it seem that two such different theories should both be wrong and yet by precisely

the same amount, that I venture to say that few will be found who are critical enough to insist on the doubt.

This concordance might be shown by giving actual values of the right-hand member of (15), for actual gases at one or more points adjoining the curve which divides solid from gas on the phase-diagram. The usage is, however, different, and it is of some value to abide by the usage, even though I am now required to make one more transformation of (15) which I have hitherto avoided. This involves the auxiliary equation,

$$dL/dT = C_p^{gas} - C_p^{sol} \quad (32)$$

which makes it possible to calculate L for any temperature, provided it be measured at any other temperature and the specific heats be known at all the temperatures in between. We may thus start from any measured value of L , calculate a value L_0 appropriate to the absolute zero, and thereafter we may write the integrals, as always heretofore, extending from zero to T .

$$L = L_0 + \int C_p^{gas} dT - \int C_p^{sol} dT \quad (33)$$

The first of these two integrals is equal for a monatomic gas to $(5/2)RT$ per mole. Since it is L/T which appears in (15), this entails a term $(5/2)R$ on the right of that equation. This term neatly blots out the term $R \ln e^{5/2}$ which is a portion of our statistical value of I as given in (31), so that after all the equation is not much worsened in appearance. It has in fact assumed the form

$$R \ln P = -L_0/T + (5/2)R \ln T - \int (C_p^{sol}/T) dT + (1/T) \int C_p^{sol} dT + J \quad (34)$$

and here J is yet another additive constant—the additive constant of the vapor-pressure equation in its commonest form—of which this may be said,

$$J = R \ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \quad (35)$$

if the statistical theory is sound and if in addition the entropy of a crystalline solid of a single kind at the absolute zero is zero.

It is evident that if the two presumptions are true, then the remainder left behind when $(3/2) \ln m$ is subtracted from the experimental value of J will have a definite value, the same for all gases. This indicates how the test is made, or rather how it is set forth in the literature. The remainder, expressed in units which need not concern us, should be -1.589 . Now,

data are available⁵ for all of the noble gases from helium through xenon; and I quote the values which they furnish for this "remainder":

He 1.59 ± 0.01 ; Ne (two experiments) 1.56 ± 0.04 , 1.59 ± 0.01
 Ar (two experiments) 1.61 and 1.61 ± 0.04 ;
 Kr 1.59 ± 0.02 ; Xe 1.588

The agreements are remarkably good, and when one remembers the contrast and the subtlety of the two theories which they ratify conjointly, one deems them among the most impressive in the whole of physics or of chemistry either. The result for He implies that $S_0 = 0$ for *liquid* helium.

There are data available also for the vapors of several metals, though for these the experimentalist's task is much harder. It will be seen that in most of the cases we may again rejoice in agreements, though within a broader range of experimental unresureness; in a few there is disagreement, and one can only wonder whether the measurer of vapor-pressure underestimated his possible error.

Na (two experiments) 1.57 ± 0.1 and 1.41 ± 0.03 ;
 K 1.47 ± 0.04 ; Mg. 1.61 ± 0.2 ; Zn 1.51 ± 0.15 ;
 Cd (two experiments) 1.63 ± 0.1 , 1.51 ± 0.1 ; Hg 1.62 ± 0.03 ;
 Tl 1.40 ± 0.3 ; Pb (two experiments) 1.7 ± 0.2 , 1.21 ± 0.26 .

So the situation with respect to monatomic gases is satisfactory on the whole and almost unblemished.⁶ But monatomic gases are but a small proportion of all vapors: has not the theory something to say as regards those which are diatomic—such as oxygen, hydrogen, nitrogen, carbon monoxide—and even those which are polyatomic?

The theory does indeed cover these; and the needed enlargement is simple to write down, if not always easy to compute. Thus far the partition-function has contained only the terms supplied by the translatory motions of the molecules in the container—terms which depend on no other quality of the molecules than their masses, and for a given mass are the same whether the molecule is composed of a single atom or of two or of many. Now to the partition-function so composed are to be added the terms deriving from the rotation and from the vibrations of the molecules. Each new term is of the familiar form $\exp(-E_i/kT)$, where now E_i is to stand for some permitted energy-value of rotation or of vibration, and the summation is

⁵ Data from the collation of Ditchburn and Gilmour (*Rev. Mod. Phys.* 13, 310, 1941), except the value for xenon which is from Clusius.

⁶ Here I must say, even if only in a footnote, that for atoms which have angular momentum there is still one more term in the additive constant occurring in the right-hand member of (30). This term may be loosely described as referring to the "disorder" arising from the fact that there are two or more different orientations of the angular momentum, between which the atoms may choose. Its exact value (zero for the inert gases, $nR \ln 2$ for the alkali metals) is derived from the spectrum of the atom. Allowance is made for this term in the computation leading to the value of the "remainder", and the agreements here tabulated for Na and K sustain the allowance. A bad disagreement for tungsten emerges from an early (1924) research by Lange.

to be carried over all values of E_i . There is less of a mental obstacle now than there was in the "translatory" terms, for the doctrine of discrete permitted energy-values in rotation is among the oldest, while that of discrete energy-states in vibration is quite the oldest, of the whole of quantum-theory. To get the energy-values E_i , the spectra are consulted. Spectrum analysis is the most highly-developed of the branches of physics, and the knowledge of the values of E_i which it affords for the better-known of the diatomic molecules—and even for some few of the triatomic—may be described as complete, daring as it may sound.

Values of entropy figured by the statistical way which I have been describing, with additions duly made to the partition-function to allow for rotation and vibration, are called "spectroscopic" entropy-values by Giauque and his colleagues of the Berkeley school. As a rule they are computed for a standard pressure and temperature, often for one atmosphere and 25°C.; let us call these P_0 and T_0 . Now as a rule the point (P_0, T_0) does not lie just off the divide which on the phase-diagram separates solid (or liquid) from gas. One may, however, use (11) for getting the entropy-difference between (P_0, T_0) and any such point (P, T) lying along the divide on the side corresponding to gas. At the point (P, T) the entropy may be evaluated by the right-hand member of (14), and to it may then be added the entropy-difference just mentioned. The sum, *computed with the assumption that S_0 is zero*, is what Giauque and his school name a "calorimetric" entropy-value. If the two agree, there is a verification of the conjoined assumptions that the statistical theory is sound, and that the crystalline solid at zero absolute has none of that disorder which is the source of entropy.

I take the following data from Eastman⁷ of the Berkeley school. Of his two tables, one comprising gases for which the data are definitely better known than they are for the rest, I quote this one only. The accuracy of the calorimetric value "is in all cases high, errors being of the order of 0.1 throughout." The supposed accuracy of the spectroscopic values is indicated by the number of significant figures to which they are carried.

	<i>Calor.</i>	<i>Spectrosc.</i>
N ₂	45.9	45.788
O ₂	49.1	49.03
HCl	44.5	44.64
HBr	47.6	47.48
HI	49.5	49.4
CO	46.2	47.316
NO	43.0	43.75
H ₂ O	44.23	45.17
N ₂ O	51.44	52.581
H ₂	29.7	31.23

⁷ *Chem. Rev.* 18, 257 (1936).

The first five are the stellar examples of concordance, therefore support for the two conjoined assumptions. In the last five the discrepancy is deemed to exceed the possibility of doubt, and some explanation ought to be found.

How is one to explain a "calorimetric" value less than the "spectroscopic"—as occurs in all five of these cases? The comparison, I recall, is essentially between $(I - S_0)$ and I . In all of these five cases, $I - S_0$ turns out to be less than I ; therefore we are tempted to assume a "disorder" in the solid, subsisting even unto the absolute zero. The case of hydrogen is the clearest, the disorder being traceable in part to the intermingling of two types of hydrogen molecule known as the "ortho" and the "para" type. In the other cases, the explanations have a vagueness which suggests that they are speculative. This is not a very satisfactory statement to end with. Yet even these discrepancies are so small, that even if there were no closer agreements one would still feel assured that the truth is to be found in some minor alteration of the theory rather in rejecting the theory altogether; and the five excellent agreements, combined with the excellent agreements for so many monatomic gases, convert this feeling of assurance into certitude.

Abstracts of Technical Articles by Bell System Authors

*Recent Developments in Burying Telephone Cables.*¹ DONALD FISHER and TEMPLE C. SMITH. The term "buried cables" has come to mean those underground cables which have no conduit protection. Due to the accelerated demand for such construction in recent years, much effort has been expended in devising methods and developing machinery for burying cables. One of the earlier methods used in this and some foreign countries was to dig a trench by hand alongside the road; unreel the cable from a moving truck, thus laying it beside the trench; work the cable over into the trench by having 30 to 50 men handle it in relays; splice the cable in the trench, and finally backfill the spoil and tamp it by hand. Later variations of this method introduced one or more of the following units of machine equipment: Power trenching machines; Caterpillar tractors with trailers to straddle the trench, laying the cable directly from the reel into the trench; Drag-line or other types of power backfillers; Power tampers or rollers.

In order to further reduce the number of operations involved, speed up the installation, and reduce the cost, large plow trains have recently been developed which, except for splicing, in ordinary soil complete the job of burying a cable in one pass over the route. The idea of plowing cable into the ground is not new. In fact the great grandfather of all the cable plows was designed by Ezra Cornell long before he established the university. His "ponderous machine" drawn by a "long line of horses" was designed for laying telegraph cable in the early 1840's, but the development was dropped when the simple expedient of carrying wires on poles and insulators was conceived.

The large plow trains recently developed for installing telephone cable are capable of burying either a single cable or a pair of cables together with as many as three properly spaced lightning-protection wires, and of cutting a slot for them as much as 50 inches deep where such a depth is required. To provide the complete plow train has required the design of many pieces of equipment which the word "plow" does not suggest to one's mind. The plows and some of this equipment are discussed in this paper.

*A Frequency-Modulated Control-Track for Movietone Prints.*² J. G. FRAYNE and F. P. HERRNFELD. A 5-mil frequency-modulated track located between sound and picture areas is proposed to control reproduction

¹ *Elec. Engg., Transactions Section*, April 1942.

² *Jour. S.M.P.E.*, February 1942.

in the theater from one or more sound-tracks. A variation of approximately one octave in the control frequency provides a 30-db change in volume range which may be used in part for volume expansion of loud sounds or as noise reduction for weak sounds. The control-track frequency is varied manually and recorded simultaneously with the sound-track in the dubbing operation, the gain of the monitoring channel being varied in accordance with the control frequency to produce automatically the enhanced volume range desired from the release print. The track is recorded in line with the standard soundtrack and does not require separate printing or reproducing apertures. It is scanned by a separate photo-sensitive surface, the output being converted from frequency to voltage variations by a frequency-discriminating network identical to that used in the monitoring channel. The output from the network, applied to the grid of a variable-gain-amplifier in the sound channel, controls automatically the volume of the reproduced sound in accordance with that observed in the dubbing operation.

*Performance of Ground-Relayed Distribution Circuits during Faults to Ground.*³ C. L. GILKESON, P. A. JEANNE and J. C. DAVENPORT, Jr. An extensive oscillographic study has been made on power distribution feeders primarily to obtain data useful in the consideration of joint use of poles by power and telephone facilities. Some of the results, chiefly those obtained from three-phase, four-wire, multigrounded neutral feeders equipped with instantaneous ground relays and for immediate breaker reclosure, are believed to be of general interest and are presented herewith. Included are data on the performance of the protective devices utilized for clearing ground faults on the feeders included in the study, the effectiveness and certain limitations of these devices, and characteristics of the faults experienced.

*A More Symmetrical Fourier Analysis Applied to Transmission Problems.*⁴ R. V. L. HARTLEY. The Fourier identity is here expressed in a more symmetrical form which leads to certain analogies between the function of the original variable and its transform. Also it permits a function of time, for example, to be analyzed into two independent sets of sinusoidal components, one of which is represented in terms of positive frequencies, and the other of negative. The steady-state treatment of transmission problems in terms of this analysis is similar to the familiar ones and may be carried out either in terms of real quantities or of complex exponentials. In the transient treatment, use is made of the analogies referred to above, and

³ *Elec. Engg., Transactions Section*, January 1942.

⁴ *Proc. I.R.E.*, March 1942.

their relation to the method of "paired echoes" is discussed. A restatement is made of the condition which is known to be necessary in order that a given steady-state characteristic may represent a passive or stable active system (actual or ideal). A particular necessary condition is deduced from this as an illustration.

*Paper Dielectrics Containing Chlorinated Impregnants.*⁵ D. A. McLEAN, L. EGERTON, G. T. KOHMAN and M. BROTHERTON. Chlorinated aromatic hydrocarbons are used extensively as impregnants for paper in electrical apparatus such as capacitors and transformers. They possess high stability toward heat and oxygen, nonflammability, and desirable electrical properties. However, the present study shows that under special conditions a type of decomposition occurs which liberates products so active chemically that, especially at elevated temperatures, under high potential gradients, and in contact with metals, autocatalytic decomposition reactions are initiated.

When aluminum electrodes are used and d-c. fields are applied, the deterioration manifests itself in a leakage current increasing with time and in the formation of partially carbonized areas in the paper. Evidence is presented that the decomposition starts by the splitting off of hydrogen chloride from the chlorinated compounds. This attacks the electrodes to form aluminum chloride, which decomposes the organic constituents of the insulation.

The deterioration is considered in relation to certain variations in composition; all components of the structure—the paper, the impregnant, and the electrode materials—play important roles in the reactions.

*Methods for Measuring the Performance of Hearing Aids.*⁶ FRANK F. ROMANOW. A hearing aid can be considered as a sound transmission system which is interposed in the path between the source of sound and the listener's ear. As such its performance can be judged by comparing the sound that reaches the ear first through the air path and then through the hearing aid. The experimental procedure to carry out this concept is, however, time consuming. To obtain a simple laboratory technique for comparative purposes, it is proposed, therefore, that the amplification of a hearing aid be measured by placing its microphone in a known sound field and observing the output of the receiver when terminated in an appropriate impedance. For an air conduction receiver this impedance takes the form of a closed cavity. For a bone conduction receiver the termination is an artificial mastoid. Since in a portable hearing aid compactness is desired,

⁵ *Indus. & Engg. Chem.*, January 1942.

⁶ *Jour. Acous. Soc. Amer.*, January 1942.

the undistorted pressure that can be developed by the set is limited in magnitude. Also the amplification is a function of the variation of the power supply voltages. Hence it is necessary that these characteristics be measured. As an illustration of the different factors involved, characteristic curves for a recently developed vacuum tube aid are shown.

*Some Mechanical Aspects of Telephone Apparatus. Part I—Development of Crossbar Switch as a Typical Unit of Automatic Dial Telephone System.*⁷ J. D. TEBO and H. G. MEHLHOUSE. One half the telephones in the world are in the United States. A total of 100,000,000 calls a day are made on this equipment, on matters large and small—routine or emergency. Especially in these days of national emergency, communication facilities have become indispensable to our defense organizations, vitally assisting in speeding up the program of national safety.

Americans have grown to accept their telephones as a necessity, seldom realizing the vastness of the system and the spirit of service in the large organization constantly striving to maintain and improve a means of communication already unexcelled. Seldom is it realized that the equipment in the home or office is only a very small part of the facilities required in this business of telephoning. A network of wire literally covering the nation from coast to coast, and intricate switching devices for interconnecting the telephones throughout the nation and most of the world all combine to transmit the spoken word quickly and faithfully.

The vastness and complexity of such a service must of necessity require a wide range of equipment which, in the Bell System, totals 44,000 kinds of apparatus involving 170,000 different parts. Some of the mechanical aspects of such equipment are presented in this paper, particularly those having to do with design and manufacture, jointly handled for the Bell System by the Bell Telephone Laboratories and Western Electric Company. Obviously, the entire range of telephone equipment cannot be included. This paper is therefore intended to deal with a specific telephone switching mechanism, known as the crossbar switch, which is used in the latest dial telephone system.

⁷ *Mech. Engg.*, May 1942.

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DEVOTED TO THE SCIENTIFIC AND ENGINEERING ASPECTS
OF ELECTRICAL COMMUNICATION

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The Mathematics of the Physical Properties of Crystals

By WALTER L. BOND

SECTION 1

INTRODUCTION

THE use of crystals as oscillating elements and as light valves in electric circuits has given the mathematics of crystalline media an engineering importance. Soon after the first simple quartz oscillators were made it was noticed that some ways of cutting the block from the natural crystal gave lower temperature coefficients of frequency than did other ways. This led to studies of the change of elastic moduli with direction and temperature and finally to the discovery that there are directions in quartz for which the shear modulus does not change with temperature.

Such computations are rather involved, and there is, in the English language, no general reference book on these new problems. The existing works were evidently not written with the idea in mind that anyone would ever actually do much numerical work with directional properties of crystals, since the methods used are not the best suited to this. The matrix algebra has the advantages of a symbolic algebra and is also, through the concept of matrix multiplication, a scheme for computing numerical results.

As the problem of temperature coefficients of frequency involves the temperature coefficient of expansion, the temperature coefficient of density and the temperature coefficient of elastic moduli, these problems must be put into the language of matrix algebra so that they will fit into the general structure being built for more difficult problems. For this reason, after an introduction to the idea of linear vector functions, through consideration of the relation between the electric field and the induction in a crystal, and a hasty sketch of symmetry types found in crystals, we proceed to the consideration of stress and strain and their relations to each other.

Following these, we take up piezo electricity and the converse piezo electric effects; these are important as they tell us the ways a crystal may be driven. We have not seen anywhere a general proof that the moduli of the converse effect are the same numbers as the moduli of the direct effect—to the first order of small quantities, though Lippman predicted the converse effect and demonstrated its magnitude to be about this; he ap-

parently didn't consider the general case of six simultaneous stress components, six strain components, three electric field components and three induction components. The fact that the mentioned relation is true only to the first order of small quantities seems to have escaped the attention of some experimenters who have sought to show non-linearity of the piezo-electric effect by demonstrating non-linearity in the converse effect.

As a basis for light valve problems, we handle the propagation of light through crystals, then the electro optic effect and the piezo optic effect.

SECTION 2

A LINEAR VECTOR FUNCTION

For almost every physical constant of an isotropic medium a crystalline medium has several constants. For instance, a piece of glass has a coefficient of thermal expansion but a crystal has many coefficients of thermal expansion, the coefficient depending on direction. It might be thought that there were no necessary relations between the coefficients in different directions but there are necessary relations.

As an example of the simplifying relations between the values of physical constants in different directions let us consider a crystal in an electric field. Measurements show that the dielectric constant varies with direction in a crystal. If the field is not in the direction of greatest dielectric constant, the displacement current might veer over a little, much as a nail tries to follow the grain of the wood. We shall assume that for any electric field vector E there corresponds an electric induction vector D which may not coincide with E . Also we assume that the magnitude of D is proportional to E , that is, if E results in D , then nE results in nD . Lastly, we assume that if E_1 results in D_1 , E_2 in D_2 . . . and E_m results in D_m , then $E_1 + E_2$. . . E_m results in $D_1 + D_2 +$. . . D_m . If these assumptions hold, then as any arbitrary field E can be expressed as the vector sum of its three components E_1 , E_2 , E_3 along three arbitrary unit vectors i , j , k , the induction vector resulting from E can be computed from the induction vectors resulting from E_1 , E_2 , and E_3 . For, let E_1 result in $D_{11}i + D_{21}j + D_{31}k$, E_2 result in $D_{12}i + D_{22}j + D_{32}k$ and E_3 result in $D_{13}i + D_{23}j + D_{33}k$, then $E_1 + E_2 + E_3 = E$ results in the induction vector:

$$\begin{aligned}
 D = & (E_1D_{11} + E_2D_{12} + E_3D_{13})i \\
 & + (E_1D_{21} + E_2D_{22} + E_3D_{23})j \dots\dots\dots(2.1) \\
 & + (E_1D_{31} + E_2D_{32} + E_3D_{33})k
 \end{aligned}$$

It is seen then, that not more than 9 constants are needed to describe the dielectric properties of a crystal. The energy required to establish the

electric field is half the product of the component of the induction in the direction of the field and the electric field. This is, therefore:

$$2W = E_1^2 D_{11} + E_2^2 D_{22} + E_3^2 D_{33} + E_2 E_3 (D_{23} + D_{32}) + E_3 E_1 (D_{31} + D_{13}) + E_1 E_2 (D_{12} + D_{21})$$

Considering then a condenser made from a unit cube of crystal, the charge is D and the energy content is W . If there is no leakage loss, the charge that can be drawn from the condenser is $D = \frac{\partial W}{\partial E}$. Whence $D_1 = \frac{\partial W}{\partial E_1} = D_{11} E_1 + \frac{1}{2} (D_{12} + D_{21}) E_2 + \frac{1}{2} (D_{13} + D_{31}) E_3$. If, therefore, the induction is derivable from a potential, $D_{12} = \frac{1}{2} (D_{12} + D_{21})$ or $D_{12} = D_{21}$. Similarly $D_{13} = D_{31}$ and $D_{23} = D_{32}$. By a proper choice of axes the remaining six D 's can be reduced to three. In the case of isotropic dielectrics $D_{11} = D_{22} = D_{33}$ and $4\pi D_{11}$ corresponds to k , the dielectric constant.

SECTION 3

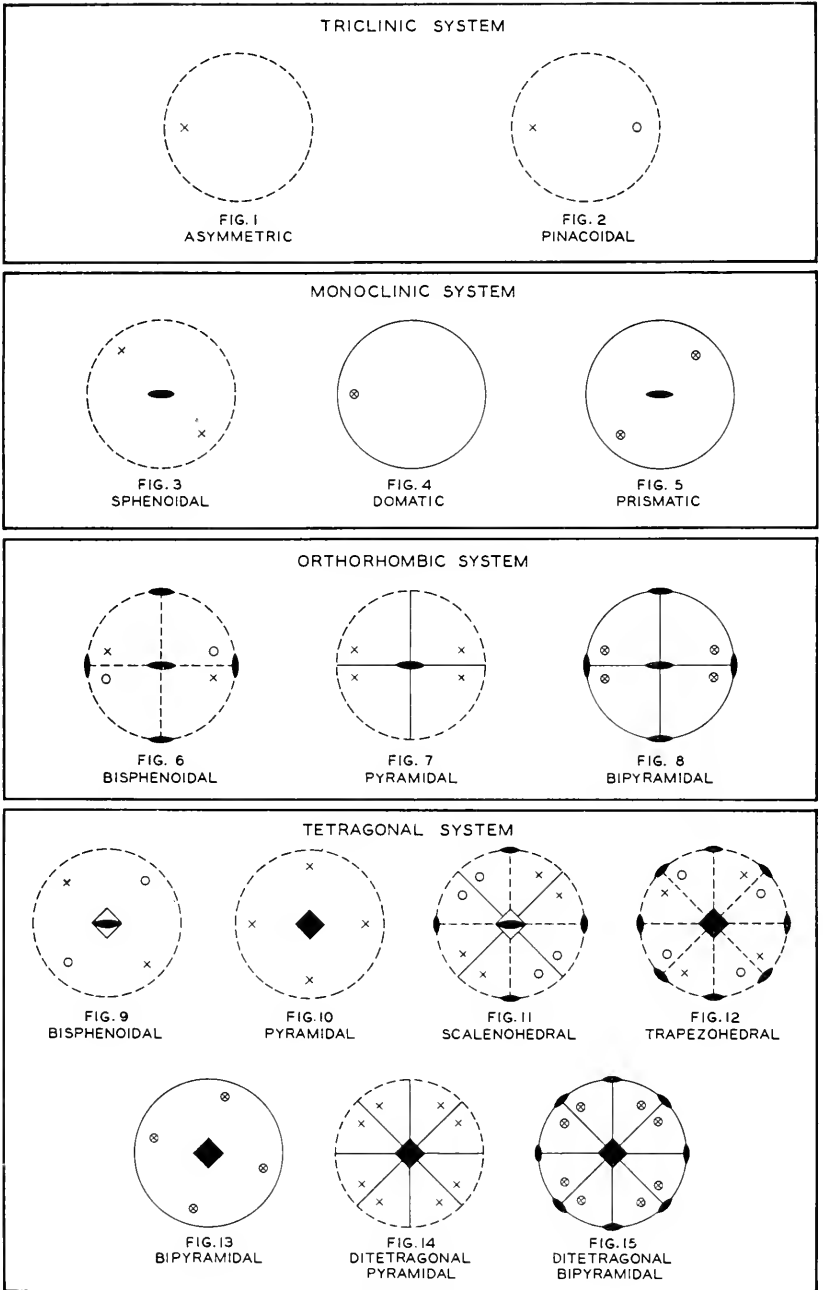
THE SYMMETRY OF CRYSTALS

If a crystal has certain sorts of symmetry the number of constants required to describe each property is materially reduced. For this reason we now turn our attention to a study of symmetry.

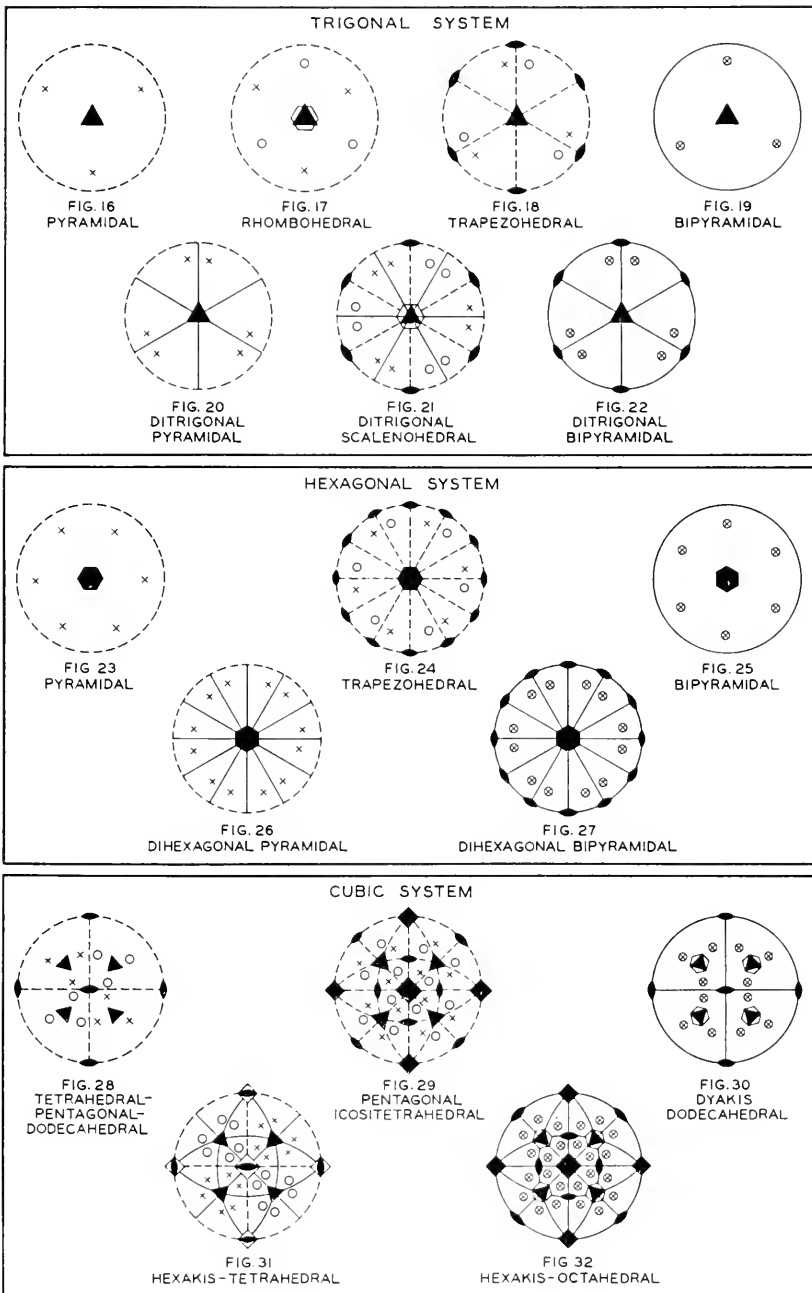
In general, plotting a vector property of the medium for a crystal gives a complicated surface which we shall call a property surface. Each property surface of a homogeneous isotropic medium is a sphere.

Because of the orderly arrangement of matter in a crystal, the property surfaces of crystalline media are commonly symmetrical. If a casting of a property surface were made it might fit into its mold in several positions. A property surface for quartz for example, if lifted from its mold and rotated through a third of a turn about the proper axis, would fit back into the mold. That is, quartz has a three fold axis. The natural requirement that molecules be laid down in a way economical of space limits the kinds of symmetry possible for crystals to axes of two fold (binary) symmetry, of three fold (trigonal), of four fold and of six fold symmetry, planes of reflection symmetry and combinations of axis-reflection symmetry, besides a simple symmetry through a center. From these elements it is possible to divide all possible property surfaces into 32 classes. No other classes built from these elements could be self-consistent.

A diagram study will prove this point. On a sphere let us mark axes of two fold symmetry by means of a solid boat shaped figure, three fold with a solid triangle, four fold with a square, six fold with a hexagon, planes of symmetry with a solid line (great circle) and combination axis reflection, by means of similar hollow figures. Finally, we shall project the sphere



Figs. 1-15—Crystal classes.



Figs. 16-32—Crystal classes.

and markings onto a plane through the center. Figures 1 to 32 is a set of such diagrams. Fig. 23 for instance shows a six fold axis. Fig. 1 represents a medium with no symmetry whatever. The cross represents a typical vector property, the vector piercing the sphere above the projection sheet. If the vector pierced below the sheet it would be marked with a circle. The dashed circle of Fig. 23 indicates the boundary of the sphere without implying it to be a plane of symmetry. The presence of six fold symmetry requires the typical vector to be shown in six places. If an axis of two fold symmetry is added at right angles to the six fold axis, it must appear six times and the typical vector must now appear twelve times, six times above and six times below the projection sheet. Continuing in this way we shall find the self-consistent classes of symmetry to be the 32 shown in the diagrams. Often the symmetry of a crystal class is expressed by means of a formula. A center of symmetry is symbolized by the letter C , a binary axis by A_2 , a trigonal axis by A_3 , a ternary axis by A_4 , a six fold axis by A_6 , a plane of reflection by P , and a combination rotation reflection by the combination symbols \mathcal{R}_4 or \mathcal{R}_6 . In this way the symmetry formula of quartz for example, is $3A_2 \cdot A_3$.

SECTION 4

MATRIX ALGEBRA

In the solution of problems of crystal physics we are involved in the handling of many sets of linear simultaneous equations. As the matrix algebra lessens the work involved in handling sets of linear simultaneous equations we turn now to a study of matrix algebra.

Several independent variables $x_1, x_2 \dots x_n$ are linearly related to several other independent variables $y_1, y_2 \dots y_m$ as

$$\begin{aligned}
 y_1 &= a_{11}x_1 + a_{12}x_2 + \dots + a_{1n}x_n \\
 y_2 &= a_{21}x_1 + \dots \\
 &\dots\dots\dots \\
 y_m &= a_{m1}x_1 + \dots \quad a_{mn}x_n
 \end{aligned}$$

or briefly

$$y_l = \sum_{j=1}^n a_{lj}x_j \quad l = 1, 2 \dots m \dots\dots\dots (4.1)$$

In most all such equations as (4.1) the variable to be summed over appears twice in the subscripts of one side. As a convention we agree to omit the summation sign and sum wherever subscripts are repeated.

Thus: $y_i = a_{ij}x_j$ is to be summed over j
again, if $x_j = b_{jk}z_k$ the z 's being a third set of variables we have:

$$y_i = a_{ij}b_{jk}z_k \text{ to be summed over } j \text{ and } k.$$

We can think of this as a special multiplication of hyperquantities a , b and z . If we define

$$c_{ik} = a_{ij}b_{jk} \dots \dots \dots (4.2)$$

we may go from the y 's to the z 's directly thru $y_i = c_{ik}z_k$. We can now consider the "table"

$$\begin{pmatrix} a_{11}a_{12} \dots a_{1n} \\ a_{21} \dots \\ a_{ml} \dots a_{mn} \end{pmatrix}$$

as being the quantity a , and the table

$$\begin{pmatrix} b_{11}b_{12} \dots b_{1m} \\ \dots \dots \dots \\ b_{pl} \dots b_{pm} \end{pmatrix}$$

as the quantity b .

These "tables" are called matrices.

Going to eq. (4.2) we see that the quantity c is to be a "table," the typical element c_{ij} of which is to be gotten by multiplying the i th row of a by the j th column of b , term by term thus:

$$c_{ij} = a_{i1}b_{1j} + a_{i2}b_{2j} + \dots$$

After a little practice it becomes almost automatic to form the ij th term of the product of two matrices by letting the index finger of the left hand follow across the i th row of the left matrix while the right index finger follows down the j th column of the right matrix. The fingers step along in synchronism and at each pause the quantities under the two fingers are multiplied and the product added algebraically to the accumulated sum.

The algebra of these special multiplications is not commutable, i.e. $ab \neq ba$.

Eq. (4.1) can be considered as a special case of eq. (4.2), in which the matrices x and y have one column only. In this manner a vector with

components $x_1 \ x_2 \ x_3$ can be considered as the matrix $\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$.

If eq. (4.1) has the same number of x 's as y 's we may solve (by means of determinants) for the x 's in terms of the y 's. We would then get a new set of equations

$$x_i = a_{ij}^{-1} y_j.$$

The significance of the a^{-1} is that the matrix product of a and a^{-1} is a matrix with ones on the major diagonal and all other terms zero. Whenever the product of two square matrices gives such a matrix (known as the idemfactor, I) they are said to be reciprocal. Only square matrices have reciprocals. Multiplying any matrix by the idemfactor leaves the matrix unchanged. We might consider, as part of our mathematical short hand, that eq. (4.1) was solved for x by multiplying through by a^{-1} , as

$$a^{-1}y = a^{-1}ax = Ix = x.$$

We must remember that the order must not be disturbed as the quantities are not commutable, and that only square matrices have reciprocals.

The major diagonal of a square matrix is the set of terms running diagonally from the upper left to the lower right.

A symmetrical matrix has any term $M_{ij} = M_{ji}$

An anti-symmetrical or skew symmetric matrix has any term $M_{ij} = -M_{ji}$ for $i \neq j$.

Rotation Theory

The matrix algebra can be used to express a vector as a function of another vector, that is to handle such relations as exist between E and P of section 2.

There is another important aspect of matrix multiplication, that of transforming a function from one set of axes to another. Let us assume that the new set of unit axes, x'_1 , x'_2 and x'_3 are merely the old ones rotated through angle ϕ about some axis A which is a unit vector passing through the origin. From Fig. 33 we see that in the expression:

$$x_1 = a_{11}x'_1 + a_{21}x'_2 + a_{31}x'_3$$

the a_{ij} 's are the cosines of the angles between x_1 and the three quantities x'_j . Conversely they are the cosines of the angles between the x'_j 's and x_1 . Consequently, if the primed unit vectors are given in terms of the unprimed ones by the three equations

$$x'_i = a_{ij}x_j$$

then the unprimed x 's are given in terms of the primed ones by the expression:

$$x_j = a_{ji}x'_i$$

This reversible relationship is well depicted by the table:

	x_1	x_2	x_3
x'_1	a_{11}	a_{12}	a_{13}
x'_2	a_{21}	a_{22}	a_{23}
x'_3	a_{31}	a_{32}	a_{33}

In this direction cosine table we can “look up” the components of any unit vector in terms of the other system.

The matrix a_{ji} is merely the matrix a_{ij} with rows and columns interchanged. a_{ji} is called the conjugate of a_{ij} . We shall denote the conjugate of any matrix M by M_c .

Obviously V' is the vector sum of the 3 components (on the new system) of each of its 3 components on the old system.

$$(V)_{\text{new}} = \begin{pmatrix} a_{11}^{-1}V_1 + a_{12}^{-1}V_2 + a_{13}^{-1}V_3 \\ a^{-1}V + \dots\dots\dots \\ \dots \quad \dots \quad \dots \end{pmatrix}$$

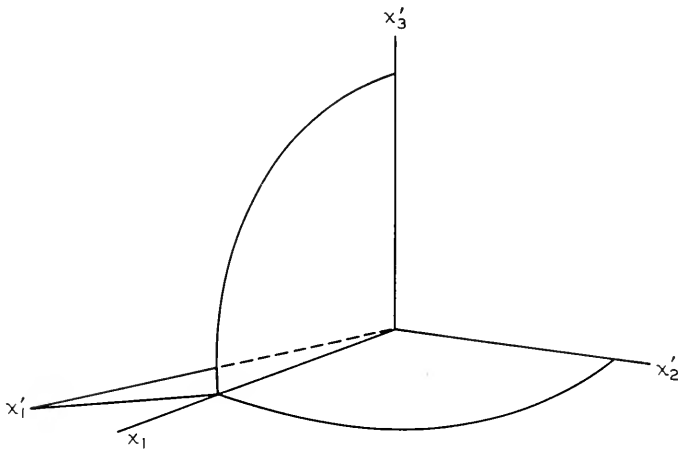


Fig. 33—The direction cosines of X_1 on $X'_1 X'_2 X'_3$.

If the expression giving the components of V on the new system is denoted by V' we may write

$$V' = a V$$

conversely

$$V = a^{-1} V'$$

Since x_1 is of unit length, the sum of the squares of its three components (on the primed system) is unity.

That is
$$a_{11}^2 + a_{12}^2 + a_{13}^2 = 1$$

similarly
$$a_{21}^2 + a_{22}^2 + a_{23}^2 = 1 \dots\dots\dots (4.3)$$

and
$$a_{31}^2 + a_{32}^2 + a_{33}^2 = 1$$

Now a_c can be considered as a rotation similar to the rotation a . Consequently their product aa_c is a similar rotation. Let us consider this product.

The squares of its terms must sum to zero, row by row as in (4.3)

$$\begin{pmatrix} a_{11}a_{12}a_{13} \\ a_{21}a_{22}a_{23} \\ a_{31}a_{32}a_{33} \end{pmatrix} \begin{pmatrix} a_{11}a_{21}a_{31} \\ a_{12}a_{22}a_{32} \\ a_{13}a_{23}a_{33} \end{pmatrix} = \begin{pmatrix} 1 & . & . \\ . & 1 & . \\ . & . & 1 \end{pmatrix}$$

Because of the relations $a_{11}^2 + a_{12}^2 + a_{13}^2 = 1$, etc., we see that the terms of the third matrix are zero for all terms not on the major diagonal. Therefore, aa_c is an idemfactor and the reciprocal matrix of a is the same as its conjugate matrix.

$$a_c = a^{-1} \dots \dots \dots (4.4)$$

Also x'_1 is of unit length, and the sum of the squares of its components on the unprimed system is unity. Thus we find:

$$\begin{aligned} a_{11}^2 + a_{21}^2 + a_{31}^2 &= 1 \\ a_{12}^2 + a_{22}^2 + a_{32}^2 &= 1 \dots \dots \dots (4.5) \\ a_{13}^2 + a_{23}^2 + a_{33}^2 &= 1 \end{aligned}$$

We now introduce from vector analysis the concept of the scalar product. The scalar product of two vectors u and v is $u_c v$. It is the product of the lengths of the two vectors and the cosine of the angle between them.

If we take the scalar product of x_1 and x_2 as expressed in the primed system we have, since they are mutually perpendicular:

$$(a_{11}, a_{12}, a_{13}) \begin{pmatrix} a_{21} \\ a_{22} \\ a_{23} \end{pmatrix} = a_{11}a_{21} + a_{12}a_{22} + a_{13}a_{23} = 0$$

Similarly multiplying x_2 and x_3 scalarly, and x_3 and x_1 we find:

$$\begin{aligned} a_{11}a_{21} + a_{12}a_{22} + a_{13}a_{23} &= 0 \\ a_{21}a_{31} + a_{22}a_{32} + a_{23}a_{33} &= 0 \dots \dots \dots (4.5) \\ a_{31}a_{11} + a_{32}a_{12} + a_{33}a_{13} &= 0 \end{aligned}$$

If we multiply x'_1 and x'_2 etc. as expressed on the unprimed system we get the relations:

$$\begin{aligned} a_{11}a_{12} + a_{21}a_{22} + a_{31}a_{32} &= 0 \\ a_{12}a_{13} + a_{22}a_{23} + a_{32}a_{33} &= 0 \dots \dots \dots (4.7) \\ a_{13}a_{11} + a_{23}a_{21} + a_{33}a_{31} &= 0 \end{aligned}$$

The vector product of two vectors u and v requires the defining of a special matrix, the cross matrix.

$$u \times = \begin{pmatrix} 0 & -u_3 & u_2 \\ u_3 & 0 & -u_1 \\ -u_2 & u_1 & 0 \end{pmatrix} \dots \dots \dots (4.8)$$

We note that this is formed by writing zeros on the major diagonal, then going back from the lower right corner writing u_1, u_2 and u_3 around the edges. We then make the lower left term negative, then operate on the opposite side of the major diagonal so as to make the matrix skew symmetric.

The reciprocal of any matrix m is

$$m_{ij}^{-1} = \frac{M_{ji}(-1)^{i+j}}{|m|} \dots\dots\dots (4.9)$$

where M_{ji} is the ji minor of $|m|$.

The cross matrix has no reciprocal as for it (4.9) becomes indeterminate.

Since the vector product of two vectors u and v is another vector perpendicular to both u and v and of a length $uv \sin(\angle uv)$ we may write, on the primed system

$x_1 \times x_2 = x_3$ in the form

$$\begin{pmatrix} 0 & -a_{13} & a_{12} \\ a_{13} & 0 & -a_{11} \\ -a_{12} & a_{11} & 0 \end{pmatrix} \begin{pmatrix} a_{21} \\ a_{22} \\ a_{23} \end{pmatrix} = \begin{pmatrix} -a_{13}a_{22} + a_{12}a_{23} \\ a_{13}a_{21} - a_{11}a_{23} \\ -a_{12}a_{21} + a_{11}a_{22} \end{pmatrix} = \begin{pmatrix} a_{31} \\ a_{32} \\ a_{33} \end{pmatrix}$$

Matrices including vectors are equal only when their corresponding terms are equal. Hence, we get the relations

$$\begin{aligned} a_{31} &= a_{12}a_{23} - a_{13}a_{22} \\ a_{32} &= a_{13}a_{21} - a_{11}a_{23} \dots\dots\dots (4.10) \\ a_{33} &= a_{11}a_{22} - a_{12}a_{21} \end{aligned}$$

Similarly we get the relations:

$$\begin{aligned} a_{11} &= a_{22}a_{33} - a_{23}a_{32} \\ a_{12} &= a_{23}a_{31} - a_{21}a_{33} \\ a_{13} &= a_{21}a_{32} - a_{22}a_{31} \dots\dots\dots (4.11) \\ a_{21} &= a_{32}a_{13} - a_{12}a_{33} \\ a_{22} &= a_{33}a_{11} - a_{31}a_{13} \\ a_{23} &= a_{31}a_{12} - a_{32}a_{11} \end{aligned}$$

The 21 relations between the a_{ij} 's allow us to complete the matrix given four terms.

Several Useful Matrix Relations

The del operator is the pseudo vector $\nabla = \begin{pmatrix} \partial/\partial x_1 \\ \partial/\partial x_2 \\ \partial/\partial x_3 \end{pmatrix} \dots\dots\dots (4.12)$

It transforms upon a rotation of axes as does an ordinary vector:

$$\nabla' = a \nabla \dots \dots \dots (4.13)$$

$$\text{grad } u = \nabla u_c, \text{ a matrix } \dots \dots \dots (4.14)$$

$$\text{div } u = \nabla_c u, \text{ a scalar } \dots \dots \dots (4.15)$$

$$\text{curl } u = \nabla \times u, \text{ a matrix } \dots \dots \dots (4.16)$$

$$\text{grad radius vector} = \nabla \rho = I, \text{ the idemfactor. } \dots \dots (4.17)$$

$$(abc \dots)^{-1} = \dots c^{-1} b^{-1} a^{-1} \dots \dots \dots (4.18)$$

$$(abc \dots) c = \dots c_c b_c a_c \dots \dots \dots (4.19)$$

$$\begin{pmatrix} a_{11} & 0 & 0 & 0 & \dots \\ 0 & a_{22} & 0 & 0 & \dots \\ 0 & 0 & a_{33} & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}^{-1} = \begin{pmatrix} 1/a_{11} & 0 & 0 & \dots \\ 0 & 1/a_{22} & 0 & \dots \\ 0 & 0 & 1/a_{33} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \dots \dots (4.20)$$

$$(\text{Scalar times matrix})^{-1} = \frac{(\text{matrix})^{-1}}{\text{scalar}} \dots \dots \dots (4.21)$$

SECTION 5

THE GEOMETRY OF ROTATIONS

As a first application of the matrix algebra let us compute the *a* matrix for a few general rotations. Although we can consider a general rotation as one of angle ϕ about the unit vector* *A*, it is easier to consider a general rotation as three successive rotations about coordinate axes.

A study of Fig. 34 shows that for a counterclockwise rotation ϕ about x_1 , the new components of a vector *V* are:

$$\begin{aligned} V'_1 &= V_1 \\ V'_2 &= V_2 \cos \phi + V_3 \sin \phi \\ V'_3 &= -V_2 \sin \phi + V_3 \cos \phi \end{aligned}$$

whence $V' = aV$ where

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \phi & \sin \phi \\ 0 & -\sin \phi & \cos \phi \end{pmatrix} \dots \dots \dots (5.1)$$

* A general rotation of amount ϕ about the unit axis *A* is given by

$$a = AA_c + (I - AA_c) \text{Cos } \phi + \text{Sin } \phi A$$

See Vector Analysis (Gibbs Wilson, Yale Press) pp. 338.

Similarly, for a counterclockwise rotation ϕ about x_2 we have

$$a = \begin{pmatrix} \cos \phi & 0 & -\sin \phi \\ 0 & 1 & 0 \\ \sin \phi & 0 & \cos \phi \end{pmatrix} \dots\dots\dots (5.2)$$

and for a counterclockwise rotation ϕ about x_3 :

$$a = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \dots\dots\dots (5.3)$$

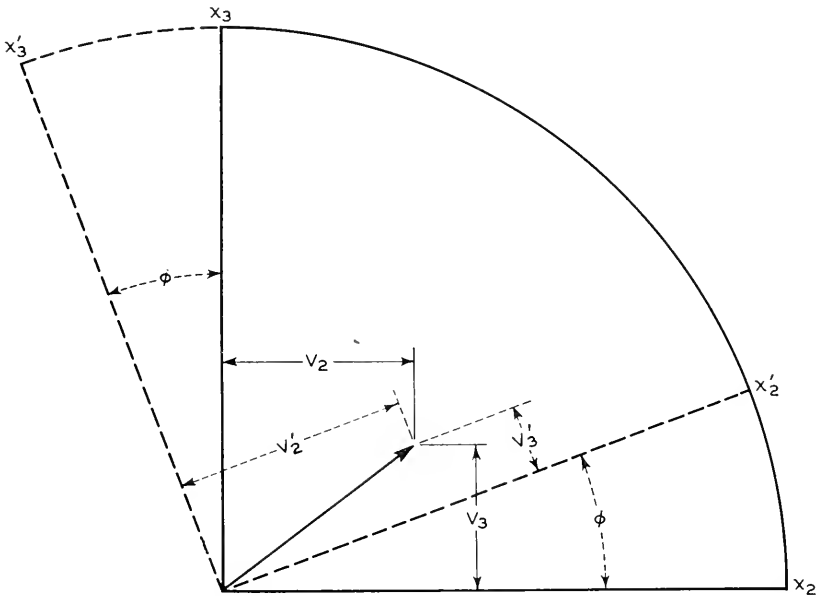


Fig. 34—The relationship between the components of a vector on one coordinate system and on another.

In the appendix we give the special transformations corresponding to the symmetry operations of the 32 crystal classes. If we have three successive rotations:

$$\begin{aligned} x' &= ax \\ x'' &= a'x' \\ x''' &= a''x'' \end{aligned}$$

the resultant rotation is

$$x''' = a''a'ax$$

or
$$x''' = Rx \dots\dots\dots (5.4)$$

where
$$R = a''a'a \dots\dots\dots (5.5)$$

The I.R.E. Orientation Angles and the I.R.E. Matrix

The Institute of Radio Engineers has proposed that, for quartz crystals, all orientations be given in terms of three rotations ϕ, θ, ψ about x_3, x_2' and x_3'' respectively, starting with the plate length along x_1 width along x_2 and thickness along x_3 . (Here x_3 is the z or optic axis, x_1 is the electric axis.)

Whence, here:

$$R = \begin{pmatrix} \cos \psi & \sin \psi & 0 \\ -\sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix} \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and carrying out the two matrix multiplications:

$$\begin{pmatrix} x_1 & x_2 & x_3 \\ \cos \phi \cos \theta & \cos \psi & \sin \phi \cos \theta \\ -\sin \phi \sin \psi & +\cos \phi \sin \psi & \cos \psi - \sin \theta \cos \psi \\ -\cos \phi \cos \theta & \sin \psi & -\sin \phi \cos \theta \\ -\sin \phi \cos \psi & +\cos \phi \cos \psi & \sin \theta \sin \psi \\ \cos \phi \sin \theta & \sin \phi \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} x_1''' \\ x_2''' \\ x_3''' \end{pmatrix} \dots (5.6)$$

If we denote the unit vectors along the length, width and thickness as P_1P_2 and P_3 respectively we have as a matrix defining the plate:

$$P = Rx \dots \dots \dots (5.7)$$

The I.R.E. orientation system is useful to the designer of crystal plates because his problem is to choose such values of ϕ, θ, ψ as to give the plate certain physical properties along its length, width and thickness. The man who cuts the plate has a different problem, that of moving the crystal (and hence the $x_1 x_2 x_3$ axes) about a fixed saw so that the plate cut parallel to the saw blade is what the designer ordered.

Let us consider such a system as shown in Figs. 37, 38 and 39. In Fig. 38 the crystal stands with its optic axis along P_3 , its + electric axis (for right hand quartz) along P . Since the shop man considers clockwise rotation as positive we now rotate the crystal through angle U_3 about P_3 clockwise, we then turn the crystal through angle U_2 clockwise about P_1 , and finally, after cutting out a slab of required thickness, we turn it clockwise through angle U_1 about P_3 to cut its length and width.

On the plate axes P_1 the crystallographic axes $x_1 x_2 x_3$ are now given by

$$x = rP \dots \dots \dots (5.8)$$

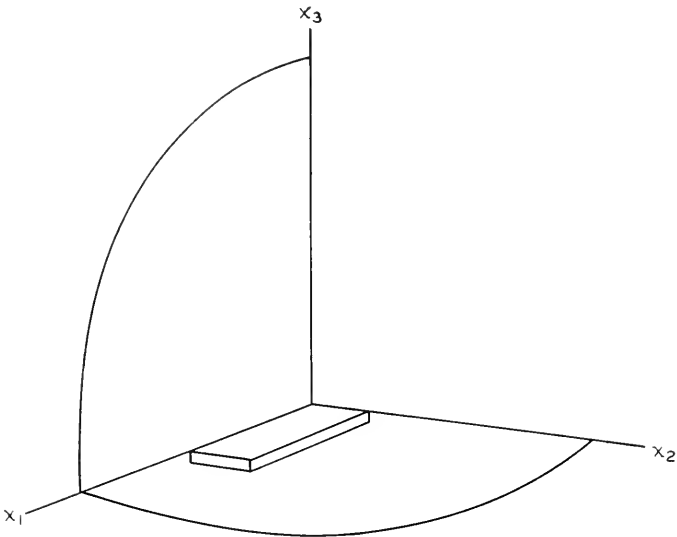


Fig. 35—The initial position $(0, 0, 0)$ for the I.R.E. direction angles.

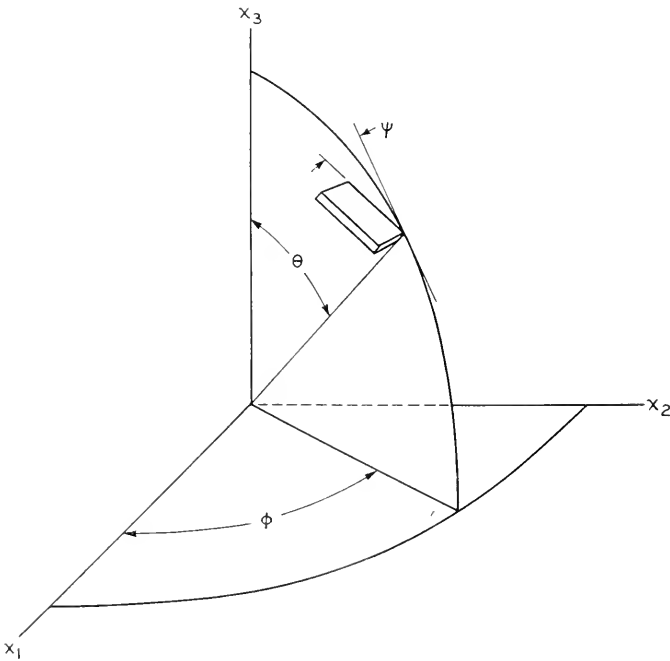


Fig. 36—The final position (Φ, Θ, Ψ) for the I.R.E. direction angles.

where

$$r = \begin{pmatrix} \cos U_1 \sin U_1 0 \\ -\sin U_1 \cos U_1 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & \theta & \theta \\ 0 & \cos U_2 \sin U_2 \\ 0 & -\sin U_2 \cos U_2 \end{pmatrix} \begin{pmatrix} \cos U_3 \sin U_3 0 \\ -\sin U_3 \cos U_3 0 \\ 0 & 0 & 1 \end{pmatrix}$$

or

$$r = \begin{pmatrix} \cos U_1 \cos U_3 & \cos U_1 \sin U_3 & \sin U_1 \sin U_2 \\ -\sin U_1 \cos U_2 \sin U_3 & +\sin U_1 \cos U_2 \cos U_3 & \\ -\sin U_1 \cos U_3 & -\sin U_1 \sin U_3 & \cos U_1 \sin U_2 \\ -\cos U_1 \cos U_2 \sin U_3 & +\cos U_1 \cos U_2 \cos U_3 & \\ \sin U_2 \sin U_3 & -\sin U_2 \cos U_3 & \cos U_2 \end{pmatrix} \quad (5.9)$$

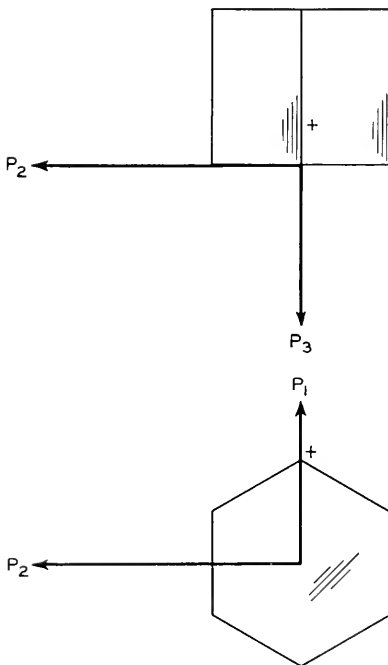


Fig. 37

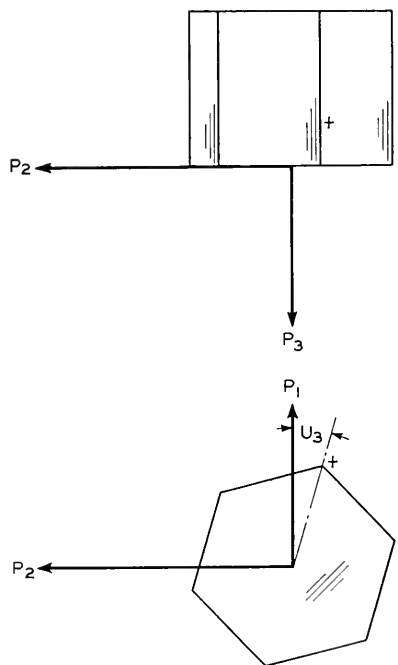


Fig. 38

Fig. 37—The $(0, 0, 0)$ position of a shop system of direction angles.

Fig. 38—The second position of a shop system.

From (5.8) we see that $P = r x$ and hence, if this is to be the same plate the designer specified by $P = R x$ we must have $R = r$ whence we may equate the terms of (5.6) and (5.9) to get the relations

$$\begin{aligned} \cos U_2 &= \cos \theta \text{ or } U_2 = \pm \theta \\ \tan U_1 &= \cot \psi \dots \dots \dots (5.10) \\ \tan U_3 &= \cot \phi \end{aligned}$$

or

$$\begin{aligned} U_1 &= \psi - 90 + n\pi \\ U_2 &= \theta \\ U_3 &= \phi - 90 + n\pi \end{aligned}$$

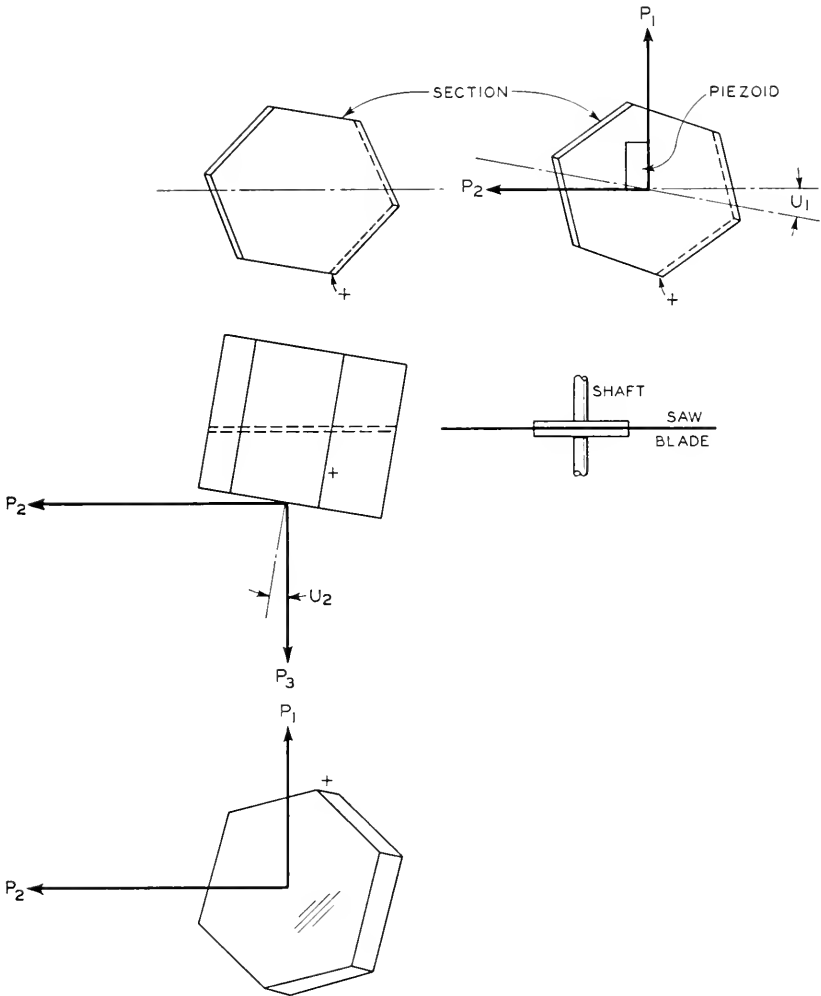


Fig. 39—Cutting the slab and trimming it to the piezoid boundaries.

Where n is any integer positive or negative, including zero. If we take

$$\begin{aligned} U_1 &= \psi - 90 \\ U_2 &= \theta \\ U_3 &= \phi + 90 \end{aligned} \dots\dots\dots (5.11)$$

The matrices are consistent term by term.

SECTION 6

CRYSTALLINE DIELECTRICS

As a first application of the matrix algebra considered as a linear vector function let us reconsider the problem of the crystal in an electric field.

The relations of chapter II, equation (1) can be written in the abbreviated form:

$$D = D_{ij}E \quad \text{where} \quad D_{rs} = D_{sr}$$

in accordance with the system of abbreviations adopted in the appendix.

If we put

$$4\pi D_{rs} = k_{rs}$$

equation (1) can be written

$$D = \frac{1}{4\pi} k_{rs} E \dots\dots\dots (6.1)$$

In order to investigate the effects of crystal symmetry in determining the least number of dielectric constants that are required for a given class of symmetry it is desirable to find the electric induction D for any system of axes. Suppose that we choose a system for axes x'_1, x'_2, x'_3 related to x_1, x_2, x_3 through the relations:

$$\begin{aligned} x_1 &= a_{11}x'_1 + a_{12}x'_2 + a_{13}x'_3 \\ x_2 &= a_{21}x'_1 + a_{22}x'_2 + a_{23}x'_3 \dots\dots\dots (6.2) \\ x_3 &= a_{31}x'_1 + a_{32}x'_2 + a_{33}x'_3 \end{aligned}$$

where a_{11} is the cosine of the angle between x_1 and x'_1 , a_{12} is the cosine of the angle between x'_1 and x_2 etc.

Equation (6.2) can be abbreviated to

$$x' = ax$$

where a is the matrix

$$a = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

It is shown in the sec. 4 that any vector $V = \begin{pmatrix} V_1 \\ V_2 \\ V_3 \end{pmatrix}$ can be written on the new system of axes as V' where $V' = aV$, conversely $V = a^{-1}V'$; a^{-1} is the matrix reciprocal to a . Since the induction D and the electric field E are simple vector functions they transform as the vector V , that is:

$$D' = aD \dots\dots\dots(6.3)$$

$$E' = aE \dots\dots\dots(6.4)$$

But by (6.1)

$$D = \frac{1}{4\pi} kE$$

whence:

$$aD = \frac{1}{4\pi} aka_c aE$$

or

$$D' = \frac{1}{4\pi} k'E' \dots\dots\dots(6.5)$$

if

$$k' = aka_c \dots\dots\dots(6.6)$$

We see that the form of (6.5) is the same as that of (6.1) for any set of axes if (6.6) is used to define the new dielectric matrix k .

To apply this relation (6.6) to a particular crystal let us consider a tetragonal crystal (which has its properties unchanged by a rotation of 90° about a four fold axis). Let us choose the four fold axis as x_3 and then rotate the axis 90° about x_3 . In this case

$$a = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ and the reciprocal matrix } a^{-1} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

whence equation (6.6) becomes:

$$k' = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} k_{11} & k_{12} & k_{31} \\ k_{12} & k_{22} & k_{23} \\ k_{31} & k_{23} & k_{33} \end{pmatrix} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} k_{22} - k_{12} & k_{23} \\ -k_{12} & k_{11} - k_{31} \\ k_{23} - k_{31} & k_{33} \end{pmatrix}$$

But because of the symmetry k is unchanged by this transformation, hence

$$k = k'$$

Two matrices can be equal only if corresponding terms are equal, hence

$$k_{11} = k_{22}, k_{12} = -k_{21} = 0, k_{23} = -k_{32} \text{ and } k_{31} = k_{23}$$

whence

$$k_{23} = k_{31} = 0.$$

We are left then, with the dielectric constant matrix for the tetragonal bisphenoidal class:

$$k = \begin{pmatrix} k_{11} & 0 & 0 \\ 0 & k_{11} & 0 \\ 0 & 0 & k_{33} \end{pmatrix}$$

Applying other transformations possible for tetragonal crystals gives no further simplification.

If we go through all the symmetry transformations possible for the 32 classes we find that cubic crystals require but one dielectric constant, hexagonal, trigonal and tetragonal crystals require two constants, orthorhombic monoclinic and triclinic crystals require 3.

As the triclinic class has no fixed axes or planes of symmetry the reduction of its 6 constants to 3 is not so obvious. It may be seen by expanding into ordinary xyz coordinates, that $\rho_c k \rho = 1$ is the equation of an ellipsoid, (ρ is the radius vector) where the six k 's are the coefficients of x^2 , y^2 , z^2 , yz , zx and xy respectively. If we choose the coordinate axes along the axes of the ellipsoid the yz , zx and xy terms drop out and only three k 's are needed. With triclinic crystals then, if we determine the axes of the ellipsoid, then choose the coordinate axes along them, only three dielectric constants are needed to completely specify the polarization in terms of the electric field. The determination of the ellipsoid axes must be made experimentally as there are no symmetry elements to guide us. It is possible to compute the positions of the axes from the 6 k 's by solving a cubic equation.

The values of the k 's depend on the frequency of the applied field. In crystals of low symmetry the ellipsoid axes for different frequencies do not necessarily coincide.

Another vector quantity of interest is the polarization, $P = D - \frac{1}{4\pi} E$.

Using (1) this becomes

$$P = \frac{1}{4\pi} (k - I)E \dots\dots\dots (6.7)$$

SECTION 7

QUADRATIC FORMS

Often the elements of a matrix are themselves functions of other quantities. In order to relate the elements of one matrix with those of another by means of a matrix multiplication, we may make a single column matrix of each of them. We then wish to know how a transformation of axes changes the elements of this single column matrix. Consider a symmetrical matrix b that relates two vectors u and v :

$$u = bv.$$

A transformation of axes, a , changes u and v to u' and v' . Multiplying $u = bv$ through by the prefactor a we have

$$au = abv.$$

We now replace au by its equivalent $a^{-1}v'$ whence:

$$u' = aba^{-1}v'$$

so that

$$u' = b'v'$$

if we define b' as

$$b' = aba^{-1} \dots\dots\dots (7.1)$$

To be in accord with common usage we now rearrange b according to the arbitrary scheme:

$$\begin{pmatrix} b_{11} \\ b_{22} \\ b_{33} \\ b_{23} \\ b_{31} \\ b_{12} \end{pmatrix} = \begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ \cdot \\ \cdot \\ B_6 \end{pmatrix}$$

We wish to know what operation to perform on B to get B' corresponding to b' . If we expand $b' = aba^{-1}$ it is easily seen that $b' = \alpha B$ where

$$\alpha = \begin{pmatrix} a_{11}^2 & a_{12}^2 & a_{13}^2 & 2a_{12}a_{13} & 2a_{13}a_{11} & 2a_{11}a_{12} \\ a_{21}^2 & a_{22}^2 & a_{23}^2 & 2a_{22}a_{23} & 2a_{23}a_{21} & 2a_{21}a_{22} \\ a_{31}^2 & a_{32}^2 & a_{33}^2 & 2a_{32}a_{33} & 2a_{33}a_{31} & 2a_{31}a_{32} \\ a_{21}a_{31} & a_{22}a_{32} & a_{23}a_{33} & a_{22}a_{33} & a_{21}a_{33} & a_{22}a_{31} \\ a_{31}a_{11} & a_{32}a_{12} & a_{33}a_{13} & a_{12}a_{33} & a_{13}a_{31} & a_{11}a_{32} \\ a_{11}a_{21} & a_{12}a_{22} & a_{13}a_{23} & a_{13}a_{23} & a_{11}a_{23} & a_{12}a_{21} \end{pmatrix} \quad (7.2)$$

Because we shall often need to form the α matrix from the a matrix we need an easily remembered mechanism for doing so. We notice that those are four kinds of terms in the α matrix and that the four kinds can be separated from each other by two center lines, one horizontal, one vertical. This gives us four squares of nine terms each and we can correlate each term of any square to a term of the a matrix by means of its position in the square. The terms of the upper left square are the squares of the corresponding terms of the a matrix. To form any term of the lower left square we cover the corresponding term of the a matrix with our finger and multiply the visible terms of that column. To form any term of the upper right square we cover the corresponding a term and write down *double* the product of the visible terms of that row. To form any term of the lower right square we find the corresponding a term, strike out that row and column and write down the *sum* of the remaining cross products. A study of the following diagram will help to remember these rules.

Terms are squares of corresponding a terms	Omission products doubled
Omission products	Sum of omission cross products

Fig. 40

SECTION 8

CRYSTAL ELASTICITY

Stress

Consider a point P in a medium acted on by forces. If a small area is chosen about P the medium on one side of the area exerts a force on the medium on the other side. The force will depend on the size of the area and

on the direction of its normal n . We shall choose a triangular area ds such that an arbitrarily chosen set of mutually perpendicular unit axes x_1, x_2, x_3 pass through the vertices of the triangle. Let us consider the conditions of equilibrium of the tetrahedral element of volume so formed. The areas normal to x_1, x_2, x_3 are ds_1, ds_2, ds_3 , respectively, and the forces per unit area acting through these faces are:

$$F_1 = \begin{pmatrix} f_{11} \\ f_{12} \\ f_{13} \end{pmatrix}, \quad F_2 = \begin{pmatrix} f_{21} \\ f_{22} \\ f_{23} \end{pmatrix}, \quad F_3 = \begin{pmatrix} f_{31} \\ f_{32} \\ f_{33} \end{pmatrix}$$

Any body forces (such as gravity) depend on a higher order of smallness (that is on the volume rather than on the area) and hence are negligible. Whence for equilibrium:

$$Fds = F_1ds_1 + F_2ds_2 + F_3ds_3$$

But

$$ds_1 = n_1ds, \quad ds_2 = n_2ds \quad \text{and} \quad ds_3 = n_3ds$$

where $\begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix}$ is the normal to the area ds . Whence we may write: $F = fn$

where f is the matrix

$$\begin{pmatrix} f_{11} & f_{12} & f_{13} \\ f_{21} & f_{22} & f_{23} \\ f_{31} & f_{32} & f_{33} \end{pmatrix}$$

For the body to be in rotational equilibrium the tangential forces must balance, hence $f_{12} = f_{21}, f_{13} = f_{31}$ and $f_{23} = f_{32}$.

Transformation of Axes

A change of axes that transforms vectors through $F' = aF$ changes $F = fn$ to $aF = afa^{-1}an$ so that if $f' = afa^{-1}$ then $F' = f'n'$.

In order to relate the stress to other quantities through a matrix we wish to convert it into a single column matrix. We put $f_{11} = X_1, f_{22} = X_2, f_{33} = X_3, f_{23} = f_{32} = X_4, f_{31} = f_{13} = X_5$ and $f_{12} = f_{21} = X_6$.

Changing to the X representation we find

$$x' = \alpha X' \dots \dots \dots (8.1)$$

where α is the matrix eq. (7.2).

Strain Theory

If the dimensions of a body change, a point $p = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$ is moved to $p + \sigma_p$

where $\sigma_p = \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$. A neighboring point $p + u$ is moved by an amount σ_{p+u} given by $\sigma_{p+u} = (\nabla\sigma_c)_c u + \sigma_p$. The movement of $p + u$ relative to p is $\sigma = \sigma_{p+u} - \sigma_p = (\nabla\sigma_c)_c u$.

The 9 components of $(\nabla\sigma_c)_c$ describe the sort of movement in the neighborhood of a point; they are the strain coefficients. If the strain matrix is $\epsilon = (\nabla\sigma_c)_c$, a transformation $x' = ax$ causes this to become $a\epsilon a_c = (a\nabla\sigma_c a_c)_c$ and if $a\nabla = \nabla'$ and $a\sigma = \sigma'$ so that $\sigma_c a_c = \sigma'_c$ we have $\epsilon' = (\nabla'\sigma'_c)_c$ if

$$\epsilon' = a\epsilon a_c \dots \dots \dots (8.2)$$

When we arrange ϵ as a single column matrix e we shall, following custom, take $e_4 = \frac{\partial\sigma_2}{\partial x_3} + \frac{\partial\sigma_3}{\partial x_2}$, $e_5 = \text{etc.}$ This has the effect of moving the 2's of the α matrix to the conjugate position so that, while x transforms as $x' = \alpha x$, e transforms as $e' = \alpha_c^{-1} e$.

We shall take tensions as positive stress elements, and elongations as positive strain elements. The shear strain, $e_c = (0, 0, 0, 0, 0, e_6)$ becomes upon rotating through 45° about x_3 , $e'_c = \left(\frac{e_6}{2}, -\frac{e_6}{2}, 0, 0, 0, 0\right)$. This shows that to be consistent, a positive shear strain about x_3 must mean an expansion along the line $x_1 = x_2$ and an equal contraction along the line $x_1 = -x_2$.

A positive shear stress is one that tends to produce a positive shear strain.

By superposing such strain elements we see that the ϵ matrix (useful in displacement problems) may be formed from the e matrix (which is useful in stress strain relation) as

$$\epsilon = \begin{pmatrix} e_1 & \frac{1}{2}e_6 & \frac{1}{2}e_5 \\ \frac{1}{2}e_6 & e_2 & \frac{1}{2}e_4 \\ \frac{1}{2}e_5 & \frac{1}{2}e_4 & e_3 \end{pmatrix} \dots \dots \dots (8.3)$$

This slightly awkward relation is used solely to make the "work done in straining" expressible as

$$2W = X_c e = e_c X \dots \dots \dots (8.4)$$

If the e 's were taken as equal to the ϵ 's the work would be: $2W = X_1 e_1 + X_2 e_2 + X_3 e_3 + 2X_4 e_4 + 2X_5 e_5 + 2X_6 e_6$. This would be awkward in some later problems.

If the scalar W is to be unaffected by a transformation a we must have $W = e_c X$ unaffected. If we write

$$W = e_c \alpha^{-1} \alpha X = e_c \alpha^{-1} X'$$

we have

$$W' = W = e'_c X'$$

if

$$e'_c = e_c \alpha^{-1}$$

when

$$e' = \alpha_c^{-1} e_c \dots \dots \dots (8.5)$$

This substantiates our previous statement.

Relation Between Stress and Strain

If the strain in an elastic body is proportioned to the stress we may write:

$$\begin{aligned} e_1 &= S_{11} X_1 + S_{12} X_2 + \dots + S_{16} X_6 \\ e_2 &= S_{21} X_1 + \dots \dots \dots \end{aligned}$$

Where the S 's are elastic moduli. In matrix notation:

$$e = SX \dots \dots \dots (8.6)$$

Conversely $X = S^{-1}e$ or if $S^{-1} = C$

$$X = Ce \dots \dots \dots (8.7)$$

The C 's are called elastic constants to distinguish them from the moduli S .

As $e = SX$, $\alpha_c^{-1}e = \alpha_c^{-1}S\alpha^{-1}\alpha X$, and since $\alpha_c^{-1}e = e'$, (the representation of e on a new axis system related to the old one through the matrix a) and αX is X' , then we may write $(\alpha_c^{-1}e) = (\alpha_c^{-1}S\alpha^{-1})(\alpha X)$ as:

$$e' = S'X' \text{ where } S' = \alpha_c^{-1}S\alpha^{-1} \dots \dots \dots (8.8)$$

Similarly operating on $X = Ce$ we find

$$X' = C'e' \text{ where } C' = \alpha C\alpha_c \dots \dots \dots (8.9)$$

The energy required to cause the strain e is

$$W = \int X_r de_r = \frac{1}{2} X_r e_r = \frac{1}{2} S_{rs} X_r X_s \dots \dots \dots (8.10)$$

whence, if W is a perfect differential,

$$S_{rs} = \frac{\partial^2 W}{\partial X_r \partial X_s} = \frac{\partial^2 W}{\partial X_s \partial X_r} = S_{sr} \dots \dots \dots (8.11)$$

Similarly

$$C_{rs} = C_{sr} \dots\dots\dots(8.12)$$

This reduces the constants and moduli to 21 of each.

If a transformation is performed that is permitted by the symmetry of the medium the elastic modulus matrix is unaltered. The monoclinic system has a binary axis. If we choose this as x_3 and rotate the axes 180°

about this by means of the matrix $a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ we have $S' =$

$$\alpha_c^{-1} S \alpha^{-1} = S.$$

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} S_{11} S_{12} S_{13} S_{14} S_{15} S_{16} \\ S_{12} S_{22} S_{23} S_{24} S_{25} S_{26} \\ S_{13} S_{23} S_{33} S_{34} S_{35} S_{36} \\ S_{14} S_{24} S_{34} S_{44} S_{45} S_{46} \\ S_{15} S_{25} S_{35} S_{45} S_{55} S_{56} \\ S_{16} S_{26} S_{36} S_{46} S_{56} S_{66} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} & -S_{14} & -S_{15} & S_{16} \\ S_{12} & S_{22} & S_{23} & -S_{24} & -S_{25} & S_{26} \\ S_{13} & S_{23} & S_{33} & -S_{34} & -S_{35} & S_{36} \\ -S_{14} & -S_{24} & -S_{34} & S_{44} & S_{45} & -S_{46} \\ -S_{15} & -S_{25} & -S_{35} & S_{45} & S_{55} & -S_{56} \\ S_{16} & S_{26} & S_{36} & -S_{46} & -S_{56} & S_{66} \end{pmatrix}$$

Equating terms, those whose signs differ in S and S' must vanish.

Proceeding in this way through the 32 crystal classes we arrive at the ten following matrices that cover the elastic behaviour of all 32 classes.

Triclinic System
21 moduli

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{12} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{13} & S_{23} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{14} & S_{24} & S_{34} & S_{44} & S_{45} & S_{46} \\ S_{15} & S_{25} & S_{35} & S_{45} & S_{55} & S_{56} \\ S_{16} & S_{26} & S_{36} & S_{46} & S_{56} & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous

.....(8.13)

Monoclinic System
 x_3 axis binary
13 moduli

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & S_{16} \\ S_{12} & S_{22} & S_{23} & 0 & 0 & S_{26} \\ S_{13} & S_{23} & S_{33} & 0 & 0 & S_{36} \\ 0 & 0 & 0 & S_{44} & S_{45} & 0 \\ 0 & 0 & 0 & S_{45} & S_{55} & 0 \\ S_{16} & S_{26} & S_{36} & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous

.....(8.14)

Phombis System
 x_3 binary
 9 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{23} & S_{23} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous
(8.15)

Tetragonal System
 x_3 a fourfold axis
 (Classes 9, 10, 13)
 7 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & S_{16} \\ S_{12} & S_{11} & S_{13} & 0 & 0 & -S_{16} \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ S_{16} & -S_{16} & 0 & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous
(8.16)

Tetragonal System
 x_3 a fourfold axis
 x_1 a twofold axis
 (Classes 11, 12, 14, 15)
 6 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{pmatrix}$$

The C matrix is entirely analogous
(8.17)

Trigonal System
 x_3 trigonal axis
 (Classes 16, 17)
 7 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & -S_{15} & 0 \\ S_{12} & S_{11} & S_{13} & -S_{14} & S_{25} & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ S_{14} & -S_{14} & 0 & S_{44} & 0 & 2S_{25} \\ -S_{25} & S_{25} & 0 & 0 & S_{44} & 2S_{14} \\ 0 & 0 & 0 & 2S_{25} & 2S_{14} & 2(S_{11} - S_{12}) \end{pmatrix}$$

The C matrix is analogous except that
 $C_{46} = C_{25}$
 $C_{56} = C_{14}$
 $C_{66} = \frac{1}{2}$
 $(C_{11} - C_{12})$
(8.18)

Trigonal System
 x_3 trigonal axis
 x_1 binary (Classes 18, 20, 21)
 6 modulii
 (alpha quartz)

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & 0 & 0 \\ S_{12} & S_{11} & S_{13} & -S_{14} & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ S_{14} & -S_{14} & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 2S_{14} \\ 0 & 0 & 0 & 0 & 2S_{14} & 2(S_{11} - S_{12}) \end{pmatrix}$$

The C matrix is analogous except that
 $C_{56} = C_{14}$
 $C_{66} = \frac{1}{2}$
 $(C_{11} - C_{12})$
(8.19)

Hexagonal System
 x_3 a sixfold axis
 x_1 a twofold axis
 (Classes 19, 22, 23, 24, 25, 26, 27)
 5 modulii

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) \end{pmatrix}$$

The C matrix is analogous except that
 $C_{66} = \frac{1}{2}$
 $(C_{11} - C_{12})$
(8.20)

Cubic System
 x_1, x_2 and x_3
 fourfold axes
 3 moduli

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{44} \end{pmatrix} \dots\dots\dots (8.21)$$

The C matrix is entirely analogous

Isotropic bodies
 2 moduli

$$S = \begin{pmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & S_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & S_2 \end{pmatrix} \dots\dots\dots (8.22)$$

The C matrix is analogous except that $C_2 = \frac{1}{2} (C_{11} - C_{12})$
 $S_2 = 2 (S_{11} - S_{12})$

Several Elastic Ratios in common use are given here for reference:

Young's Modulus: A tension stress X divided by the component of strain in the direction of X , $Y_i = \frac{X_i}{e_i}$. If the coordinate axes are chosen so that the stress lies along X_1 , $Y_1 = \frac{1}{S_{11}}$. To find the value of Y in an arbitrary direction, (θ, φ) find S' for a transformation that puts X' in the direction (θ, φ)

$$S' = \alpha_c^{-1} S \alpha^{-1}$$

Where α is taken as form (21.4). Whence we obtain:

$$\begin{aligned} \left(\frac{1}{Y_{\theta, \varphi}} \right) &= c_1^4 s_2^4 S_{11} + s_1^4 s_2^4 S_{22} + c_2^4 S_{33} + s_1^2 s_2^2 c_2^2 S_{44} + c_1^2 c_2^2 s_2^2 S_{55} + c_1^2 s_1^2 s_2^4 S_{66} \\ &+ 2c_1^2 s_1 c_2 s_2^3 S_{66} + 2c_1 s_1^2 c_2 s_2^3 S_{46} + 2c_1 s_1 c_2^2 s_2^2 S_{66} + 2c_1 s_1^3 s_2^4 S_{26} \\ &+ 2c_1^3 s_1 s_2^4 S_{16} + 2c_1^3 s_2^3 c_1 S_{15} + 2c_1^2 s_1 s_2^3 c_2 S_{14} + 2c_1^2 c_2^2 s_2^2 S_{13} \\ &+ 2c_1^2 s_1^2 s_2^4 S_{12} + 2s_1^2 c_2^2 s_2^2 S_{23} + 2s_1 s_2 c_2^2 S_{34} + 2c_1 s_1 c_2^2 s_2^2 S_{45} \\ &+ 2c_1 c_2^3 s_2 S_{35} + 2c_1 s_1^2 c_2 s_2^3 S_{25} + 2s_1^3 c_2 s_2^3 S_{24} \dots\dots\dots (8.23) \end{aligned}$$

Rigidity Modulus: The shearing stress divided by the component of shear about the axis of shearing stress. For shear about x_1 ,

$$N_1 = \frac{1}{S_{44}} \dots\dots\dots (8.24)$$

Its value in another directions can be found as $Y_{\theta, \varphi}$ was above.

The bulk modulus: The change in volume per unit volume for unit hydrostatic pressure is the bulk modulus, H . For a stress $X_c = (1, 1, 1, 0, 0, 0)$

$$e = (S_{11} + S_{12} + S_{31}, S_{12} + S_{33} + S_{23}, S_{31} + S_{23} + S_{33}, \dots)$$

$$H = (\epsilon_1 + \epsilon_2 + \epsilon_3 = S_{11} + S_{22} + S_{33} + 2S_{12} + 2S_{31} + 2S_{23}) \dots \dots \dots (8.25)$$

This is obviously independent of the choice of axes.

The Temperature Coefficient of the Elastic Modulii and Constants

If

$$C = C^\circ + th + t^2h^1 + t^3h^2 + \dots \dots \dots (8.26)^*$$

and

$$S = S^\circ + th + t^2H^1 + t^3H^2 + \dots \dots \dots (8.27)$$

(C° and S° denote the values of the C 's and S 's for some standard temperature $t = 0$) then as the transformations are

$$C' = \alpha C \alpha_c \text{ and } S' = \alpha_c^{-1} S \alpha^{-1} \text{ or}$$

$$C' = \alpha (C^\circ + th + t^2h^1 + t^3h^1' \dots) \alpha_c$$

and

$$S' = \alpha_c^{-1} (S^\circ + tH + t^2H^1 + t^3H^1 \dots) \alpha^{-1}$$

we see that

$$C' = C^{\circ 1} + th' + t^2h^{1'} \dots \dots \dots (8.28)$$

$$S' = S^{\circ 1} + tH' + t^2H^{1'} \dots \dots \dots (8.29)$$

where

$$h' = \alpha h \alpha_c \text{ etc.} \dots \dots \dots (8.30)$$

$$H' = \alpha_c^{-1} H \alpha^{-1} \text{ etc.} \dots \dots \dots (8.31)$$

That is, the h 's transform as the C 's do, and the H 's transform as the S 's do. Consequently we may copy their respective forms from the C and S matrices for any particular crystal class.

When the temperature coefficients of the constants or modulii are known in the form:

$$C_{ij} = C_{ij}^\circ (1 + tT_{c_{ij}}) \dots \dots \dots (8.32)$$

$$S_{ij} = S'_{ij} (1 + tT_{s_{ij}}) \dots \dots \dots (8.33)$$

* The n of t^n denotes the n th power of the scalar t ; the n of h^n is merely another matrix, it does not mean a power.

we may write:

$$h_{ij} = C_{ij}^{\circ} T_{c_{ij}} \dots \dots \dots (8.34)$$

$$H_{ij} = S_{ij}^{\circ} T_{s_{ij}} \dots \dots \dots (8.35)$$

Multiplying (5) by (6) we get:

$$SC = I = S^{\circ}C^{\circ} = S^{\circ}C^{\circ} + t(S^{\circ}h + HC^{\circ}) + t^2(S^{\circ}h^1 + Hh + h^1C^{\circ}) + \dots$$

whence, for this relation to hold for all values of t :

$$S^{\circ}h + HC^{\circ} = 0 \dots \dots \dots (8.36)$$

whence

$$\begin{aligned} h &= -C^{\circ}HC^{\circ} \\ H &= -S^{\circ}hS^{\circ} \end{aligned} \dots \dots \dots (8.37)$$

also

$$S^{\circ}h^1 + Hh + H^1C^{\circ} = 0 \dots \dots \dots (8.38)$$

so that

$$\begin{aligned} h^1 &= hS^{\circ}h - C^{\circ}H^1C^{\circ} \\ H^1 &= HC^{\circ}H - S^{\circ}h^1S^{\circ} \end{aligned} \dots \dots \dots (8.39)$$

From these we can compute the h 's given the H 's and vice versa.

SECTION 9

TEMPERATURE EXPANSION

The change in the dimensions of a crystal caused by a temperature change can be considered as a strain. The shift of the terminus of a vector l relative to its origin is given from the strain matrix ϵ by the equation $\Delta l = t\epsilon l$

Since ϵ is symmetric a proper choice of axes makes it possible to make the strain per degree a diagonal matrix,

$$\Delta l = tAl \quad \text{where} \quad A = \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} \dots \dots \dots (9.1)$$

As l and Δl both transform as vectors, a transformation a causes A to transform as

$$A' = aAa^{-1} \dots \dots \dots (9.2)$$

The elongation per unit length per degree in the direction (θ, Φ) is

$$\Delta l_{\theta\varphi} = \begin{pmatrix} \cos \theta \sin \varphi, & \sin \theta \sin \varphi, & \cos \varphi \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} \begin{pmatrix} \cos \theta \sin \varphi \cdot \cdot \\ \sin \theta \sin \varphi \cdot \cdot \\ \cos = \varphi \cdot \cdot \end{pmatrix}$$

whence

$$\Delta l_{\theta\varphi} = A_1 \cos^2 \theta \sin^2 \varphi + A_2 \sin^2 \theta \sin^2 \varphi + A_3 \cos^2 \varphi \dots \dots \dots (9.3)$$

The strain can easily be extended to a function of t and t^2 as follows:

$$\Delta l = tAl + t^2Bl \dots \dots \dots (9.4)$$

Applying the prefactor a to both sides and putting the idemfactor in between A and l and between B and l in the form $I = a^{-1}a$ we have:

$$\begin{aligned} a\Delta l &= t(aAa^{-1})al + t^2(aBa^{-1})al \quad \text{or} \\ \Delta l' &= t A'l' + t^2 B'l' \quad \text{where} \\ A' &= aAa^{-1} \quad B' = aBa^{-1} \dots \dots \dots (9.5) \end{aligned}$$

SECTION 10

TEMPERATURE VARIATION OF THE ISOTHERMAL ELASTIC MODULI AND STRESS VARIATION OF THE TEMPERATURE EXPANSION COEFFICIENTS

We can write the isothermal elastic modulus matrix at temperature $\theta + t$ as

$$S^i = S^{i\theta} + tH \dots \dots \dots (10.1)$$

and the coefficient of temperature expansion at constant stress X as

$$\bar{A} = \bar{A}^\theta + LX \dots \dots \dots (10.2)$$

Let us take a unit cube of crystal about the cycle indicated in the table; starting with the cube in the unstressed unstrained state at absolute temperature θ :

Operation	Change in Stress	Change in Strain	Temp.
Heat at zero stress	0	$t\bar{A}^\theta$	θ to $\theta + t$
Apply X isothermally	X	$(S^{i\theta} + tH)X$	$\theta + t$
Cool at Const. X	0	$-t(\bar{A}^\theta + LX)$	$\theta + t$ to θ
Apply $-X$ isothermally	$-X$	$-S^{i\theta}X$	θ

If we sum the strain changes in this cycle to zero we have

$$H = L$$

so that we may write

$$S = S^{\circ} + tH \dots \dots \dots (10.1)$$

$$\bar{A} = \bar{A}^{\circ} + tHX \dots \dots \dots (10.3)$$

This tells us that we may determine the temperature coefficients of the elastic moduli by measuring the effect of stress on the temperature expansion coefficients.

In a similar way we find that if the isothermal elastic constant matrix at temp. $\theta + t$ is:

$$C^i = C^{i\circ} + th \dots \dots \dots (10.4)$$

then the relation between temperature and stress at constant strain e is

$$X = tB \dots \dots \dots (10.5)$$

where

$$B = B^{\circ} + he \dots \dots \dots (10.6)$$

The Difference between the Specific Heats at Constant Stress and Constant Strain

Writing for the specific heats at constant stress and at constant strain σ^p and σ^v , respectively, we can perform the following cycle:

Operation	Change in Stress	Change in Strain	Temperature	Work In	Heat Out	Entropy
Heat at zero stress . . .	—	tA°	θ to $\theta + t$	0	$-\rho t \sigma^p$	$\frac{-\rho t \sigma^p}{\theta + t/2}$
Restore zero strain isothermally	—	$-tA^{\circ}$	$\theta + t$	$\frac{t^2}{2} A_c^{\circ} C A^{\circ}$	Q	$\frac{Q}{\theta + t}$
Cool at zero strain . . .	—	0	$\theta + t$ to θ	0	$\rho t \sigma^v$	$\frac{\rho t \sigma^v}{\theta + \frac{t}{2}}$

Equating the sum of the entropy changes to zero:

$$Q = \left(1 + \frac{t}{2\theta} - \frac{t^2}{4\theta^2} \dots \right) \rho t (\sigma^p - \sigma^v)$$

Equating the work in to the heat out:

$$(\sigma^p - \sigma^v) = \frac{\theta}{\rho} \bar{A}_c^{\circ} C \bar{A}^{\circ} \dots \dots \dots (10.7)$$

Isothermal and Adiabatic Elastic Moduli

Let us take a unit crystal cube at temperature θ , apply any stress X adiabatically, heat it to bring the temperature back to θ at constant stress then release it isothermally. The cycle is analyzed in the table:

Operation	Change in Stress	Change in Strain	Temperature	Work In	Heat Out	Entropy Change
Apply X adiabatically	X	$S^a X$	θ to $\theta - t$	$\frac{1}{2} X_c S^a X$	0	0
Heat to θ at const. X	0	$t(\bar{A}^\circ + HX)$	$\theta - t$ to θ	$tX_c(\bar{A}^\circ + HX)$	$-t\rho\sigma^p$	$\frac{-t\rho\sigma^p}{\theta - t/2}$
Remove X isothermally	$-X$	$-S^{i\circ} X$	θ	$-\frac{1}{2} X_c S^{i\circ} X$	Q	Q/θ

Summing the strains to zero:

$$(S^{i\circ} - S^a)X = t(\bar{A}^\circ + HX)$$

If we equate the total entropy change to zero we obtain an expression for Q that can be substituted in the relation "work in = Heat out." This gives us:

$$-\frac{1}{2} X_c (S^{i\circ} - S^a)X + tX(\bar{A}^\circ + HX) = \frac{1}{2} \frac{t^2 \rho \sigma^p}{\theta}$$

and from these two expressions we derive, writing ϕ for $S^{i\circ} - S^a$:

$$\phi = \frac{\theta}{\rho\sigma^p} (\bar{A}^\circ + HX)(\bar{A}^\circ + HX)_c \dots \dots \dots (10.8)$$

which is, to the first order of the small quantities X :

$$\phi = \frac{\theta}{\rho\sigma^p} \bar{A}^\circ \bar{A}^\circ_c + 2HX\bar{A}^\circ_c \dots \dots \dots (10.9)$$

and since $X = C\epsilon$ we have also

$$\frac{\theta}{\rho\sigma^p} (\bar{A}^\circ + 2HC\epsilon)\bar{A}^\circ \dots \dots \dots (10.10)$$

Whence we see that as the stress approaches zero as a limit ϕ approaches

$\phi^\circ = \frac{\theta}{\rho\sigma^p} \bar{A}^\circ \bar{A}^\circ_c$. If we write similarly $C^{i\circ} - C^a = \psi$ we have multiplying $S^{i\circ} = S^a + \phi$ by $C^{i\circ} = C^a + \psi$ and dropping higher orders of small quantities:

$$\psi = -C^{i\circ} \phi C^{i\circ} \dots \dots \dots (10.11)$$

For example we have for quartz at 20° Centigrade

$$\phi^{\circ} = \frac{293 \times 10^{-12}}{2.65 \times 7.37 \times 10^6} \begin{pmatrix} 14.4 \\ 14.4 \\ 7.8 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (14.4 \ 14.4 \ 7.8 \ 0 \ -0 \ 0)$$

$$= \begin{pmatrix} 3.13 & 3.13 & 1.69 & 0 & 0 & 0 \\ 3.13 & 3.13 & 1.69 & 0 & 0 & 0 \\ 1.69 & 1.69 & .907 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} 10^{-15} \quad \text{and as}$$

$$S^{io} = 10^{-15} \times \begin{pmatrix} 1298 & -166 & -152 & -431 & 0 & 0 \\ -166 & 1298 & -152 & 431 & 0 & 0 \\ -152 & -152 & 990 & 0 & 0 & 0 \\ -431 & 431 & 0 & 2005 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2005 & 862 \\ 0 & 0 & 0 & 0 & 862 & 2928 \end{pmatrix}$$

whence $\phi_{11} = S_{11}^{io} (1 - .00241)$

$$\phi_{12} = S_{12}^{io} (1 - .0189)$$

$$\phi_{13} = S_{13}^{io} (1 - .0111)$$

$$\phi_{33} = S_{33}^{io} (1 - .000917)$$

For Rochelle Salt we have:

$$\phi = \frac{293 \times 10^{-12}}{1.79 \times 15.5 \times 10^6} \begin{pmatrix} 59.9 \\ 38.1 \\ 44.8 \\ 4 \\ 0 \\ 0 \end{pmatrix} \quad (59.9 \ 38.1 \ 44.8 \ 0 \ 0 \ 0)$$

$$= \begin{pmatrix} 38.0 & 24.2 & 28.5 & 0 & 0 & 0 \\ 24.2 & 15.4 & 18.1 & 0 & 0 & 0 \\ 28.5 & 18.1 & 21.3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \times 10^{-15}$$

$$\text{As } S^{i_o} = \begin{pmatrix} 4690 & -795 & -2180 & 0 & 0 & 0 \\ -795 & 3205 & 1691 & 0 & 0 & 0 \\ -2180 & 1691 & 2815 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6060 & 0 & 0 \\ 0 & 0 & 0 & 0 & 3060 & 0 \\ 0 & 0 & 0 & 0 & 0 & 8020 \end{pmatrix} \times 10^{-15}$$

So that

$$\begin{aligned} \phi_{11} &= S_{11}^{i_o} (1 - .0080) & \phi_{12} &= S_{12}^{i_o} (1 - .0305) \\ \phi_{22} &= S_{22}^{i_o} (1 - .0050) & \phi_{13} &= S_{13}^{i_o} (1 - .0103) \\ \phi_{33} &= S_{33}^{i_o} (1 - .0076) & \phi_{23} &= S_{23}^{i_o} (1 - .0107) \\ \phi_{44} &= S_{44}^{i_o} \\ \phi_{55} &= S_{55}^{i_o} \\ \phi_{66} &= S_{66}^{i_o} \end{aligned}$$

At the temperature of maximum piezo activity the components of ϕ for Rochelle are smaller by about $3\frac{1}{2}\%$.

SECTION 11

THE PIEZO-ELECTRIC EFFECT

Some crystals develop an electric charge when subjected to mechanical stresses. As far as the effect is linear it may be expressed by:

$$\begin{aligned} D_1 &= d_{11}X_1 + d_{12}X_2 \cdots d_{16}X_6 \\ D_2 &= d_{21}X_1 + \cdots \dots \dots \dots \dots \dots \dots (11.1) \\ D_3 &= d_{31}X_1 + \cdots \dots \dots \dots \dots \dots \dots \dots \dots \end{aligned}$$

or in matrix notation

$$D = dX \dots \dots \dots \dots \dots \dots (11.2)$$

where the 18 constants d_{ij} are called piezo-electric constants, and D is the electric induction.

On rotating the axes by means of a transformation a , the vector D becomes D' where $D' = aD$. The stress transforms as $X' = \alpha X$ whence $D = dX$ becomes $D' = ad\alpha^{-1}X'$ or $D' = d'X'$ where:

$$d' = ad\alpha^{-1} \cdots \dots \dots \dots \dots \dots (11.3)$$

If transformations permitted by symmetry are performed, the d matrix is unchanged. Class 3 has a binary axis only, if we choose this as x_3 and perform the transformation

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ we find:}$$

$$d = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$d = \begin{pmatrix} -d_{11} & -d_{12} & -d_{13} & d_{14} & d_{15} & -d_{16} \\ -d_{21} & -d_{22} & -d_{23} & d_{24} & d_{25} & -d_{26} \\ d_{31} & d_{32} & d_{33} & -d_{34} & -d_{35} & d_{36} \end{pmatrix}$$

For this to be consistent with the original d matrix the terms with conflicting signs must vanish.

Applying similar analyses to each of the 32 classes we arrive at the set of matrices:

Class 1 (asymmetric)
No symmetry

$$d = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \quad (11.01)$$

Class 2 (triclinic pinacoidal), center of symmetry $d = 0 \dots \dots \dots$ (11.02)

Class 3 (monoclinic sphenoidal)
 x_3 is binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & d_{36} \end{pmatrix} \quad \begin{matrix} \text{(sucrose)} \\ (11.03) \end{matrix}$$

Class 4 (monoclinic domatic)
 x_3 plane is plane of symmetry

$$d = \begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & 0 & d_{26} \\ 0 & 0 & 0 & d_{34} & d_{35} & 0 \end{pmatrix} \quad (11.04)$$

Class 5 (monoclinic prismatic) center of symmetry, $d = 0 \dots \dots \dots$ (11.05)

Class 6 (Orthorhombic bisphenoidal)
 x_1, x_2, x_3 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad \begin{matrix} \text{(Rochelle)} \\ (11.06) \end{matrix}$$

Class 7 (Orthorhombic Pyramidal)
 x_3 binary, x_1 and x_2 planes of symmetry

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.07)$$

Class 8 (Orthorhombic bipyramidal), center of symmetry, $d = 0$ (11.08)

Class 9 (Tetragonal bisphenoidal)
 x_3 is quaternary alternating

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & -d_{15} & d_{14} & 0 \\ d_{31} & -d_{31} & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (11.09)$$

Class 10 (Tetragonal pyramidal)
 x_3 is quaternary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.10)$$

Class 11 (Tetragonal scalenohedral)
 x_3 quaternary, x_1 and x_2 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (11.11)$$

Class 12 (Tetragonal trapezohedral)
 x_3 quaternary, x_1 and x_2 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (11.12)$$

Class 13 (Tetragonal bipyramidal) center of symmetry, $d = 0$ (11.13)

Class 14 (Ditetragonal pyramidal)
 x_3 quaternary
 x_1 and x_2 planes of symmetry

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.14)$$

Class 15 (Ditetragonal bipyramidal) center of symmetry, $d = 0$ (11.15)

Class 16 (Trinonal pyramidal)
 x_3 trigonal

$$d = \begin{pmatrix} d_{11} - d_{11} & 0 & d_{14} & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.16)$$

Class 17 (Trigonal rhombohedral) center of symmetry, $d = 0$ (11.17)

Class 18 (Trigonal trapezohedral)
 x_3 trigonal, x_1 binary

$$d = \begin{pmatrix} d_{11} - d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{(Quartz)} \quad (11.18)$$

Class 19 (Trigonal bipyramidal)
 x_3 trigonal, x_3 plane of symmetry

$$d = \begin{pmatrix} d_{11} - d_{11} & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (11.19)$$

Class 20 (Ditrigonal pyramidal)
 x_3 trigonal, x_2 plane of symmetry

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad \text{(tourmaline)} \quad (11.20)$$

Class 21 (Ditrigonal scalenohedral) center of symmetry, $d = 0$ (11.21)

Class 22 (Ditrigonal

bipyramidal)

 x_3 trigonal, x_3 plane of symmetry x_2 plane of symmetry

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (11.22)$$

Class 23 (Hexagonal

pyramidal)

 x_3 Hexagonal

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.23)$$

Class 24 (Hexagonal

trapezohedral)

 x_3 hexagonal, x_1 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (11.24)$$

Class 25 (Hexagonal bipyramidal) center of symmetry, $d = 0$ (11.25)

Class 26 (Dihexagonal

pyramidal)

 x_3 hexagonal, x_2 plane

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (11.26)$$

Class 27 (Dihexagonal bipyramidal) center of symmetry, $d = 0$ (11.27)

Class 28 (Cubic tetrahedral-

pentagonal-dedocahedral)

 x_1, x_2, x_3 binary

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{pmatrix} \quad (11.28)$$

Class 29 (Cubic pentagonal-icositetrahedral) $d = 0$ (11.29)Class 30 (Cubic, dyakisdodecahedral) center of symmetry, $d = 0$ (11.30)

Class 31 (Cubic, hexakis-tetrahedral)

 x_1, x_2, x_3 quaternary alternating

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{pmatrix} \quad (11.31)$$

Class 32 (Cubic, hexakis-octahedral) center of symmetry, $d = 0$ (11.32)

Whenever a center of symmetry exists the piezo-electric property vanishes since a center of symmetry requires $d' = (-I) dI = -d = -d'$. Also $d = 0$ for the pentagonal icositetrahedral class.

Classes 6, 11, 12, 24, 28 and 31 polarize only by shear.

Classes 1, 3, 4, 7, 10, 14, 16, 20, 23, 26 can be polarized by hydrostatic pressure. As an example of this let us consider tourmaline (which is ditrigonal pyramidal). For hydrostatic pressure, $X_1 = X_2 = X_3, X_4 = X_5 = X_6 = 0$, whence from the polarization stress matrices we find, $D_1 = 0, D_2 = 0, D_3 = (2d_{31} + d_{23}) \times \text{pressure}$. As $d_{31} = 0.75 \times 10^{-8}$ and $d_{33} = 5.8 \times 10^{-8}$ for tourmaline, we get 7.3 abcoulombs per cm^2 per dyne per cm^2 .

SECTION 12

THE CONVERSE PIEZO-ELECTRIC EFFECT

A stress X causes an electric induction

$$D = dX \dots\dots\dots(11.2)$$

and a strain

$$e = SX \dots\dots\dots(8.7)$$

If the charge is allowed to leak away a further strain occurs, at constant stress. This is the strain that would be gotten if the stress were originally applied with surfaces rendered conducting:

$$e^\circ = S^\circ X \dots\dots\dots(12.1)$$

In the first sort of stress, the work per unit volume done on the crystal by establishing the stress X is:

$$W = \frac{1}{2}X_c e = \frac{1}{2}X_c SX \dots\dots\dots(8.4)$$

The energy stored electrically in the medium is:

$$W_E = 2\pi D_c k^{-1} D \dots\dots\dots(12.2)$$

while the work done on a conducting crystal is:

$$W^\circ = \frac{1}{2}X_c S^\circ X \dots\dots\dots(12.3)$$

If a crystal be stressed in its insulated state by expenditure of energy W , the charges then absorbed by an external circuit taking up energy W_E , the strain changes from e to e° at constant stress so that the stresses perform additional work

$$W_a = X_c(e^\circ - e) = X_c(S^\circ - S)X$$

and the crystal is left containing energy W° . Whence

$$W^\circ = W - W_E + W_a \dots\dots\dots(12.4)$$

or:

$$\frac{1}{2}X_c S^\circ X = \frac{1}{2}X_c SX - 2\pi D_c k^{-1} D + X_c(S^\circ - S)X$$

so that:

$$X_c(S^\circ - S)X = 4\pi D_c k^{-1} D$$

If we substitute $D = dX$ we find

$$X_c(S^\circ - S)X = 4\pi X_c d_c k^{-1} dX$$

so that:

$$S^{\circ} - S = 4\pi d_c k^{-1} d \dots \dots \dots (12.5)$$

The change in strain caused by rendering the surfaces conducting is:

$$e^{\circ} - e = (S^{\circ} - S)X = 4\pi d_c k^{-1} dX \dots \dots \dots (12.6)$$

If the crystal be now insulated and the stress removed, an induction of opposite sign will occur and because of the assumed linear dependence of D on X the new induction will be equal to the negative of the previous one. The induction $D = -dX$ indicates an electric field:

$$E = 4\pi k^{-1} D = 4\pi k^{-1} dX \dots \dots \dots (12.7)$$

Also, the strain will alter by an amount $-e''$, where, since the action takes place with non-conducting surfaces:

$$e'' = SX$$

This leaves a strain on the crystal, of amount:

$$e' = e^{\circ} - e'' = (S^{\circ} - S)X \dots \dots \dots (12.8)$$

From (12.6), (12.7) and (12.8) it follows that:

$$e' = d_c E \dots \dots \dots (12.9)$$

As the medium is in just the condition that an electric field E would put the unstressed medium, (12.9) is the equation of the converse piezo-electric effect. It is to be noted that the set of constants that relates polarization and stress is the conjugate of the set that relates electric field and strain. For convenience in notation the converse effect will be written as

$$e = gE \dots \dots \dots (12.10)$$

where

$$g = d_c \dots \dots \dots (12.11)$$

Rewriting (13) as $\alpha_c^{-1} e = (\alpha_c^{-1} g a^{-1}) a E$ we see that

$$e' = g' E'$$

where

$$g' = \alpha_c^{-1} g a \dots \dots \dots (12.12)$$

SECTION 13

THE CONVERSE PIEZO-ELECTRIC EFFECT AS A NON-LINEAR FUNCTION

If the strain of a crystal is not strictly a linear function of the electric field causing it we must relate the components of strain to field terms of the second power as well as to first power terms. That is, the equation $e = gE$ (which gives the strain e in terms of the electric field E through the 18 constants g) must be modified to include terms $E_i E_j$. All such terms are included in the symmetric matrix $(E E_c)$.

A transformation a that replaces E by $a_c E'$ also replaces E_c by $E'_c a$ so that $(E E_c)$ is replaced by $(a_c E' E'_c a)$, that is $(E E_c)$ being self-conjugate, transforms similarly to the stress matrix. We may rearrange this as a one column matrix similar to the stress matrix X , as follows:

$$(E E_c) = \begin{pmatrix} E_1^2 \\ E_2^2 \\ E_3^2 \\ E_2 E_3 \\ E_3 E_1 \\ E_1 E_2 \end{pmatrix} = \bar{E} \dots \dots \dots (13.1)$$

We may now relate the strain to E and \bar{E} through the two matrices g and G :

$$e = gE + G\bar{E} \dots \dots \dots (13.2)$$

If transformations permitted by the symmetry of the crystal are performed, g' must equal g and G' must equal G , this allows us to simplify the matrices; g is no different than before and hence vanishes for all types having centers of symmetry (and for the pentagonal icositetrahedral class).

Rewriting (1) as $\alpha_c^{-1} e = (\alpha_c^{-1} g a^{-1}) a E + \alpha_c^{-1} G a^{-1} a E$ we see that

$$e' = g' E' + G' \bar{E}$$

where

$$\begin{aligned} g' &= \alpha_c^{-1} g a \\ G' &= \alpha_c^{-1} G \alpha^{-1} \dots \dots \dots (13.3) \end{aligned}$$

The matrix G transforms as the elastic moduli matrix does but $G_{ij} \neq G_{ji}$. Applying $G' = \alpha_c G \alpha$ we arrive at the set of matrices that follow

Triclinic (36 constns)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} & G_{15} & G_{16} \\ G_{21} & G_{22} & G_{23} & G_{24} & G_{25} & G_{26} \\ G_{31} & G_{32} & G_{33} & G_{34} & G_{35} & G_{36} \\ G_{41} & G_{42} & G_{43} & G_{44} & G_{45} & G_{46} \\ G_{51} & G_{52} & G_{53} & G_{54} & G_{55} & G_{56} \\ G_{61} & G_{62} & G_{63} & G_{64} & G_{65} & G_{66} \end{pmatrix} \quad (13.4)$$

Monoclinic (20 constns)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & G_{13} \\ G_{21} & G_{22} & G_{23} & 0 & 0 & G_{26} \\ G_{31} & G_{32} & G_{33} & 0 & 0 & G_{36} \\ 0 & 0 & 0 & G_{44} & G_{45} & 0 \\ 0 & 0 & 0 & G_{54} & G_{55} & 0 \\ G_{61} & G_{62} & G_{63} & 0 & 0 & G_{66} \end{pmatrix} \quad (13.5)$$

Orthorhombic (12 constns)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & 0 \\ G_{21} & G_{22} & G_{23} & 0 & 0 & 0 \\ G_{31} & G_{32} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{66} \end{pmatrix} \quad (13.6)$$

Tetragonal Classes 9, 10, 13
(10 constns)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & G_{16} \\ G_{12} & G_{11} & G_{13} & 0 & 0 & -G_{16} \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & G_{45} & 0 \\ 0 & 0 & 0 & -G_{45} & G_{44} & 0 \\ G_{61} - G_{61} & 0 & 0 & 0 & 0 & G_{66} \end{pmatrix} \quad (13.7)$$

Tetragonal Classes 11,
12, 14, 15) (7 constns)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{13} & 0 & 0 & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{66} \end{pmatrix} \quad (13.8)$$

Trigonal (Classes 16, 17)
(10 constns)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} - G_{25} & 0 \\ G_{12} & G_{11} & G_{13} - G_{14} & G_{25} & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ G_{41} - G_{41} & 0 & G_{44} & G_{45} 2G_{52} \\ -G_{52} & G_{52} & 0 & -G_{45} & G_{44} 2G_{41} \\ 0 & 0 & 0 & 2G_{25} & 2G_{14} 2(G_{11} - G_{22}) \end{pmatrix} \quad (13.9)$$

Trigonal (Classes 18, 20, 21)
(8 constants)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} & 0 & 0 \\ G_{12} & G_{11} & G_{13} & -G_{14} & 0 & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ G_{41} & -G_{41} & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 2G_{41} \\ 0 & 0 & 0 & 0 & 2G_{14} & 2(G_{11} - G_{12}) \end{pmatrix} \quad (13.10)$$

Trigonal (Classes 19, 22)
(6 constants)

Also Hexagonal (Classes 23, 24, 25, 26, 27)

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{13} & 0 & 0 & 0 \\ G_{31} & G_{31} & G_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(G_{11} - G_{12}) \end{pmatrix} \quad (13.11)$$

Cubic (Classes 28, 29, 30,
31 and 32) (5 Constants)

$$\begin{pmatrix} G_{11} & G_{12} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{12} & G_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{44} \end{pmatrix} \quad (13.12)$$

Isotropic Bodies
(2 Constants)

$$\begin{pmatrix} G_{11} & G_{12} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{11} & G_{12} & 0 & 0 & 0 \\ G_{12} & G_{12} & G_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & G & 0 & 0 \\ 0 & 0 & 0 & 0 & G & 0 \\ 0 & 0 & 0 & 0 & 0 & G \end{pmatrix} \quad (13.13)$$

$$G = 2(G_{11} - G_{12})$$

According to this analysis, all bodies suffer a change in dimensions when subjected to an electric field. These strains resulting from a field are generally much smaller than those strains $e = gE$ present only in crystals lacking a center of symmetry. For example, quartz has a strain of about $6.5 \times 10^{-8} \text{ cms/cm/ab volt}$. Glass in a field of 1000 practical volts per cm has a strain of about 4×10^{-12} , in a 100,000 volt field it has 4×10^{-8} . Rubber in the 1000 volt field strains by about 7×10^{-8} and in the 100,000 volt field by about 7×10^{-4} . The 1st order quartz strain in these fields would be about 2.2×10^{-7} and 2.2×10^{-5} respectively.

THE SECOND ORDER PIEZO-ELECTRIC EFFECT

If the induction stress relation is not strictly linear one can assume the induction to depend also on second order terms of the stress:

$$D = dX + p(\overline{XX}_c)$$

where (\overline{XX}_c) is a single column matrix formed from the 21 elements of XX_c and p is a matrix of the 63 elements $p_{11,1} \dots p_{33,3}$.

Since X transforms as $X' = \alpha X'$, (XX_c) transforms as $X'X'_c = \alpha XX_c \alpha_c$. In the same way that α was formed from a we can form a matrix $\bar{\alpha}$ that transforms the single column matrix (\overline{XX}_c) through $(\overline{XX}_c)' = \bar{\alpha}(\overline{XX}_c)'$.

$$aD = ad\alpha^{-1} X + ap(\bar{\alpha})^{-1} \bar{\alpha}(\overline{XX}_c) \text{ or}$$

$$D' = d'X' + p'(\overline{XX}_c)'$$

where

$$d' = ad\alpha^{-1} \text{ and } p' = ap(\bar{\alpha})^{-1}$$

The first order effect is the same as before. With the relation $p' = ap(\bar{\alpha})^{-1}$ we could perform the operations of symmetry permitted by the 32 crystal classes and obtain the reduced matrices. However since $\bar{\alpha}$ has 484 elements we shall limit ourselves to crystals with centers of symmetry.

As X is unchanged by an inversion through the origin, α is the idemfactor for this transformation and a is $-I$, also $(\bar{\alpha}) = I$. Therefore $D' = -D = D$ so that D vanishes.

It is to be noted that although there is a sort of reciprocity between the first order piezo effect and the converse effect, in that the matrices for one are the conjugates of the matrices of the other, there is no such reciprocity in the second order effects: if a center of symmetry exists no polarization can be brought about by stress either as a first order effect or as a second order effect; if a center of symmetry exists an electric field can cause a strain through the second order effect but not through the first order effect.

Dielectric Constants at Constant Stress and at Constant Strain

Let us consider a unit crystal cube, initially unstressed, unstrained and in zero electric field. We write k^p and k^v for the dielectric constant matrices at constant stress and constant strain, respectively, C^E as the elastic constant matrix at constant electric field E , C^o as the same for zero field. We study a cycle consisting of a strain caused by application of an electric field E at zero stress followed by a stress applied at constant E to reduce the strain to zero and completed by conducting away the electric charges at zero strain so that the body is left in its original state. The cycle is described by the table:

Operation	Change in Stress	Change in Strain	Change in Displacement Current	Change in Field	Energy Put In
Apply $E \dots$	0	$d_c E$	$\frac{1}{4\pi} k^p E$	$E \frac{1}{8\pi}$	$E_c k^p E$
Apply $-\epsilon \dots$	$-C^E d_c E$	$-d_c E$	$-\frac{1}{4\pi} (k^p - k^v) E$	$0 \frac{1}{2}$	$E_c d C^E d_c E -$
Apply $-E \dots$	$C d_c E$	0	$-\frac{1}{4\pi} k^v E$	$\frac{1}{4\pi}$	$E_c (k^p - k^v) E$
				$-E - \frac{1}{8\pi}$	$E_c k^v E$

whence $C = C^E$; also

$$k^p - k^v = 4\pi d C d_c \dots \dots \dots (13.14)$$

SECTION 14

PYRO-ELECTRICITY

If the electric polarization brought about by heating some kinds of crystals is simply a function of the uniform temperature change, that is if this polarization can be produced by taking the whole body quickly from the

uniform temperature t_0 to the uniform temperature $t_0 + t$ the pyro-electric effect could be described by the equation:

$$\begin{pmatrix} D_1 \\ D_2 \\ D_3 \end{pmatrix} = t \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} \dots\dots\dots (14.1)$$

where ρ is the pyro-electric matrix.

This can be approached in another way by considering the polarization as due to the uniform strain. We may hence write, since $X = Ce$: (i.e. stress matrix = elastic constant matrix times the strain matrix)

$$P = dX = dCe$$

where e is the strain brought about by the temperature change t . If

$A = \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix}$ is the temperature expansion matrix we have:

$$P = t dC \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Now since d has 3 rows and the A matrix has but one column the product dCA has 3 rows and one column so that we may define ρ as dCA .

As D of $D = t\rho$ transforms by $D' = aD$, so does ρ :

$$\rho' = a\rho$$

When a center of symmetry exists a permitted transformation is $a = -I$, whence $\rho = -\rho' = -\rho$ so that $\rho = 0$. No pyro-electric effect (on this theory) could exist for a crystal with a center of symmetry.

If a binary axis exists and is chosen as x_3 we have

$$\begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} = \begin{pmatrix} -\rho_1 \\ -\rho_2 \\ \rho_3 \end{pmatrix}$$

whence for this case

$$\rho = \begin{pmatrix} 0 \\ 0 \\ \rho_3 \end{pmatrix} \dots\dots\dots (14.2)$$

If another binary axis exists at right angles to this one we find $\rho = 0$.

This is seen seriously to limit the number of classes showing this kind of pyro-electric effect. In fact we find $\rho = 0$ for classes 2, 5, 6, 8, 9, 11, 12, 13, 15, 17, 18, 19, 21, 22, 24, 25, 27, 28, 29, 30, 31 and 32. The expression

$\rho = \begin{pmatrix} 0 \\ 0 \\ \rho_3 \end{pmatrix}$ describes the pyro-electric effect in the classes, 3, 7, 10, 14, 16, 20,

23 and 26, while the expression $\rho = \begin{pmatrix} \rho_1 \\ \rho_2 \\ 0 \end{pmatrix}$ describes class 4, and only class

1 is described by

$$\rho = \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} \dots \dots \dots (14.3)$$

It is to be noted then that this theory excludes many classes ordinarily described as pyro-electric, such crystals as quartz in Class 18 for example. Consequently it would seem that whether or not this effect exists we must seek elsewhere for the explanation of the effect in quartz.

The effect can easily be explained as due to non-uniform temperature, which causes stress which in turn give rise to electric phenomena in piezo active crystals. For example a suddenly chilled crystal has its outer layers in a state of tension. This would produce just the pattern of positive and negative charges that one actually observes. As to whether the first effect exists, much argument between Lord Kelvin and others seems to have left the question still uncertain.

In pyro-electric crystals we would expect to find a difference in the piezo constants measured isothermally or adiabatically. If a temperature change t causes an electric displacement $D = \rho t$ the application of an electric field E should cause a temperature change t given by a relation such as:

$$t = \varphi E \dots \dots \dots (14.4)$$

Also the temperature coefficient of expansion, A_s (for a crystal with faces rendered conducting) would differ from the coefficient A_i (for a crystal with an insulated surface).

If a crystal at temperature t_0 has suddenly applied to it a field E the temperature rises to $t_0 + \varphi E$ and the crystal strains, because of the converse piezo effect, by amount $\epsilon = g_a E$ where g_a is the adiabatic converse piezo matrix. If the field is now removed isothermally a further strain $g_i E$ takes place. If the faces are short-circuited and the temperature restored to t_0 a further strain $A_s t = A_s \varphi E$ takes place and the crystal is then in its

initial state. Equating the sum of the strains to zero we find $(g_a - g_i)E = A_s \varphi E$ or

$$g_a - g_i = A_s \varphi \dots \dots \dots (14.5)$$

Let the initial state of a crystal be, temperature = t_0 , stress, strain and field = 0. If the (electrically insulated) crystal is heated by amount t , a strain $A_i t$ is caused and also an electric displacement $D = \rho t$. There now exists an electric field $E = r \pi k^{-1} \rho t$. Let this field be discharged at constant temperature, giving a further strain of $g_i E = 4 \pi g_i k^{-1} \rho t$. The crystal is now short-circuited and if the initial temperature is restored a strain $-A_s t$ follows. The crystal is now in its initial state. If we equate the sum of the strains to zero we find:

$$A_i - A_s = 4 \pi g_i k^{-1} \rho \dots \dots \dots (14.6)$$

SECTION 15

THE THERMO-ELECTRIC EFFECT IN CRYSTALS

It should be possible for an electric field to be set up by a temperature gradient. Let us assume that the vector T is the temperature gradient and is related to the vector field E through the matrix Π by means of the equation:

$$E = \Pi T \quad \text{where} \quad \Pi = \begin{pmatrix} \Pi_{11} & \Pi_{12} & \Pi_{13} \\ \Pi_{21} & \Pi_{22} & \Pi_{23} \\ \Pi_{31} & \Pi_{32} & \Pi_{33} \end{pmatrix} \dots \dots \dots (15.1)$$

Examination shows that Π transforms through

$$\Pi' = a \Pi a_c \dots \dots \dots (15.2)$$

For Class 1 the Π matrix has the 9 terms of (15.1). Class 2 has a center of symmetry. For a center of symmetry $a = -I$ but $a = -I$ causes no change in (15.2) so that class 2 has 9 constants. The thermo electric effect is not killed by the presence of a center of symmetry. The ordinary thermo-electric effect of metals is a case in point.

If x_3 is a binary axis $a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ and Π reduces to

$$\Pi = \begin{pmatrix} \Pi_{11} & \Pi_{12} & 0 \\ \Pi_{21} & \Pi_{22} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \dots \dots \dots (15.3)$$

Examination shows this form to answer for classes 3 and 4 and 5.

If x_1 and x_3 are binary (15.3) reduces to

$$\Pi = \begin{pmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{22} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \dots \dots \dots (15.4)$$

which described classes 6, 7 and 8.

For x_3 quaternary alternating:

$$\Pi = \begin{pmatrix} \Pi_{11} & \Pi_{12} & 0 \\ -\Pi_{12} & \Pi_{11} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \dots \dots \dots (15.5)$$

This is found to handle classes 9 and 10. If x_3 is quaternary alternating and x_1 is binary:

$$\Pi = \begin{pmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{11} & 0 \\ 0 & 0 & \Pi_{33} \end{pmatrix} \dots \dots \dots (15.6)$$

which is found to cover classes 11, 12, 13, 14 and 15. For classes 16, 17, 19, 23 and 25 Π reduces to the form (15.5).

If x_3 is trigonal and x_1 is binary the matrix is (15.5) which then handles cases 18, 20, 21, 22, 24, 26 and 27.

For cubic crystals, not only are x_1, x_2 and x_3 binary as for matrix (15.4) but the vector $\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$ is an A_3 , for which $a = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$ whence, for classes 28, 29, 30 and 31 we find the matrix:

$$\Pi = \begin{pmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{11} & 0 \\ 0 & 0 & \Pi_{11} \end{pmatrix} \dots \dots \dots (15.6)$$

Reports of a pyro electric effect in quartz should probably be attributed to nonuniform heating exciting the piezo electric effect. Reports of a pyro electric effect in such crystals as topaz and colemanite which have a center of symmetry and hence cannot be piezo electric should probably be attributed to this thermo electric effect.

SECTION 16

THE PROPAGATION OF LIGHT IN CRYSTALLINE MEDIA

Maxwell's equations are:

$$C \nabla \times B = 4\pi j$$

$$C \nabla \times E = -B$$

when C is the velocity of light in free space, E is the (vector) electric field, j is the induction current and B is the magnetic induction. In a crystalline medium the current is given by $4\pi j = k\dot{E}$ where k is the dielectric constant (matrix), whence:

$$C\nabla \times B = k\dot{E} \dots\dots\dots (16.1)$$

$$C\nabla \times E = -\dot{B} \dots\dots\dots (16.2)$$

As the divergence of the Curl is always zero:

$$\begin{aligned} \nabla_c k\dot{E} = \nabla_c j = 0 \\ \nabla_c B = 0 \end{aligned} \dots\dots\dots (16.3)$$

applying $\frac{\partial}{\partial t}$ to (16.1) and substituting (16.2) in the result:

$$\begin{aligned} -C^2\nabla \times \nabla \times E = k\ddot{E} \text{ or} \\ C^2(\nabla_c\nabla - \nabla\nabla_c)E = k\ddot{E} \dots\dots\dots (16.4) \end{aligned}$$

We shall try as a solution:

$$\dot{E} = \dot{E}_0 e^{i(qn_c r - \omega t)} \dots\dots\dots (16.5)$$

where E_0 is the vector amplitude of the electric field, i is $\sqrt{-1}$, r is the radius vector from the origin to any point, q is a constant, n is the unit normal (at r) of surfaces of equal phase, and ω is 2π times the frequency of E .

Substituting (16.5) in (16.4) we find:

$$\dot{E} - n\dot{E}_c n = \frac{\omega^2}{q^2 c^2} k\dot{E} \dots\dots\dots (16.6)$$

Examination of (16.5) shows that $\frac{\omega}{q}$ is the phase velocity along n . Writing $4\pi k^{-1}j$ for \dot{E} and V^2 for $\frac{\omega^2}{q^2}$ we have:

$$k^{-1}j - nj_c k^{-1}n = \frac{V^2}{c^2} j \dots\dots\dots (16.7)$$

This equation is independent of the absolute value of j so let us restrict j to being a unit vector.

$$\nabla_c k\dot{E} = 0 = \nabla_c k\dot{E}_0 e^{i(qn_c r - \omega t)} = j_c n i q e^{i(qn_c r - \omega t)}$$

whence $j_c n = 0 \dots\dots\dots (16.8)$

That is, the current is always normal to the direction of propagation.

Multiplying (16.7) thru by the prefactor j_c and cancelling the term in $j_c n$ we have:

$$j_c k^{-1} j = \frac{V^2}{c^2} \dots \dots \dots (16.9)$$

This tells us that the velocity is a single valued function of the direction of the current.

With the idemfactor I , (16.7) may be written:

$$\left(k^{-1} - \frac{V^2}{c^2} I \right) j = n(k^{-1} j)_c n$$

If we multiply this thru by $\left(k^{-1} - \frac{V^2}{c^2} I \right)^{-1}$ we get

$$j = \left(k^{-1} - \frac{V^2}{c^2} I \right)^{-1} n(k^{-1} j)_c n \dots \dots \dots (16.10)$$

Multiplying this thru by n_c and dropping the scalar factor $(k^{-1} j)_c n$:

$$n_c \left(k^{-1} - \frac{V^2}{c^2} I \right)^{-1} n = 0 \dots \dots \dots (16.11)$$

If the axes are so chosen that k is a diagonal matrix (16.9) and (16.11) become:

$$\frac{V^2}{c^2} = \frac{j_1^2}{k_{11}} + \frac{j_2^2}{k_{22}} + \frac{j_3^2}{k_{33}} \dots \dots \dots (16.12)$$

$$\frac{n_1^2}{\frac{1}{k_{11}} - \frac{V^2}{C^2}} + \frac{n_2^2}{\frac{1}{k_{22}} - \frac{V^2}{C^2}} + \frac{n_3^2}{\frac{1}{k_{33}} - \frac{V^2}{C^2}} = 0 \dots \dots \dots (16.13)$$

Examination of (16.13) shows that (16.11) must have two values of V^2 for each value of the vector normal n . As V^2 is a single valued function of j there must be two distinct values of j (j' and j'' say) for any particular n ; and given n , only waves having their current vectors in the directions of j' and j'' can be propagated. A ray in the direction N but not having its j in one of the directions j' or j'' will be broken up into two components having their current vectors along j' and j'' respectively.

If the velocity V_1 corresponds to j' and V_2 to j'' we have by means of (16.10) since $n' = n''$:

$$j'_c j'' = n_c \left(k^{-1} - \frac{V_1^2}{c^2} I \right)^{-1} \left(k^{-1} - \frac{V_2^2}{c^2} I \right)^{-1} n(k^{-1} j')_c n(k^{-1} j'')_c n$$

(The quantities in the braces are scalar)

By means of the identity

$$(u^{-1} - v^{-1}) = -u^{-1}(u - v)v^{-1}$$

since

$$k^{-1} - \frac{V_1^2}{c^2} I - \left(k^{-1} - \frac{V_2^2}{c^2} I \right) = \frac{V_2^2 - V_1^2}{c^2} I$$

the idemfactor can be multiplied into an adjacent matrix giving

$$\begin{aligned} n_c \left(k^{-1} - \frac{V_1^2}{c^2} I \right)^{-1} \left(k^{-1} - \frac{V_2^2}{c^2} I \right)^{-1} n \\ = \frac{c^2}{V_2^2 - V_1^2} n_c \left(k^{-1} - \frac{V_1^2}{c^2} I \right)^{-1} - \left(k^{-1} - \frac{V_2^2}{c^2} I \right)^{-1} n \\ = 0 - 0 = 0 \end{aligned}$$

so that j' and j'' are mutually perpendicular.

SECTION 17

THE ELECTRO-OPTIC EFFECT

The velocity of light in a crystalline medium is a single valued function of the unit current vector j

$$\frac{V^2}{c^2} = j_c k^{-1} j \dots \dots \dots (16.11)$$

where c is the velocity of light in vacuo and k is the dielectric matrix, also $j = \dot{D}$ where \dot{D} is $\frac{dD}{dt}$.

We developed the induction as a linear function of the electric field, deriving the relation:

$$4\pi D = kE \dots \dots \dots (6.1)$$

If the induction is not a linear function of the electric field we can improve on eq. (6.1) by adding second order terms:

$$\begin{aligned} 4\pi D_i = k_{i1}E_1 + k_{i2}E_2 + k_{i3}E_3 + k_{i1}E_1^2 + k_{i2}E_2^2 + k_{i3}E_3^2 \\ + \frac{1}{2} h_{i4}E_2E_3 + \frac{1}{2} h_{i4}E_3E_2 + \dots \frac{1}{2} h_{i6}E_1E_2 \end{aligned}$$

or

$$\begin{aligned} 4\pi D_i = (k_{i1} + h_{i1}E_1 + \frac{1}{2} h_{i6}E_2 + \frac{1}{2} h_{i5}E_3) E_1 \\ + (k_{i2} + \frac{1}{2} h_{i6}E_1 + h_{i2}E_2 + \frac{1}{2} h_{i4}E_3) E_2 \\ + (k_{i3} + \frac{1}{2} h_{i5}E_1 + \frac{1}{2} h_{i4}E_2 + h_{i3}E_3) E_3 \dots \dots \dots (17.1) \end{aligned}$$

Examination of (17.1) suggests that we might consider the k 's as being linearly modified by the field. Writing k as a single column matrix:

$$K = \begin{pmatrix} k_{11} \\ k_{22} \\ k_{33} \\ k_{23} \\ k_{13} \\ k_{12} \end{pmatrix} = \begin{pmatrix} K_1 \\ K_2 \\ \cdot \\ \cdot \\ \cdot \\ K_6 \end{pmatrix}$$

we may write

$$K = K^\circ + h E \dots \dots \dots (17.2)$$

where K° is the dielectric matrix for vanishingly small fields.

We can develop the modified reciprocal matrix in the same manner:

$$k^{-1} = \begin{pmatrix} k_{11}^{-1} & k_{12}^{-1} & k_{13}^{-1} \\ k_{12}^{-1} & k_{22}^{-1} & k_{23}^{-1} \\ k_{13}^{-1} & k_{23}^{-1} & k_{33}^{-1} \end{pmatrix} \quad K^{-1} = \begin{pmatrix} K_1^{-1} \\ K_2^{-1} \\ \cdot \\ \cdot \\ \cdot \\ K_6^{-1} \end{pmatrix} = \begin{pmatrix} k_{11}^{-1} \\ k_{22}^{-1} \\ k_{33}^{-1} \\ k_{22}^{-1} \\ k_{13}^{-1} \\ k_{12}^{-1} \end{pmatrix}$$

where

$$K^{-1} = K^{-1^\circ} + z E \dots \dots \dots (17.3)$$

It is to be noted that K^{-1} is not the reciprocal of K but merely a symbol for the single column matrix formed from k^{-1} in the usual way. Taking reciprocals of both sides of $k' = \alpha k a_c$ we find $(k^{-1})' = \alpha k^{-1} a_c$. That is, k^{-1} transforms exactly as did k . Whence, K^{-1} transforms exactly as K does, i. e.

$$K^{-1'} = \alpha K^{-1}$$

We can rewrite (17.3) as

$$\alpha K^{-1} = \alpha K^{-1^\circ} + (\alpha z a_c) a E$$

or

$$K^{-1'} = (K^{-1^\circ})' + z' E' \\ z' = \alpha z a_c \dots \dots \dots (17.4)$$

In case $\alpha^{-1} = \alpha c$ the z 's transform as do the conjugates of the piezo-electric constants, d . Of the transformations permitted by the symmetry

of the 32 crystal classes only those of the trigonal and hexagonal systems fail to have $\alpha^{-1} = \alpha_c$. These 12 classes must be examined individually but the other classes may have their z matrices copied from the corresponding d_c matrices.

Applying $z' = \alpha z a_c$ for a rotation of 120° about x_3 we find for class 16

$$z = \begin{pmatrix} z_{11} & -z_{22} & z_{13} \\ -z_{11} & z_{22} & z_{13} \\ 0 & 0 & z_{33} \\ z_{41} & z_{51} & 0 \\ z_{51} & -z_{41} & 0 \\ -z_{22} & -z_{11} & 0 \end{pmatrix}$$

The remaining 11 classes may be derived from class 16 by operations for which either $\alpha^{-1} = \alpha_c$ or a center of symmetry exists. Consequently, we may form our z matrices from the d_c 's in all cases if we leave out the 2's.

The electro-optic effect can be put in terms of the polarization instead of the field by substituting in (17.3).

$$E = 4\pi (k - I)^{-1} P \quad \text{whence} \\ K^{-1} = K^{-1^\circ} + \eta P \dots \dots \dots (17.5)$$

where

$$\eta = 4\pi z (k - I)^{-1} \dots \dots \dots (17.6)$$

Conversely

$$z = \frac{1}{4\pi} \eta (k - I)$$

The η matrices transform exactly as did the z 's and hence may be formed from the d_c 's but omitting the 2's.

SECTION 18

THE PIEZO-OPTICAL EFFECT

If the dielectric constants of a crystal are changed by the application of stress, this may be represented by:

$$K^{-1} = (K^{-1})^\circ + \pi X \dots \dots \dots (18.1)$$

where the 36 constants $\pi_{11} \dots \pi_{66}$ are stress-optical constants.

We may then form k^{-1} as

$$k^{-1} = \begin{pmatrix} k_{11}^{-1} + \pi_{1i} X_i & k_{12}^{-1} + \pi_{6i} X_i & k^{-1} + \pi_{5i} X_i \\ k_{12}^{-1} + \pi_{6i} X_i & k_{22}^{-1} + \pi_{2i} X_i & k_{23}^{-1} + \pi_{4i} X_i \\ k_{13}^{-1} + \pi_{5i} X_i & k_{23}^{-1} + \pi_{4i} X_i & k_{33}^{-1} + \pi_{3i} X_i \end{pmatrix} \dots \dots \dots (18.2)$$

As the velocity of a light ray of unit current vector j is given by

$$j_c k^{-1} j = \frac{V^2}{c^2} \dots \dots \dots (16.9)$$

We can, by (18.2) and (16.9), compute the change in the velocity caused by the stress, if we know the constants π .

Altering (18.1) to $\alpha K^{-1} = \alpha K^{-1^\circ} + \alpha \pi \alpha^{-1} \alpha X$ we see that:

$$K^{-1'} = K^{-1^\circ} + \pi' X' \quad \text{where} \quad \pi' = \alpha \pi \alpha^{-1} \dots \dots \dots (18.3)$$

The alteration of K^{-1} can be expressed as a function of the strain by substituting ce for X in (18.1).

$$K^{-1} = K^{-1^\circ} + \pi ce = K^{-1^\circ} + me \dots \dots \dots (18.4)$$

$$m = \pi c, \quad \pi = ms \dots \dots \dots (18.5)$$

Operating in (18.4) as we did on (18.1) we find m transforms as

$$m' = \alpha m \alpha_c \dots \dots \dots (18.6)$$

Applying the crystal symmetry operation to these matrices shows that they reduce to the following

Triclinic system 36 constants	$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & \pi_{15} & \pi_{16} \\ \pi_{21} & \pi_{22} & \pi_{23} & \pi_{24} & \pi_{25} & \pi_{26} \\ \pi_{31} & \pi_{32} & \pi_{33} & \pi_{34} & \pi_{35} & \pi_{36} \\ \pi_{41} & \pi_{42} & \pi_{43} & \pi_{44} & \pi_{45} & \pi_{46} \\ \pi_{51} & \pi_{52} & \pi_{53} & \pi_{54} & \pi_{55} & \pi_{56} \\ \pi_{61} & \pi_{62} & \pi_{63} & \pi_{64} & \pi_{65} & \pi_{66} \end{pmatrix}$	The m matrix is entirely analogous (18.7)
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Monoclinic system α_3 is binary 20 constants	$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & \pi_{16} \\ \pi_{21} & \pi_{22} & \pi_{23} & 0 & 0 & \pi_{26} \\ \pi_{31} & \pi_{32} & \pi_{33} & 0 & 0 & \pi_{36} \\ 0 & 0 & 0 & \pi_{44} & \pi_{45} & 0 \\ 0 & 0 & 0 & \pi_{54} & \pi_{55} & 0 \\ \pi_{61} & \pi_{62} & \pi_{63} & 0 & 0 & \pi_{66} \end{pmatrix}$	The m matrix is entirely analogous (18.8)
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Orthorhombic system α_3 is binary 12 constants	$\begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{21} & \pi_{22} & \pi_{23} & 0 & 0 & 0 \\ \pi_{31} & \pi_{32} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{66} \end{pmatrix}$	The m matrix is entirely analogous (Rochelle salt) (18.9)
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Tetragonal system
 x_3 is a four-fold axis
 (Classes 9, 10 & 13)
 9 Constants

$$\left(\begin{array}{cccccc} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & \pi_{16} \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & -\pi_{16} \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ \pi_{61} & -\pi_{61} & 0 & 0 & 0 & \pi_{66} \end{array} \right) \dots \dots \dots (18.10)$$

The m matrix is entirely analogous

Tetragonal system
 x_3 is a four-fold axis
 x_1 is a binary axis
 (Classes 11, 12, 14 & 15)
 7 Constants

$$\left(\begin{array}{cccccc} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{66} \end{array} \right) \dots \dots \dots (18.11)$$

The m matrix is entirely analogous

Trigonal system
 x_3 is a trigonal axis
 (Classes 16 & 17)
 11 Constants

$$\left(\begin{array}{cccccc} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & -\pi_{25} & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & \pi_{25} & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & \pi_{41} & 0 & \pi_{44} & \pi_{45} & 2\pi_{52} \\ -\pi_{52} & \pi_{52} & 0 & -\pi_{45} & \pi_{44} & 2\pi_{41} \\ 0 & 0 & 0 & \pi_{25} & \pi_{14} & (\pi_{11} - \pi_{12}) \end{array} \right) \dots \dots \dots (18.12)$$

The m matrix is analogous except that
 $m_{46} = m_{52}$
 $m_{56} = m_{41}$
 $m_{66} = \frac{m_{11} - m_{12}}{2}$

Trigonal system
 x_3 is a trigonal axis
 x_1 is a binary axis
 (Classes 18, 20 & 21)
 8 Constants

$$\left(\begin{array}{cccccc} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & -\pi_{41} & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 2\pi_{41} \\ 0 & 0 & 0 & 0 & \pi_{14} & (\pi_{11} - \pi_{12}) \end{array} \right) \dots \dots \dots (18.13)$$

The m matrix is analogous except that
 $m_{56} = m_{41}$
 $m_{66} = \frac{m_{11} - m_{12}}{2}$
 (quartz)

Hexagonal system
 x_3 is a sixfold axis
 x_1 is a binary axis
 (Classes 19, 22, 23, 24, 25, 26 & 27)
 6 Constants

$$\left(\begin{array}{cccccc} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & (\pi_{11} - \pi_{12}) \end{array} \right) \dots \dots \dots (18.14)$$

The m matrix is analogous except that
 $m_{66} = \frac{m_{11} - m_{12}}{2}$

Cubic system
 3 Constants

$$\left(\begin{array}{cccccc} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{44} \end{array} \right) \dots \dots \dots (18.15)$$

The m matrix is entirely analogous

For isotropic bodies, the π matrix is formed by setting $\pi_{44} = (\pi_{11} - \pi_{12})$ in the π matrix of the cubic system; the m matrix is similarly formed by putting $m_{44} = \frac{m_{11} - m_{12}}{2}$.

Isotropic bodies

$$\left(\begin{array}{cccccc} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{11} - \pi_{12} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{11} - \pi_{12} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{11} - \pi_{12} \end{array} \right) \begin{array}{l} \text{The } m \text{ matrix has} \\ \\ m_{44} \text{ etc} = \frac{m_{11} - m_{12}}{2} \\ \\ \dots\dots\dots (18.16) \end{array}$$

SECTION 19

APPLICATION OF THE ELECTRO AND PIEZO OPTICAL EFFECT

In the equations $K^{-1} = K^{-1^0} + zE$ and $K^{-1} = K^{-1^0} + mE$, etc. the K^{-1} 's are to be used in forming k^{-1} for the equation giving the velocity of the light used namely $\frac{V^2}{C^2} = j_c k^{-1} j$. Obviously then K^{-1^0} should be formed from the squares of the reciprocals of the refractive indices, the lower three members being zero. After applying the electric field or strain a transformation of coordinates may be necessary to re-diagonalize, i.e. make $K_4^{-1'} = K_5^{-1'} = K_6^{-1'} = 0$. From the re-diagonalized K^{-1} we may write the new principle refractive indices by taking the reciprocals of the square roots of $K_1^{-1'}$, $K_2^{-1'}$ and $K_3^{-1'}$. It should be noted that if $K_i^{-1'} = K_i^{-1^0} + \Delta_i$ then

$$\mu_i' + \Delta\mu_i = \mu_i' - \frac{\mu_i'^3}{2} \Delta_i \dots\dots\dots (19.1)$$

For a given direction of the wave normal there are two velocities, a wave splitting into two components traveling with different velocities. By definition the refractive indices, μ_a and μ_b in a given direction are the normal velocities in that direction divided into the velocity of light in free space. Whence in a path length l there are $\frac{l\mu_a}{\lambda}$ waves in one component and $\frac{l\mu_b}{\lambda}$ waves in the other, where λ is the wave-length in vacuum. Consequently if l is the thickness of the crystal along that path the two components can recombine after passing through the medium but they are out of phase by $\gamma = \frac{l}{\lambda} (\mu_a - \mu_b)$ whole waves so that the light which entered as plane polarized will leave elliptically or circularly polarized, except when 2γ is an integer.

The quantity $B = \mu_a - \mu_b$ is known as the birefringence.

$$\gamma = \frac{lB}{\lambda} \dots\dots\dots(19.2)$$

If a phase difference of $\frac{1}{30}$ wave can be just detected, using a wave length of 6000 Å and a path length $l = 1$ cm the just detectable birefringence would be $B = \frac{\gamma\lambda}{l} = 2 \times 10^{-6}$; if the path were 10 cms the detectable B would be 0.2×10^{-6} . Obviously this detectable difference between refractive indices is much smaller than could be detected by measuring each refractive index and subtracting.

It is customary to choose the coordinate system so that looking along x_2 the very lowest refractive index is for polarization in the plane of x_1 and the very highest for polarization in the plane of x_3 . That is, the x_2 axis is the axis along which light should be passed to get the greatest birefringence.

Birefringence in any Direction

If the axes are so chosen that K is diagonal and $K_3 > K_2 > K_1$ then, somewhere in the plane perpendicular to x_2 are two directions, the optic axes, along which there is a single normal velocity. These directions make* equal angles V with the x_3 axis where

$$\begin{aligned} \sin V &= \pm \sqrt{\frac{K_1^{-1} - K_2^{-1}}{K_1^{-1} - K_3^{-1}}} \\ \text{or} \\ \cos V &= \pm \sqrt{\frac{K_2^{-1} - K_3^{-1}}{K_1^{-1} - K_3^{-1}}} \dots\dots\dots(19.3) \end{aligned}$$

Also the two refractive indices μ_a and μ_b for a wave normal making angles g_1 and g_2 with these optic axes satisfy the equation:

$$\begin{aligned} \frac{2}{\mu_a} &= (K_1^{-1} + K_3^{-1}) + (K_1^{-1} - K_3^{-1}) \cos (g_1 - g_2) \\ \frac{2}{\mu_b} &= (K_1^{-1} + K_3^{-1}) + (K_1^{-1} - K_3^{-1}) \cos (g_1 + g_2) \end{aligned}$$

whence

$$\begin{aligned} 2 \left(\frac{1}{\mu_a} - \frac{1}{\mu_b} \right) &= \frac{2(\mu_b - \mu_a)(\mu_a + \mu_b)}{\mu_a^2 \mu_b^2} \\ &= (K_1^{-1} - K_3^{-1}) \cos (g_1 - g_2) - \cos (g_1 + g_2) \end{aligned}$$

* Theory of Optics, P. Drude, pg. 320.

as $B = \mu_b - \mu_a$ is the birefringence we have:

$$B = \frac{\mu_a^2 \mu_b^2}{\mu_a + \mu_b} (K_1^{-1} - K_3^{-1}) \sin g_1 \sin g_2 \dots \dots \dots (19.4)$$

By spherical trigonometry:

$$\begin{aligned} \cos g_1 &= \cos V \cos \theta + \sin V \sin \theta \cos \phi \\ \cos g_2 &= \cos V \cos \theta - \sin V \sin \theta \cos \phi \end{aligned} \dots \dots \dots (19.5)$$

where θ is the angle the wave normal makes with x_3 and ϕ is the angle the plane containing the normal and x_3 makes with x_1 .

From (19.5) it follows that:

$$\begin{aligned} \sin g_1 \sin g_2 &= \\ \sqrt{(1 - \cos^2 V \cos^2 \theta - \sin^2 V \sin^2 \theta \cos^2 \phi)^2} & \\ - 4 \sin^2 V \cos^2 V \sin^2 \theta \cos^2 \theta \cos^2 \phi \dots \dots \dots & (19.6) \end{aligned}$$

Hence if the rediagonalized K^{-1} is

$$\begin{pmatrix} K_1^{-1} + \Delta_1 \\ K_2^{-1} + \Delta_2 \\ K_3^{-1} + \Delta_3 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

then

$$\begin{aligned} B &= \frac{\mu_a^2 \mu_b^2}{\mu_a - \mu_b} \\ \sqrt{(K_1^{-1} - K_3^{-1} + \Delta_1 - \Delta_3) - (K_2^{-1} - K_3^{-1} + \Delta_2 - \Delta_3) \cos^2 \theta} & \\ - (K_1^{-1} - K_2^{-1} + \Delta_1 - \Delta_2) \sin^2 \theta \cos^2 \phi^2 - 4(K_1^{-1} - K_2^{-1} & \\ + \Delta_1 - \Delta_2)(K_3^{-1} - K_3^{-1} + \Delta_2 - \Delta_3) \sin^2 \theta \cos^2 \theta \cos^2 \phi \dots & (19.7) \end{aligned}$$

$$B = B_0 + \frac{\mu^3}{2} (\Delta_1 \Delta_3) \sin g_1 \sin g_2 \dots \dots \dots (3')$$

For most practical purposes we may take

$$\frac{\mu_a^2 \mu_b^2}{\mu_a + \mu_b} = \frac{\mu^3}{2}$$

where μ is some intermediate value of the refractive index.*

* Note: It might seem that as $K_i^{-1} = K_i^{-10} + \Delta_i$ gives us $\mu_i = \mu_i^0 - \frac{\mu_i^2}{2} \Delta_i + \frac{3}{8} \mu_i^5 \Delta_i^2 \dots$ we could form the 3 principal birefringences directly from the μ 's instead of using $(6a \dots e)$. From the μ expressions we would get $B_3 = \mu_2 - \mu_1 - \frac{1}{2}(\mu_2^3 \Delta_2 - \mu_1^3 \Delta_1) + \frac{3}{8}$ which differs from $6b$ if $\mu_2 \neq \mu_1$. Equation $6b$ is correct; the one from the μ expression is an approximation.

In a few special cases (18.7) may be simplified. If (ϕ, θ) falls along an optic axis $g_1 = V - V^\circ$ and $g_2 = V + V^\circ$ whence

$$B_A = \frac{\mu^3}{2} [(\Delta_1 - \Delta_2) \cos^2 V^\circ - (\Delta_2 - \Delta_3) \sin^2 V^\circ] \dots (19.61)$$

if $\theta = 0$

$$B = \mu_2 - \mu_1 + \frac{\mu_1^2 \mu_2^2}{\mu_1 + \mu_2} (\Delta_1 - \Delta_2) \dots (19.62)$$

if $\theta = 90^\circ$

$$B = (\mu_3 - \mu_1)(1 - \cos^2 \phi \sin^2 V^\circ) + \frac{\mu^3}{2} (\Delta_1 - \Delta_3 - (\Delta_1 - \Delta_2) \cos^2 \phi) \dots (19.63)$$

if $\phi = 0$

$$B = (\mu_3 - \mu_1)(\sin^2 V^\circ - \sin^2 \theta) + \frac{\mu^3}{2} (\Delta_1 - \Delta_2 - (\Delta_1 - \Delta_3) \sin \theta) \dots (19.64)$$

if $\phi = 90^\circ$

$$B = (\mu_3 - \mu_1)(1 - \cos^2 \theta \cos^2 V^\circ) + \frac{\mu^3}{2} (\Delta_1 - \Delta_3 - (\Delta_2 - \Delta_3) \cos \theta) \dots (19.65)$$

The Electro Optics of Quartz

For quartz, in the equation $K^{-1} = K^{-1^\circ} + zE$

$$Z = \begin{pmatrix} z_{11} & 0 & 0 \\ -z_{11} & 0 & 0 \\ 0 & 0 & 0 \\ z_{41} & 0 & 0 \\ 0 & -z_{41} & 0 \\ 0 & -z_{11} & 0 \end{pmatrix} \begin{array}{l} \text{If } E \text{ is in practical volts*} \\ Z_{11} = 0.47 \times 10^{-10} \\ Z_{41} = 0.20 \times 10^{-10} \end{array}$$

Obviously the E_3 component produces no effect so we shall examine the effects due to the components E_1 and E_2 separately. If $E = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} E_1$

$$K^{-1} = \begin{pmatrix} K_1^{-1^\circ} + z_{11}E_1 \\ K_1^{-1^\circ} - z_{11}E_1 \\ K_3^{-1^\circ} \\ z_{41}E_1 \\ 0 \\ 0 \end{pmatrix} \text{ which can be diagonalized}$$

* Computed from F. Pockels data, see his Lehrbuch der Kristall-Optik, (B. G. Tuebner).

by a small rotation about x_1 of amount $\theta = \frac{-z_{41}E_1}{K_1^{-1} - K_3^{-1}}$ giving

$$K^{-1} = \begin{pmatrix} K_1^{-1} + z_{11}E_1 \\ K_1^{-1} - z_{11}E_1 \\ K_3^{-1} \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \text{and} \quad \mu = \begin{matrix} \mu_1 - \frac{\mu_1^3}{2} \times 0.47 \times 10^{-10} E_1 \\ \mu_1 + \frac{\mu_1^3}{2} \times 0.47 \times 10^{-10} E_1 \\ \mu_3 \end{matrix}$$

The greatest "added birefringence" is gotten by viewing along x_3 , when $\Delta B = 1.544^3 \times 0.47 \times 10^{-10} E_1$. If $E_1 = 10^4 \Delta B = 1.73 \times 10^{-6}$ a quantity detectable if the path length is about 1 cm. Viewing along x_3 (the optic axis) is complicated by the rotation of the plane of polarization in quartz. Homogeneous strains have never been found to alter this rotation, but the rotation complicates and partly masks the birefringence phenomena. If

$$E = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} E_2 \text{ we find}$$

$$K^{-1} = \begin{pmatrix} K_1^{-1} \\ K_1^{-1} \\ K_3^{-1} \\ 0 \\ -z_{41}E_2 \\ -z_{11}E_2 \end{pmatrix}$$

Rotating the coordinate axes through 45° about x_3 then applying the transformation

$$a = \begin{pmatrix} 1 & 0 & \underline{a} \\ 0 & 1 & -\underline{a} \\ -\underline{a} & \underline{a} & 1 \end{pmatrix}$$

where

$$\underline{a} = \frac{1}{K_1^{-1} - K_3^{-1}} z_{41} E_2$$

we find:

$$K^{-1''} = \begin{pmatrix} K_1^{-1} + z_{11}E_2 \\ K_1^{-1} - z_{11}E_2 \\ K_3^{-1} \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \mu = \begin{matrix} \mu_1 - \frac{\mu_1^3}{2} z_{11} E_2 \\ \mu_1 + \frac{\mu_1^3}{2} z_{11} E_2 \\ \mu_3 \end{matrix}$$

which is identical to the μ for field along x_1 , but the final axes in this case do not coincide with the final axes for $E = E_1$, but again, the greatest added birefringence is utilized by viewing along x_3 . In the second case the Nicols would be best set along x_1 and x_2 , i.e., at 45° to x'_1 and x'_2 whereas in the first case they would be best set at 45° to x_1 and x_2 .

The strain Optics of Quartz

$$K^{-1} = K^{-1^0} + m\epsilon,$$

$$m = \begin{pmatrix} m_{11} & m_{12} & m_{13} & m_{14} & 0 & 0 \\ m_{12} & m_{11} & m_{13} & -m_{14} & 0 & 0 \\ m_{31} & m_{31} & m_{33} & 0 & 0 & 0 \\ m_{41} & m_{41} & 0 & m_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & m_{44} & m_{41} \\ 0 & 0 & 0 & 0 & m_{14} & \frac{m_{11} - m_{12}}{2} \end{pmatrix} \quad \text{where}^* \begin{matrix} m_{11} = .138 \\ m_{12} = .250 \\ m_{13} = .259 \\ m_{14} = .029 \\ m_{31} = .258 \\ m_{33} = .098 \\ m_{41} = -.042 \\ m_{44} = -.0685 \end{matrix}$$

If the strain is a simple tension along x_1 ,

$$K^{-1} = \begin{pmatrix} K_1^{-1^0} + m_{11} \epsilon_1 \\ K_1^{-1^0} + m_{12} \epsilon_1 \\ K_3^{-1^0} + m_{41} \epsilon_1 \\ m_{41} \epsilon_1 \\ 0 \\ 0 \end{pmatrix} \quad \text{which diagonalizes,} \quad K^{-1'} = \begin{pmatrix} K_1^{-1^0} + m_{11} \epsilon_1 \\ K_1^{-1^0} + m_{12} \epsilon_1 \\ K_3^{-1^0} + m_{31} \epsilon_1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

through a small transformation to:

applying 18.63 or 18.64 we find the birefringence along x_1 to be:

$$B_{11} = \mu_3 - \mu_1 + \frac{\mu^3}{2} (m_{12} - m_{31}) \epsilon_1 = .0091 - .0148 \epsilon_1$$

Similarly the birefringence along x_2 is $B_{12} = .0091 - .225 \epsilon_1$ and $B_{13} = 0 - .207 \epsilon_1$. With a strain of 10^{-4} , which is about a tenth of the breaking strain, B_{13} would be 20.7×10^{-6} , a quantity detectable in a thickness of one millimeter.

The values of $B_{21} \cdots B_{43}$ corresponding to birefringence along x_6 for a tension along x_2 etc., can be computed in just the same way. But $B_{51} \cdots B_{63}$ require rotations of 45° about x_3 to diagonalize, so the birefringences can be computed by setting $\theta = 45^\circ$ in equations (19.6).

* Lehrbuch der Kristalloptik—F. Pockels.

The following table summarizes these simple strain birefringence effects, the rows indicating the strain and the columns the direction of light passage.

$B_0 - .0148 \underline{e_1}$	$B_0 - .222 \underline{e_1}$	$.207 \underline{e_1}$
$B_0 + .222 \underline{e_2}$	$B_0 - .0148 \underline{e_2}$	$.207 \underline{e_2}$
$B_0 - .298 \underline{e_3}$	$B_0 - .298 \underline{e_3}$	0
$B_0 + .0536 \underline{e_4}$	$B_0 - .0536 \underline{e_4}$	$-.107 \underline{e_4}$
$(B_0 + 0$	$B_0 + 0$	$-.107 \underline{e_5})$
$(B_0 + 0$	$B_0 + 0$	$.208 \underline{e_6})$

(the parentheses indicate the 45° transformations).

A similar table for the electro-optic effect in quartz is

$B_0 - .87 \times 10^{-10} E_1$	$B_0 + .87 \times 10^{-10} E_1$	$1.74 \times 10^{-10} E_1$
$B_0 + 0$	$B_0 + 0$	$1.74 \times 10^{-10} E_1$
$B_0 + 0$	$B_0 + 0$	0

Since a driving voltage of $E_1 = 100$ volts may, due to the building up of oscillations, cause a periodic strain of $e = 10^{-4}$ in a quartz plate, it would seem from the foregoing that 99.99% of any birefringence change must be due to the mechanical effect.

The 18° Cut Crystal

A crystal, the thickness of which is along the electric axis, x_1 , the width making an angle $\theta' \doteq 18^\circ$ with the optic axis, x_3 , can be caused to oscillate with a simple motion along its length. (If θ' is not about 18° or 72° the oscillation is not a simple extension along the length, as is shown by the node which then lies diagonally across the crystal.) On a set of axes defined by the edges of the crystal block, x'_1 being in the direction of the thickness or x_1 , x'_3 in the direction of the width and makes an angle θ' with x_3 , x'_2 is the length and makes an angle θ' with x_2 ; on these block axes the strain is \underline{e}'_2 . Rotating the axes about x'_1 through an angle θ' we find the strain expressed on the crystal axes to be:

$$e = \alpha^{-1} e' = \begin{pmatrix} 0 \\ \cos^2 \theta' \\ \sin^2 \theta' \\ -\sin \theta' \cos \theta' \\ 0 \\ 0 \end{pmatrix} \underline{e}'_2$$

whence

$$K^{-1} = K^{-1^{\circ}} + me \text{ gives us}$$

$$K^{-1} = \begin{pmatrix} K_1^{-1^{\circ}} + (m_{12} \cos^2 \theta' + m_{13} \sin^2 \theta' - m_{14} \sin \theta' \cos \theta') \underline{e_2'} \\ K_1^{-1^{\circ}} + (m_{11} \cos^2 \theta' + m_{13} \sin^2 \theta' + m_{14} \sin \theta' \cos \theta') \underline{e_2'} \\ K_3^{-1^{\circ}} + (m_{31} \cos^2 \theta' + m_{33} \sin^2 \theta') \underline{e_2'} \\ \quad - (m_{41} \cos^2 \theta' + m_{44} \sin \theta' \cos \theta') \underline{e_2'} \\ 0 \\ 0 \end{pmatrix}$$

A small transformation removes the 4th term without altering the others to the first power of small quantities.

To obtain the birefringence along the width x_3' , we set $\theta = \theta'$ in equation (18.65):

$$B_{3'} = (\mu_3 - \mu_1) \sin^2 \theta' + \frac{\mu^3}{2} \left\{ m_{12} \cos^2 \theta' - m_{11} \cos^4 \theta' + (m_{13} - m_{33}) \sin^4 \theta' - m_{14} \sin^2 \theta' \frac{1 + \cos^2 \theta'}{2} - m_{31} \sin^2 \theta' \cos^2 \theta' \right\} \underline{e_2'}$$

which, for $\theta' = 18^{\circ}$ is $B_3' = .00087 + .20 \underline{e_2'}$

For the birefringence along the length x_2' we set

$$\theta = 90^{\circ} + \theta' \text{ in (6e) giving:}$$

$$B = (\mu_3 - \mu_1) \cos^2 \theta' + \frac{\mu^3}{2} \{ m_{12} \cos^2 \theta' - m_{31} \cos^4 \theta' + (m_{13} - m_{11} - m_{33}) \sin^2 \theta' \cos^2 \theta' - m_{14} \sin \theta' \cos \theta' (1 + \sin^2 \theta') \} \underline{e_2'}$$

which, for $\theta' = 18^{\circ}$ is $B_2 = .00824 + .049 \underline{e_2'}$.

SECTION 20

TRANSVERSE ISOTROPY

A material that has identical properties in all directions normal to a given line is called transversely isotropic. Any line parallel to this line may be considered as an axis of transverse isotropy.

Dielectric Properties, Optical Properties, Thermal Expansion

With respect to these, a transversely isotropic material behaves as does a uniaxial crystal, only two constants being needed to describe each. For example, the displacement current in terms of the electric field and the dielec-

tric constant matrix is $D = \frac{1}{4\pi} kE$ where, if x_3 is the axis of transverse isotropy:

$$D = \begin{pmatrix} D_{11} & 0 & 0 \\ 0 & D_{11} & 0 \\ 0 & 0 & D_{33} \end{pmatrix} \dots\dots\dots (20.1)$$

Elasticity

We must find the forms of S and C , (the elastic modulus and elastic constant matrices) that are not changed by rotations about the axis of transverse isotropy. We can simplify the work by starting with the crystal class that has hexagonal symmetry only. On applying the transformation $S' = \alpha_c S \alpha = S$ for arbitrary rotations about X_3 we find no further simplification follows. Hence the S and C matrices can be copied from those for the Hexagonal Pyramidal Class.

The Piezo-Electric Effect

Again choosing x_3 as the axis of transverse isotropy and starting with hexagonal symmetry about X_3 we find that in order to be invariant to all rotations about X_3 the matrix must simplify to:

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \dots\dots\dots (20.2)$$

A pitch solidified in an electric field would probably exhibit this kind of piezo electric behaviour. It might also be expected to show an electro optic effect governed by a matrix like the conjugate of the above matrix.

SECTION 21

APPENDIX

Transformations

A counterclockwise rotation of the axes through an angle ϕ about the x_1 axis is represented by the matrices a and α as follows (where c is written for $\cos \phi$ and s for $\sin \phi$):

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & c & s \\ 0 & -s & c \end{pmatrix}, \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & c^2 & s^2 & 2sc & 0 & 0 \\ 0 & s^2 & c^2 & -2sc & 0 & 0 \\ 0 & -sc & sc & c^2 - s^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & c & -s \\ 0 & 0 & 0 & 0 & s & c \end{pmatrix} \dots\dots\dots (21.1)$$

A counterclockwise rotation about x_2 is given by:

$$a = \begin{pmatrix} c & 0 & -s \\ 0 & 1 & 0 \\ s & 0 & c \end{pmatrix}, \quad \alpha = \begin{pmatrix} c^2 & 0 & s^2 & 0 & -2sc & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ s^2 & 0 & c^2 & 0 & 2sc & 0 \\ 0 & 0 & 0 & c & 0 & s \\ sc & 0 & -sc & 0 & c^2 - s^2 & 0 \\ 0 & 0 & 0 & -s & 0 & c \end{pmatrix} \dots \dots \dots (21.2)$$

A counterclockwise rotation about x_3 is given by:

$$a = \begin{pmatrix} c & s & 0 \\ -s & c & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} c^2 & s^2 & 0 & 0 & 0 & 2cs \\ s^2 & c^2 & 0 & 0 & 0 & -2cs \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & c & -s & 0 \\ 0 & 0 & 0 & -s & c & 0 \\ -cs & cs & 0 & 0 & 0 & c^2 - s^2 \end{pmatrix} \dots \dots \dots (21.3)$$

In case one wants only the value of a tensor property in a given direction not all the elements of a and α need be used, but only a row or column. A special case is that of computing such a property in the direction (θ, ϕ) of polar coordinates. The x'_1 axis is chosen in this direction; x'_2 and x'_3 are not determined. Writing c_1 for $\cos \theta$, c_2 for $\cos \phi$, s_1 for $\sin \theta$ and s_2 for $\sin \phi$ the required matrices are

$$\begin{pmatrix} c_1 s_2 \dots \\ a_c = s_1 s_2 \dots \\ c_2 \dots \end{pmatrix}, \quad \alpha^{-1} = \begin{pmatrix} c_1^2 s_2^2 \dots \\ s_1^2 s_2^2 \dots \\ c_2^2 \dots \\ s_1 s_2 c_2 \dots \\ c_1 c_2 s_2 \dots \\ c_1 s_1 s_2^2 \dots \end{pmatrix} \dots \dots \dots (21.4)$$

From these the (11) term can be computed for any tensor.

A few special transformations needed constantly are: A rotation of 180° about x_3 :

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \dots \dots (21.5)$$

A rotation of 90° about x_3 :

$$a = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \dots (21.6)$$

A reflection in the plane perpendicular to x_3 :

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \dots (21.7)$$

A cyclic interchange where x_2 replaces x_1 , etc.:

(The line making equal angles with x_1 , x_2 , and x_3 is a three-fold axis)

$$a = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \dots (21.8)$$

A cyclic interchange, where $-x_3$ replaces x_1 , etc.:

(The line making equal angles with x_1 , x_2 , and x_3 is a six-fold axis of the second sort)

$$a = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \dots (21.9)$$

A rotation of 90° about x_3 combined with a reflection in the x_3 plane:

$$a = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}, \quad \alpha^{-1} = \alpha_c \dots (21.10)$$

A rotation of 60° about x_3 :

$$\alpha = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \alpha = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \dots (21.11)$$

To form α^{-1} substitute $-\sqrt{3}$ for $\sqrt{3}$ in α .

A rotation of 60° about x_3 combined with a reflection in x_3 :

$$\alpha = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \alpha = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \dots (21.12)$$

To form α^{-1} substitute $-\sqrt{3}$ for $\sqrt{3}$ in α .

A rotation of 120° about x_3 :

$$\alpha = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \alpha = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \frac{\sqrt{3}}{4} & -\frac{\sqrt{3}}{4} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \dots (21.13)$$

To form α^{-1} substitute $-\sqrt{3}$ for $\sqrt{3}$ in α .

Inversion through the origin (a center of symmetry)

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} = I \dots \dots \dots (21.14)$$

$\alpha^{-1} = \alpha_c$

A rotation of 180° about x_1 :

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix} \quad \alpha^{-1} = \alpha_c \dots (21.15)$$

A reflection in x_1 plane:

$$a = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix} \quad \alpha^{-1} = \alpha_c \dots (21.16)$$

A reflection in the x_2 plane:

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \alpha = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix} \quad \alpha^{-1} = \alpha = \alpha_c \dots (21.17)$$

In computing the electro-optic and mechanico-optic effects we need a transformation that will restore to diagonality a matrix that has very small but symmetrical off diagonal terms. This transformation we call a small transformation. Such a transformation has its matrix differing but slightly from an idemfactor.

$$\text{If} \quad \bar{k} = \begin{pmatrix} k_{11} + \Delta_{11} & \Delta_{12} & \Delta_{31} \\ \Delta_{12} & k_{22} + \Delta_{22} & \Delta_{23} \\ \Delta_{31} & \Delta_{23} & k_{33} + \Delta_{33} \end{pmatrix}$$

we assume that it can be re-diagonalized to the matrix k' by means of the

$$\text{transformation: } k' = \delta \bar{k} \delta, \text{ where } \delta = \begin{pmatrix} 1 & \delta_{12} & \delta_{13} \\ \delta_{21} & 1 & \delta_{23} \\ \delta_{31} & \delta_{32} & 1 \end{pmatrix}$$

Since $\delta_{11} \delta_{21} + \delta_{12} \delta_{22} + \delta_{13} \delta_{23} = 0$ we find that, to the first order of small quantities $\delta_{ij} = -\delta_{ji}$.

Expanding $\delta \bar{k} \delta$ to the first order of small quantities and equating the non-diagonal terms to zero we find that:

$$\delta_{12} = \frac{\Delta_{12}}{k_{11} - k_{22}}; \quad \delta_{23} = \frac{\Delta_{23}}{k_{22} - k_{33}} \quad \text{and} \quad \delta_{31} = \frac{\Delta_{31}}{k_{33} - k_{11}}$$

Therefore, to the first order of small quantities Δ_{ij} :

$$\delta \equiv \begin{pmatrix} k_{11} + \Delta_{11} & \Delta_{12} & \Delta_{31} \\ \Delta_{12} & k_{22} + \Delta_{22} & \Delta_{23} \\ \Delta_{31} & \Delta_{23} & k_{33} + \Delta_{33} \end{pmatrix} \delta, = \begin{pmatrix} k_{11} + \Delta_{11} & 0 & 0 \\ 0 & k_{22} + \Delta_{22} & 0 \\ 0 & 0 & k_{33} + \Delta_{33} \end{pmatrix}$$

where $\delta = \begin{pmatrix} 1 & \frac{\Delta_{12}}{k_{11} - k_{22}} & \frac{-\Delta_{31}}{k_{33} - k_{11}} \\ \frac{-\Delta_{12}}{k_{11} - k_{22}} & 1 & \frac{\Delta_{23}}{k_{22} - k_{33}} \\ \frac{\Delta_{31}}{k_{33} - k_{11}} & \frac{-\Delta_{23}}{k_{22} - k_{33}} & 1 \end{pmatrix}$ is the transformation $x' = x \dots \dots \dots (21.18)$

The electro and piezo-optic effects of biaxial crystals can be handled by these infinitesimal transformations, but uniaxial crystals and cubic crystals may require finite rotations to re-diagonalize the k^{-1} matrix. In the

case of cubic crystals we note that $\begin{pmatrix} k & 0 & 0 \\ 0 & k & \Delta \\ 0 & \Delta & k \end{pmatrix}$ may be diagonalized by a

rotation of 45° about x_1 , giving

$$\begin{pmatrix} k & 0 & 0 \\ 0 & k + \Delta & 0 \\ 0 & 0 & k - \Delta \end{pmatrix} \dots \dots \dots (21.19)$$

$$\begin{pmatrix} k & 0 & \Delta_2 \\ 0 & k & \Delta_1 \\ \Delta_2 & \Delta_1 & k \end{pmatrix} \text{ becomes } \begin{pmatrix} k & 0 & \sqrt{\Delta_1^2 + \Delta_2^2} \\ 0 & k & 0 \\ \sqrt{\Delta_1^2 + \Delta_2^2} & 0 & k \end{pmatrix} \text{ upon rotation through angle}$$

$\tan^{-1} \frac{\Delta_1}{\Delta_2}$ about x_3 and diagonalizes by then rotating through 45° about x_2 giving:

$$k'' = \begin{pmatrix} k + \sqrt{\Delta_1^2 + \Delta_2^2} & 0 & 0 \\ 0 & k & 0 \\ 0 & 0 & k - \sqrt{\Delta_1^2 + \Delta_2^2} \end{pmatrix} \dots \dots (21.20)$$

The work can be handled with single column matrices K instead of using the square matrices k . If k is a diagonal single column matrix (i.e., the single column matrix of a diagonal matrix), then the almost diagonal matrix $K + \Delta$ is diagonalized by the transformation:

$$\begin{pmatrix} 1 & 0 & 0 & 0 & \frac{2\Delta_5}{K_1 - K_3} & \frac{2\Delta_6}{K_1 - K_2} \\ 0 & 1 & 0 & \frac{2\Delta_4}{K_2 - K_3} & 0 & \frac{-2\Delta_6}{K_1 - K_2} \\ 0 & 0 & 1 & \frac{-2\Delta_4}{K_2 - K_3} & \frac{-2\Delta_5}{K_1 - K_3} & 0 \\ 0 & \frac{-\Delta_4}{K_2 - K_3} & \frac{\Delta_4}{K_2 - K_3} & & \frac{-\Delta_6}{K_1 - K_2} & \frac{-\Delta_5}{K_1 - K_3} \\ \frac{-\Delta_5}{K_1 - K_3} & 0 & \frac{\Delta_5}{K_1 - K_3} & \frac{\Delta_6}{K_1 - K_2} & 1 & \frac{\Delta_4}{K_1 - K_3} \\ \frac{-\Delta_6}{K_1 - K_2} & \frac{\Delta_6}{K_1 - K_2} & 0 & \frac{\Delta_5}{K_1 - K_3} & \frac{\Delta_4}{K_2 - K_3} & 1 \end{pmatrix} \begin{pmatrix} K_1 + \Delta_1 \\ K_2 + \Delta_2 \\ K_1 + \Delta_3 \\ \Delta_4 \\ \Delta_5 \\ \Delta_6 \end{pmatrix} = \begin{pmatrix} K_1 + \Delta_1 \\ K_2 + \Delta_2 \\ K_3 + \Delta_3 \\ 0 \\ 0 \\ 0 \end{pmatrix} \dots \dots (21.21)$$

which transforms vectors as $x' = \delta x$ where

$$\delta = \begin{pmatrix} 1 & \frac{\Delta_6}{K_1 - K_2} & \frac{\Delta_5}{K_1 - K_3} \\ \frac{-\Delta_6}{K_1 - K_2} & 1 & \frac{\Delta_4}{K_2 - K_3} \\ \frac{-\Delta_5}{K_1 - K_3} & \frac{-\Delta_4}{K_2 - K_3} & 1 \end{pmatrix} \dots \dots \dots (21.22)$$

If K_1 , K_2 and K_3 are not all different the preceding analysis falls down as some terms become infinite; a finite transformation is needed in this case. The difficulty can generally be dodged by applying a 45° rotation about one of the axes. Sometimes the easiest solution is to rotate through an angle ϕ about a coordinate axis then solve for the value of ϕ that will vanish certain terms. As examples of these devices we give the following:

$$\begin{pmatrix} K_1 \\ K_1 \\ K_1 \\ \Delta_4 \\ 0 \\ 0 \end{pmatrix} \text{ rotated } 45^\circ \text{ about } x_1 \text{ becomes } \begin{pmatrix} K_1 \\ K_1 + \Delta_4 \\ K_1 - \Delta_4 \\ 0 \\ 0 \\ 0 \end{pmatrix} \dots \dots (21.23)$$

$$\begin{pmatrix} K_1 \\ K_1 \\ K_1 \\ \Delta_4 \\ \Delta_5 \\ 0 \end{pmatrix} \begin{matrix} \text{rotated through} \\ \tan^{-1} \frac{\Delta_4}{\Delta_5} \text{ about} \\ x_3 \text{ is} \end{matrix} \begin{pmatrix} K_1 \\ K_1 \\ K_1 \\ 0 \\ \sqrt{\Delta_4^2 + \Delta_5^2} \\ 0 \end{pmatrix} \begin{matrix} \text{and ro-} \\ \text{tated } 45^\circ \\ \text{about } x_2 \\ \text{is} \end{matrix} \begin{pmatrix} K + \sqrt{\Delta_4^2 + \Delta_5^2} \\ K \\ K - \sqrt{\Delta_4^2 + \Delta_5^2} \\ 0 \\ 0 \\ 0 \end{pmatrix} \dots (21.24)$$

- D = electric induction
- E = electric field
- k = dielectric constant matrix (square)
- K = dielectric constant matrix (single column)
- a = transformation matrix for vectors
- α = transformation matrix for tensors (of stress tensor sort)
- X = stress matrix (single column)
- e = strain matrix (square)
- ϵ = strain matrix (single column)
- S = elastic modulus matrix
- C = elastic constant matrix
- H = temperature change of elastic modulus matrix

- h = temperature change of elastic constant matrix
 T_s = temperature coefficient of elastic modulus terms
 T_c = temperature coefficient of elastic constant terms
 A = temperature expansion matrix
 d = piezo-electric constant matrix
 g = inverse piezo effect matrix
 G = electro-striction matrix
 Z = electro-optic matrix
 π = stress optic matrix
 m = strain optic matrix
 P = polarization = elec. mom. per unit vol. = surface charge per unit area
 η = susceptibility = $\frac{P}{E}$

Table of Equations	Transformations
$D = \frac{1}{4\pi} kE$ $e = SX$ $X = Ce$ $S = C^{-1}$ $h = -C^{\circ}HC^{\circ}$ $H = -S^{\circ}hS^{\circ}$ $\Delta l = tAl + l^2Bl$ $D = dX$ $e = gE$ $g = d_c$ $K^{-1} = K^{-1^{\circ}} + ZE$ $K^{-1} = K^{-1^{\circ}} + \pi X$ $K^{-1} = K^{-1^{\circ}} + me$ $P = \frac{k - I}{4\pi} E = \pi E$ $\pi = \frac{k - I}{4\pi}$	<p>The form</p> $\begin{matrix} x & y & z \\ x' & l_1 & m_1 & n_1 \\ y' & l_2 & m_2 & n_2 \\ z' & l_3 & m_3 & n_3 \end{matrix}$ <p>is the transformation $a = \begin{matrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{matrix}$</p> $A' = aAa^{-1}$ $D' = aD$ $E' = aE$ $k' = aka_c$ $K' = \alpha K$ $X' = \alpha X$ $e' = \alpha_c^{-1}e$ $C' = \alpha C\alpha_c$ $S' = \alpha_c^{-1}S\alpha^{-1}$ $h' = \alpha h\alpha_c$ $H = \alpha_c^{-1}H\alpha^{-1}$ $h_{ij} = C_{ij}^{\circ}TC_{ij}$ $H_{ij} = S_{ij}^{\circ}TS_{ij}$ $d' = ad\alpha^{-1}$

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The Metallurgy of Fillet Wiped Soldered Joints*

By E. E. SCHUMACHER, G. M. BOUTON, G. S. PHIPPS

THE seriousness of the present tin scarcity has stimulated large consumers of this vital metal to develop drastic conservation measures in order to extend the available supplies to cover the emergency period. By devising new soldering methods and alloys the Bell System has contributed a substantial share in the tin conservation effort. Fortunately, the changes, as far as can now be determined, have not introduced weakness into the soldered joints. Some of the new procedures now used were already in the process of development at the onset of the emergency, while others were devised under its stress. In some instances, the newly developed solders were found to be more difficult to use than the alloys previously available, and would not have been introduced under normal conditions. One major change made that previously had been under consideration will result in large tin savings. Unless service difficulties are encountered, this modification gives promise to remain after the emergency has passed. The change involves a reduction in the amount of solder placed on a wiped joint between the cable sheath and the sleeve. Instead of the customary full size wiped joint a wipe of fillet proportions is formed. Through this change, a solder saving of over 60% per joint can be realized.

Plumbers and cable splicers have for many years joined lead pipes and cable sheath by a soldering process called "wiping." The name is an apt description of the operation. In wiping a joint the sections to be united are heated by pouring molten solder over their surfaces and manipulating the resulting semi-liquid mass by wiping with cloth pads to a well rounded symmetrical form such as is shown in Fig. 1. The operation requires considerable skill on the part of the splicer and close control of the solder composition. At first consideration, the problem of tightness in such joints seems simple but experience shows that even under the best conditions the fissures frequently found in the solder occasionally link to form a path that allows leakage to occur. In the case of telephone cables not maintained under gas pressure, such leaks permit the entrance of water to wet the paper covered conductors, thereby impairing the insulation value and causing service interruptions. By going to an extreme and wiping off all the solder in excess of a fillet, it has been found that many causes of porosity are eliminated. Figures 2 and 3 show cross sections of joints wiped the old and new

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Fig. 1—A conventionally wiped joint between telephone cable and sleeve (third size).

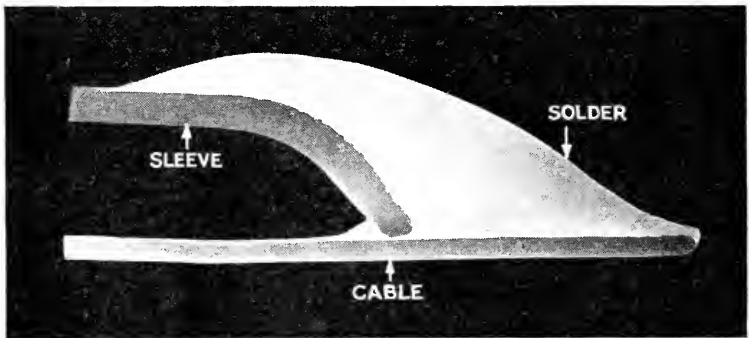


Fig. 2—A section taken from a joint wiped conventionally (magnification $1\frac{1}{2} \times$).

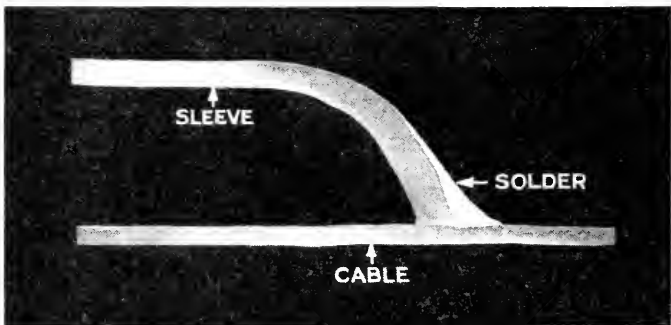


Fig. 3—A section taken from a joint wiped using the fillet technique (magnification $1\frac{1}{2} \times$).

ways. The saving in solder and consequently in strategic tin is evident. The field splicing forces find that joints are easier to make by the new method and are less apt to be porous.

Several interesting metallurgical considerations which are responsible for the success of the fillet wipe will now be discussed briefly. Much has been written about the wiping process of soldering cable joints and the many requirements of a good wiping solder have been frequently listed. The success of the procedure here described is dependent upon a few fundamental characteristics of lead-tin alloys in the process of freezing which have sound metallurgical explanations.

For an understanding of the defects possible in a soldered joint wiped in the usual manner, the simple solidification phenomena of metals may be considered. As is well known, molten metal in a crucible when allowed to cool with free circulation of air will begin freezing near the walls of the vessel and with a few exceptions, will end with a concave surface due to solidification shrinkage. Restricting the discussion to a simple lead-tin wiping solder, solidification progresses as follows: a lead-tin solid solution commences to freeze and forms a rather porous cylinder touching the crucible walls and extending to a height corresponding to the volume of the melt at that time; on further cooling, dendrites of lead-tin solid solution grow inward toward the center of the crucible and at the same time many tiny new crystals form throughout the liquid. There are thus taking place simultaneously, shrinkage of metal as it becomes solid, shrinkage of previously frozen solid as it cools, and shrinkage of the remaining liquid as the temperature drops. The originally solidified outer cylinder, adhering to the crucible walls remains essentially at its original height. The level of the semi-liquid portion nearer the center of the crucible continuously falls until the precipitated crystallites formed in the body of the melt make a loosely piled mass extending from the upper surface to the bottom of the crucible. Further shrinkage of the liquid then leaves these primary crystallites at approximately this level while the liquid recedes, leaving fissures between them. This can be beautifully observed by means of a binocular microscope focussed on the surface of a solidifying crucible of wiping solder or, on the top surface of a solidifying wiped joint.

Further insight into the mechanism of wiping solder solidification may be gained by another simple illustration. If two solder strips are cast by pouring small quantities of molten solder, one on a cold iron surface, and the other on a cloth-covered board and both are then bent cold to produce specimens as shown in Fig. 4, the chill cast sample will exhibit fewer cracks resulting from shrinkage than the slowly cooled one. In the slowly cooled sample primary crystallites form throughout the solidifying mass and pack at a level above that which the final volume of completely solid solder

warrants. The sample cast on the cold plate starts to freeze at its surface in contact with the iron plate and, because of the rapid extraction of heat by the cold iron, it continues to freeze in a rapidly advancing smooth front until the last liquid at the top is solid. Because of the steep temperature gradient there is little opportunity for nucleation and dendrite formation in the upper liquid. The surface of this melt is therefore smooth and free from the fissures that are caused by the shrinkage of the eutectic away from

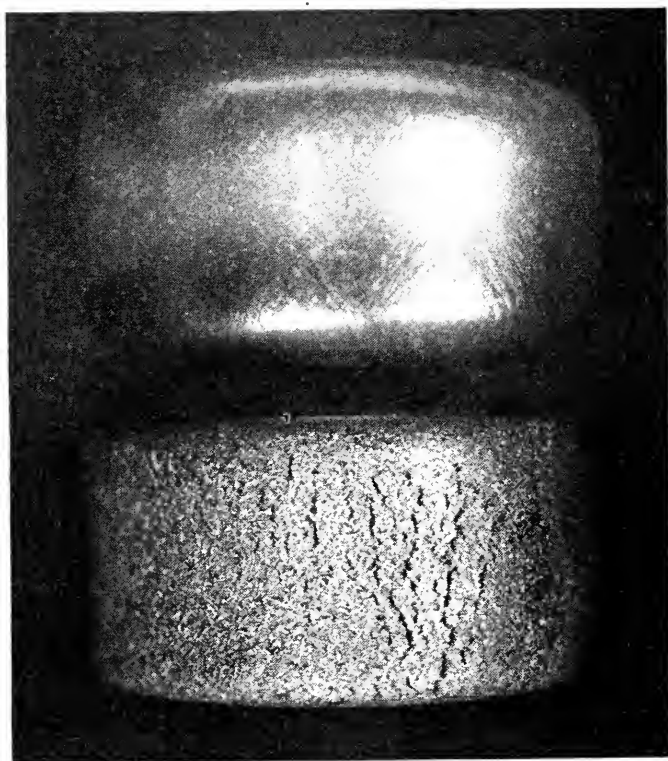


Fig. 4—Bent strips illustrating the effect of variations in cooling rate on the structure of wiping solders are here shown. The upper strip was chill cast and shows a sound ductile surface. The lower strip of the same solder was slowly cooled and upon bending exposes fissures between the crystallites at the surface (magnification $3\times$).

the dendrites in the slowly cooled sample. Recession of the liquid in the slowly cooled sample leaves a multitude of shrinkage channels which, if they occurred at the critical portion of a wiped joint, would cause leaks.

Another illustration may be useful in demonstrating the processes taking place in connection with joint wiping. Solder may be allowed to solidify in a crucible until its surface is quite firm to a probe. If, at this stage, the

crucible is tilted sideways to a position shown in Fig. 5 a portion of the remaining eutectic may be poured out leaving spongy regions. This loss of eutectic is observed frequently during the formation of the old massive type joints which may lose several drops by drainage after the splicer has completed his shaping operations. It is also shown by the greater number of pores in the top half of a joint compared to the bottom and the somewhat grayer surface appearance of the top.



Fig. 5—An ingot of wiping solder which had been tilted while in the crucible before completely solidified. The lower lip represents eutectic drainage from the partially solidified mass (magnification $1\frac{1}{2} \times$).

Although a solidification range in which quantities of liquid and solid metal may exist at equilibrium is an essential feature of a wiping solder, another factor of major importance is the nucleation rate of the alloy. Wiping solders having high nucleation rates will develop quickly a myriad of points or nuclei throughout the melt from which further crystallization will proceed, while an alloy of low nucleation rate will develop relatively few of these points in the same time and consequently grow fewer and larger crystals. The former alloy will have a texture similar to fine clay while the latter will behave like coarse sand and water when subjected to wiping

tests. In the fine clay-like texture there are more solid particles present than in the water-sand type of texture and therefore there is more surface available for the retention of the liquid in the former type of semi-solid mass. Drainage is thus greatly retarded with the result that porosity is materially lessened. The type of texture determines in a large measure the ease of shaping and potential porosity of a wiping solder.

Having examined elementary forms of solidification, attention may now be focussed on the setting up of the wiped joint itself. In practice, the parts to be joined are cleaned and fluxed. Circumferential paper pasters are then applied to the sheath and sleeve to restrict the spread of the solder. The splicer then pours hot solder from a ladle over the prepared parts and catches the excess in a cloth held in contact with the bottom of the joint. The caught solder is repeatedly pushed back around the cable with a wiping motion to aid "tinning" or alloying and to distribute the heat. After a few such operations the prepared surfaces can be seen to be thoroughly wetted by the solder. At this stage a portion of the caught solder is mixed in the ladle with more hot solder and the mass which now has a clay-like consistency is poured on the joint and molded into place using cloth pads. When solidification has proceeded to a condition where the solder can support itself in position, manipulation is stopped. From this point on, loss of heat takes place by conduction away from the joint by the sheath and sleeve, by radiation, and by air convection currents at the surface of the solder. As a result of this combination of heat losses final solidification takes place in the interior of the solder mass near the important sheath-sleeve junction. The action that causes pipes to form in castings draws the eutectic from the critical area between the sheath and the end of the sleeve. If the solder has the proper characteristics there will be a shell of solder which does not have interconnecting shrinkage cavities, drainage cavities or fissures due to the wiping operation and the finished joints will be gas tight. If the solder is unduly coarse or has insufficient liquid eutectic at the time the mass is too rigid to manipulate further, the resulting joint may leak.

The new fillet wiping technique is similar to the old up to the step where the splicer molds the mass to shape. At this point the new technique consists in wiping the solder to a small fillet similar to that shown in Fig. 3. The resulting joint has much less solder and therefore much less total shrinkage and tendency to draw eutectic from the space between the sheath and sleeve. Also, at the temperature where wiping is discontinued there is insufficient volume of solder left by the fillet wiping technique to permit drainage drops to accumulate and fall from the bottom of the joint. Thermal conduction along the sheath and sleeve cause rapid solidification of the solder at the joint, eliminating the possibility of drainage. Experience has shown a consistently high percentage of sound joints when fillet wiping is

rigidly practiced. During the development period of the fillet wiping technique examination of the few fillet type wiped joints that were found to leak showed quantities of solder present much in excess of that required. Under the microscope such joints showed the tell-tale sponginess where the eutectic had been drawn away from the junction in the course of final solidification.

Physical tests on joints made using the fillet wipe between sections of telephone cable and sleeving, have demonstrated that fillet joints similar in size to that shown in Fig. 2 made with 38% tin, 0.1% arsenic, balance lead wiping solder are stronger in tensile strength, creep and fatigue than the cable itself.

The application of the new technique has gone much further toward saving tin than any known permissible change in the composition of solder. Using the old technique, a reduction of only one per cent in the nominal tin content of a lead-tin wiping solder resulted in widespread occurrence of leaky joints, indicating that little tin could be saved by a simple change in solder specification. This observation was to be expected since many studies had been conducted over the years to reduce the tin content in wiping solders to the minimum consistent with the production of satisfactory joints. Tin has always been much more expensive than lead and for large users of solder a reduction of one per cent in the tin content might result in savings of many thousands of dollars annually.

While the use of the fillet wipe results in large savings in tin other avenues for conserving this strategic metal are available such as the substitution of ternary and quaternary alloys containing less tin than that required by the binary lead-tin wiping solders. A satisfactory alloy of this type was developed which contains 13% tin, 23% bismuth, 0.1% arsenic, balance lead. Though readily available a short time ago, bismuth now has become too restricted to be used extensively in solders. A wiping solder is now being introduced into service in which, through the inclusion of a small quantity of antimony, it has been possible to reduce the tin content. This material appears suitable for fillet wiping although it requires more skill to use than the 38% tin, 0.1% arsenic, balance lead wiping solder. Other compositions may be usable that contain less than normal tin, but on the whole, the savings accomplished by composition modifications will be small compared to those produced by the new wiping technique that has been described.

IN SUMMATION

By virtue of its small solder volume the fillet wipe reduces tin consumption and produces joints less liable to leakage than the conventional wiped joints. The reasons for the success of this type of joint are based on the sound metallurgical principles herein described. The use of the fillet wipe promises to survive the period of restricted tin consumption.

A Mathematical Theory of Linear Arrays

By

S. A. SCHELKUNOFF

A MATHEMATICAL theory, suitable for appraising and controlling directive properties of linear antenna arrays, can be based upon a simple modification of the usual expression for the radiation intensity of a system of radiating sources. The first step in this modification is closely analogous to the passage from the representation of instantaneous values of harmonically varying quantities by real numbers to a symbolic representation of these quantities by complex numbers. The second step consists in a substitution which identifies the radiation intensity with the norm¹ of a polynomial in a complex variable. The complex variable itself represents a typical direction in space. This mathematical device permits tapping the resources of algebra and leads to a pictorial representation of the radiation intensity.

An *antenna array* is a spatial distribution of antennas in which the individual antennas are geometrically identical, similarly oriented, and energized at similarly situated points. The first and the last properties insure that the *form* of the current distribution is the same in all the elements of the array and that consequently the array is composed of antennas with the same radiation patterns. The difference between individual elements consists merely in the relative phases and intensities of their radiation fields. The second property means that the radiation patterns of the individual elements are similarly oriented and that consequently the *radiation pattern of the array is the product of the radiation patterns of its typical element and the "space factor"*. The *space factor* of an array is defined as the *radiation pattern* of a similar array of *non-directive* elements. Hence in studying the effect of spatial arrangement of antennas, we may confine ourselves to non-directive elements and thus materially simplify the analysis.

An array is *linear* if points, similarly situated on the elements, are colinear. In this paper we are concerned mostly with linear arrays of *equispaced* sources although in conclusion we shall have an occasion to say a few words about more general types.

¹ The norm of a complex number is the square of its absolute value.

RADIATION INTENSITY AND FIELD STRENGTH

Consider a linear array of n equispaced nondirective sources (Fig. 1). Apart from the inverse distance factor, the instantaneous field strength of the array in the direction making an angle θ with the line of sources may be expressed as follows

$$\begin{aligned} \sqrt{\Phi_i} &= A_0 \cos(\omega t + \vartheta_0) + A_1 \cos(\omega t + \psi + \vartheta_1) + A_2 \cos(\omega t + 2\psi + \vartheta_2) \\ &+ \cdots + A_{n-2} \cos(\omega t + \overline{n-2} \psi + \vartheta_{n-2}) + \cos(\omega t + \overline{n-1} \psi), \quad (1) \\ \psi &= \beta \ell \cos \theta - \vartheta, \quad \beta = \frac{2\pi}{\lambda}. \end{aligned}$$

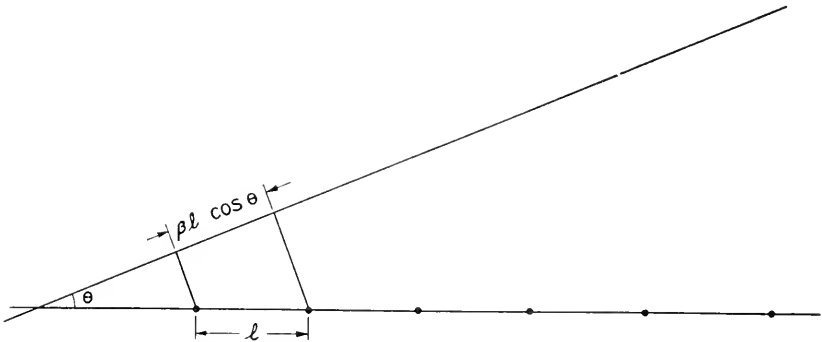


Fig. 1—A linear array of equispaced non-directive sources. If two sources are of equal intensity and in phase, their fields at a distant point are substantially equal in intensity but differ in phase by $\beta \ell \cos \theta$ where $\ell \cos \theta$ is the projection of the distance between the sources upon the particular spatial direction under consideration. If the sources are unequal, an allowance must be made for the relative field intensities in proportion to magnitudes of the sources and the phases must be adjusted for the phase difference between the sources.

In this equation: $A_0, A_1, \cdots, A_{n-1} = 1$ are the relative amplitudes of the elements of the array; ϑ is a progressive phase delay, from left to right, between the successive elements of the array; $\vartheta_1, \vartheta_2, \cdots, \vartheta_{n-2}, \vartheta_{n-1} = 0$ represent the phase deviations from the above progressive phase delay; $\beta = 2\pi/\lambda$ is the phase constant, where λ is the wavelength. The *radiation intensity*, that is the power radiated per unit solid angle, is proportional to the square of the amplitude of $\sqrt{\Phi_i}$.

Forming another expression similar to (1) but with sines in the place of cosines, multiplying the result by $i = \sqrt{-1}$ and adding it to (1), we have

$$\begin{aligned} \sqrt{\Phi'_i} &= [A_0 e^{i\vartheta_0} + A_1 e^{i\psi+i\vartheta_1} + A_2 e^{2i\psi+i\vartheta_2} + \cdots \\ &+ A_{n-2} e^{i(n-2)\psi+i\vartheta_{n-2}} + e^{i(n-1)\psi}] e^{i\omega t}. \quad (2) \end{aligned}$$

The true instantaneous value of the field strength is the real part of (2).

Hence the amplitude $\sqrt{\Phi}$ of the field strength² is the absolute value of (2); thus³

$$\sqrt{\Phi} = \left| a_0 + a_1 z + a_2 z^2 + \cdots + a_{n-2} z^{n-2} + z^{n-1} \right|, \quad (3)$$

$$z = e^{i\psi}, \quad \psi = \beta \ell \cos \theta - \vartheta, \quad a_m = A_m e^{i\vartheta_m}.$$

In this equation: $a_0, a_1, a_2, \cdots, a_{n-2}, a_{n-1} = 1$ are complex numbers representing the relative amplitudes of the elements of the array and the phase deviations of these elements from a given progressive phasing. Thus if all the coefficients are real and positive, they represent the relative amplitudes of the elements of the array. If the algebraic sign of a particular coefficient is reversed, the phase of the corresponding element is changed by 180° ; if some coefficient is multiplied by i or $-i$, the phase of the corresponding element is respectively accelerated or delayed by 90° ; and in general the phase acceleration is equivalent, in our scheme, to a multiplication by a unit complex number $e^{i\vartheta}$. Some coefficients may be equal to zero and the corresponding elements of the array will be missing. In view of this possibility, we shall call ℓ the "apparent" separation between the elements; it is the greatest common measure of actual separations. When the elements are equispaced the apparent separation is the actual separation.

Thus we have the fundamental

*Theorem I: Every linear array with commensurable separations between the elements can be represented by a polynomial and every polynomial can be interpreted as a linear array.*⁴

The total length of the array is the product of the apparent separation between the elements and the degree of the polynomial. The degree of the polynomial is one less than the "apparent" number of elements. The actual number of elements is at most equal to the apparent number.

The above analytical representation of arrays is accomplished with the aid of the following transformation

$$z = e^{i\psi}, \quad (4)$$

in which $\psi = \beta \ell \cos \theta - \vartheta$ is a function of the angle θ made by the line of sources with a typical direction in space. Since ψ is always real, the absolute value of z equals unity and z itself is always on the circumference of the unit circle (Fig. 2). As θ increases from 0° (which is in a direction of the line of sources) to 180° (which is in the opposite direction), ψ decreases and

² For brevity's sake, we shall call $\sqrt{\Phi}$ itself the "field strength."

³ Equation (3) could be derived directly from the physics of the situation in the same manner as (1). The foregoing method of transition from (1) to (3) serves only the purpose of showing the relationship between a less familiar formula and a very well known one.

⁴ If the separations are not commensurable the arrays are represented by an algebraic function with incommensurable exponents.

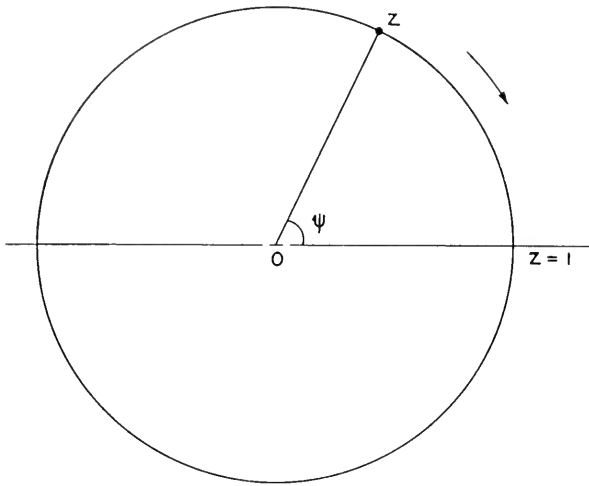


Fig. 2—A typical direction in space is represented by a complex variable which is represented in a complex plane by a point lying on the circumference of a circle of unit radius, having its center at the origin. As the angle θ made by a typical direction with the line of sources, increases from 0° to 180° , point z moves clockwise.

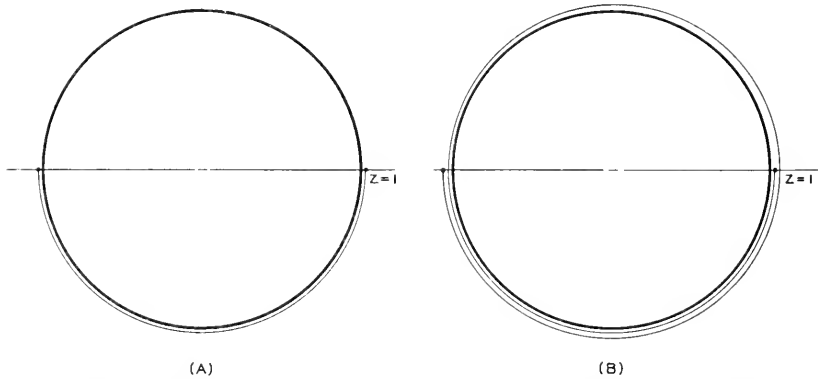


Fig. 3—(A) The active range of z , corresponding to $\vartheta = \beta\ell$ and one-quarter wave-length separation between the elements. (B) The active range of z , corresponding to $\vartheta = \beta\ell$ and $\ell = \frac{3}{4}\lambda$.

z moves in the clockwise direction. When $\theta = 0$, $\psi = \beta\ell - \vartheta$; and when $\theta = 180^\circ$, $\psi = -\beta\ell - \vartheta$. Hence the range $\bar{\psi}$ described by z is

$$\bar{\psi} = 2\beta\ell. \tag{5}$$

When the separation ℓ between the successive elements of the array is equal to one-half wavelength, the range of $z = 2\pi$ and as θ varies from 0° to 180° , z describes a complete cycle and returns to its original position.

In this case there is a one-to-one correspondence between the points of the circumference of the unit circle and conical surfaces coaxial with the line of sources. Such conical surfaces, called radiation cones, are loci of directions in which the radiation intensities are equal. If the separation between the elements $< \lambda/2$, the range of z is smaller than 2π and z describes only a portion of the unit circle (Fig. 3A). Finally, if $\ell > \lambda/2$, then the path of z overlaps itself (Fig. 3B). Such a path, winding upon itself, will be called a *Riemann circle*. In this instance, one and the same point on the circle may correspond to several radiation cones; but if we regard different positions of z along its path as distinct points on the Riemann circle, then there will be a one-to-one correspondence between the points on the circle and the radiation cones.

Since the radiation intensity is a periodic function of ψ , the space factor of a given array will repeat itself if the separation between the elements is greater than one-half wavelength.

COMPOSITION OF SPACE FACTORS

Since the product of two polynomials is a polynomial, we obtain the following corollary to Theorem I

Theorem II: There exists a linear array with a space factor equal to the product of the space factors of any two linear arrays.

In other words, there is a linear array such that its radiation intensity in any given direction is the product of the radiation intensities in this direction of any two given arrays. Thus we have

$$\begin{aligned}\sqrt{\Phi_1} &= |a_0 + a_1z + a_2z^2 + \cdots + a_{n-1}z^{n-1}|, \\ \sqrt{\Phi_2} &= |b_0 + b_1z + b_2z^2 + \cdots + b_{m-1}z^{m-1}|, \\ \sqrt{\Phi_1} \sqrt{\Phi_2} &= |(a_0 + a_1z + \cdots + a_{n-1}z^{n-1})(b_0 + b_1z + \cdots + b_{m-1}z^{m-1})| \\ &= |a_0b_0 + (a_0b_1 + a_1b_0)z + (a_0b_2 + a_1b_1 + a_2b_0)z^2 + \cdots|.\end{aligned}\tag{6}$$

The coefficients of the expanded product represent the amplitudes and the phases of the derived array.

Naturally the process may be repeated and a linear array can be constructed with its space factor equal to the product of the space factors of any number of linear arrays or to any power of the space factor of any array.

For example, let us start with a pair of equal sources, represented by

$$\sqrt{\Phi} = |1 + z|,\tag{7}$$

and construct a linear array with the space factor equal to the square of (7). The field strength of the required array will be

$$\sqrt{\Phi} = |1 + z|^2 = |1 + 2z + z^2|.\tag{8}$$

This array consists of three elements with amplitudes proportional to 1, 2, 1. If the elements of the original couplet are one-quarter wavelength apart and 90° out of phase, the couplet is “unidirectional”. The space factor of such a couplet is depicted by Curve A in Fig. 4. The space factor of the triplet represented by (8) is shown by Curve B. In the directions in which the couplet radiates half as much or a third as much power as in the principal direction, the triplet radiates correspondingly only a quarter or a ninth of the power radiated in the principal direction.

The above considerations suggest a simple method for suppressing subsidiary radiation lobes. It is well known that in a uniform linear array⁵

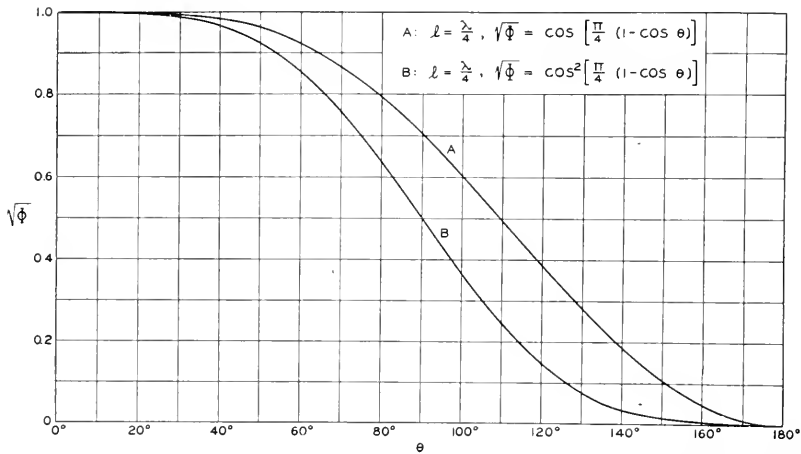


Fig. 4—Space Factors—Curve A is the space factor of a unidirectional couplet in which $\ell = \lambda/4$. Curve (B) represents the space factor of an array with amplitudes proportional to 1, 2, 1.

the difference in levels of the principal maximum of radiation and the first subsidiary is substantially independent of the number of elements, provided this number is sufficiently large. Thus in the limit, the first subordinate maximum is 13.5 decibels below the principal maximum. Consequently for the array with its space factor equal to the square of the space factor of the uniform array, the limiting difference in levels must be 26.9 decibels.

Since the uniform array is represented by

$$\sqrt{\Phi} = | 1 + z + z^2 + \dots + z^{n-1} |, \tag{9}$$

⁵ A “uniform” array is an array made up of sources of equal strength with a uniform progressive phase delay.

the other array is given by

$$\begin{aligned}\sqrt{\Phi} &= |1 + z + \cdots + z^{n-1}|^2 \\ &= |1 + 2z + 3z^2 + \cdots + nz^{n-1} + (n-1)z^n \\ &\quad + \cdots + 2z^{2n-3} + z^{2n-2}|.\end{aligned}\tag{10}$$

Thus the amplitudes of the individual sources are proportional to 1, 2, 3, \cdots , $n-1$, n , $n-1$, \cdots , 3, 2, 1. Figure 5 depicts the effect of such "triangular" amplitude distribution.

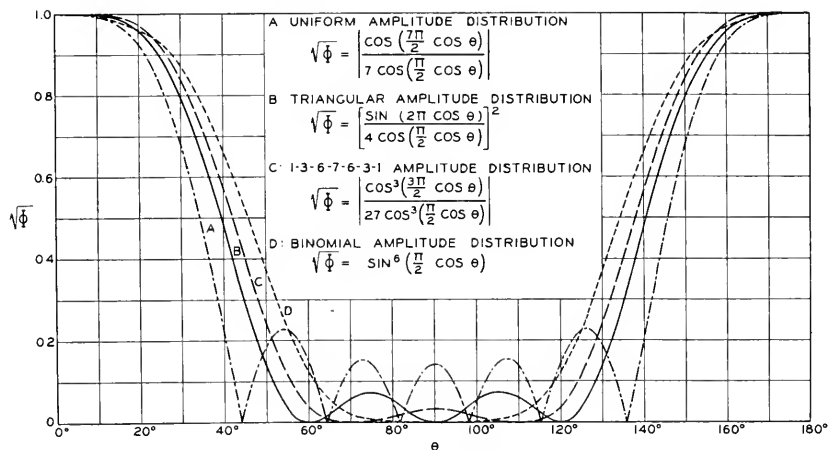


Fig. 5—Space Factors—(A) is for a uniform array and (B) for an array with "triangular" amplitude distribution.

Evidently we could raise (9) to any given power

$$\sqrt{\Phi} = |1 + z + z^2 + \cdots + z^{n-1}|^m.\tag{11}$$

This process does not change the number of separate radiation lobes. The so-called "binomial" distribution of amplitudes was first suggested by John Stone Stone.⁶ His scheme is a special case of (11) if we let $n = 2$. For the effect of the binomial amplitude distribution see Fig. 5.

The relative merits of two forms for the radiation intensity as given by (1) and (3) can now be appraised in the light of the foregoing examples. Using (1), we have for the instantaneous radiation intensity of the uni-directional couplet

⁶ U. S. Patents 1,643,323 and 1,715,433.

$$\begin{aligned} \sqrt{\Phi_i} &= \cos \omega t + \cos\left(\omega t + \frac{\pi}{2} \cos \theta - \frac{\pi}{2}\right) \\ &= \cos \omega t + \sin\left(\omega t + \frac{\pi}{2} \cos \theta\right). \end{aligned} \tag{12}$$

By just inspecting this equation, we find no evidence for existence of a linear array with a space factor equal to the square of the space factor of the couplet. Still less obvious is the method of obtaining proper amplitude ratios.

ARRAYS OF ARRAYS

The foregoing method of composition of space factors is in reality an analytical expression of geometric construction of "arrays of arrays". Consider, for instance, a pair of equiphase sources of equal strengths

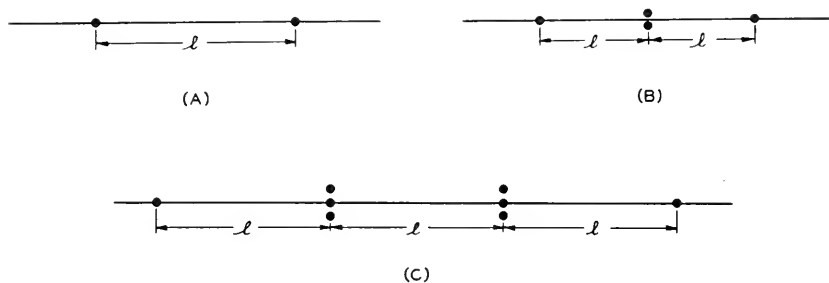


Fig. 6

(Fig. 6A). Take two such pairs as elements of an array of the same type (Fig. 6B). The middle sources add up to a single source of strength two. If the operation is repeated by taking (B) as elements of (A) or by taking (A) as elements of (B), then (C) is obtained; the amplitudes of (C) are proportional to 1, 3, 3, 1.

Each shift of a source to the right through distance l is represented analytically as multiplication by z . An algebraic identity

$$(a_0 + a_1z + a_2z^2)z = a_0z + a_1z^2 + a_2z^3 \tag{13}$$

is an expression of an obvious fact that each element of an array is shifted through the same distance as the entire array. Similarly a given change in the strength and the phase of the array is achieved by making the same change in all its elements; this fact is expressed by the identity

$$b(a_0 + a_1z + a_2z^2) = ba_0 + ba_1z + ba_2z^2. \tag{14}$$

In general, if an array represented by

$$f(z) = a_0 + a_1z + a_2z^2 + \cdots + a_{n-1}z^{n-1} \quad (15)$$

is taken as the element of an array given by

$$F(z) = b_0 + b_1z + b_2z^2 + \cdots + b_{m-1}z^{m-1}, \quad (16)$$

then the resulting array of arrays is represented by

$$f(z)F(z) = b_0f(z) + b_1zf(z) + b_2z^2f(z) + \cdots + b_{m-1}z^{m-1}f(z). \quad (17)$$

DECOMPOSITION THEOREM

Consider now a pair of non-directive sources with strengths proportional to 1, $-t$; then

$$\sqrt{\Phi} = |z - t|. \quad (18)$$

Geometrically, the complex number $z - t$ is represented by a line drawn from point t to point z (Fig. 7A). Accordingly, the *radiation intensity*

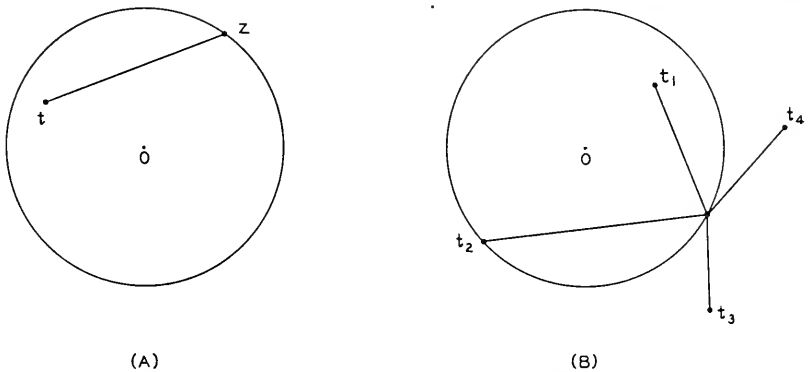


Fig. 7—The radiation intensity of a linear array is represented by the square of the product of the lines joining the null points of $\sqrt{\Phi}$ to a point z on the unit circle.

of the pair of sources is represented by the distance between t and z . If $\sqrt{\Phi}$ vanishes for some particular direction in space, it vanishes for all directions making the same angle with the line of sources; these directions form a *cone of silence* of the radiation system. Obviously, a radiating couplet has a cone of silence if and only if the null point of $\sqrt{\Phi}$ is in the range of z ; in particular, there can be no cone of silence unless the null is on the unit circle.

By the fundamental theorem of algebra a polynomial of degree $(n - 1)$ has $(n - 1)$ zeros (some of which may be multiple zeros) and can be factored into $(n - 1)$ binomials; thus

$$\sqrt{\Phi} = |(z - t_1)(z - t_2) \cdots (z - t_{n-1})|. \quad (19)$$

Each binomial represents the directive pattern of a pair of elements separated by distance l . Hence

Theorem III: *The space factor of a linear array of n apparent elements is the product of the space factors of $(n - 1)$ virtual couplets with their null points at the zeros of $\sqrt{\Phi}$: t_1, t_2, \dots, t_{n-1} .*

Accordingly the radiation intensity of an array is equal to the square of the product of the distances from the null points of the array to that point z on the unit circle which corresponds to the chosen direction (Fig. 7B). To each null point lying in the range of z , there corresponds one and only one *cone of silence* provided each null point is counted as many times as z happens to pass it in describing the complete range.

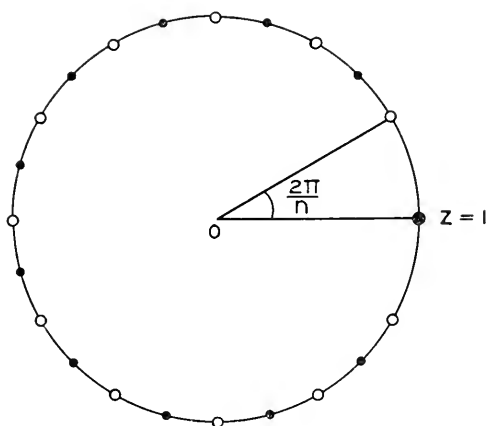


Fig. 8—The null points of a uniform linear array and the point $z = 1$ representing the direction of the greatest radiation divide the unit circle into equal parts. The hollow circles represent the null points and the solid circles the points of maximum radiation.

By summing the geometric progression (9) the radiation intensity of a uniform array can be represented as follows

$$\sqrt{\Phi} = \left| \frac{z^n - 1}{z - 1} \right|. \quad (20)$$

Hence the null points of such an array are the n -th roots of unity, excluding $z = 1$. Since z is a unit complex number,⁷ any power of it is also a unit complex number. Moreover, each multiplication by $z = e^{i\psi}$ represents a displacement through an arc of ψ radians. Hence the n -th roots

⁷ A *unit complex number* is a complex number whose absolute value is equal to unity.

of unity divide the circle into n equal parts (Fig. 8). Analytically we have

$$z^n - 1 = 0, \quad t_m = e^{-\frac{2m\pi i}{n}}, \quad m = 1, 2, 3, \dots, n-1, \quad (21)$$

$$\psi_m = -\frac{2m\pi}{n}, \quad \cos \theta_m = \frac{\vartheta}{\beta\ell} - \frac{2m\pi}{n\beta\ell}.$$

When $z = 1$, $\sqrt{\Phi}$ is evidently a *principal* maximum. Other maxima of smaller magnitude, the so-called *subordinate* or *subsidiary* maxima, occur approximately half way between the null points. The general

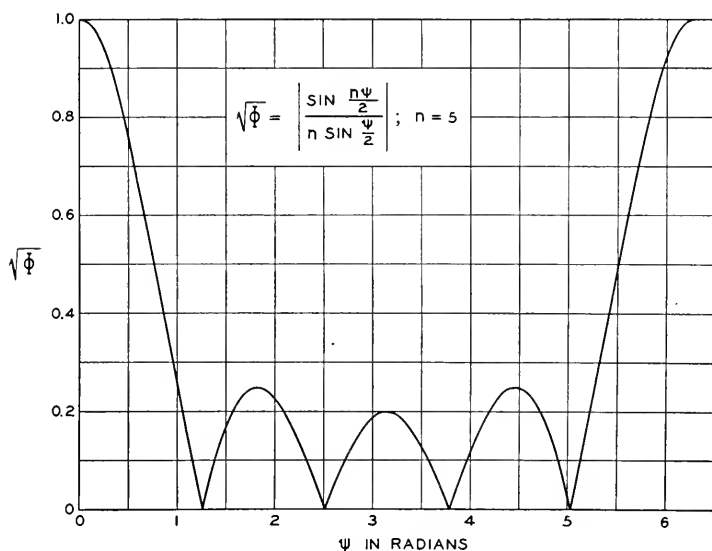


Fig. 9—The field strength $\sqrt{\Phi}$ as a function of ψ for $n = 5$. The principal maximum is reduced to unity.

behavior of the field strength can readily be understood if we follow z around the unit circle. When plotted against ψ , $\sqrt{\Phi}$ has the shape shown in Fig. 9. This is a universal radiation characteristic which can be interpreted for any particular spacing and phasing between the elements with the aid of the curve for $\psi + \vartheta = \beta\ell \cos \theta$ (Fig. 10).

It is easy to estimate the relative level of the first subordinate maximum. For a fairly large number of elements, the difference in levels is determined largely by the distances of the maximum points from the *nearest* null points. The distances are approximately equal to the circular arcs joining the corresponding points. Since the arcs joining the first subordinate maximum with the nearest null points are nearly half as long as

those for the principal maximum, the first subordinate maximum of the field strength is about one-quarter of the principal maximum. In other words, the subordinate maximum is approximately 12 decibels below the principal maximum.

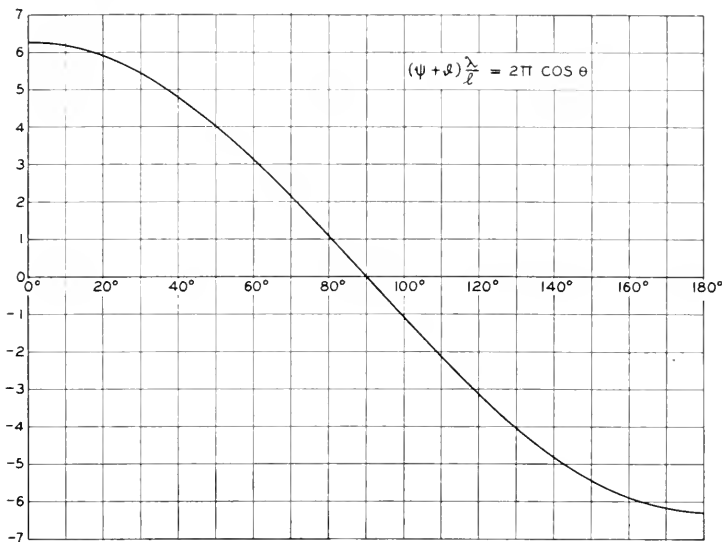


Fig. 10

A more accurate value for this difference in levels can be obtained by first rewriting (20) in the form

$$\sqrt{\Phi} = \left| \frac{z^{\frac{n}{2}} - z^{-\frac{n}{2}}}{z^{\frac{1}{2}} - z^{-\frac{1}{2}}} \right| = \frac{\sin \frac{n\psi}{2}}{\sin \frac{\psi}{2}} \tag{22}$$

and then substituting successively $\psi = 0$ and $\psi = \frac{3\pi}{n}$, one for the principal maximum and the other for the first subordinate. Accordingly we obtain

$$\frac{\sqrt{\Phi(0)}}{\sqrt{\Phi\left(\frac{3\pi}{n}\right)}} = n \sin \frac{3\pi}{2n} \tag{23}$$

If n is large $\sin \frac{3\pi}{2n}$ is approximately equal to $\frac{3\pi}{2n}$ and the field strength ratio becomes $\frac{3\pi}{2} = 4.71$. This ratio corresponds to the difference in levels equal to 13.5 decibels.

DIRECTIVITY OF ARRAYS

The "decomposition theorem" of the preceding section throws considerable light on directive properties of arrays. The number of elements in the array is one greater than the number of virtual couplets. Hence to secure the greatest possible directivity with a given number of elements, the virtual couplets must be properly combined.

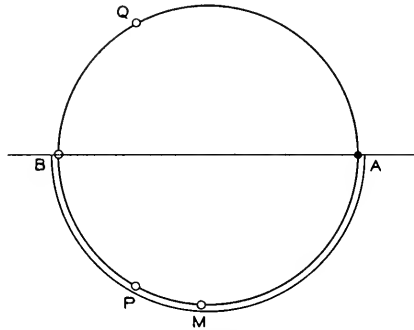


Fig. 11—The null points of several three-element arrays. The spacing between the elements is $\lambda/4$ and the progressive phase delay is $T/4$ (T equals period).

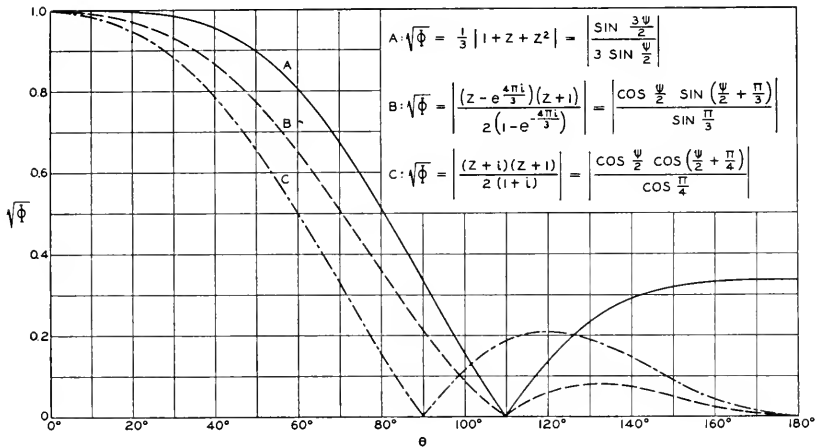


Fig. 12—Comparison of directivity of several three-element arrays. The spacing between the elements is $\lambda/4$; the direction of principal radiation is $\theta = 0^\circ$. Curve (A) refers to the uniform array, (B) to an array with nulls at P and B (see Fig. 11), and Curve (C) refers to an array with its nulls at B and M.

For example, the null points of a uniform array of three elements, one-quarter wavelength apart, are at P and Q (Fig. 11). If $\vartheta = \pi/2$, the range of z consists of the lower half of the unit circle and principal radiation takes place in the direction $\theta = 0$. Evidently, the virtual couplet with its null

at Q is comparatively nondirective. Substituting for this couplet another couplet with a null at B should improve the directivity of the array. This is indeed the case: In Fig. 12, Curve A depicts directive properties of the uniform array and Curve B depicts those of an array with its nulls at P and B . The field strength of the second array is

$$\begin{aligned}\sqrt{\Phi} &= \left| (z - e^{-\frac{2\pi i}{3}})(z + 1) \right| = \left| z^2 + (1 - e^{-\frac{2\pi i}{3}})z - e^{-\frac{2\pi i}{3}} \right| \\ &= \left| 1 + z\sqrt{3}e^{-\frac{i\pi}{6}} + z^2e^{-\frac{i\pi}{3}} \right|, \quad z = \frac{\pi}{2}(\cos\theta - 1); \end{aligned} \quad (24)$$

hence the amplitudes of the elements are proportional to 1, $\sqrt{3}$, 1 and the total progressive phase delay in the direction of maximum radiation is $\frac{\pi}{2} + \frac{\pi}{6} = \frac{2\pi}{3}$ radians.

The minor lobe of the second array is substantially smaller than that of the first array. The major lobes, however, are equally "wide"⁸ although one lobe is somewhat sharper than the other. The width of the major lobe can be reduced at the expense of increasing the minor lobe by moving the null from P to M (Fig. 11). The effect of this change is shown by Curve C (Fig. 12). The corresponding field strength is⁹

$$\begin{aligned}\sqrt{\Phi} &= |(z + i)(z + 1)| = |z^2 + (1 + i)z + i| \\ &= |1 - i(1 + i)z - iz^2| = \left| 1 + \sqrt{2}e^{-\frac{i\pi}{4}}z + e^{-\frac{i\pi}{2}}z^2 \right|; \end{aligned} \quad (25)$$

hence the amplitudes are proportional to 1, $\sqrt{2}$, 1 and the total progressive phase delay is $\frac{\pi}{2} + \frac{\pi}{4} = \frac{3\pi}{4}$.

For arrays of six elements, one-quarter wavelength apart and with $\vartheta = \pi/2$, we have Fig. 13. Curve A represents the directive characteristic of a uniform array, with its nulls as shown in Fig. 14A, and Curve B shows the directive properties of an array with its nulls equispaced on the lower half of the unit circle as shown in Fig. 14B.

If the spacing between the elements is $\ell = \lambda/8$ and if the phase delay $\vartheta = \pi/2$, then the effect of distribution of the null points is even more pronounced (Figs. 15 and 16). This time z is confined to the fourth quadrant of the unit circle. In Fig. 15, $n = 3$; Curve A corresponds to an array with equal amplitudes in which case the nulls are equispaced on the complete unit circle (Fig. 17A) and Curve B corresponds to an array with its nulls equi-

⁸ If the "width" of a lobe is measured by the angle of the cone of silence enclosing the lobe.

⁹ When transforming the expressions for $\sqrt{\Phi}$, it is well to remember that the absolute value of a complex quantity does not change if this quantity is multiplied by a unit complex number.

spaced within the range of z (Fig. 17B). In Fig. 16, $n = 6$; Curve A represents an array with nulls distributed evenly on the complete circle and Curve B represents an array with nulls evenly spaced in the range of z .

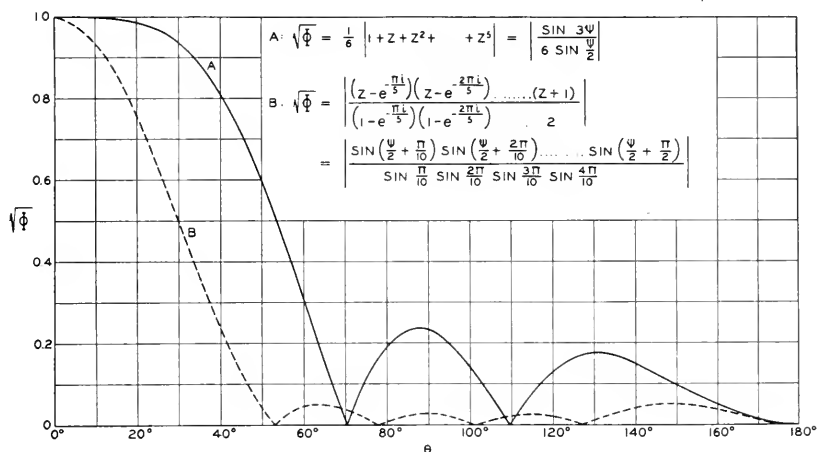


Fig. 13—Directive properties of 2 six-element arrays with $\ell = \lambda/4$. Curve (A) refers to a uniform array and Curve (B) refers to an array with its nulls equispaced in the range of z .

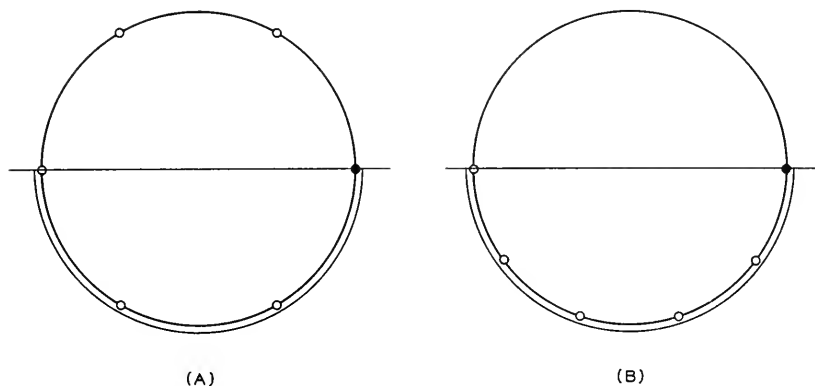


Fig. 14—Disposition of null points for the arrays with directive characteristics as shown in Fig. 13.

If the total length of an array is kept constant but the number of elements is increased, the array may be made more directive; Figure 18 illustrates this point. This increase in directivity can be secured only if the null points of the array are properly distributed within the range of z ; in Fig. 18

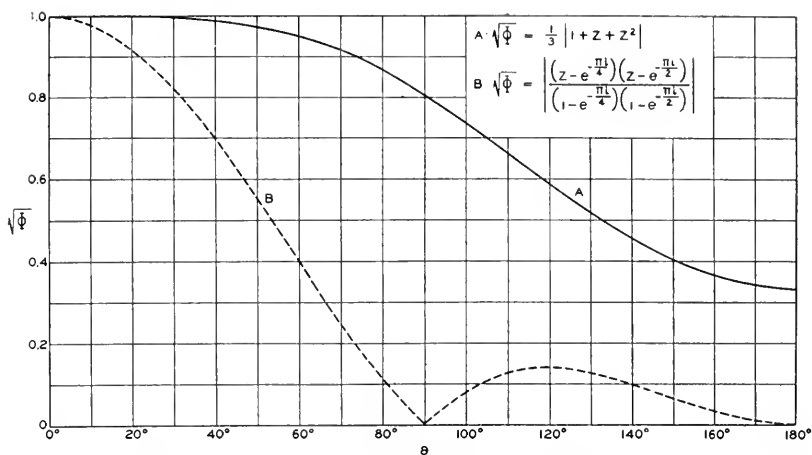


Fig. 15—Directive properties of three-element linear arrays with $\ell = \lambda/8$. Curve (A) refers to a uniform array and Curve (B) to an array with its nulls equispaced in the range of ε .

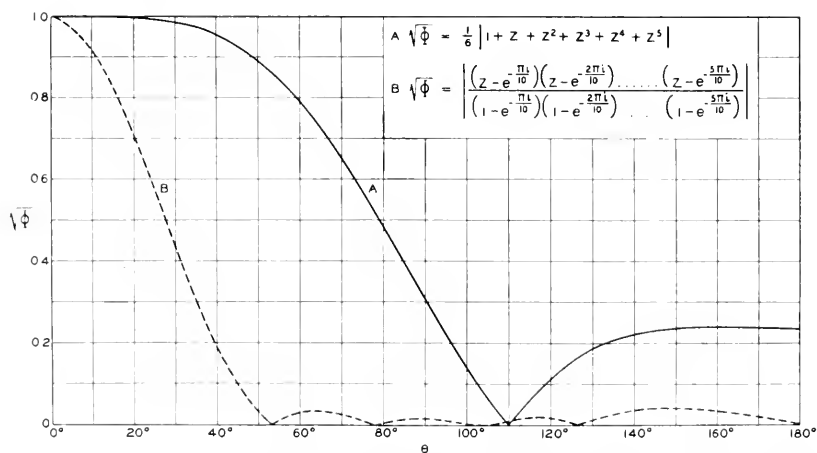


Fig. 16—Directive properties of six-element linear arrays with $\ell = \lambda/8$. Curve (A) refers to a uniform array and Curve (B) to an array with its nulls equispaced in the range of ε .

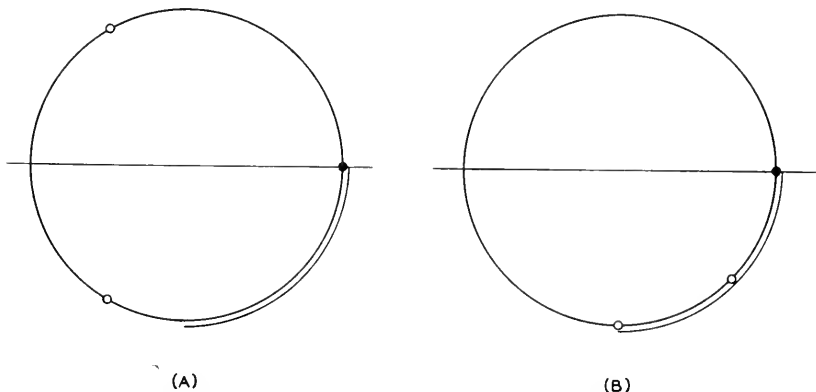


Fig. 17—Disposition of nulls for the arrays whose directive properties are shown in Fig. 15.

the null points are evenly spaced in the range of α , appropriate to each separation between the elements.

If the elements of the array are directive, the null points should be distributed with due reference to the directive pattern of the elements in order that a further increase in directivity could be secured.

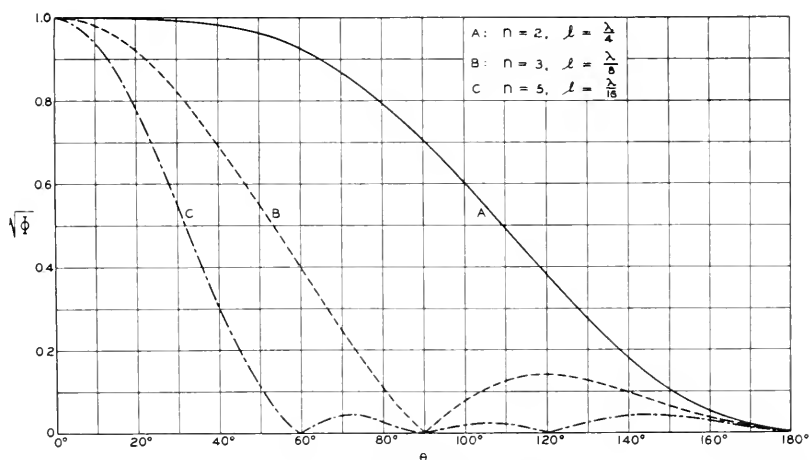


Fig. 18—Directive properties of linear arrays with total length equal to $\lambda/4$. (A), $n = 2$, $l = \lambda/4$; (B), $n = 3$, $l = \lambda/8$; (C), $n = 5$, $l = \lambda/16$.

MULTI-DIMENSIONAL ARRAYS

The simplest method of constructing multi-dimensional arrays is to take a linear array as an element of another linear array. The axis of the second array may be chosen to make any angle with the axis of the first array. In this way only a special class of multi-dimensional arrays can be formed. Analytical expressions for the radiation intensities of more general arrays can be formulated in terms of two or more complex variables. These variables, however, will not be independent and a given direction in space will be represented by a group of related points, one point on each circle representing the particular complex variable. At this time we shall not be concerned with any developments applicable to such general multi-dimensional arrays.

ARRAYS WITH PRESCRIBED SPACE FACTORS

If the minimum separation between the elements does not exceed $\lambda/2$, it is theoretically possible to design a linear array with a space factor given by an arbitrary function $f(\psi)$ or $F(\theta)$ of direction of radiation. Naturally the number of required elements will be usually infinite; with a finite number of elements the space factor may only be approximate.

Consider an array with an *odd* number of elements $n = 2m + 1$. Since the modulus of z is unity the polynomial (3) can be divided by z^m without affecting $\sqrt{\Phi}$; thus

$$\sqrt{\Phi} = | a_0 z^{-m} + a_1 z^{-m+1} + a_2 z^{-m+2} + \dots + a_m + a_{m+1} z + \dots + a_{2m} z^m |. \tag{26}$$

Let us now assume that the coefficients equidistant from the ends of the polynomial are conjugate complex; then the polynomial is real and we can drop the bars. Thus setting

$$a_m = A_0, \quad a_{m+k} = A_k - iB_k, \quad k > 0, \quad a_{m-k} = a_{m+k}^*, \tag{27}$$

where the A 's and B 's are real; we have

$$\begin{aligned} a_{m+k} z^k + a_{m-k} z^{-k} &= (A_k - iB_k) e^{ik\psi} + (A_k + iB_k) e^{-ik\psi} \\ &= 2A_k \cos k\psi + 2B_k \sin k\psi. \end{aligned} \tag{28}$$

Consequently, (26) becomes

$$\sqrt{\Phi} = \sum_{k=0}^m \epsilon_k (A_k \cos k\psi + B_k \sin k\psi), \tag{29}$$

where ϵ_k is the Neumann number.¹⁰

If now we wish $\sqrt{\Phi}$ to be a prescribed function $f(\psi)$ of the variable ψ , we need only expand this function in a Fourier series

$$\sqrt{\Phi} = f(\psi) = \sum_{k=0}^{\infty} \epsilon_k (p_k \cos k\psi + q_k \sin k\psi), \tag{30}$$

and approximate it with any desired accuracy by means of a finite series (29). Once the A 's and B 's are known, we calculate the a 's from (27).

It must be remembered that the real independent variable is not ψ but θ and the directive pattern is to be assigned as a function of θ . Besides being dependent on θ , ψ is a function of the distance ℓ between the successive elements of the array. Since θ varies from 0° to 180° , the range of ψ is $\bar{\psi} = 2\beta\ell$. The function $f(\psi)$ is prescribed within this range. On the other hand the period of the expressions (29) and (30) is 2π . This means that if $\bar{\psi} > 2\pi$, that is if $\ell > \lambda/2$, it is impossible to obtain the desired directive pattern with our scheme, because the pattern repeats itself automatically as ψ increases or decreases by 2π . But if $\ell < \lambda/2$, we have a considerable latitude in the design; outside the range of ψ , we can supplement $f(\psi)$ by an arbitrary function of ψ . It is only when $\ell = \lambda/2$ that there is a unique class of linear arrays that will produce a directive pattern given by the first

¹⁰ $\epsilon_0 = 1, \epsilon_k = 2$ when $k \neq 0$.

$(m + 1)$ terms of (30). Dr. T. C. Fry of these Laboratories has suggested that leaving ℓ undetermined and fixing the number of elements, an array could be designed which would have the best fit to the prescribed pattern. In this connection, the "best fit" means the least mean square deviation of the approximating pattern from the given pattern.

If $\sqrt{\Phi}$ is given as a function $F(\theta)$ of θ , then by virtue of the definition of ψ we can write

$$F(\theta) = F\left(\cos^{-1} \frac{\psi + \vartheta}{\beta \ell}\right) = f(\psi). \quad (31)$$

Let us now consider a simple example for the sake of illustrating the method. Let $f(\psi)$ be defined by

$$\begin{aligned} f(\psi) &= 0, & 0 < \psi < \pi, \\ &= 1, & \pi < \psi < 2\pi. \end{aligned} \quad (32)$$

We shall assume that the separation between the elements is one-half wavelength. This makes the range of ψ equal to 2π . It is also seen that regarded as a function of θ , $f(\psi)$ retains its essential characteristic: being equal to zero over one-half of the range and to unity over the remaining half.

Expanding (32) into a Fourier series we have

$$f(\psi) = \frac{1}{2} - \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{\sin(2k-1)\psi}{2k-1}. \quad (33)$$

Consequently

$$\begin{aligned} A_0 &= \frac{1}{2}, A_k = 0 \text{ if } k \neq 0; \\ B_k &= 0, \text{ if } k \text{ is even;} \\ B_k &= -\frac{1}{k\pi}, \text{ if } k \text{ is odd.} \end{aligned} \quad (34)$$

Figure 19 shows several approximations to $f(\psi)$ by means of a finite number of elements. The curve S_m corresponds to an approximation by the finite series (29). If S_9 is deemed to be a sufficiently good approximation to the given directive pattern, then

$$\begin{aligned} \sqrt{\Phi} &= \frac{1}{\pi} \left| \frac{1}{9} + \frac{1}{7} z^2 + \frac{1}{5} z^4 + \frac{1}{3} z^6 + z^8 + \frac{i\pi}{2} z^9 \right. \\ &\quad \left. - z^{10} - \frac{1}{3} z^{12} - \frac{1}{5} z^{14} - \frac{1}{7} z^{16} - \frac{1}{9} z^{18} \right|. \end{aligned} \quad (35)$$

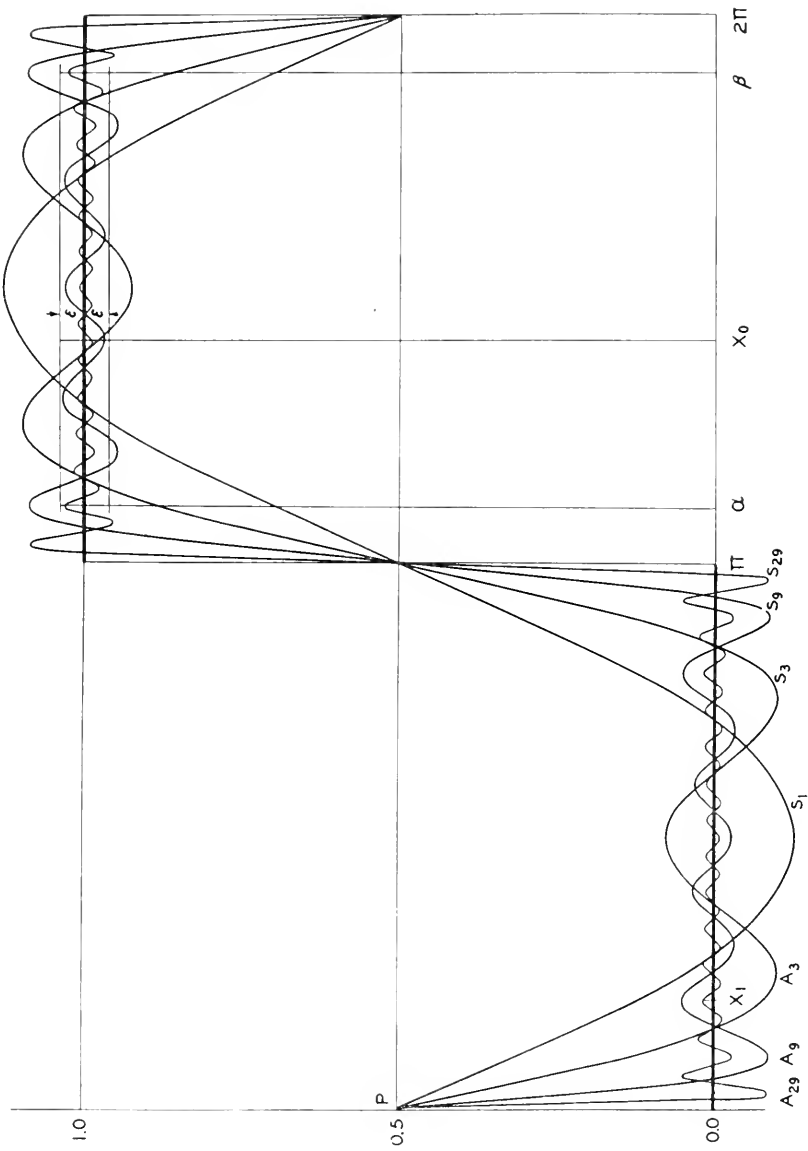


Fig. 19

The total length of this array is $(n - 1) \frac{\lambda}{2} = 2m \frac{\lambda}{2} = 9\lambda$. All elements except the three central ones are separated by one wavelength since the odd powers of z except z^0 are missing.

END-ON ARRAYS WITH EQUISPACED NULL POINTS

We now pass to a more detailed analysis of end-on arrays with null points equispaced on a given circular arc.

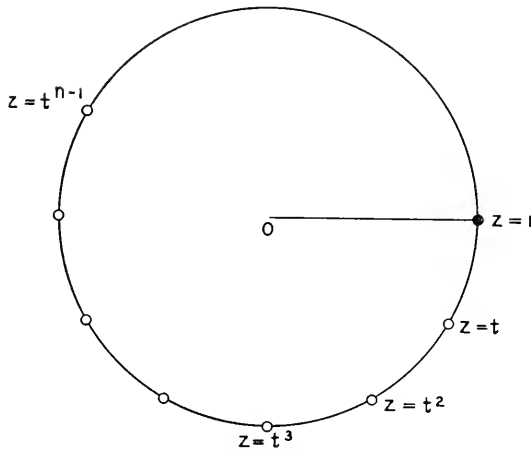


Fig. 20

For an end-on array $\vartheta = \beta l$ and

$$z = e^{i\psi}, \quad \psi = \beta l(\cos \theta - 1). \quad (36)$$

The range of z begins at $z = 1$ and extends clockwise to a point determined by $\psi = -2\beta l$. Let $n - 1$ null points be equispaced on an arc of length $\bar{\psi}$ as shown in Fig. 20; the field strength is then

$$\sqrt{\bar{\Phi}} = |(z - t)(z - t^2) \cdots (z - t^{n-1})|, \quad t = e^{-\frac{i\bar{\psi}}{n-1}}. \quad (37)$$

This can be expressed as

$$\begin{aligned} \sqrt{\bar{\Phi}} = 2^{n-1} & \left| \sin \frac{1}{2} \left(\psi + \frac{\bar{\psi}}{n-1} \right) \right. \\ & \times \sin \frac{1}{2} \left(\psi + \frac{2\bar{\psi}}{n-1} \right) \cdots \sin \frac{1}{2} \left(\psi + \frac{(n-1)\bar{\psi}}{n-1} \right) \left. \right|. \end{aligned} \quad (38)$$

The angle of the cone of silence enclosing the major radiation lobe is determined from

$$\beta\ell(\cos \theta_1 - 1) = -\frac{\bar{\psi}}{n-1}; \quad (39)$$

thus

$$1 - \cos \theta_1 = \frac{\bar{\psi}}{(n-1)\beta\ell}, \quad \sin \frac{\theta_1}{2} = \sqrt{\frac{\bar{\psi}}{2(n-1)\beta\ell}}. \quad (40)$$

If the arc $\bar{\psi}$ is equal to the range of z , then (40) becomes

$$1 - \cos \theta_1 = \frac{2}{n-1}, \quad \sin \frac{\theta_1}{2} = \frac{1}{\sqrt{n-1}}. \quad (41)$$

In this case, the size of the first cone of silence is determined *solely by the number of elements*. On the other hand, if $\bar{\psi} = 2\pi - 2\pi/n$, the nulls are equispaced on the unit circle and we have an ordinary uniform array; then

$$1 - \cos \theta_1 = \frac{2\pi}{n\beta\ell} = \frac{\lambda}{n\ell}, \quad \sin \frac{\theta_1}{2} = \sqrt{\frac{\lambda}{2n\ell}}. \quad (42)$$

This time the size of the first cone of silence depends upon the total length $L = (n-1)\ell$ of the array measured in wavelengths.

When the number of elements in the first case and the total length of the array in the second are large, then we have approximately

$$\theta_1' = \frac{2}{\sqrt{n-1}}, \quad \theta_1'' = 2 \sqrt{\frac{\lambda}{2n\ell}}. \quad (43)$$

For a large n the ratio of the two cone angles is approximately

$$\frac{\theta_1'}{\theta_1''} = \sqrt{\frac{2\ell}{\lambda}}. \quad (44)$$

For example, if $\ell = \lambda/8$, the angle of the major lobe in the first case is one-half of that in the second case or one-quarter if we are to compare the solid angles.

Equispacing the null points in the range of z not only makes the major lobe narrower but it also makes it sharper. Thus at the point lying halfway between the point of maximum radiation and the first null point, the field strength relative to the principal maximum is

$$\chi = \frac{\sin \frac{\bar{\psi}}{4(n-1)} \sin \frac{3\bar{\psi}}{4(n-1)} \sin \frac{5\bar{\psi}}{4(n-1)} \cdots \sin \frac{(2n-3)\bar{\psi}}{4(n-1)}}{\sin \frac{\bar{\psi}}{2(n-1)} \sin \frac{2\bar{\psi}}{2(n-1)} \sin \frac{3\bar{\psi}}{2(n-1)} \cdots \sin \frac{(n-1)\bar{\psi}}{2(n-1)}}. \quad (45)$$

For a quarter wavelength separation between the elements $\bar{\psi} = \pi$ and this ratio is equal to

$$x = \frac{1}{\sqrt{2(n-1)}} \quad (46)$$

so that the drop in the radiation intensity becomes $[10 \text{ Log}_{10} (n-1) + 3]$ decibels. On the other hand, for a long uniform array the corresponding drop is independent of n and is equal to 4 decibels.

Another consequence of equispacing the null points in the range of z consists in substantial suppression of subsidiary radiation lobes. The first subordinate maximum is situated approximately halfway between the first two null points where $\psi = -\frac{3\bar{\psi}}{2(n-1)}$; thus the field strength there, relative to the principal maximum, is

$$x = \frac{\sin \frac{\bar{\psi}}{4(n-1)} \sin \frac{\bar{\psi}}{4(n-1)} \sin \frac{3\bar{\psi}}{4(n-1)} \cdots \sin \frac{(2n-5)\bar{\psi}}{4(n-1)}}{\sin \frac{\bar{\psi}}{2(n-1)} \sin \frac{2\bar{\psi}}{2(n-1)} \sin \frac{3\bar{\psi}}{2(n-1)} \cdots \sin \frac{(n-1)\bar{\psi}}{2(n-1)}} \quad (47)$$

For a quarter wavelength separation this field strength becomes

$$\begin{aligned} x &= \frac{2^{-\frac{2n-3}{2}} \sin \frac{\pi}{4(n-1)}}{\sqrt{2(n-1)} 2^{-\frac{2n-3}{2}} \sin \frac{(2n-3)\pi}{4(n-1)}} \\ &= \frac{\sin \frac{\pi}{4(n-1)}}{\sqrt{2(n-1)} \sin \frac{2(n-3)\pi}{4(n-1)}} \end{aligned} \quad (48)$$

When n is sufficiently large, we have approximately

$$x = \frac{\pi}{4(n-1) \sqrt{2(n-1)}} \quad (49)$$

and the subsidiary maximum is $[30 \text{ Log}_{10} (n-1) + 5]$ decibels below the principal maximum. Each time the number of elements is doubled, the level of the subsidiary maximum is diminished by about 9 decibels. Thus an array of the type (37) with $\bar{\psi} = 2\beta l$ has very sharp directive properties.

In order to find the relative amplitudes and phase deviations of the elements of the array represented by (37), we expand $\sqrt{\Phi}$ into a single polynomial as follows¹¹

$$\begin{aligned} \sqrt{\Phi} &= |(1 - t^{-1}z)(1 - t^{-2}z) \cdots (1 - t^{-n+1}z)| \\ &= \left| 1 + \sum_{k=1}^{n-1} (-)^k \frac{(1 - t^{-n+1})(1 - t^{-n+2}) \cdots (1 - t^{-n+k})}{(1 - t^{-1})(1 - t^{-2}) \cdots (1 - t^{-k})} t^{-\frac{k(k+1)}{2}} z^k \right| \\ &= \left| 1 + \sum_{k=1}^{n-1} (-)^k \frac{(t^{-\frac{n-1}{2}} - t^{\frac{n-1}{2}}) \cdots (t^{-\frac{n-k}{2}} - t^{\frac{n-k}{2}})}{(t^{-\frac{1}{2}} - t^{\frac{1}{2}})(t^{-1} - t) \cdots (t^{-\frac{k}{2}} - t^{\frac{k}{2}})} t^{-\frac{kn}{2}} z^k \right| \quad (50) \\ &= \left| 1 + \sum_{k=1}^{n-1} (-)^k \frac{\sin \frac{(n-1)\bar{\psi}}{2(n-1)} \cdots \sin \frac{(n-k)\bar{\psi}}{2(n-1)}}{\sin \frac{\bar{\psi}}{2(n-1)} \cdots \sin \frac{k\bar{\psi}}{2(n-1)}} e^{\frac{ikn\bar{\psi}}{2(n-1)}} z^k \right|. \end{aligned}$$

Hence the progressive phase delay from one antenna to the next is equal to

$$\vartheta = \pi - \frac{n\bar{\psi}}{2(n-1)} \text{ and the amplitudes are in the ratio}$$

$$\begin{aligned} 1, \quad & \frac{\sin \frac{(n-1)\bar{\psi}}{2(n-1)}}{\sin \frac{\bar{\psi}}{2(n-1)}}, \quad \frac{\sin \frac{(n-1)\bar{\psi}}{2(n-1)} \sin \frac{(n-2)\bar{\psi}}{2(n-1)}}{\sin \frac{\bar{\psi}}{2(n-1)} \sin \frac{2\bar{\psi}}{2(n-1)}}, \\ & \frac{\sin \frac{(n-1)\bar{\psi}}{2(n-1)} \sin \frac{(n-2)\bar{\psi}}{2(n-1)} \sin \frac{(n-3)\bar{\psi}}{2(n-1)}}{\sin \frac{\bar{\psi}}{2(n-1)} \sin \frac{2\bar{\psi}}{2(n-1)} \sin \frac{3\bar{\psi}}{2(n-1)}}, \quad \dots, \quad 1. \end{aligned} \quad (51)$$

The amplitudes of the elements equidistant from the ends of the array are equal. In the special case of an end-on array with nulls equispaced in the range of z , $\bar{\psi} = 2\beta\ell$ and $\vartheta = \beta\ell$; hence the progressive phase delay from one antenna to the next is $\pi - \frac{\beta\ell}{n-1}$.

While (50) serves well for finding the amplitude and phase distribution in the individual elements of the array, another form is more general for calculating the directive properties. In order to obtain this form we set

¹¹ Chrystal's Algebra, Vol. 2, p. 340, (1926).

$$p_0 = 1, \quad p_{n-1-k} = p_k, \quad p_k = \frac{\sin \frac{(n-1)\bar{\psi}}{2(n-1)} \cdots \sin \frac{(n-k)\bar{\psi}}{2(n-1)}}{\sin \frac{\psi}{2(n-1)} \cdots \sin \frac{k\bar{\psi}}{2(n-1)}} \quad (52)$$

$$\varphi = \psi + \frac{\bar{\psi}}{2} + \frac{\bar{\psi}}{2(n-1)} + \pi,$$

divide the last expression in (50) by $e^{\frac{i(n-1)\varphi}{2}}$ and combine the terms equidistant from the ends. Thus we obtain

$$\begin{aligned} \sqrt{\Phi} = 2 \cos \frac{(n-1)\varphi}{2} + 2p_1 \cos \frac{(n-3)\varphi}{2} \\ + 2p_2 \cos \frac{(n-5)\varphi}{2} + \cdots, \end{aligned} \quad (53)$$

where the last term is $2p_{\frac{n}{2}-1} \cos \frac{\varphi}{2}$ if n is even and $p_{\frac{n-1}{2}}$ if n is odd.

Let D be the maximum value of $\sqrt{\Phi}$; then the gain of the array over a single source is given by

$$G = 10 \text{Log}_{10} \frac{4\pi D^2}{\iint \Phi d\Omega} = 10 \text{Log}_{10} \frac{2D^2}{\int_0^\pi \Phi \sin \theta d\theta} \text{ decibels}, \quad (54)$$

where Ω is the solid angle and the integration is extended over a unit sphere. For an end-on array with nulls equispaced in the range of z , the maximum radiation is in the direction $\psi = 0$. Thus we shall have

$$\begin{aligned} D = 2 \cos \frac{(n-1)\varphi_0}{2} + 2p_1 \cos \frac{(n-3)\varphi_0}{2} \\ + 2p_2 \cos \frac{(n-5)\varphi_0}{2} + \cdots, \end{aligned} \quad (55)$$

where

$$\varphi_0 = \beta l + \frac{\beta l}{n-1} + \pi. \quad (56)$$

A convenient expression for the radiation intensity can be obtained from (50) by taking its norm

$$\begin{aligned} \Phi = [p_0 + p_1 e^{i\varphi} + p_2 e^{2i\varphi} + \cdots + p_{n-1} e^{i(n-1)\varphi}] \\ \cdot [p_0 + p_1 e^{-i\varphi} + \cdots + p_{n-1} e^{-i(n-1)\varphi}]. \end{aligned} \quad (57)$$

Since the set of coefficients $p_0, p_1, p_2 \dots p_{n-1}$ is symmetric about the center, we find

$$\begin{aligned} \Phi = & 2p_0^2 \cos (n-1)\varphi + 2(p_0p_1 + p_1p_0) \cos (n-2)\varphi \\ & + 2(p_0p_2 + p_1p_1 + p_2p_0) \cos (n-3)\varphi \\ & + 2(p_0p_3 + p_1p_2 + p_2p_1 + p_3p_0) \cos (n-4)\varphi + \dots \quad (58) \\ & + 2(p_0p_{n-2} + p_1p_{n-3} + p_2p_{n-4} + \dots + p_{n-2}p_0) \cos \varphi \\ & + (p_0p_{n-1} + p_1p_{n-2} + p_2p_{n-3} + \dots + p_{n-1}p_0). \end{aligned}$$

Since

$$\int_0^\pi \Phi \sin \theta d\theta = \frac{1}{\beta\ell} \int_{\varphi_1}^{\varphi_0} \Phi d\varphi, \quad (59)$$

$$\varphi_0 = \beta\ell - \vartheta + \frac{\bar{\psi}}{2} + \frac{\bar{\psi}}{2(n-1)} + \pi, \quad \varphi_1 = \varphi_0 - 2\beta\ell$$

we can write

$$\begin{aligned} \int_0^\pi \Phi \sin \theta d\theta = & \frac{1}{\beta\ell} \left[\frac{2p_0^2 \sin (n-1)\varphi}{n-1} + \frac{2(p_0p_1 + p_1p_0) \sin (n-2)\varphi}{n-2} \right. \\ & \left. + \dots + (p_0p_{n-1} + p_1p_{n-2} + \dots + p_{n-1}p_0)\varphi \right]_{\varphi_1}^{\varphi_0}. \quad (60) \end{aligned}$$

For an end-on array with nulls equispaced in the range of z , (60) becomes

$$\begin{aligned} \int_0^\pi \Phi \sin \theta d\theta = & \frac{2}{\beta\ell} \left[\frac{2(-)^{n-1} p_0^2}{n-1} \sin (n-1)\beta\ell \cos \frac{(n-1)\beta\ell}{n-1} \right. \\ & + \frac{2(-)^{n-2} (p_0p_1 + p_1p_0)}{n-2} \sin (n-2)\beta\ell \cos \frac{(n-2)\beta\ell}{n-1} + \dots \quad (61) \\ & \left. + (p_0p_{n-1} + p_1p_{n-2} + \dots + p_{n-1}p_0)\beta\ell \right]. \end{aligned}$$

Substituting in (54), we shall obtain the gain of the array.

Similar expressions can be obtained for an end-on array in which the amplitudes of the individual elements are equal. Thus we have

$$\begin{aligned} \Phi = & \frac{1}{n^2} [e^{i(n-1)\psi} + e^{i(n-2)\psi} + \dots + e^{i\psi} + 1] \\ & \cdot [1 + e^{-i\psi} + e^{-2i\psi} + \dots + e^{-i(n-1)\psi}] \quad (62) \\ = & \frac{1}{n^2} [2 \cos (n-1)\psi + 4 \cos (n-2)\psi \\ & + 6 \cos (n-3)\psi + \dots + 2(n-1) \cos \psi + n], \end{aligned}$$

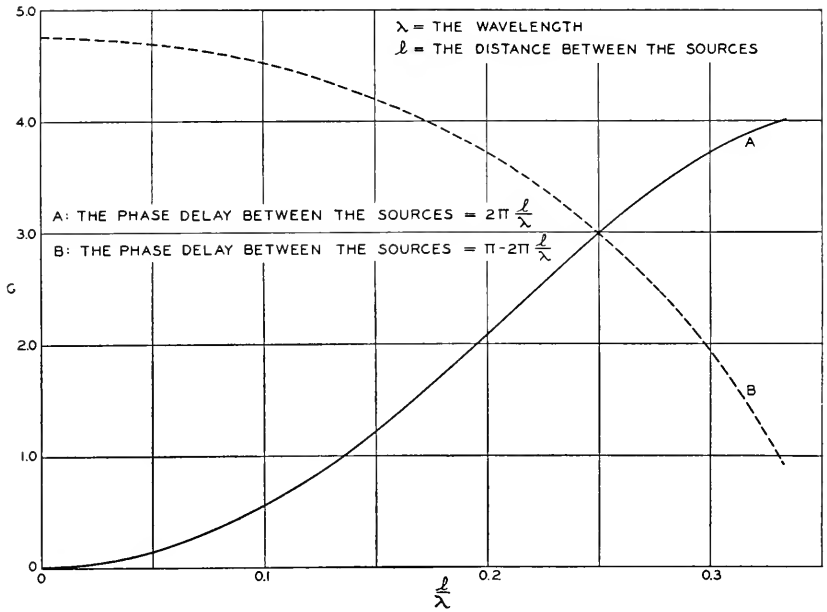


Fig. 21—The directive gain in decibels of a pair of sources with equal amplitudes. (A), the phase delay between the sources is $2\pi\ell/\lambda$; (B), the phase delay between the sources is $\pi - 2\pi\ell/\lambda$.

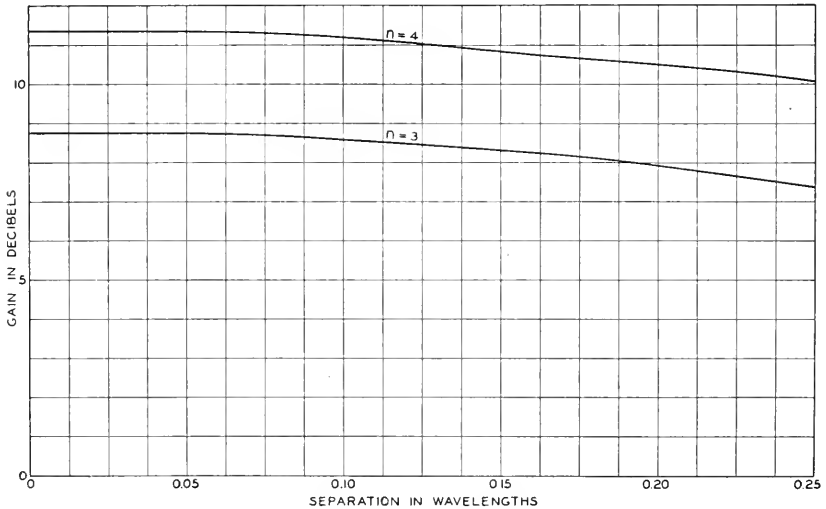


Fig. 22—The gain as a function of separation in wavelengths: n is the number of elements.

where $\psi = \beta\ell (\cos \theta - 1)$. In this case $D = 1$ and

$$\int_0^\pi \Phi \sin \theta \, d\theta = \frac{2}{n^2 \beta\ell} \left[n\beta\ell + \frac{\sin 2(n-1)\beta\ell}{n-1} + \frac{2 \sin 2(n-2)\beta\ell}{n-2} \right. \\ \left. + \dots + \frac{3 \sin 2(n-3)\beta\ell}{n-3} + \dots + (n-1) \sin 2\beta\ell \right]. \quad (63)$$

When the separation between the elements is exactly an integral number of quarter wavelengths, (63) becomes

$$\int_0^\pi \Phi \sin \theta \, d\theta = \frac{2}{n} \quad (64)$$

and consequently the gain is

$$G = 10 \text{ Log}_{10} n. \quad (65)$$

Figure 21 contrasts the directive gain of a pair of sources of equal strength with the phase delay $2\pi\ell/\lambda$ (Curve A) with a directive gain of another pair of sources of equal strength but with the phase delay $\pi - 2\pi\ell/\lambda$ (Curve B). In one case the directive gain diminishes with separation between the elements and in the other it increases. Figure 22 shows the directive gain of three-element and four-element end-on arrays with nulls equispaced in the range of z .

As the separation between the elements decreases, the directive gain of an end-on array with nulls equispaced in the range of z increases but the radiation intensity per ampere-meter decreases. This circumstance would be of no importance if we had perfect conductors at our disposal to make transmitting and receiving antennas; but in reality parasitic losses in themselves cannot be removed and the efficiency of an array decreases, therefore, with the separation between the elements. This decrease in efficiency will impose an upper limit on the overall gain that can be obtained with small antenna arrays in spite of the fact that the directive gain could be made very large.

Likewise the band width diminishes as the distance between the elements decreases. This imposes another limitation on arrays of this type.

Memorial to the Classical Statistics

By KARL K. DARROW

ONE of the most elusive and perplexing, hazy and confusing of the parts of theoretical physics is that which bears the name of "statistical mechanics".* On the principle that a tree is to be judged by its fruits, this must be ranked as high as the tree which bore the golden apples of the Hesperides; for among its fruits are the Maxwell-Boltzmann distribution-law, the black-body radiation law, the value of the chemical constant, the Fermi distribution-law for the electrons in metals, the alternating intensities in band-spectra—and indeed the tree might lay a valid claim to the whole of quantum-theory. The singular thing is that such wonderful fruits should have grown from, or should have been grafted upon, so badly-rooted a tree. To change the metaphor, one frequently feels that the superstructure is sustaining the foundations, and the premises are flowing from the consequences, rather than the other way about. Perhaps anyone who feels this way should be disqualified from writing about the subject; but on the present occasion, the attempt is going to be made.

Statistical mechanics—hereinafter to be called "S.M." at times for short—did not of course arise from any desire to solve the problems suggested above, which came late. It seems to have sprung from attempts to answer older questions, of which the following may serve as an example. Consider a gas in a box, with an electric fan or something of the sort fitted inside to stir it up. The gas having been stirred up, the fan is stopped, leaving it in a state of surging and whirling about within the confines of the box. Very shortly, however, the surging and the whirling cease, the gas having passed of itself into a state of tranquillity and uniformity—uniform density, uniform pressure, uniform temperature. From this state it never departs, unless stirred up afresh. There is a tendency of the gas to go of itself from the state of surging into the state of uniformity, and no tendency at all for it to go from the state of uniformity back into the state of surging. This is very unlike the behavior of a pendulum, which having fallen from one end of the arc of its sweep to the middle thereof, moves on to the opposite end, retraces its path and returns to its first situation. Why should the gas behave that other way?

* I acknowledge with gratitude the incentive given me by Smith College to explore this subject, by offering me the opportunity of giving a course on statistical and chemical physics in the spring semester of 1942.

For an answer to this question and others of the kind, S.M. offers the following statement:

BASIC THEOREM OF STATISTICAL MECHANICS

A system is more likely to be found in a state of greater probability than in a state of lesser probability

It may be that no reader of these lines has ever seen the basic theorem of S.M. set forth with such merciless candor, though in many a sober treatise there is an elaborate statement which when analyzed turns out to be just this and nothing more. Of course it is a tautological statement, and has no value except insofar as it may help to drive some contradictory notion out of the student's mind or to prepare that mind for some meaning or other which is not yet in the statement but may be added to it later. Actually it can serve both these offices.

To be expelled from the mind of the student is first of all the idea that S.M. is going to give him a description of the way in which the gas proceeds from the surging state to the uniform. From an astronomer he may learn the orbit of the moon from apogee to perigee. From an authority on ballistics he may find the trajectory of the bullet from the muzzle of the gun to the bull's eye on the target. From a railroad office he may get a timetable showing the passage of the train from mile to mile over the rails from Boston to Chicago. All this sort of thing is out of the range of statistical mechanics! If a railroad acted like a surging gas and its timetable were devised in the spirit of S.M., one would go to the office and be told that the trains were enormously more likely to be in Boston than in Chicago or anywhere in between. From this one would be expected to infer that at any moment chosen at random the chance of finding a train anywhere along the line except in Boston would be practically nil—unless indeed one got a train and put it on the rails at Springfield, and even this would be of little use for getting to Chicago, since at every subsequent instant the train would almost certainly be in Boston. Not a very useful timetable, and not a very useful railroad!

S.M. thus starts off with a renunciation. It renounces the prospect of telling just how the gas proceeds from the surging state to the uniform state. To that smooth unbroken sequence of times and places whereby the moon finds its way through the heavens and the bullet through the air and the train along the rails, there is no counterpart presented.

This of course is a serious matter, for the smooth unbroken sequence is inseparably linked—or almost inseparably linked—with the notion of cause-and-effect, the notion of natural law, the notion of man as a being who can foretell the future. Mechanics harmonizes with these notions; for mech-

anics is the science which professes that, given the positions and momenta and the forces in a system of particles at 10 A.M. sharp, it can predict the positions and momenta of all the particles at 11 A.M. and every instant in between and all through the endless future. Statistical mechanics, for all the implications of its name, is nowhere nearly so audacious.

Suppose the electric fan, or whatever stirring-gadget was employed, was stopped an instant before 10 A.M. sharp. S.M. limits itself to affirming that at 11 A.M. the most probable state for the gas in the container—the immensely most probable state, the almost-certain state—is the uniform state. It also says the same thing exactly for 10:15 A.M., and for 10:01 A.M., and even for 10 A.M. sharp. If at 10 A.M. sharp the gas is in a state of wild and furious surging, S.M. does not deny the fact, but sees no reason for revising its own affirmation. If at 10:01 A.M. the gas is settling down but has not yet quite reached the uniform state, that again does not deter S.M. from standing by its assertion. Whenever a freak of chance or act of man may have produced one of the states which it calls improbable, S.M. just says “wait, and you shall have the state which *I* am going to talk about.” To further questions it can only say “I know my limits”—and that is what its basic theorem says for it.

If now the negative aspect of the basic theorem is sufficiently clear, we may address ourselves to the task of giving the theorem a positive meaning. For this there is but one way: the word “probability” must be replaced with some word or phrase or mathematical expression which does have a meaning. After this is done we can of course restore the word “probability” as an equivalent for that other word or expression. The basic theorem will then be tautological upon the surface only, for actually it will have the meaning conferred upon it by the definition of its key-word.

Various meanings have been offered for the key-word, by various people who have been successful in getting useful results out of statistical mechanics. Until 1924 the dominant meaning was that imposed by Gibbs and Boltzmann. From this meaning arises the form of S.M. which is called “the classical statistics”. (The word “statistics”, by the way, is a bad but common abbreviation for “statistical mechanics”.) This is the topic of the present article. In 1924 there was proposed a novel meaning for the key-word, which led to results sometimes agreeing with, sometimes differing from, those attained by the classical statistics. Where the results of the two agreed, they agreed with experiment also; where the results of the two disagreed, experiment sustained the new one. This event has left the classical statistics in a strange situation, in which one cannot exclude the possibility that all of its remarkable achievement is due to a happy but deceptive chance. The classical statistics may indeed be only a past episode in the history of scientific thought, and it is for this reason that I have given to the article the

strange and sombre title "Memorial to the Classical Statistics". Yet even as a past episode, it is worthy of remembrance; its didactic value may yet be great; and perhaps the human mind may some day stretch its powers to the point of conceiving the classical and the new statistics as aspects of a single whole, as it has lately stretched itself to the extent of uniting the wave-picture and the corpuscular picture of matter and of light.

THE MAXWELL STATISTICS

Since the main concern of S.M. is with the "most probable state", one sees that its principal content must be made up of assertions about that most probable state. Maxwell made such an assertion. He wrote down a formula for the distribution-in-velocity of the molecules of a gas. It is the formula now called "the Maxwell-Boltzmann distribution-law", which is so well known to the readers of this journal that I will not bother to write it down until there is actual need for having it on the page. Maxwell might have said bluntly: "This is the distribution which I will assume for the most probable state"; and having said so, left it at that. He did not leave it at that, and presumably he would have been dissatisfied so to leave it, as most of us would be. Instead, he postulated a pair of attributes for the most probable state, and showed that if these are the attributes, then the distribution is according to that formula.

The attributes which Maxwell postulated are "isotropy" and "independence".

The former is easy enough. One assumes that in the most probable state, the distribution of velocities of the molecules is isotropic. Nothing can usefully be added to this simple statement.

The latter is a little harder to grasp. Perhaps it can best be exhibited by describing a couple of imagined cases for which it would not be valid. Suppose for instance that all of the molecules have the same speed—the same magnitude of velocity, though their velocity-vectors be pointed in all directions. Let this common value of speed be denoted by V , and let any direction chosen at random be made the axis of x in an ordinary coordinate-frame. If a molecule happened to be travelling with such a velocity that the component thereof along the x -axis, v_x let us call it, was just equal to V , then it would be a certainty that v_y and v_z , the y and z components of the velocity, were both of them zero. If a molecule happened to be travelling in such a way that v_x was zero, then either v_y or v_z or both of them would have to be different from zero, and the square root of the sum of the squares of v_y and v_z would have to be equal to V . There would consequently be a *correlation* between the values of the three components, and the probable—may even the possible—values of any one of them would be affected by those of the other two. If the molecules had a uniform distribution of speeds up

to a maximum value of V , there would still be a correlation of a similar sort, though not so marked a one: the higher the velocity-component in the x -direction, the lower would the y and the z components be likely to be. One could imagine distributions for which the higher the velocity-component in the x -direction, the higher would the y and the z components be likely to be.

The "assumption of independence" is, that in the most probable state there is no correlation at all. Whether the x -component of the velocity of a molecule is high or low is a detail which has no influence whatever on the possible or the probable values of the y and the z components. Low values of v_y go just as well and just as abundantly with low values of v_x as with high, and reversely.

The Maxwell-Boltzmann law, as I said, is the distribution-law which conforms to both the assumption of isotropy and the assumption of independence. So the question arises: do those two assumptions have the quality of plausibility and of convincingness, which make the average person say "Surely these must be the attributes of the most probable state of a gas!" I do not know what result a referendum on this question would give, but it is my guess that most physicists would feel more satisfied with these than they would with the Maxwell-Boltzmann distribution-law if it were tossed out to them with the bare affirmation "This is assumed to be the attribute of the most probable state". Clearly this is how Maxwell felt, and there is no better guide than the intuition of a Maxwell.

The foregoing question is something else than the question whether the assumptions, and the Maxwell-Boltzmann distribution-law which follows from them, are truly the attributes of the most probable state. It is a strange historical fact that not for many years after the promulgation of this famous law, and not till after both of its sponsors were dead, was there any proper test of it. The derivations of the law were exercises in abstract and un-remunerated thought. Nevertheless experiment—applied to thermionic electrons, to molecules of ordinary gases, to thermal neutrons—came at long last to justify Maxwell. To any who may feel that the assumption of independence is in itself too reasonable to require any proof, I disclose that in other forms of statistics this assumption is declared to be false, except as an approximation.

The "Maxwell statistics" therefore consists in the main of the statement:

The most probable state of a gas is that in which isotropy and independence prevail among the velocity-vectors of the molecules.

We now require some terminology and some notation.

I take for granted an understanding of the terms "velocity-vector" and "distribution-in-velocity", these being learned by physicists out of kinetic theory if not out of S.M. A velocity-vector may be replaced by a point

which serves just as well for all of its purposes and even better for some. Let the velocity-components $v_x, v_y,$ and v_z be laid out along the axes of a Cartesian coordinate-frame, and the vector for any molecule be drawn from the origin: the point at its tip is the point in question. Point and coordinate-frame are said to be "in velocity-space". Statistical mechanics prefers as a rule to deal with the momenta of the molecules rather than their velocities. This is for valid and powerful reasons, one of which is that the transition to the case of photons becomes much easier.¹ In the case of material gases it makes no practical difference, since the momentum of a molecule is its velocity-vector multiplied by the mass of the molecule which is practically a constant, and every statement about the distribution-in-velocity can with the utmost ease be translated into a statement about the distribution-in-momentum and *vice versa*. The momentum-vector may be replaced by the point at its tip, having coordinates p_x, p_y and p_z in a coordinate-frame in "momentum-space". If we consider together with these the three coordinates x, y, z of the molecule in ordinary space, we may say that we are locating the molecule in six-dimensional space. I have yet to meet someone who claims that he can visualize a six-dimensional space, and yet there is no doubt that the phrase fulfills a psychological need and has a practical value. The six-dimensional space of these particular six variables is called "the μ -space".

It seems odd to bring in the μ -space before considering by itself the three-dimensional "ordinary" or "coordinate-space" in which the gas is located. Is there nothing to be said about the most probable distribution of the molecules in the coordinate-space? Well, "every schoolboy knows" that the state to which a gas tends and in which it remains is a state of uniform density. Maxwell, I think, accepted this as one of the facts behind which one cannot, or does not, go. For a complete statement of the Maxwell statistics I therefore offer the following:

A gas is very much more likely to be in its "most probable state" than in any other. The most probable state is that in which isotropy and independence prevail among the momentum-vectors, while the distribution in coordinate-space is uniform.

So in the Maxwell statistics the distribution-in-momentum of the molecules is *derived* from assumptions ostensibly more basic, while the distribution-in-ordinary-space is simply *affirmed*. If a theory could be devised in which both were derived from assumptions apparently more basic, one would be likely to feel that something had been gained. Now this is a characteristic, and one of the principal virtues, of Boltzmann's theory known as the "Boltzmann Statistics" or as the "Classical Statistics".

¹Another reason has to do with "Liouville's theorem," for which unfortunately I cannot make room without overloading this article.

THE BOLTZMANN STATISTICS

Boltzmann invented a way of appraising the probability of any imagined state of a gas, which has the following very remarkable features:

(a) It gives so sharp a definition to the key-word "probability", that not only can the state of maximum probability be identified, but the ratio of the probabilities of any two states can be computed.

(b) For the distribution-in-momentum of the molecules in the most probable state, it derives a formula identical with that which springs from the Maxwell statistics. This of course is why the formula is known as the Maxwell-Boltzmann law.

(c) For the distribution-in-space of the molecules in the most probable state, it derives the uniform distribution.

All this does not entail that the Boltzmann statistics is necessarily right. It does, however, lead to consequences, which it is the privilege and the affair of experimental physics to verify or to reject.

I can now write down a phrase into which the Boltzmann statistics, and equally well those which came later, can be fitted:

The probability of a state is the number of different ways in which the state can be realized.

This is another of those oracular sayings which acquire a meaning only after some meaning is given to the key-word, which in this case is *ways*. I could now rewrite the basic theorem without the word "probability", and so can the reader; but the only effect would be to transfer the mystery out of the word "probability" and into the word "way". Boltzmann, however, assigned a meaning to the latter word. It is this meaning which we now must strive to realize.

For this purpose I propose a game of which the outfit consists of a sack, an enormous number N of balls, and a smaller number M of baskets. The game is played by reaching into the sack, drawing out the balls one after another, and tossing them into the baskets. All of the balls feel precisely alike to the hand, so that there is never the least inclination to put one aside and pick up another as one's hand gropes around in the sack. Nevertheless when one looks at the balls after they have fallen into the baskets, one sees that they are nicely adorned with the integer numbers running from 1 to N . Incidentally the baskets also are numbered. It is this numbering which gives point to the game.

Someone or other—someone who might be designated as the caller, after the man who calls the figures of a square-dance—has prescribed a sequence of M numbers N_1 and N_2 and N_3 and so on to N_M , all of them positive integers and totalling up to N . A single inning of the game consists in drawing all of the balls out of the sack one after another, and dropping the first N_1 which come out into the basket I, the next N_2 which emerge into the

basket II, and so on until every one of the balls is reposing in one or another basket. Now along comes the umpire with pencil and pen, and he writes down on one sheet of his pad of paper the numbers of all the balls which are in basket I, and on a second sheet the numbers of all which are in II, and so on until he has got an inventory of the contents of all of the baskets. *The inventory does not state the order in which the balls in any basket were dropped into that basket.* That order is blotted out and forgotten. *The inventory states which balls are in which baskets,* and lets it go at that.

This does not seem a very entertaining game, but entertainment is not what it is for. The present question is: how many different inventories can there be, consistent with that sequence of figures $N_1, N_2, N_3, \dots, N_M$ which the caller prescribed at the start?

The answer is obtained in what must seem, to anyone meeting for the first time such a question, a strangely devious way.

First we evaluate the whole number of different *orders* in which the balls can be drawn from the sack. This is N -factorial or $N!$; for the first ball to emerge may be any one of the N , and the next may then be any one of the $(N-1)$ remaining, and the next may then be any one of the $(N-2)$ remaining, and so on to the end.

If each order corresponded to a different inventory, $N!$ would be our answer. Clearly this is so, if and only if there are as many baskets as balls and one ball in every basket. In all other cases $N!$ is larger, and often colossally larger, than the number which we seek. It is necessary now to see that this great multitude of $N!$ different orders falls into groups composed of X orders apiece, all of those in a single group corresponding to a single inventory—necessary to see this, and to calculate X ; whereupon we shall find that X , the “number of orders per inventory”, is the same for all of the inventories—so that the number which we seek is $N!$ divided by this common value of X .

It seems to be helpful to think of some one inventory, and of some one order which leads to that inventory. By a certain amount of mental effort, which varies from person to person, it can be seen that this particular order is but one among $N_1! N_2! N_3! \dots N_M!$ different orders all leading to the very same inventory. For think of the N_1 numbered balls which lie in the first of the baskets: there are $N_1!$ different orders in which they could have come out of the sack, and every one of these corresponds to the very same inventory. Think next of the N_2 numbered balls which rest in the second basket: they might have come out of the sack in $N_2!$ different orders, without changing the inventory. Think now of the contents of both of these baskets at once. Each of the $N_2!$ orders in which the second basketful may come out of the sack may follow on any one of the $N_1!$ orders in which it is possible for the first basketful to emerge. The product $N_1! N_2!$ is therefore the total

number of ways in which the first $(N_1 + N_2)$ of the balls might have come out of the sack without changing the inventory.

The process of proof need not be carried further. X has been evaluated. It bears no earmark of whatever particular inventory the student may have chosen to adopt at the beginning. It depends only upon the sequence of numbers N_1, N_2, \dots, N_M fixed by the caller, which sequence I will hereafter term a "distribution".

The number of inventories—or "complexions", to use a commoner word—for the distribution N_1, \dots, N_M is therefore given by the formula,

$$W = N!/N_1! N_2! \dots N_M! = N!/IIN_i! \quad (1)$$

The theorem to which we are advancing affirms that this number has its maximum value for the uniform distribution—the distribution in which the caller assigns the same number of balls, N/M , to each of the baskets.

The usual argument for this statement may be put as follows: Let us assume the uniform distribution, with $A = (N/M)$ balls in each basket, and compare its value of W with that of one of the neighboring distributions such as the one in which there are $(A + 1)$ balls in the first of the baskets, $(A - 1)$ in the second and A in each of the rest. It is not even necessary to get out a pencil and paper to see that W for the latter is less than W for the former, being in fact just $A/(A + 1)$ times as great. The same is evidently true for disarrangements of the uniform distribution which involve more than two baskets and more than one ball per basket. The conclusion is clinched by the obvious fact that when all of the balls are in any one basket, W has its least possible value, *viz.* unity. (To unite this formally with the previous statements, one must follow the mathematicians' practice of using a symbol $0!$ or "zero-factorial" and giving it the value unity).

We shall have to play this not so very entertaining game on several occasions in S.M., altering the meaning of the balls and the meaning of the baskets from one occasion to the next. The reader has probably guessed that the balls stand for the molecules. The guess is right in the classical statistics, wrong in the newer forms. To get at the meaning of the baskets, suppose the gas contained in a box of volume V , the interior of which is divided up by impalpable coordinate-planes into compartments or cells all of the same volume V_0 . The baskets stand for the cells.

Now we have the theorem that W is greatest for the uniform distribution of the balls in the baskets, and the assertion that the most probable state of a gas is the state of uniform density, all ready to be fitted together. The process of fitting-together is of the simplest. W is christened the "probability" of the state described by the "distribution" N_1, N_2, \dots, N_M , the quantities N_i now standing for the numbers of molecules in the various cells. Not only is the state of uniformity the most probable one by this definition,

but so long as the number of molecules N is many times as great as the number of compartments M —a condition easy to realize—those distributions which are markedly far from uniform have probabilities which are fantastically smaller than the value of W for the uniform state.

The Boltzmann statistics manages thus to derive the assertion aforesaid—the assertion that the uniform distribution in ordinary space is of all the most probable—from a principle which (at least in appearance) is more fundamental. It has indeed a couple of bothersome points—more than a couple perhaps, but there are two in particular which the newer statistics will attempt to assuage. One of these is the size to be assigned to the cells V_0 ; but we are borrowing trouble to think too much of that now, since whatever choice be made so long as N/M be large will not affect the achievement just cited. The other is, that one would much rather think of the molecules of a gas (of a single chemical kind) as being alike absolutely, than as being distinguished one from another by a mysterious something-or-other represented in this theory by numbers painted on balls. In the Boltzmann statistics, however, the numbers must stay on the balls.

We go over into the momentum-space, setting up a coordinate-frame and representing the molecules by dots, the coordinates of which are the momentum-components p_x, p_y, p_z of the molecules in question. To each position of a dot corresponds an energy-value, equal to $(1/2m)(p_x^2 + p_y^2 + p_z^2)$; we will call it E . E vanishes at the origin, and has a constant value over any spherical surface centered at the origin. To any distribution of the dots will correspond a specific value for the total energy of the gas. For this we need a symbol different from E ; and as we shall have a good deal to do with thermodynamics later on, I choose the thermodynamical symbol U . The average energy of the molecules of the gas will then be U/N , to be denoted by \bar{U} .

The entry of E and U into the situation is of the first importance. It is in fact all that will save us from the highly unwanted conclusion that the most probable distribution in the momentum-space is the uniform one, just as it was in the coordinate-space. To see why it makes so great a difference is not altogether easy. I think that the reflections which follow may give an inkling of the reason.

The momentum-space must be taken either as infinite or as finite. If we take it as infinite and demand a distribution of uniform density, then the density goes to zero and at the same time the energies of the molecules go to infinity, producing an impossible situation. Let us then take it as finite, blocking off all of the parts of it which lie beyond a certain sphere centered at the origin. Assume a uniform distribution within the sphere. This will correspond to a certain value of U . (The student may suppose, if it makes him happier, that the U -value was preassigned and the radius of the "certain sphere" chosen accordingly.) The W -value of this distribution will surely

be greater than that for any non-uniform distribution, whether of the same U or of a different U , confined within the sphere. However, by blocking off the whole of the momentum-space beyond the sphere, we have barred a whole lot of distributions corresponding to the same U and having some of their dots beyond the sphere. By no means have we proved that the W -value for the uniform distribution within the sphere is greater than that for any and all of the barred distributions. Now if we can agree that the blocking-off of part of the momentum-space is a silly thing to do and unacceptable to Nature, the argument for the uniform distribution is spoiled, and we have to look for a new idea.

At this point it seems best to go through the mathematical process for finding the distribution of greatest W in the coordinate-space and the momentum-space, just as that process is presented in the textbooks.

We return to equation (1) and make it a manageable one by having recourse to that godsend of statistical mechanics, the "Stirling approximation", which may be written thus:

$$\ln N! = N \ln N - N + \ln \sqrt{2\pi N} \quad (2)$$

This is valid only for large values of N , though writers on S.M. never seem to remember how large the values must be. For still larger values of N we can drop off the last two terms, arriving at a sort of super-Stirling approximation which however itself is commonly called *the* Stirling approximation:

$$\ln N! = N \ln N \quad (3)$$

Putting (3) into (1), we find:

$$\ln W = N \ln N - \sum N_i \ln N_i \quad (4)$$

Defining some quantities w_i by the equations $N_i = N w_i$, we make this over into:

$$\ln W = - N \sum w_i \ln w_i \quad (5)$$

having availed ourselves of the obvious fact that $\sum w_i$ is equal to unity.

We might now convert this into an equation for W , but this would be a waste of time and energy, since whenever W has a maximum so also will $\ln W$. With $\ln W$, therefore, we operate from now on. Making small variations in the quantities N_i , and making therefore small variations—call them δw_i —in the quantities w_i , we find in first approximation for the ensuing change in $\ln W$,

$$\delta \ln W = - N \sum (1 + \ln w_i) \delta w_i \quad (6)$$

Now we are restricting ourselves to variations in the quantities N_i which leave unchanged the total number of molecules in the cells, or of balls in the baskets—to variations, therefore, for which

$$\sum N_i = N = \text{constant}, \quad \sum \delta w_i = 0 \quad (7)$$

This restriction being introduced into (6), $\delta \ln W$ proceeds to vanish if and only if w_i has the same value for all of the cells. Now, the vanishment of $\delta \ln W$ is a necessary condition for having a maximum of W at the situation in question. I do not refer to it as a sufficient condition, because it admits of a minimum or of what is technically known as a “stationary” value of W in the situation in question. However it has already been shown, without the aid of the Stirling approximation, that the expression to which we are approximating is greater for the uniform distribution than for the neighboring non-uniform ones. It may therefore be accepted that here we have a maximum of W for the uniform distribution, and have reached the old result in a new way; an achievement nearly useless, were it not a prelude to the performance in momentum-space.

I continue to use the symbols W and N and N_i and w_i , but now with reference to the distribution of the representative dots in momentum-space. A new symbol, E_i , shall signify the energy of a molecule in the i th cell of the momentum-space. We wish at all costs to avoid the conclusion that the stable distribution in the momentum-space is the uniform one. Boltzmann managed to avoid it, and his was the following way:

Let us write, for the number of molecules in the i th cell, the expression:

$$Nw_i = NA \exp(-BE_i) \quad (8)$$

and insert it into (6). We shall find:

$$\delta \ln W = -N \sum (1 + \ln A - BE_i) \delta w_i. \quad (9)$$

Of the three terms on the right, two vanish for all variations in which the total number of molecules remains the same. The third does not—but it *will* vanish for a restricted class of these variations, to wit, those and those only for which the total energy of all the molecules remains the same; for $N \sum w_i E_i$ is precisely that total energy.

Some writers at this point ask the student to imagine a gas in a container being completely cut off from energy-interchange with the container-walls and with the whole of the outside world, and therefore being limited to the particular U -value with which it started out. Others import the word “temperature” which I am desperately (and vainly) trying to keep out until I am ready to bring it formally into the discourse, and aver that the gas is nearly or quite so limited if the walls of the container have the same temperature as the gas itself. The student may take his choice, but must suppose that

under such conditions Nature rejects that distribution which so to speak is "stable against" every conceivable variation, and elects that peculiar distribution which is stable not against any conceivable variation but only against the possible ones. Perhaps this is because the uniform distribution would entail the consequences mentioned on page 117, or perhaps there is no sense in saying that it is "because" of this or "because" of that. Anyhow, the peculiar distribution is the one which the data sustain.

However I have not really defined the peculiar distribution as yet, having merely thrown the symbols A and B into equation (8) as though they stood for completely disposable constants. It can readily be seen that at the most there can be but one disposable constant, for A and B interlinked by the obvious equation:

$$\Sigma w_i = A \Sigma \exp(-BE_i) = 1 \quad (10)$$

But even B is not disposable, if the total energy U and the average energy per molecule \bar{U} are preassigned; for there is another obvious equation:

$$\bar{U} = \Sigma E_i w_i = A \Sigma E_i \exp(-BE_i) \quad (11)$$

What with equations (10) and (11), there is no longer anything disposable about the constants A and B . The peculiar distribution in the momentum-space is completely defined. It is the Maxwell-Boltzmann distribution-law obtained from the Maxwell statistics, and sometimes known as the "canonical" distribution.

To summarize now the Boltzmann statistics as on page 113 the Maxwell statistics was summarized:

A gas is more likely to be found in its most probable state than in any other. The probability of a state is found by imagining it as a distribution of numbered molecules among cells, in the coordinate-space and in the momentum-space. That of any distribution is measured by the number of inventories compatible therewith. By this criterion the most probable distribution in coordinate-space is the uniform one, and by this criterion carefully hedged about, the most probable distribution in momentum-space is the Maxwell-Boltzmann or canonical one. It is necessary to liken molecules of a single kind to numbered balls, differing in no way except the numbering.

This point was reached by statistical mechanics about fifty years ago. Had it not been for Planck's wish and tenacious will to explain the black-body radiation-law, it might have been the stopping-point.

A HELPFUL AND TROUBLESOME COINCIDENCE BETWEEN TWO DIFFERENT QUANTITIES

Let us return to the game with the sack, the balls and the basket, played in the manner which led to good results when applied to the molecules in the coordinate-space.

The most probable distribution is the one evoked by the caller, when he calls for an equal number of balls in every basket. If there are N balls and M baskets, this means N/M balls to each basket, and a maximum number of inventories which I will call W_{\max} . Looking back to equation (1), we see that W_{\max} is a fraction the numerator of which is N -factorial, while the denominator is (N/M) -factorial raised to the power M . Taking logarithms and using the super-Stirling approximation, we find:

$$\ln W_{\max} = N \ln M \quad (12)$$

The logarithm of the probability of the most probable distribution (of numbered balls in numbered baskets, or molecules in equal cells of coordinate-space) is equal to the logarithm of the number of baskets (cells), multiplied by the number of balls (molecules).

Next suppose the caller, in a fit of uncontrollable zest for the game, calling in succession every one of the conceivable distributions. What is the total number of inventories compatible with all of them together? To sum over every conceivable expression of the type of (1) seems a hopeless assignment, but there is a short-cut to the result.

Fix a particular order for the drawing of the balls from the sacks—it may as well be the very order of their numbering. The first of the balls to be drawn may be tossed into any one of the baskets, giving M distinct “possibilities”. The second may be tossed into any one of the baskets, the same or another, giving in conjunction with the fate of the first M^2 different possibilities. The third may be tossed—but we leap to the conclusion. There are M^N possibilities altogether, and *these are the inventories*. Thus the total number of inventories consistent with all of the distributions, which I will call W_{tot} , is a number whereof the logarithm is,

$$\ln W_{\text{tot}} = N \ln M \quad (13)$$

But this is the same as the expression for $\ln W_{\max}$!

The meaning of this strange coincidence can only be, that when N and N/M are both so great that the super-Stirling approximation is a good one, then the *logarithm* of the number of inventories belonging to the most probable distribution is nearly as great as the *logarithm* of the total number of inventories belonging to all of the distributions put together—so nearly as great, that either *logarithm* is a good approximation to the other.

In the foregoing very important paragraph, I have italicized the word “logarithm” because if it were left out the statement would become a false one. The statement is not true if applied to the numbers themselves. W_{tot} is manyfold greater than W_{\max} , and the ratio between the two actually increases with rising N . So does the difference between $\ln W_{\text{tot}}$ and $\ln W_{\max}$ increase with rising N , but not so fast as either by itself; wherefore the truth

of the statement. The student may convince himself of this by applying the second-degree Stirling approximation (equation 2)².

I have called this both a helpful and a troublesome coincidence. It may be deemed a helpful one, because the expression for the total number of inventories is easier to derive and easier to remember than the expression for the number of inventories belonging to the most probable distribution. If therefore one has good ground for believing (as here is the case) that the logarithms of the two are approximately equal, one may serenely remember and use $\ln W_{\text{tot}}$ instead of $\ln W_{\text{max}}$. The troublesome feature is, that some expositors speak of $\ln W_{\text{tot}}$ throughout and never allude to $\ln W_{\text{max}}$, thus confusing the student to an extent which (if my experience is typical) may well be serious. I shall later dwell on the fact that $\ln W$ for any distribution is regarded as a measure of the entropy of that distribution, and $\ln W_{\text{max}}$ therefore as a measure of the entropy of the most probable distribution. Some people imply that $\ln W_{\text{tot}}$ is the true measure of the entropy of the gas, instead of being an approximation to it. They commit no numerical error in so doing, but they blot out the most remarkable quality of the Boltzmann statistics, to wit, the clear distinction which it makes between the most probable distribution and those of lesser probability. This mistake is more commonly made in treating the newer statistics. Here I am not so sure that it is a mistake, but I think so.

MEANINGS OF THE WORD "STATE"

The word "state", which turns up continually in this essay, is one of those words of which a proper definition is hardly less than a full description of the theory which employs it. When the theory changes so also does the meaning of the word. In the welter of statistical theories, the word "state" has several different meanings. In thermodynamics also it has more than one meaning, but one is preeminent.

Thermodynamics usually concerns itself with gases (not to speak of liquids and solids) which are in what I earlier called a "uniform" state: uniform density, uniform pressure, uniform temperature. For a gas of a single kind ("kind" being a word which it is the business of chemistry to define) it is a fact of experience that any two of these three variables suffice to define the third and also all of the other variables which thermodynamics cares about. Of these others there are two in particular which I mention at this point, the

² Actually if one goes from the "most probable state" $N_i = \text{const.} = N/M$ to the "next most probable" in which one ball is taken out of one of the baskets and put into another, the change in W is in the ratio of (N/M) to $(N/M) + 1$, which is practically no change at all when N/M is so high as is commonly taken. This shows that the statement could not be true if it were made about the numbers W_{max} and W_{tot} rather than about the logarithms thereof. It certainly looks as though the statement could not be true even when made of the logarithms, but this is evidently one of the cases where "intuition" is a fallible guide.

energy and the entropy. This makes five altogether, and any two of the five suffice to determine the state,—THE STATE, the uniform state, the only one about which thermodynamics really knows or cares. When asked about what I earlier called “a surging state”, thermodynamics mutters something to the effect that the entropy of such a state is smaller than that of THE STATE, and then puts an end to the conversation by refusing to commit itself further. Thermodynamics takes no cognizance of the molecular structure of matter. A gas might be a continuum, for all that it knows or cares.

Statistical mechanics talks about a mental image of the gas, in the form of a flock of dots in the coordinate-space and another flock of dots in the momentum-space, or one may call them a single flock of dots in the μ -space. In Boltzmann statistics, the “state” of this image is what I have been calling the “distribution”. The most probable state of the image—to wit, the one with the greatest number of inventories or complexions—is identified with THE STATE of thermodynamics. All of the rest belong to the category of which thermodynamics would say, that the entropy is smaller than it is for THE STATE. But since according to S.M. they belong to a category for which the probability is smaller than it is for THE STATE, one sees a connection between entropy of the gas and probability of the image beginning to take shape.

Now it is time to make a formal introduction of the concepts of entropy and temperature—the latter word having already sneaked into this article two or three times in spite of all my efforts to keep it out.

FORMAL ENTRANCE OF ENTROPY AND TEMPERATURE

For a substance, meaning now a gas, of a single kind, entropy and temperature are defined by the equation,

$$dU = TdS - PdV \quad (14)$$

P stands for pressure, V for volume, and S for entropy. For energy I use the symbol U already employed in that sense—but notice that formerly it stood for the kinetic energy of the molecules! To use the same symbol in both senses implies that the energy of the gas is entirely the kinetic energy (of translatory motion) of the molecules. This identification turns out to be valid for the “monatomic” gases, which are luckily numerous and well-studied. To these we confine ourselves throughout this article. T stands for the temperature called absolute; this being the only kind of temperature which will ever figure in this article, the adjective henceforth is discarded. Density was the fifth variable in my list given above, but volume is usually preferred to it. To make them equally useful, the quantity of gas must be stated; here it will be taken as one gramme-molecule.

It is evident that the equation is a comparison between two states. Do not go astray by supposing that these are like two of the states which we have been considering, having the same U and V and differing in the number of inventories! These on the contrary are two examples of THE STATE—of the thermodynamic state, of the most probable state—of a gas, differing in the values of some at least among the five variables. The quantities dU and dS and dV are the differences between the U -values and the S -values and the V -values of the two states, while P and T may be taken as referring to either, the smallness of the difference between the two states—implied by the differential notation—permitting of this.

It is also evident from my wording that the one equation is being used to define the two quantities S and T . This is unluckily no verbal slip, nor is it a temporary shortcut to be replaced by a royal road as the argument proceeds. The meanings of entropy and temperature are so coiled up together in thermodynamics, that it is impossible to take them apart unmutilated. One cannot seize either by storm and then invest the other, at least not without the aid of statistical theory: one has to surround them both in a single campaign. As Eddington has vigorously written, this is a common thing in physics. Electric force is defined as that which acts on electric charge, electric charge as that which is acted upon by electric force, and so on. . . . Common as it may be, it is probably nowhere else so harassing as in thermodynamics. There are three ways of intruding upon the vicious circle.

First, to apprehend both concepts in a single mental act. This is the counsel of perfection.

Second, to use a temporary definition of temperature, with the promise of confirming or correcting it later. The ideal-gas thermometer is the device used for this purpose in thermodynamics. Anyone trained in this way is likely to think for the rest of his life of temperature as the primary concept, entropy as a derived one—as indeed was the case, when thermodynamics started.

Third, to produce a theory which makes a pronouncement as to the nature of entropy.

This last is the major office of statistical mechanics. To those who accept it, entropy becomes the primary concept and temperature the derived one, and both are visualized by the aid of the key-word "probability" of the basic theorem, interpreted in some particular way.

OLD STATISTICAL THEORY OF ENTROPY

In the classical statistics, the entropy of a distribution is considered to be the logarithm of the number of inventories or complexions compatible with that dis-

tribution, multiplied by a constant (always denoted by k) which is adjusted to bring about agreement with experiment:

$$\text{entropy } S = k \ln W. \quad (15)$$

To illustrate this doctrine and to evaluate k , I now take the student back to the coordinate-space, where a box of volume V populated with N molecules is divided mentally into M equal cells of volume V_0 , and the most probable distribution is characterized by the value $N \ln M$ for the logarithm of the probability. The entropy—or no, not the entire entropy of the gas, but merely what I will call “the contribution of the volume of the entropy” and denote by S_e —is then supposed to be $kN \ln M$, or:

$$S_e = kN \ln V - kN \ln V_0 \quad (16)$$

Reverting to the equation (14) in which the definitions of entropy and temperature were tangled up together, and rearranging it, we get:

$$TdS = dU + PdV \quad (17)$$

Now, an “ideal gas” is defined by two attributes. First, there exists between its pressure and its volume and its temperature the relation $P = aT/V$, wherein a stands for a constant. Second, its energy U depends upon the temperature only, and not upon any other variable, in particular not upon the volume. Therefore we may write:

$$TdS = C_v dT + (aT/V)dV \quad (18)$$

C_v here standing for something of which we need only know that it is a function of T alone. Integrating, we find:

$$S = R \ln V + (\text{function of temperature}) + \text{constant} \quad (19)$$

and lo! it is seen that the dependence of entropy on volume is precisely of the sort which the theory is fitted to explain.

The next step is to adjust the value of the constant k . The constant a aforesaid is proportional to the amount of gas in the box, proportional therefore to N : it is the constant ratio of a to N to which k must be equated. For the amount of gas let us choose one gramme-molecule. Then a assumes the value always symbolized by R and called the “gas-constant”, and N assumes the value usually symbolized by N_0 and called the “Avogadro number”. Both of these are known from experiment, and k is fixed by the equation

$$k = R/N_0 \quad (20)$$

The constant k is named in Boltzmann’s honor, though in his time its value was not known because the value of N_0 was only vaguely apprehended.

Now we have settled what I called “the contribution of volume to en-

trophy". It remains to interpret the rest of the right-hand member of (19), which I will call "the contribution of temperature to entropy". To do this we must re-enter the momentum-space.

From (15) and (5) and (8) we get, for the entropy S_m of the flock of dots in the momentum-space:

$$\begin{aligned} S_m &= -k \ln W = -kN \sum w_i \ln w_i \\ &= -kNA \sum (\ln A - BE_i) e^{-BE_i} \end{aligned} \quad (21)$$

Refreshing our memory from (10), we see that the first term of this expression reduces to $-kN \ln A$. Refreshing our memory from (11), we see that the second term reduces to $+kNB\bar{U}$ or kBU . Referring now to one gramme-molecule of gas, I put R for Nk , and find:

$$S_m = -R \ln A + kBU \quad (22)$$

S_m is hereby given as a function of U , but a more complicated function than appears on the surface, since A depends upon B (equation 10) and B upon V (equation 11). Yet when we differentiate S_m with respect to U , and in so doing take account of these complications, it turns out that we might as well have been oblivious of them! for the result is the same as though A and B were constants:

$$dS_m/dU = kB \quad (23)$$

Now the temperature, which has so often slipped into this argument in ways more or less surreptitious, is about to make its formal and ceremonious entry into the statistical picture. We turn back to equation (17), and deduce:

$$dS/dU = 1/T \quad (24)$$

The derivative here standing on the left is the derivative of entropy with respect to energy under the condition of constant volume: a thermodynamicist would write it $(\partial S/\partial U)_v$. It is therefore properly to be identified with the derivative in (23), and we make the two identical by putting:

$$B = 1/kT \quad (25)$$

Now taking the entropy S to be the sum of S_c and S_m , we find:

$$S = S_c + S_m = -R \ln A + U/T + R \ln V - R \ln V_0 \quad (26)$$

and this is to be compared with (19), the thermodynamic expression for entropy, which I repeat to make the comparison easier:

$$S = \int (C_v/T) dT + R \ln V + \text{constant} \quad (27)$$

Comparing these, we see first of all that $R \ln V$ appears in both, as was already stated. It also seems at first glance that $(-R \ln A + U/T)$ is to be identified with the integral in (27), and that $-R \ln V_0$ is to be identified with the constant in (27). This however is not necessarily the case, for $(-R \ln A + U/T)$ may prove to include constant terms. Indeed they do; and we must proceed to evaluate both A and U in terms of T in order to round off the task.

I recall equation (10) and write it thus:

$$1/A = \Sigma \exp(-E_i/kT) \quad (28)$$

This is a summation, to which each cell contributes one term having the value of E appropriate to that cell— E_i for the i th cell. Of the volumes of these cells I have thus far said nothing, except that all are equal. I continue to say nothing further, but I give to their common volume the symbol H_0 . Let us now form the integral:

$$\iiint \exp(-E/kT) dp_x dp_y dp_z, \quad E = (1/2m)(p_x^2 + p_y^2 + p_z^2) \quad (29)$$

the range of integration extending over the whole of momentum-space. This integral may be described as follows. Let the momentum-space be divided into cells of unit volume. Each of these cells of unit volume makes a contribution

$$\exp(-\bar{E}/kT)$$

to the integral, \bar{E} standing now for the average value of E in the cell in question. The integral is the sum of all of these contributions. Now let us inquire how much of a contribution is made by this same cell of unit volume to the summation (28). This second contribution is made up of $1/H_0$ terms, one for each of the cells of volume H_0 which occupy the cell of unit volume. The values E_i corresponding to these cells will not be exactly equal to the value \bar{E} corresponding to the entire cell of unit volume; but to the degree of approximation which is now being used, the difference may be neglected. The summation (28) is then equal to $1/H_0$ times the integral (29). Now the value of the integral (29) is given in all tables of definite integrals, and in terms of our symbols it amounts to

$$(2\pi mkT)^{3/2}$$

so we come to the conclusion:

$$\begin{aligned} \ln A &= -\ln(2\pi mkT)^{3/2} + \ln H_0 \\ &= -\frac{3}{2} \ln T - \ln(2\pi mk)^{3/2} + \ln H_0 \end{aligned} \quad (30)$$

Now we have attended to every term in (26) except the term U/T . Nearly every reader will remember that the average kinetic energy of an atom of a monatomic gas at temperature T is $\frac{3}{2}kT$. I therefore leave out the derivation of this result, except for showing the student how to begin on it: the first step is to go back to equation (11) where an expression was given for \bar{U} , and in that expression to replace the summation $\sum E_i \exp(-BE_i)$ by $(1/H_0)$ times the integral $\iiint E \exp(-BE) dp_x dp_y dp_z$. It follows that U/T is $(3/2)Nk$, which for one gramme-molecule of gas is $(3/2)R$, which I write as $R \ln e^{3/2}$.

The picture of entropy for a monatomic gas limned by the Boltzmann statistics, is now completed. Entropy is the function which follows:

$$S = \frac{3}{2} R \ln T + R \ln V + R \ln \frac{(2\pi m k e)^{3/2}}{V_0 H_0} \quad (31)$$

The dependence on volume is correct, *i.e.*, just the same as in the thermodynamic formula. The dependence on temperature is correct, for $(3/2)R$ is the value of the specific heat at constant volume per gramme-molecule of a gas, the quantity C_v of equation (18). The additive constant, as to the value of which thermodynamics says nothing, is fixed when the volumes V_0 and H_0 of the elementary cells in the ordinary space and the momentum-space are fixed.

MIXTURES OF GASES

Now we will go through the mental operation which is called "considering a mixture" of two different monatomic gases, N' atoms of the one and N'' atoms of the other, in the same box and (necessarily) in the same momentum-space. Let me denote by U' and U'' , respectively, the energies of these two gases; and by $N'_i = N'w'_i$ and $N''_i = N''w''_i$, respectively, the numbers of atoms of the two kinds in the i th cell of momentum-space.

If we seek the most probable distribution of the first gas in the momentum-space, making the stipulation that we will admit only such variations of the quantities w'_i as leave N' and U' unchanged—well, of course, we get the same result as before, the distribution (8), with N' in place of N and (let me say) A' in place of A and B' in place of B . A' will depend upon B' and B' will depend upon U'/N' . If we do the like with the second gas, we get anew to the distribution (8) with N'' , A'' and B'' in place of N' , A' and B' . A'' will not be the same as A' nor will B'' be the same as B' , unless it happens that U''/N'' is equal to U'/N' . There is no cause for surprise in this. In acting this way we are only treating each gas by itself, and have as yet done nothing which can be regarded as "considering a mixture".

Let us however seek the most probable distribution of the two gases, mak-

ing the stipulation that we will admit only such variations of the quantities w'_i and w''_i as leave N' and N'' and the sum of the energies U' and U'' —not however the individual energies U' and U'' —unchanged. In acting this way we are doing something which may be regarded as “considering a mixture”, since we are allowing for the possibility that energy may pass from the one gas to the other and the other to the one. Equally well are we considering the case of two gases separated by a partition through which energy may pass, but not the atoms. Since in such a case we really ought to take into account the atoms and the energy of the partition also, we must appease the critics by providing that the partition shall be very thin.

Choose any set of values of the quantities N'_i , which is to say, any particular distribution of the first gas; and choose any set of values of the quantities N''_i , which is to say, any particular distribution of the second gas. Go back to equation (1) and put primes on all the symbols N , N_1 , N_2 , \dots on the right-hand side of that equation. The resulting expression gives the total number of inventories or complexions of the first gas. Take off the primes and affix double primes to each of these symbols. The resulting expression gives the total number of inventories or complexions of the second gas. Every complexion of either may coexist with any complexion of the other. Therefore the total number of complexions of the pair of gases is the product of the two expressions. It is this product which is W for the pair of gases, be they mixed or side-by-side.

With use of the Stirling approximation, the logarithm of W for the pair is the sum of two such expressions as we have seen in (5):

$$\ln W = -N'\Sigma w'_i \ln w'_i - N''\Sigma w''_i \ln w''_i \quad (32)$$

and its variation is:

$$\delta \ln W = -N'\Sigma(1 + \ln w_i)\delta w_i - N''\Sigma(1 + \ln w''_i)\delta w''_i \quad (33)$$

Let us now give a trial to the tentative distribution,

$$w'_i = A' \exp(-B'E_i), \quad w''_i = A'' \exp(-B''E_i) \quad (34)$$

On substituting this into (33) we find that if B' is unequal to B'' , the distribution has a stationary value of W with respect only to such variations as leave the energies of the two gases separately unchanged—the result which we had before. If however B' and B'' are the same, then W is stationary with respect to variations which leave the sum of the energies unchanged, either being allowed to gain or lose so long as the other loses or gains by an equal amount. Since each B is controlled by the corresponding U/N , the distribution (33) has a stationary value of W for variations of the type in question if and only if the average energy of the atoms of each gas is the same. Since each B controls the corresponding A , this condition of

equal average energy makes the distributions of the two gases just the same.

We have already seen that kB is the reciprocal of the temperature: for it is the reciprocal of $(\partial U/\partial S)_v$ in our statistical picture, and the definition of absolute temperature T is precisely that T is this derivative. The statement to which we have come is, that *the most probable state of the mixture is the one in which T is the same for both components*. It is often expressed in this way: classical statistics shows that for two (or more) gases in equilibrium with each other, the temperature must be the same. It is indeed a fact of experience, and a most important one, that when two systems (be they gases or be they not) are in thermal equilibrium, their temperatures *are* the same. This has not hitherto been mentioned, and yet we seem to have derived it. Quite a rabbit for the magician of the classical statistics to have pulled out of the hat!

However, skeptical people who see a rabbit pulled out of a hat are inclined suspect that either the rabbit was in the hat beforehand, or else there is no rabbit. Let us inquire into the contents of the hat and see whether we can find the rabbit there.

The first (and the last) question to be asked is: what *is* the difference between "different" kinds of gas in the statistical picture?

To the physicist or the chemist, different kinds of gas will be (for example) mercury and helium. These differ in their spectra, boiling-points, chemical properties, and quantities of other features. None of these features however appears in the theory, and therefore none of them can contribute to the result. The atoms also differ in mass, and for a moment this seems to be a difference of which the statistical picture takes account, since the letter m appears in some of our equations. However, it appears only in the ultimate equations, those such as (29) in which the distribution-in-momentum is expressed. It does not appear in the original form of the Maxwell-Boltzmann distribution-in-energy, the form shown in equation (8). It appears in particular in the last term of equation (31), but not elsewhere. Apart from this it may be said that *in the classical statistics, all gases are the same gas*.

This is a paradox, but only one of two. The other paradox is, that *in the classical statistics two parts of the same gas are different gases*. This second paradox arises from the numbering of the molecules, which is an essential feature of the classical statistics.

Therefore in the statistical picture a mixture of N' atoms of mercury and N'' atoms of helium is distinguished by the fact that the mercury atoms bear one set of integer numbers (say those from 1 to N') and the helium atoms another set (say those from $N' + 1$ to $N' + N''$). But if the atoms were all helium atoms or all mercury atoms, they would also be divisible in many

different ways into a set of N' atoms bearing one set of numbers and a set of N'' atoms bearing another set of numbers. Each set would obviously have to have the same distribution, with the same A and the same B , as any other set or as the totality of all the atoms. This conclusion, which is self-evident in the case in which all the atoms are called "mercury", remains true when some of the atoms are called "mercury" and others are called "helium". We have done nothing but change the names of some of the atoms; we have not imported into our theory anything which differentiates one kind of atom from another kind. No wonder we have arrived at the conclusion that all kinds have the same distribution-in-energy, the same A , the same B and the same temperature! The rabbit was indeed in the hat, but it does not look like so much of a rabbit.

The classical statistics therefore doesn't recognize any of the real differences between atoms of different kinds, except for alterations in the last term of (31); but it does make an artificial difference which creates the astonishing result, that any two samples of the same gas are different gases! At this point we may begin to wonder whether this peculiarity, which has led to so apparently brilliant a result in respect of the equality of temperatures in thermal equilibrium, might elsewhere lead us astray. It does; and here appears the rift in the lute of classical statistics.

THE RIFT IN THE LUTE

Let us imagine two boxes of equal size separated by a common partition, each containing a gas consisting of N atoms, both gases at the same temperature. We will baptize one gas "mercury" and the other gas "helium". Let an opening be made through the partition. It is known that in such a situation in Nature, the two gases diffuse into one another, the final and permanent condition being that in which the mercury and the helium are equally distributed between the two boxes. The process of diffusion is an example of what in thermodynamics is called an "irreversible" process. The state of uniform mixing ought to correspond to the most probable state in the statistical picture. But what does the statistical theory say?

The statistical theory says nothing about diffusion and nothing about mixing. The statistical theory takes account of nothing but the facts that the mercury had at its disposal the volume V before and the volume $2V$ after the breaking of the partition, and ditto for the helium. The value V contains M cells ($M = V/V_0$) and the volume $2V$ contains $2M$ cells. The (approximate) probabilities of the uniform distribution are M^N before and $(2M)^N$ after. The latter is greater than the former; the entropy goes up by $Nk \ln 2$ for each gas, by $2 Nk \ln 2$ for the two of them, when the private preserve of each is thrown open to the other. This gain is what is called the

“entropy of mixing” though as we have seen it is really the “entropy of expansion”. It is the alteration in the second term of the righthand member of (31).

But now suppose both of the boxes hold helium. One may indeed continue to suppose that when the partition is opened each one of the two samples of helium undergoes an expansion, doubling its volume. The entropy would then go up by $2Nk \ln 2$. However this looks so silly a thing to say that no one, I feel almost secure in affirming, has ever said it. The natural thing to say is, that the $2N$ atoms of helium distributed through the two boxes at uniform temperature and uniform pressure have just the same entropy-value whether or not the partition is broken.

What does the classical statistics say about this situation? Its answer can be foretold. Since the two samples of helium are different by virtue of the different numberings of the two sets of atoms, the classical statistics insists that the entropy increase by $2Nk \ln 2$ when the partition is broken, even though the gases are the same. This is indeed, if I may pervert the poem, “the little rift within the lute, which makes the classical statistics mute.” The achievement of predicting the uniform distribution in ordinary space, the achievement of predicting the Maxwell-Boltzmann distribution-law in momentum-space, the achievement of providing the proper relation between temperature and mean kinetic energy—all of these are unsettled by this calamity.

Were I writing a strictly logical article I should quit at this point. Nothing further can apparently be done, except to tamper with the classical statistics in an effort to remove the unwanted result which has sprung forth to plague us. To violate the logic of the classical statistics in order to banish the undesired while keeping the desired results is a very questionable act. In theoretical physics, it is not admissible that the end justifies any and all means. Nevertheless so successful a feat of tampering has been done, that I cannot refrain from mentioning it as I close.

Let me first express in a slightly different way the nature of the “rift”. Compare two samples of the same gas at the same temperature, one consisting of N atoms in a volume V , the other consisting of xN atoms in a volume xV . That which is called entropy in thermodynamics—and therefore that which *is* entropy, since it is the privilege of thermodynamics to give the definition of entropy—is x times as great for the latter as for the former. But that which the classical statistics calls entropy—or, as we must admit, miscalls entropy—is not x times as great for the latter as for the former. It would be, if there were x times as many atoms but just the same number of cells. However, there are x times as many atoms but also x times as many cells into which to put them. The number of complexions is approximately M^N in the former case and $(xM)^{xN}$ in the latter, M standing

for the number of cells in the former box. The thing miscalled entropy is $kN \ln M$ in the first case and $(kxN \ln M + kxN \ln x)$ in the second case. It is the term $kxN \ln x$ which is the rift.

Clearly we could abolish this term by allowing the volume of the cells to swell in the ratio $x:1$ when going from the former case to the latter. This is the same as making H_0 proportional to the number of atoms in the sample of gas which happens to be under study. Since in equation (31) the volumes V_0 and H_0 (of the elementary cells in ordinary space and in momentum-space) are indissolubly bound together in the product $V_0 H_0$, this is the same as making $V_0 H_0$ equal to some constant multiplied by the number of atoms under study.

Such, if I interpret correctly, was the idea proposed by Sackur in 1912. While it does the task required, it is an "*ad hoc*" assumption of the most barefaced character. If the gas under study is at first divided into two parts by a partition and the partition is then abolished, the cells must be supposed to swell up at the moment when the partition vanishes.

We can also abolish the fatal term by going back to equation (1) for the number of complexions, and removing the factor $N!$ in the numerator and replacing it by unity. We then have unity divided by the original denominator, which in the (most probable) case of the uniform distribution is $(N/M)!$ raised to the power M , as I remarked on page 121. Using the super-Stirling approximation, we find that the logarithm of one fraction is $(N \ln M - N \ln N)$. The factor $N!$ which we formerly had in the numerator killed off the term $(-N \ln N)$, but now that we have taken it out, this term survives. If now we say that k times the logarithm of $W/N!$ shall be the picture of entropy in the classical statistics, then the term $(-kN \ln N)$ comes over into the right-hand member of (31). It may be amalgamated with the last term already standing there; and when this is done, we find $V_0 H_0$ multiplied by N exactly as Sackur put it there, and with the same wished-for result.

This, if I interpret correctly, is the idea proposed in 1913 by Tetrode. It does the task required of it, but its drawback is that the removal of the factor $N!$ from the right-hand member of (1), a drastic piece of surgery as it were, violates the system of the classical statistics.³

I was not, however, thinking merely of this achievement when on Page 132 I spoke of "a remarkably successful feat of tampering." To show the

³ This may seem too strong a statement. We are, after all, only asked to accept $k \ln (W/N!)$ as our picture of entropy, instead of $k \ln W$; why be reluctant? But in effect, as I see it, we are asked first to accept $k \ln Wf$ as our picture of entropy, f being an arbitrary function of N ; and then we are asked so to choose f , that the dependence of $k \ln Wf$ on N shall conform to the actual behavior of entropy. This is different from and much less impressive than our original procedure, which consisted in first realizing that W is the number of complexions, and then discovering that $k \ln W$ depends on volume and on temperature in just the right ways for entropy.

magnitude of the achievement, I will rewrite equation (31) with two alterations. The first consists in replacing R with Nk , so that the expression shall refer not to a gramme-molecule of gas but to any number N of atoms. The second consists in following Tetrode by affirming that the entropy is not $k \ln W$, but k times the logarithm of $W/N!$ I follow him still further by using, not the super-Stirling approximation in which $N \ln N$ is written for $\ln N!$, but the better approximation in which $(N \ln N - N)$ or $(N \ln N - N \ln e)$ is written for $\ln N!$ The result is:

$$S = (3/2)Nk \ln T + Nk \ln V - Nk \ln N \\ + Nk \ln [(2\pi mk^{3/2} e^{5/2}/V_0 H_0)] \quad (35)$$

This quantity newly chosen as the picture of "entropy" depends on volume and on temperature in the right way, as did the other. The dependence on N the number of atoms is now correct, and no wonder, for the new quantity was chosen with that purpose. There is a fourth term in the right-hand member which is proportional to N , and its value is completely determined if the value of $V_0 H_0$ is fixed. The value which it takes when N is made equal to N_0 may be called "the chemical constant"; but this name has been spoiled through being used with several different meanings, and should probably be abandoned.

When to $V_0 H_0$, the volume of the elementary cell in six-dimensional space, there is given the value h^3 —the cube of Planck's constant—the resulting value of the fourth term is excellently confirmed by experiments on all of the noble gases, and (with less precision) by experiments on many of the monatomic vapors of metallic elements. This is the achievement known as "the verification of the Sackur-Tetrode formula" and it is indeed a grand one.

Anyone versed in thermodynamics will probably regard this not as a grand result, but as an incomprehensible one! Are we not taught in thermodynamics that nothing is ever measured about entropy except the *differences* between its values under different conditions, so an additive constant like the one in question must drop out of every verifiable equation, and its value can never be found? How then can it make sense to speak of confirming the value of the fourth term on the right-hand side of (35)?

Well, actually it *is* a difference which is measured: the difference between the entropy of the gas at any convenient temperature and volume and the entropy of its solidified crystalline form at the absolute zero. This difference is found to be such, that if for the entropy of the gas one puts the value (35) with h^3 substituted for $V_0 H_0$, then for the entropy of the crystalline solid at the absolute zero one finds the value: *zero*. This result—this conclusion that the entropy of a crystal is zero at the absolute zero—is in itself so desirable and welcome that it is taken as the confirmation of the

Sackur-Tetrode formula. By "desirable and welcome" I mean that it is harmonious with the idea that *entropy is a measure of disorder*, an idea plausible in itself and fruitful in its applications. A chemical element perfectly crystallized at the absolute zero is supposed to be the exemplar of supreme order, and therefore its entropy ought to be nil. But this is an enormous subject requiring at least one other article, and I am glad that my attempt at writing such an article stands already in print in the June (1942) issue of this Journal.

Here then is the astonishing history of the Classical Statistics. By a strangely artificial device, the numbering of atoms deemed identical, it arrived at the proper distributions—that is, the distributions ratified by experiment—in ordinary space and in momentum-space. It then proposed a picture of entropy partially right, yet wrong in its dependence on the number of atoms, and therefore fatally wrong. With another artificial and dubious device, it corrected itself by adopting a new picture of entropy, this time depending in the right way upon the number of atoms. With a third artificial device (the introduction of Planck's constant in a peculiar way) it completed the formula for entropy in a manner leading to the consequence that the entropies of solidified crystallized elements are zero at absolute zero. All of these feats and more were subsequently achieved by the New Statistics, in a manner which I hope to explore on a later occasion.

Abstracts of Technical Articles by Bell System Authors

*Poles and Pole Treatment.*¹ REGINALD H. COLLEY. Studies made of pole use and drainage on the southern pine forest have brought out that if the demand for poles 35-feet and longer were to continue at the present rate, a situation would soon develop in which these poles would be at a premium. It would seem wise to use as many circumference classes as possible and to broaden the use of poles of other species whenever it is practicable to do so. Successful full length treatment of red pine, lodgepole pine, western cedar and Douglas fir poles will help to broaden this use.

There has been a definite trend toward greater mechanization in pole production. Machine shaving smooths the pole surface and accelerates drying. Poles with square cut roofs and slab gains are all-purpose poles, one design taking the place of four. New types of preservative treatment—greensalt, creosote-petroleum-pentachlorphenol and salt-creosote—are of promise and must be considered, when current restrictions are removed, in those cases where clean poles are mandatory.

Interesting breaking test data are reported which show that the modulus of rupture of pole top sections average 90 per cent of the modulus of the poles as a whole, and that pole tops are sufficiently strong to meet their specified class breaking loads. This is of considerable importance where poles are guyed.

Current groundline treatment methods, it is pointed out, should be applied to untreated poles in line that are worth saving at the time of inspection, as a part of the regular inspection procedure.

*Hearing, the Determining Factor for High-Fidelity Transmission.*² HARVEY FLETCHER. This paper gives the requirements for ideal systems for the transmission of speech and music. These requirements are based on: 1. Measurements of the threshold and frequency limits of the hearing of more than 500,000 people at the New York and San Francisco World's Fairs; 2. measurements of the discomfort level of sound; 3. measurements of room noise in a wide variety of locations; and 4. measurements of the frequency limits and the maximum and minimum levels of speech, orchestral music, and various instruments of the orchestra.

From this information and from judgment tests it is concluded that substantially complete fidelity in the transmission of orchestral music is

¹ *Elec'l. Engg.*, Transactions Section, September 1942.

² *Proc. I. R. E.*, June 1942.

obtained by use of a system having a volume range of 65 decibels and a frequency range from 60 to 8000 cycles per second. Substantially complete fidelity for the transmission of speech is obtained by a system having a frequency range from 100 to 7000 cycles per second and a volume range of 40 decibels.

Preliminary experiments comparing a single-channel system and a two-channel stereophonic (auditory perspective) system showed that stereophonic transmission with an upper frequency limit of 5000 cycles per second was preferred to single-channel transmission with an upper limit of 15,000 cycles per second. A definite improvement was obtained in the stereophonic system by using three channels instead of two.

*A New Direct Crystal-Controlled Oscillator for Ultra-Short-Wave Frequencies.*³ W. P. MASON and I. E. FAIR. An ultra-high-frequency crystal oscillator is described which utilizes a mechanical harmonic of an AT or BT crystal. With the oscillator frequencies as high as 197 megacycles, harmonics as high as the 23rd have been excited. Taking the second electrical harmonic of the oscillator, frequencies as high as 300 megacycles, or 1 meter have been obtained. Since a mechanical harmonic is used, the crystal can be of a practical size to handle and adjust. The harmonic vibration of the AT and BT crystals have as low a temperature coefficient as the fundamental mode, and temperature coefficients of less than two parts per million per degree centigrade are easily obtained. Stability curves for this type of oscillator are shown and the results indicate that at 120 megacycles stabilities in the same order of magnitude as for ordinary crystal oscillators can be obtained. Without temperature or voltage control it appears likely that the frequency should remain constant to ± 0.0025 per cent.

Some measurements have been made of the properties of harmonic crystals at high frequencies. It was found that the Q of a crystal is independent of the frequency but in general increases with harmonic order. The ratio of capacitances r of a crystal increases as the square of the harmonic order. It is shown that in order to obtain a positive reactance in the crystal $Q > 2r$. This relation will only be satisfied for harmonics of AT crystals less than the 7th. As a result oscillator circuits such as the Pierce circuit cannot be used to drive crystals at high harmonic frequencies. A discussion of oscillator circuits is given and it is shown that a capacitance-bridge oscillator circuit with the crystal in one arm is the best type to use for high-frequency harmonic crystals.

*War Activities of the Bell Telephone System.*³ KEITH S. MCHUGH. The scope of the Bell System's nation-wide service is, even in peace, difficult to

³ *Proc. I. R. E.*, October 1942.

⁴ *Bell Telephone Magazine*, November 1942.

visualize in its entirety. In war, when practically every phase of the national effort to overthrow the Axis aggressors depends in some part on swift communication, both the extent and the importance of the System's contributions to the winning of the conflict are beyond summarizing. In the past two years, numerous articles in the *Bell Telephone Magazine* (listed at the end of this article), and in the employee publications of the Associated Companies, have described many aspects of the System's cooperation with the armed forces, with industry, and with the civilian population. Now, nearly a year after Pearl Harbor, it seems appropriate to review both the System's preparations for the national emergency and the steps which it has taken since war became no longer a threat but a fact. To the extent that it is possible in limited space, this article rounds out the previous fragmentary parts of the whole picture.

*The Number of Two-Terminal Series-Parallel Networks.*⁵ JOHN RIORDAN and C. E. SHANNON. This paper is concerned with the number of ways n abstract (electrical) elements may be connected in series-parallel arrangements and in particular with the way the number behaves for n large. After a proof of a generating identity for the numbers given without proof by P. A. MacMahon in 1892, the paper gives recurrences and schemes of computation by means of which MacMahon's table for the numbers is extended from $n = 10$ to $n = 30$. The behaviour for n large is shown to be of the form

$$A \lambda^n n^{-3/2}$$

with A a fixed constant and λ a real number between $2 + \sqrt{2} = 3.414$ and 4 and closer to the former than the latter; indeed an approximating function for which λ is about 3.56 agrees with the numbers within 3% over the range 7 to 20. These results are used to show that almost all switching functions of n variables require at least

$$(1 - \epsilon) \frac{2^n}{\log_2 n} \quad \epsilon > 0$$

switching elements (make or break contacts) in series-parallel realization.

*The Electrical Oscillations of a Perfectly Conducting Prolate Spheroid.*⁶ ROBERT M. RYDER. The forced oscillations of a perfectly-conducting prolate spheroid of eccentricity nearly unity are shown to be decomposable into "harmonics" corresponding to different modes of vibration, each harmonic being quantitatively connected with a certain portion of the impressed electric field which drives the antenna. The harmonics contribute additively to the current and field of the spheroid; each offers a characteristic imped-

⁵ *Jour. Mathematics and Physics*, August 1942.

⁶ *Jour. Applied Physics*, May 1942.

ance to the driving field, and the properties of the antenna are a composite depending upon the proportions of the various harmonics present. The behavior of the harmonics with frequency is discussed qualitatively; analytical expressions obtained are useful chiefly at the resonant frequencies of the antenna, where the most important harmonic becomes sinusoidal in character.

*On Radiation from Antennas.*⁷ S. A. SCHELKUNOFF and C. B. FELDMAN. This paper presents some theoretical remarks and experimental data relating to applications of the transmission-line theory to antennas. It is emphasized that the voltage, the current, and the charge are affected by radiation in different ways, a fact which should be considered in any adaptation of line equations to antennas.

It is shown experimentally and theoretically that in an antenna of length equal to an integral number of half wave-lengths, which is energized at a current antinode, the effect of radiation on the current and the charge (but not on the voltage) can roughly be represented by adding to the resistance of the wires another fairly simple term.

*The Use of Secondary Electron Emission to Obtain Trigger or Relay Action.*⁸ A. M. SKELLETT. The use of secondary electrons to obtain trigger action similar to that of a thyratron is described. An experimental tube and the necessary circuits by which this action is achieved are discussed. This combination gives the features of a triode with a relay or on and off feature, resulting in an amplifier, oscillator, modulator, or other vacuum tube device which may be turned on or off abruptly at high or low frequencies. In addition, it can be used to replace thyratrons in many of their circuits where very low impedance is not necessary and is capable of much greater speeds of operation in such applications.

*A New Frequency-Modulation Broadcasting Transmitter.*⁹ A. A. SKENE and N. C. OLMSTEAD. A new frequency-modulation transmitter is described which uses a novel amplifier circuit permitting an unusually simple mechanical design and an economical vacuum-tube complement.

The choice and design of circuit components, governed by both mechanical and electrical considerations, are discussed in detail.

*A Secondary Frequency Standard Using Regenerative Frequency-Dividing Circuits.*¹⁰ F. R. STANSEL. A secondary frequency standard is described

⁷ *Proc. I. R. E.*, November 1942.

⁸ *Jour. Applied Physics*, August 1942.

⁹ *Proc. I. R. E.*, July 1942.

¹⁰ *Proc. I. R. E.*, April 1942.

in which standard frequencies are derived from a 5-megacycle oscillator by a series of frequency dividers. The advantage of obtaining standard frequencies by frequency division rather than by frequency multiplication is pointed out and the characteristics of the regenerative frequency dividers used are discussed.

*Some Mechanical Aspects of Telephone Apparatus.*¹¹ J. D. TEBO and H. G. MEHLHOUSE. *Part I.* It is seldom realized that the vastness of the Bell System requires such an enormous amount of equipment and wires for handling the 100,000,000 calls per day made by the people in the United States. A total of 44,000 kinds of apparatus involving 170,000 different parts are required. The crossbar switch, described in this article, is the specific telephone switching mechanism used in the latest dial telephone system.

Of particular interest in the crossbar switch is the design of contact springs. These springs are essentially thin, metal beams of a rectangular cross section but of varying cross sectional area along their length. They are clamped at one end and are subject to bending as compound cantilevers. Since the clamping is necessarily between relatively soft insulating materials, the determination of the effective length of the spring in determining its true deflection curve required the use of unique methods. Likewise, since the springs are punched out of sheet stock at an angle to the grain direction of the material, the modulus of elasticity does not remain the same for equal cross sections of the same material. Consideration of these points was necessary in determining the strength of the magnets for operating the contact springs, as well as to insure that the stresses introduced in the springs would not be excessive.

To study the motions of the various parts of the switch, both high speed motion pictures and the "rapid record" oscillograph were used. The oscillograph was provided with means for obtaining "shadowgrams" of the actual movement of parts simultaneously with the changes in the electrical characteristics of the magnets and contacts. The use of both the camera and oscillograph provided valuable data for making improvements, both in design and operating characteristics.

Part II. The manufacture of crossbar apparatus is accomplished on a product basis; that is, the entire range of manufacturing operations is segregated into one division, and practically all operations from raw material to the completed product are performed in this division. More than 150 kinds of parts totaling an annual demand of 200,000,000 individual pieces are required to produce the crossbar switches.

To produce these parts requires a number of special machines, tools, and

¹¹ *Mech. Engg.*, May 1942 and June 1942.

operations. Of particular interest are the use of special progressive punch and die tools, coil winding, contact welding and conveyORIZED assembly and adjustment.

The use of heavy presses with large progressive punches and dies was necessitated by the degree of accuracy required for this grade of equipment. For example, the vertical unit base, weighing only $\frac{3}{4}$ lb., is produced by a 75,000 lb. press, using a 3,500 lb. tool. Again, since 40,000,000 contact springs are required annually, each of which must be attached to insulators, automatic presses, conveyor belts and handling devices are required. Welding two contacts on each spring is accomplished by special welding presses using rolls of contact metal tape, each contact being cut off just prior to the welding process. A quality of less than one defective contact out of 20,000 is maintained.

The coils are wound in special machines in "sticks" of 5 to 7 coils with .0007 inch thick cellulose acetate between each layer. A wire of a gage size halfway between $\#37$ and $\#38$ B & S is used on most of the coils because of critical capability conditions—the annual amount of wire of this size being 125,000 lbs.

Assembly and adjustment of the switches proceeds on conveyor belts from one end of a large room to the other—the procedure being set up in such a way as to create a continuous flow of completed parts for wiring into the large frames ready for installation in telephone exchanges.

*Regulated Rectifiers in Telephone Offices.*¹² D. E. TRUCKSESS. For many years rectifiers of the garage type were used in converting alternating current to direct current for charging batteries used for communication purposes. These batteries furnish power for relay operation, for talking, and filament and plate supplies for repeaters. The rectifiers were of the manual-control type where the operator selected the charging current by means of tap switches or rheostats.

With the development of the thyatron type of tube, a rectifying means was made available in which the grid of the rectifier tube could be used to control its own output current by an electronic circuit. Rectifier circuits were designed to maintain a constant output voltage. If a regulated rectifier is connected to a battery and the constant rectifier voltage is 2.15 volts per cell, the load current will automatically come from the rectifier and not from the battery. Also the battery will draw from the rectifier sufficient additional current to maintain its charge. If the circuit voltage is held within limits of less than plus or minus one per cent, the maintenance of the battery is reduced and its life is extended.

The thyatron tube differs from the vacuum tube in that the grid does

¹² *Elec'l. Engg.*, Transactions Section, August 1942.

not have a continuous control of the plate current. When a positive potential is applied to the plate, current does not flow until the magnitude of the negative grid voltage is reduced to the critical value, at which time the plate current flows, and the magnitude of the plate current depends upon the voltages and impedances in the circuit. The grid has no further control, and plate current flows until it is stopped by reducing the plate voltage to zero.

Thyratron tubes use various gases and mixtures of gases. The earliest type used mercury vapor, but this type of tube is quite sensitive to temperature changes. The grid characteristics are shifted materially by changes in the room temperature in which it is operated, and in low temperatures it is almost a vacuum tube. Thyratron tubes using argon gas are not affected by temperature changes, but high-pressure argon tubes have a low inverse voltage which limits their application to low-voltage rectifiers. Tubes using low-pressure argon have a higher inverse voltage, but are accompanied by a high arc drop which makes their efficiency low. A mixture of mercury vapor and argon has been found which provides the temperature-stable grid characteristic of the argon tube and the low arc drop of the mercury-vapor tube. This type of tube has been very successful with certain regulating circuits, particularly at voltages less than 60 volts.

Five kinds of regulating circuits are used in telephone offices to hold the output voltage of rectifiers constant. The selection of the circuit to be used depends upon the magnitude of the current, d-c voltage, and type of rectifying means to be used. Two forms of regulating circuits using thyratron tubes and one using two-element high-pressure tubes were developed. A fourth circuit using all vacuum tubes was adapted for telephone use. The fifth kind uses a negative resistance.

In this paper a table shows the voltage and current output, type of control of the rectifiers, and the rectifying means that have found widespread use in the Bell System.

The regulated rectifier finds its applications in telephone offices where constant voltage, independent of load and a-c line-voltage variations, is required to supply filament grid bias and plate voltage to telephone repeaters. Certain measuring circuits require a regulated rectifier to supply a stabilized voltage. Regulated rectifiers also find applications where constant voltage is of secondary importance but an automatic power plant is desired for maintaining storage batteries in a fully charged condition to be ready to supply the power for telephone offices if the a-c power fails. A further compensation of regulating the voltage is the increase in life obtained from storage batteries if they are not continually being charged and discharged but are fully floated.

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THE BELL SYSTEM TECHNICAL JOURNAL

DEVOTED TO THE SCIENTIFIC AND ENGINEERING ASPECTS
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For the purposes of record and assistance to librarians, and for the information of subscribers, it is to be noted that there was no April 1943 issue of the Bell System Technical Journal.

It is also to be noted that there was only one issue of Volume 21 of the Bell System Technical Journal. It was the issue of June 1942.

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No. 2

A Mineral Survey for Piezo-Electric Materials

By W. L. BOND

BECAUSE of the increasing interest in piezoelectric materials in many branches of science an exhaustive study of the minerals was undertaken with the object of finding all the materials that could possibly be of use for piezo-electric elements. Much help was derived from existing data.¹

Considerations of symmetry show us that for a crystal to be piezo-electrically active it must belong to a crystal class that has no center of symmetry (the Pentagonalicositetrahedral class of the cubic system, however, although it has no center of symmetry cannot be piezo active).² This makes twenty classes of possible piezo activity and twelve classes that could not possibly be active. About 90% of the crystals found in nature fall in those classes having centers of symmetry.

Although the mineralogical data are incomplete in their assignment of minerals to definite classes in the seven systems, the existing data give a start in the choosing of minerals likely to have useful piezo-electric properties.

All available data were gone through to obtain the following list of minerals classified by crystal structures. As many of the non-centric ones as were obtainable in the United States were tested by the method of Geibe and Scheibe³ (resonance in a thermionic oscillator circuit). Whenever the authorities differed on the classification of a mineral it was so examined if obtainable.

In the mineral list, each mineral is numbered according to the number of the class in Groth's *Physikalische Kristallographie*, as follows: (*) indicating classes of possible activity:

*1 Assymetric) Triclinic system
2 Pinacoidal)

¹ Dana—A System of Mineralogy, Ford—Dana's Textbook of Mineralogy; Groth—Chemische Kristallographie; Landölt Börnstein—Tabellen; International Critical Tables; Zeitschrift für Kristallographie.

² W. Voigt, *Kristal physik*.

³ *Zeits f Physik* 33, pg. 761 (1925).

- *3 Sphenoidal } Monoclinic system
- 4 Domatic }
- 5 Prismatic }
- *6 Bisphenoidal } Orthorhombic system
- *7 Pyramidal }
- 8 Bipyramidal }
- *9 Bisphenoidal } Tetragonal system
- *10 Pyramidal }
- *11 Scalenohedral }
- *12 Trapezohedral }
- 13 Bipyramidal }
- *14 Ditetragonal Pyramidal }
- 15 Ditetragonal Bipyramidal }
- *16 Pyramidal } Rhombohedral system
- 17 Rhombohedral }
- *18 Trapezohedral }
- *19 Bipyramidal }
- *20 Ditrifonal pyramidal }
- 21 Ditrifonal Scalenohedral }
- *22 Ditrifonal Bipyramidal }
- *23 Pyramidal } Hexagonal system
- *24 Trapezohedral }
- 25 Bipyramidal }
- *26 Dihexagonal Pyramidal }
- 27 Dihexagonal Bipyramidal }
- *28 Tetrahedral-Pentagonal-Dodecahedral } Cubic system
- 29 Pentagonal Icositetrahedral }
- 30 Dyakis-Dodecahedral }
- *31 Hexakis-tetrahedral }
- 32 Hexakis Octahedral }

In addition to the above classification, the following list of minerals is annotated with the following symbols:

- A = active by test
- I = inactive by test
- R = unavailable or rare
- M = mineral occurs only massive, amorphous or in other unsuitable form
- S = crystal always very small
- H = mineral is always non-homogeneous
- U = unstable
- C = electrically conducting
- ? = class not absolutely certain

CLASSIFIED LIST OF MINERALS

Actinolite	5	Allanite	5	Amosite	M
Adelite	5	Allemontite	21	Ampangabeite	8?UI
Aegirite	5?I	Allophane	M	Amphibole	5?HI
Aenigmatite	2	Almandite	32	Analcime	32
Aeschynite	8	Altaite	32	Ancylite	8
Alabandite	*31I	Aluminite	M	Andalusite	8
Alamosite	5	Alunite	21	Andesine	2
Albite	2	Alunogen	M	Andorite	8
Algodonite	H	Amblygonite	2	Andradite	32
Allactite	5?SI	Amesite	5	Anemousite	2

Anglesite	8	Bismite	21?I	Chillagite	10?
Anhydrite	8	Bismuthinite	8	Chloanthite	30
Ankerite	17	Bismutite	M	Chlorastrolite	H
Annabergite	5	Blödite	5	Chlorite	5
Annerodite	8	Blomstrandine	8?M1	Chloritoid	5
Anomite	5	Boleite	15?I	Chlormanganokalite	21
Anorthite	2	Boracite	*7A	Chloropal	M
Anorthoclase	2	Borax	5	Chloraphoenicite	I
Anthophyllite	8	Borickite	M	Chlorospinel	32
Antigorite	5?H	Bornite	*111	Chondrodite	5
Antlerite	M	Boulangerite	8	Chromite	32
Apatite	25I	Bournonite	8	Chrysoberyll	8
Aphrosiderite	?I	Braunite	15	Chrysolite	8
Aphthitalite	21	Breithauptite	*20I	Cinnabar	*18I
Apophyllite	15	Britholite	27?S	Claudetite	5
Aragonite	8	Brochantite	8	Clausthalite	M
Ardennite	8	Bromyrite	32	Cleveite	32
Ardunite	M	Brookite	8	Clinochlor	5
Arfvedsonite	5	Brucite	21	Clinoclasite	5
Argentite	32	Brushite	5	Clinohedrite	*4A
Argentojarosite	I	Bunsenite	32	Clinohumite	5
Argyrodite	32	Bytownite	2	Clinozoisite	5
Arrhenite	H			Cobaltite	*28C
Arseniosiderite	8	Cabrerite	5	Cohenite	M
Arsonolite	32	Cacoxnite	M	Colemanite	5
Arsenophyrite	8	Calamine	*7A	Collinsite	I
Ascharite	M	Calaverite	5	Collophanite	M
Astrakanite	5	Calciothorite	M	Coloradoite	M
Astrophyllite	8?I	Calcite	21	Columbite	8
Atacamite	8	Caledonite	8	Connellite	25
Auerlite	15	Calomel	15	Cookeite	M
Augite	5I	Campylite	25	Cordylite	21
Aurichalcite	M	Cancrinite	27	Coronetite	?I
Automolite	32	Canfieldite	32	Corundum	21
Aventurine	2	Cannizzarite	?I	Corynite	28I
Axinite	2	Carnallite	8	Cotunnite	8
		Carnotite	1	Covellite	*18?I
Babingtonite	2	Carpholite	5	Crestmoreite	M
Baddeleyite	5	Caryocrite	21	Cristobalite	M
Baldauite	?R	Cassiterite	15	Crocidolite	M
Barkevikite	5	Castorite	5	Crocoite	5
Barite	8	Caswellite	I	Cronstedtite	*16A
Barytocalcite	5	Catapleite	5	Crookesite	M
Bastnäsite	I	Celestite	8	Cryolite	5
Baumhauerite	5	Celsian	5	Cryolithionite	32
Bauxite	M	Cenosite	8?I	Cuprite	32
Beaverite	?S	Cerargyrite	32	Cuproscheelite	I
Bechilite	M	Cerite	8	Cyanite	2
Beckelite	32?S	Cerrusite	8	Cyrtolite	I
Bementite	8?I	Cervantite	8?		
Benitoite	*22I	Chabazite	21?I	Dahllite	M
Beraunite	1	Chalcanthite	2	Danburite	8
Bertrandite	*7I	Chalcedony	8?M	Datolite	5
Beryl	27	Chalcocite	8	Dawsonite	M
Beryllonite	8	Chalcolamprite	32	Dechenite	8
Berzelianite	MR	Chalcophyllite	21?I	Delessite	?SI
Berzelite	32?I	Chalcopyrite	*11C	Dellafosite	I
Betafite	32	Chalcosiderite	2	Delorenzite	8
Bindheimite	M	Chalcositbite	8	Delvauxite	M
Binnite	32?I	Chamosite	M	Demantoid	32
Biotite	5	Chiastolite	8	Deschloizite	8
Bischofite	5	Childrenite	8?I	Desmine	5

Deweylite	M	Freyalite	M	Heulandite	5
Diamond	31?I	Frieselite	8	Hielmite	8?I
Diaphorite	8	Fritzscheite	15	Hieratite	32
Diaspore	8	Fuchsite	I	Hillebrandite	M
Diopside	5			Hiortdahlite	2
Diopase	17	Gadolinite	5	Hisingerite	M
Dixenite	?SI	Gageite	I	Hodgkinsonite	5?I
Dolemite	17	Gahnite	32	Hoferite	M
Domeykite	8	Galena	32	Hokutolite	H
Douglasite	5	Ganomalite	I	Holmquistite	5?HI
Dufrenite	8	Garnet	32	Hopeite	8
Dufrenoyite	5	Gastaldite	5	Howlite	M
Dumortierite	8	Gay-Lussite	5	Huebnerite	5
Dysanalyte	32	Gedrite	8	Humite	8
Dyscrasite	8	Gehlenite	15	Hussakite	*13
		Germanite	32	Hutchinsonite	8
Edingtonite	*6A	Gersdorflite	30	Hyalophane	5
Eleonorite	?R	Geyselite	M	Hydroboracite	5
Ellsworthite	MR	Gilsonite	M	Hydromagnesite	5
Elpidite	8	Gismondite	5	Hydrozincite	M
Embolite	32	Glaserite	21	Hypersthene	8
Emerald	27	Glauberite	5		
Emmonsite	?SI	Glaucodot	8	Ilmenite	17
Emplectite	8	Glaucinite	M	Ilmnerutile	15
Enargite	8	Glaucophane	5	Isemannite	M
Enstatite	8	Gmelinite	17	Ilvaite	8
Eosphorite	8?HI	Gothite	8	Inesite	2
Epidesmine	8?SI	Goslarite	*6I	Iodembolite	32?I
Epididymite	8	Graphite	21	Iodobromite	32
Epidote	5	Greenockite	*20IS	Iodyrite	*26?I
Epistilbite	*4?A	Griffithite	M	Iolite	8
Epistolite	5	Grossularite	32		
Epsomite	*6A	Guanajuatite	8?	Jadeite	5
Erikite	8	Gummite	M	Jamesonite	5?SI
Erythrite	5	Gymnite	M	Jarosite	21
Erythrosiderite	8	Gypsum	5	Jeffersonite	5?I
Euclase	5			Jenkinsite	M
Euchroite	8?I	Hackmanite	I	Jezekeite	5?
Eucolite	21	Haidingerite	?S	Johnstrupite	5
Eucairite	M	Halite	32	Jordanite	5
Eudialyte	21	Halloysite	M	Joseite	M
Eudidylite	5	Hambergite	8		
Eulytite	*31I	Hancockite	5?S	Kainite	5
Euxenite	8	Hanksite	27	Kalinite	30
		Hardystonite	M	Kaolinite	5
Fairfieldite	2	Harmotome	5	Kasolite	I
Fassaite	5	Hatchettolite	32?I	Kelihaute	5
Faujasite	32	Hauerite	*28I	Kentrolite	8
Fayalite	8	Hausmannite	*11I	Kermesite	5?SI
Ferberite	5	Haunynite	*31I	Kieserite	5
Fergusonite	*10I	Hedenbergite	5	Klaprotholite	8
Ferrierite	I	Hedyphane	M	Klebelbergite	?S
Florencite	21	Heintzite	5	Knopite	32?I
Fluocerite	27	Hellandite	5	Kobaltmanganerz	M
Fluorite	32	Heloite	*28?R	Koenenite	21
Forsterite	8	Helvite	*31I	Koppite	32
Forshagite	M	Hematite	21	Kornerupine	8
Fouquerite	I	Hercynite	32	Krennerite	5
Fowlerite	2	Herderite	8	Krochnkite	8
Francolite	25	Herregrundite	5	Kunzite	2
Franklinite	32	Hessite	32		
Freibergite	*31C	Hetaerolite	M		

Labradorite	2	Melanite	32	Noselite	*31I
Langbanite	17	Melanocerite	21	Nowmeite	M
Langbeinite	*28A	Melanophlogite	?SI		
Langite	8	Melanterite	5	Ochrolite	I
Lanthanite	8	Melilite	15	Octahedrite	15
Lapis-lazuli	H	Meliphanite	*9?A	Okenite	M
Laumontite	5	Mellite	15	Oligoclase	2
Laurionite	8	Mendozite	30	Olivenite	8
Laurite	*28	Menilite	M	Olivine	8
Lautarite	5	Merwinite	I	Omphacite	M
Lavenite	5	Mesolite	5	Onofrite	31
Lawsonite	8	Metacinnabarite	*31I	Opal	M
Lazulite	5	Meta Torbernite	I	Orpiment	8
Lazurite	5	Metavoltine	?SI	Orthoclase	2
Leadhillite	5	Miargyrite	5	Osmiridium	21
Lehnerite	I	Microcline	2	Otavite	21
Lehrbachite	M	Microlite	32	Ottrelite	2?I
Leonite	5	Microperthite	?HS		
Lepidolite	5	Microsommitte	?SI	Pachnolite	5
Lepidomelane	H	Miersite	*31R	Pandermite	5
Leucite	*31?I	Milarite	27*	Paragonite	5
Leucophanite	*6A	Millerite	*20I	Parahoeppite	2
Leucophoenicite	5?I	Mimetene	25	Paralaurionite	5
Libethenite	8	Mimetite	25, 231	Paratakamite	21?
Limonite	M	Minium	?S	Paravavxite	I
Linarite	5	Mirabilite	5	Pargasite	5
Linnaeite	32?	Mizzonite	13	Parisite	21
Licroconite	5?I	Molybdenite	27	Patronite	M
Liskeardite	M	Molybdate	8	Pearceite	5
Lithiophilite	8	Monazite	5	Pectolite	5
Loewite	15	Monticellite	8	Penninite	5
Loellingite	8	Montmorillonite	M	Pentlandite	32
Loparite	I	Montroydit	8	Perclyte	32?I
Lorandite	5	Morensonite	6	Periclase	32
Loranskit	8?	Morganite	27	Peristerite	2
Ludlamite	5?I	Mosandrite	5	Perovskite	8?
Ludwigite	M	Mossite	15	Perthite	?H, S
		Motttramite	M	Petalite	5
Magnesite	21	Muellerite	M	Petzite	32?
Magnetite	32	Muscovite	5	Pharmacolite	5
Magnetoplumbite	I	Muthmannite	*7R	Pharmacosiderite	*31I
Malachite	5			Phenacite	17
Malacon	I	Nadorite	8?I	Phillipsite	5
Mallardite	MI	Nagyagite	8	Phlogopite	5
Manganhedenbergite	5?I	Natrolite	8	Phosgenite	15
Manganite	8	Natron	5	Phosphoferrite	M
Manganophyllite	I	Naumannite	32	Phosphophyllite	5
Manganosite	32	Nemalite	M	Phosphosiderite	I
Manganotantalite	8?	Neotantalite	32	Phosphuranylite	M
Marcasite	8	Neotocite	M	Pickeringite	M
Margarite	5?RI	Nephelite	*23I	Picotite	32
Margarosanite	2	Nephrite	M	Picromerite	5
Margasite	5	Neptunite	5	Piedmontite	5
Marialite	13	Nesquehonite	8?I	Pinakiolite	I
Marignacite	32	Nicolite	*20I	Pinguite	M
Marmolite	M	Nickolsonite	8	Pinite	M
Marshite	*31I	Nickelbluete	5	Pinnoite	*10I
Martite	32?I	Nickeleisen	32	Pirssonite	*7
Mascagnite	8	Niter	8	Pisolate	M
Matlockite	15?I	Nocerite	21?SI	Pitchblende	32
Maucherite	15?I	Northrupite	32	Plagionite	5?I
Meionite	15I			Plattnerite	15

Pleonast	32	Romeite	32?I	Stilpnosiderite	M
Plumbojarosite	21	Roscoelite	?S	Stolzite	13
Polianite	15	Rosenbushite	5	Strengite	8
Pollucite	?I	Rowlandite	M	Stromeyerite	8
Polybasite	5	Ruby	21	Strontianite	8
Polycrase	8	Rumpfitz	M	Struvite	*7A
Polydymite	32?	Rutherfordine	5	Sulfoborite	8?R
Polyhalite	5?I	Rutile	15	Sulfur	8 or 7
Polymignite	8			Sulvanite	M
Powellite	13C	Saflorite	8	Sussexite	M
Prehnite	*7I	Sal-ammoniac	*28	Svanbergite	21
Priorite	8?I	Salite	5	Sychnodymite	32
Prismatine	8	Samarskite	8	Sylvanite	5
Probertite	M	Sanidine	5	Sylvite	*28I
Prochlorite	5?I	Sapphirine	5	Symplesite	?SI
Proustite	*20C	Sarcolite	*10?I	Syndaliphite	5?
Pseudobrookite	8?S	Sartorite	5?S	Synganite	5
Pseudomalachite	M	Sassolite	2		
Psilomelane	M	Scheelite	13I	Tachyphalinite	15
Psittacinite	M	Schefferite	5	Tachyhydrite	21M
Ptilolite	?S	Schirmerite	M	Talc	5
Pucherite	8	Schizolite	2	Tantalite	8
Pumpellyite	I	Schorlomite	32	Tapiolite	15
Pyroargyrite	*20I	Schreibersite	M	Tarbutite	2
Pyrite	30	Schrockingerite	8	Tasmanite	?S
Pyroaurite	21	Schrotterite	M	Teallite	8?S, I
Pyrochlore	32	Schwartzengergite	?S	Tengerite	M
Pyrochroite	*20?I	Schwetziite	*31	Tennantite	*31I
Pyrolusite	8?HI	Scolecite	*4A	Tenorite	8
Pyromorphite	25	Scorodite	8	Tephroite	8
Pyrope	32?	Semseyite	5?I	Tetradymite	21
Phyrophanite	17	Senarmontite	32	Tetrahydrite	*31C
Pyrophyllite	8	Sepiolite	M	Thalenite	5
Pyropissite	M	Serpentine	5	Thaumasite	M
Pyrosmallite	I	Serpierite	8?S	Thenardite	8
Pyrostilpnite	5	Shortite	*7A	Thermonatrite	8
Pyroxene	5	Siderite	21	Thomsonolite	5
Pyroxmangite	2	Sillimanite	8	Thomsonite	8
Pyrrhotite	*20?C	Sipylite	*10I	Thorianite	32
		Skemmatite	H	Thorite	15
Quartz	*18A	Skutterudite	30	Thortveitite	8?I
Quenselite	I	Smaltite	*38I	Thuringite	M
Quercyite	M	Smithsonite	21	Tiemannite	*31A
Quisqweite	M	Sodalite	*31?I	Tiger-eye	M
		Sodaniter	21	Tilasite	5?I
Ralstonite	32	Spencerite	5	Titanite	5?I
Rammelsbergite	8	Spessartite	32	Titanmagneteisen	32
Raspite	5	Sphalerite	*31A	Topaz	8
Realgar	5	Spinel	32	Topazolite	32
Rhabdophanite	M	Spodumene	5	Torbernite	15
Rhodochrosite	21	Spurrite	5?I	Tourmaline	*20A
Rhodolite	I	Staffelite	M	Trechmannite	17
Rhodonite	2	Stannite	*11I	Tremolite	5
Rhomite	2	Staurolite	8	Tridymite	32?I
Richterite	I	Steenstrupine	21	Trimerite	2
Richardite	M	Stephanite	*7RI	Triphylite	5
Riebeckite	5	Sternbergite	8	Triplite	5
Rinkite	5	Stibiconite	M	Triplidite	5
Rinneit	21	Stibiotantalite	*7A	Tritomite	21?
Ripidolite	5	Stibnite	8?I	Trogerite	5?
Risorite	32?I	Stichtite	I	Troilite	M
Riversideite	M	Stilbite	5?	Trona	5

Troostite	17	Variscite	8?S	Wollastonite	5
Tscheffkinite	M, H	Vauxite	I	Wulfenite	*10
Tschermigite	30	Vermiculite	I	Wurtzite	*20A
Tungstenite	M	Vesuvianite	15		
Tungstite	8	Villiamite	32?I		
Turgite	I	Vivianite	5	Xanthoconite	21
Turquois	2	Volborthite	I	Xanthophyllite	5?I
Tychite	32	Voltaite	32?I	Xanthoxenite	5?S
Tyrolite	M	Vonsenite	8?I	Xenotime	15
Tysonite	27				
Ulexite	M	Wad	M	Yttrialite	M
Ullmannite	30	Wagnerite	5	Yttrocerite	M
Uralite	?III	Walpurgite	2	Yttrifluorite	32
Uraninite	32	Warwickite	I	Yttrokrasite	8
Uranocricite	8?	Wavellite	I	Yttrotantalite	8
Uranophone	M	Wernerite	*10I		
Uranopilite	M	Whewellite	5	Zeratite	M
Uranosphaerite	M	Whitneyite	MI	Zaophyllite	I
Uranospinite	8?	Wilkite	I	Zeunerite	15
Uranothallite	8	Wilkeite	I	Zincite	*19?I
Uranothorite	M	Willemitte	17	Zinkenite	8
Uranotile	2	Wilsonite	I	Zinwaldite	5
Utahite	?S	Witherite	8	Zircon	15
Uvanite	8?S	Wittichenite	8	Zirkelite	32
Uvarogite	32	Woehlerite	5	Zoisite	8
Valentinite	8	Wolfachite	8	Zorgite	M
Vanadinite	25I	Wolframite	5	Zuonyite	*31AS

Of the 830 minerals listed 70 belong to classes that allow piezo-activity but only 17 are found to be active by the Giebe and Scheibe test. (Our test of Iodyrite was negative but Greenwood and Tomboulion⁴ found it to be active; on the other hand, we found Scolecite to be active while they report it inactive.) It may be that others of the remaining 56 classes have such small piezo-electric constants as to be undetectable. Others may be incorrectly classified as to symmetry.

Of these active materials, quartz is the most important. Because of its excellent mechanical properties (stability, etc.) as well as for its relative cheapness it seems destined to remain one of the most important piezo materials.

Tourmaline is also important because of the high magnitude of its elastic moduli in certain directions; however, it cannot be obtained in large pieces of satisfactory homogeneity.

Sphalerite is very difficult to handle because of its many cleavage planes, and appears to give little promise of becoming practically useful. Its activity is quite marked.

Homogeneous crystals of calamine appear to be very rare, so that workable crystals large enough for ordinary piezo-electric application are unobtainable. Most of the material occurs massive.

⁴On Piezo Electricity—Greenwood and Tomboulion—Zeits. f. Krist. Jan. 1932.

Epsomite gives a marked response but the crystals are generally small and they do not weather well. There is some possibility, however, that they can be made artificially.

Boracite gives a marked response, but boracite alters slowly. Its impermeance may bar it for some uses.

Stibiotantalite occurs only in thin scales, and the necessary cuts must be made in the most wasteful way. Twinning is prevalent and the composition varies widely.

Scolecite occurs only as small crystals a few millimeters in diameter and a centimeter or so in length, uniformly twinned.

Iodyrite has been found to be active by other investigators. It is electrically conductive, very soft and not very common.

Struvite is soft, unstable, and occurs only in small crystals.

Zunyite occurs only in minute crystals.

Langbeinite slowly changes its crystal structure. It may be made artificially so may be of some use if it can be kept from alteration.

Leucophanite and Meliphanite are related minerals. Neither seems to occur in good (i.e., homogeneous and untwinned) crystals of usable size.

Wurtzite does not appear very active but *good* crystals were not obtainable.

Tiemannite crystals were also unobtainable, but fragments of massive tiemannite responded. Crystals might respond more energetically if they were obtainable, but minerals that are too difficult to get would not be of practical use.

Epistilbite occurs only in small specimens, uniformly twinned.

The mineral clinohedrite is strongly active but crystals are very rare.

Cronstedtite and Edingtonite are very weakly active. Crystals of these are very rare.

The Fundamental Equations of Electron Motion (Dynamics of High Speed Particles)

By L. A. MacColl

I. INTRODUCTION

In work relating to the motion of electrons and other particles it is fairly common to assume that the particles obey the laws of Newtonian dynamics. That is, briefly, it is assumed that the rectangular coordinates (x, y, z) of the particle under consideration satisfy the differential equations

$$m\ddot{x} = X, \quad m\ddot{y} = Y, \quad m\ddot{z} = Z,$$

where m is the mass of the particle (assumed constant), X , Y , and Z are the components of the applied force, and the dots indicate differentiation with respect to the time t .

However, it is well recognized now that the above equations are not strictly correct, and that they merely represent an approximation which is adequate when the speed of the particle is sufficiently small compared with the speed of light. The system of dynamics based upon the correct equations¹ (which will be exhibited presently) is commonly called *relativistic dynamics*, not because any knowledge of the theory of relativity is essential to its understanding and use², but because it is in agreement with the theory of relativity (which Newtonian dynamics is not), because it was first developed in connection with work on the theory of relativity, and because even yet virtually all of the expositions of the subject are to be found in books and papers dealing primarily with the theory of relativity.

Just where the dividing line should be set between cases in which Newtonian dynamics is an adequate approximation and cases in which it is necessary to use relativistic dynamics is, of course, a rather vague question which cannot be answered simply and definitely. We may note, however,

¹ It is not the purpose of this article to discuss questions of fundamental physics, or the physical validity of any particular equations. For purposes of discussion, we assume outright that relativistic dynamics is at least more nearly correct than is Newtonian dynamics.

² The theory of relativity can be described briefly as a theory of the relations between the descriptions of phenomena in terms of different systems of reference. We shall *not* be concerned with this theory, because we shall be employing the same reference system throughout most of our discussion. In the final section of the paper we shall consider purely geometrical transformations of the coordinate system. These transformations, however, involve nothing that is really characteristic of the theory of relativity in the usual sense.

that according to relativistic dynamics the mass of a five thousand volt electron is about one per cent greater than the mass of an electron at rest. From this we can infer that, while Newtonian dynamics may be adequate for many purposes in our studies of electron motion, we do not have any great amount of margin, and that it will be necessary to use relativistic dynamics whenever we wish to obtain really good results concerning the motion of even moderately high speed electrons.

This article is purely expository. Its purpose is to set forth the fundamental equations and theorems of relativistic particle dynamics in a clear and concise form, unencumbered with any material relating to the theory of relativity proper. Almost all of the material is to be regarded as already known, but apparently it is only to be found in an inconvenient and scattered form. The incomplete bibliography at the end of the paper gives references to some of the more accessible sources of this and other related material.

II. THE ELEMENTARY DIFFERENTIAL EQUATIONS OF MOTION

Our discussion might be begun in any one of a number of ways, and no doubt the different approaches would appeal unequally to different readers. Considering the nature and purposes of this article, the author has deemed it best to begin by writing down at once the differential equations of motion of a particle (according to relativistic dynamics) in their most elementary form. Then, for the purposes of this discussion, these equations will have the status of a fundamental assumption. It need hardly be said that the equations are not written down arbitrarily. On the contrary, they represent the consensus of modern opinion as to the laws under which particles really do move.³ The grounds, experimental and theoretical, for this opinion are set forth in various of the works cited in the bibliography.

For the time being, until the contrary is stated in the final section, we employ a fixed rectangular coordinate system. Instead of denoting the coordinates of the particle by x , y , and z , as we have done provisionally in the Introduction, we shall denote them by x_1 , x_2 , and x_3 . Then \dot{x}_1 , \dot{x}_2 , and \dot{x}_3 denote the components of the velocity of the particle. The components of the force acting on the particle will be denoted by X_1 , X_2 , and X_3 . For the time being we need only note that the force may depend upon the coordinates, the velocity, and the time; later on we shall introduce some more explicit assumptions about the force. The symbol c will be used to denote the speed of light in vacuo.

³ The validity of these laws is not unrestricted. It is limited on the one hand by the quantum phenomena which become appreciable on the atomic scale, and on the other hand by certain phenomena revealed by the general theory of relativity which become appreciable on the cosmic scale.

We assume that the particle moves, under the influence of the force (X_1, X_2, X_3) , so that its coordinates satisfy the system of differential equations

$$\frac{d}{dt} \frac{m_0 \dot{x}_n}{\sqrt{1 - (v^2/c^2)}} = X_n, \quad (n = 1, 2, 3), \quad (1)$$

where m_0 is a positive constant characteristic of the particle, and v^2 is an abbreviation for the expression $\dot{x}_1^2 + \dot{x}_2^2 + \dot{x}_3^2$.* The positive value of the square root is the significant one; and wherever square roots appear in the subsequent work it will be understood, unless the contrary is stated, that the positive values are intended.

A few remarks may help bring out the significance of the foregoing assumption and its relations to the corresponding fundamental assumption of Newtonian dynamics.

We call the constant m_0 the *rest-mass* of the particle, and we assume (in accordance with the experimental evidence) that m_0 is identical with the mass of the particle which is used in Newtonian dynamics. In relativistic dynamics the quantity m defined by the equation

$$m = \frac{m_0}{\sqrt{1 - (v^2/c^2)}}$$

is called the *mass* of the particle. We note that as v/c approaches zero the mass approaches the rest-mass (whence the appropriateness of the latter term), and that as v/c approaches unity the mass increases without limit.

Consider the vector having the components p_1, p_2, p_3 defined by the formulae

$$p_n = \frac{m_0 \dot{x}_n}{\sqrt{1 - (v^2/c^2)}}. \quad (2)$$

We call this vector the *momentum* of the particle. The momentum is equal to the velocity of the particle multiplied by the mass.

Now equations (1) assert that the time-rate of change of the momentum of the particle is equal to the applied force.

We have already observed that as v/c approaches zero the relativistic mass of a particle approaches the Newtonian mass. We now note that as v/c approaches zero the components of the relativistic momentum approach the values

$$p_n = m_0 \dot{x}_n, \quad (2')$$

* We might merely say that v is the speed of the particle. However, for our immediate purposes, it is important not to lose sight of the fact that v is a certain particular function of the components of velocity.

which are precisely the components of the momentum according to the Newtonian theory.

Finally, as v/c approaches zero, the differential equations of motion (1) approach the forms⁴

$$\frac{d}{dt} (m_0 \dot{x}_n) = X_n, \quad (1')$$

which are the Newtonian differential equations of motion.

Thus we see that Newtonian dynamics is in effect a simplified approximate form of relativistic dynamics which is valid when the speed of the particle under consideration is sufficiently small compared with the speed of light.

Let us carry out the indicated differentiations in equations (1), and then solve the resulting equations for the quantities $m_0 \ddot{x}_1$, $m_0 \ddot{x}_2$, $m_0 \ddot{x}_3$. The work is straightforward, and need not be given here. We obtain the following set of formulae:

$$\begin{aligned} m_0 \ddot{x}_1 &= (1 - v^2 c^{-2})^{-1/2} \begin{vmatrix} X_1 & \dot{x}_1 \dot{x}_2 c^{-2} & \dot{x}_1 \dot{x}_3 c^{-2} \\ X_2 & 1 - (\dot{x}_1^2 + \dot{x}_3^2) c^{-2} & \dot{x}_2 \dot{x}_3 c^{-2} \\ X_3 & \dot{x}_2 \dot{x}_3 c^{-2} & 1 - (\dot{x}_1^2 + \dot{x}_2^2) c^{-2} \end{vmatrix}, \\ m_0 \ddot{x}_2 &= (1 - v^2 c^{-2})^{-1/2} \begin{vmatrix} 1 - (\dot{x}_2^2 + \dot{x}_3^2) c^{-2} & X_1 & \dot{x}_1 \dot{x}_3 c^{-2} \\ \dot{x}_1 \dot{x}_2 c^{-2} & X_2 & \dot{x}_2 \dot{x}_3 c^{-2} \\ \dot{x}_1 \dot{x}_3 c^{-2} & X_3 & 1 - (\dot{x}_1^2 + \dot{x}_2^2) c^{-2} \end{vmatrix}, \\ m_0 \ddot{x}_3 &= (1 - v^2 c^{-2})^{-1/2} \begin{vmatrix} 1 - (\dot{x}_2^2 + \dot{x}_3^2) c^{-2} & \dot{x}_1 \dot{x}_2 c^{-2} & X_1 \\ \dot{x}_1 \dot{x}_2 c^{-2} & 1 - (\dot{x}_1^2 + \dot{x}_3^2) c^{-2} & X_2 \\ \dot{x}_1 \dot{x}_3 c^{-2} & \dot{x}_2 \dot{x}_3 c^{-2} & X_3 \end{vmatrix}. \end{aligned} \quad (3)$$

These equations are, of course, the differential equations of motion (1) written in a new, but equivalent, form.

If, at some particular instant, the particle is moving parallel to the x_1 -axis, so that $\dot{x}_2 = \dot{x}_3 = 0$, the equations (3) reduce *at that instant* to the forms:

$$\frac{m_0 \ddot{x}_1}{(1 - v^2 c^{-2})^{3/2}} = X_1, \quad \frac{m_0 \ddot{x}_2}{(1 - v^2 c^{-2})^{1/2}} = X_2, \quad \frac{m_0 \ddot{x}_3}{(1 - v^2 c^{-2})^{1/2}} = X_3.$$

These equations show that a particle of rest-mass m_0 , moving with speed v , responds to a force parallel to the velocity as would a Newtonian particle⁵ of mass

$$m_\ell = \frac{m_0}{(1 - v^2 c^{-2})^{3/2}},$$

⁴ If this conclusion is not entirely evident, the reader is referred to equations (3), from which the conclusion follows at once.

⁵ I.e. an ideal particle which obeys the laws of Newtonian dynamics.

and that the particle responds to a force perpendicular to the velocity as would a Newtonian particle of mass

$$m_t = \frac{m_0}{(1 - v^2/c^2)^{1/2}}.$$

For this reason, it was usual in the early work on relativistic dynamics to ascribe two masses to a particle: the *longitudinal mass* m_l , and the *transverse mass* m_t . However, in general this procedure leads only to inconveniences, and it has been almost entirely abandoned.

This concludes our discussion of the elementary differential equations of motion. Without any further general theory of relativistic dynamics it is possible to solve many interesting and important problems. For instance, it can be shown easily that the trajectory of a particle subjected to a force which is constant in magnitude and direction is a catenary (rather than a parabola, which is the curve predicted by Newtonian dynamics).⁶ In the following sections we shall discuss some of the less elementary parts of the subject.

III. THE LAGRANGIAN EQUATIONS

In the foregoing the components of the applied force have been any functions of the coordinates, the components of the velocity, and the time. However, in problems concerning the motion of electrons, and for that matter in many other physical problems also, we are usually concerned with forces of a somewhat special kind. Throughout the remainder of the article we shall assume that the force belongs to this special class.

We consider four given functions of the coordinates and time, namely

$$V(x_1, x_2, x_3, t), \quad A_n(x_1, x_2, x_3, t), \quad (n = 1, 2, 3),$$

and we assume that the components of the force are given by the formulae

$$\begin{aligned} X_1 &= -\frac{\partial V}{\partial x_1} - \frac{\partial A_1}{\partial t} + \dot{x}_2 \left[\frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2} \right] - \dot{x}_3 \left[\frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1} \right], \\ X_2 &= -\frac{\partial V}{\partial x_2} - \frac{\partial A_2}{\partial t} + \dot{x}_3 \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right] - \dot{x}_1 \left[\frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2} \right], \\ X_3 &= -\frac{\partial V}{\partial x_3} - \frac{\partial A_3}{\partial t} + \dot{x}_1 \left[\frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1} \right] - \dot{x}_2 \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right]. \end{aligned} \quad (4)$$

Let us suppose, for purposes of illustration, that we are considering the motion of an electron. Then the physical interpretation of our assumption

⁶ L. A. MacColl, *American Mathematical Monthly*, Vol. 45 (1938), pp. 669-676.

concerning the force is the following. $V(x_1, x_2, x_3, t)$ is the potential energy of the electron in an electromagnetic field; that is

$$V(x_1, x_2, x_3, t) = -\epsilon\varphi(x_1, x_2, x_3, t),$$

where ϵ is the absolute value of the electronic charge, and $\varphi(x_1, x_2, x_3, t)$ is the scalar potential of the field. The functions $A_n(x_1, x_2, x_3, t)$ are related to the components $a_n(x_1, x_2, x_3, t)$ of the vector potential of the field by the equations

$$A_n(x_1, x_2, x_3, t) = -\epsilon a_n(x_1, x_2, x_3, t).$$

The terms $-\partial A_n/\partial t$ are $-\epsilon$ times the contributions of the vector potential to the components of the electric force. The quantity $\partial A_3/\partial x_2 - \partial A_2/\partial x_3$ is $-\epsilon B_1$, where B_1 is the x_1 -component of the magnetic induction; and similarly for the quantities $\partial A_1/\partial x_3 - \partial A_3/\partial x_1$ and $\partial A_2/\partial x_1 - \partial A_1/\partial x_2$.* In other cases also, equations (4), which may degenerate considerably, can be interpreted without difficulty.

Now we define a function $L(x_1, x_2, x_3, \dot{x}_1, \dot{x}_2, \dot{x}_3, t)$ of the coordinates, the components of the velocity, and the time, as follows:

$$L = -m_0c^2(1 - v^2c^{-2})^{1/2} - V + \dot{x}_1A_1 + \dot{x}_2A_2 + \dot{x}_3A_3. \quad (5)$$

We call this the Lagrangian function.

We write the equations

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{x}_n} - \frac{\partial L}{\partial x_n} = 0, \quad (n = 1, 2, 3), \quad (6)$$

carry out the indicated differentiations, and readily verify that the resulting equations are identical with those obtained by substituting the expressions (4) in equations (1). Hence, equations (6) are merely a form of the differential equations of motion. We call equations (6) the Lagrangian equations. The chief importance of these equations is due to the ease with which they enable us to use coordinate systems which are not rectangular. This will be discussed in the final section.

In the Newtonian case, i.e. the case in which the speed of the particle is small compared with the speed of light, the Lagrangian function reduces approximately to the form

$$L = -m_0c^2 + \frac{m_0}{2}(\dot{x}_1^2 + \dot{x}_2^2 + \dot{x}_3^2) - V + \dot{x}_1A_1 + \dot{x}_2A_2 + \dot{x}_3A_3. \quad (5')$$

* These relations between the A 's and the components of the vector potential, and between the partial derivatives of the A 's and the components of the magnetic induction, are based upon the use of the M.K.S. system of units. If we measure the electromagnetic quantities in other units, certain constant proportionality factors may appear in the relations.

If we employ the function (5') in equations (6), we do indeed get the Newtonian differential equations. Since the constant term $-m_0c^2$ is of no effect in the formation of the differential equations of motion, it is ordinarily omitted in writing the Newtonian form of the Lagrangian function.

IV. HAMILTON'S CANONICAL EQUATIONS

Let us write

$$p_n + A_n = \pi_n. \quad (7)$$

Solving equations (2) for $\dot{x}_1, \dot{x}_2, \dot{x}_3$, we get the result

$$\begin{aligned} \dot{x}_n &= c p_n [m_0^2 c^2 + p_1^2 + p_2^2 + p_3^2]^{-1/2} \\ &= c(\pi_n - A_n) [m_0^2 c^2 + (\pi_1 - A_1)^2 + (\pi_2 - A_2)^2 + (\pi_3 - A_3)^2]^{-1/2}. \end{aligned} \quad (8)$$

Also, it is readily seen that the differential equations (1) can be written, with the aid of equations (7) and (8), in the form

$$\begin{aligned} \dot{\pi}_n &= -\frac{\partial V}{\partial x_n} + \dot{x}_1 \frac{\partial A_1}{\partial x_n} + \dot{x}_2 \frac{\partial A_2}{\partial x_n} + \dot{x}_3 \frac{\partial A_3}{\partial x_n} \\ &= -\frac{\partial V}{\partial x_n} - c \frac{\partial}{\partial x_n} [m_0^2 c^2 + (\pi_1 - A_1)^2 + (\pi_2 - A_2)^2 + (\pi_3 - A_3)^2]^{1/2}. \end{aligned} \quad (9)$$

Now let us define a function $H(x_1, x_2, x_3, \pi_1, \pi_2, \pi_3, t)$ as follows:

$$H = c[m_0^2 c^2 + (\pi_1 - A_1)^2 + (\pi_2 - A_2)^2 + (\pi_3 - A_3)^2]^{1/2} + V. \quad (10)$$

Then equations (8) take the forms

$$\dot{x}_n = \frac{\partial H}{\partial \pi_n}, \quad (11)$$

and equations (9) take the forms

$$\dot{\pi}_n = -\frac{\partial H}{\partial x_n}. \quad (12)$$

The function H is called the Hamiltonian function. The six equations (11) and (12), which are equivalent to the three equations (1), are called Hamilton's canonical equations of motion. These equations are of great importance in all of the deeper theoretical work in dynamics.

An easy calculation shows that we have the identity

$$H + L = \pi_1 \dot{x}_1 + \pi_2 \dot{x}_2 + \pi_3 \dot{x}_3. \quad (13)$$

In the Newtonian case the Hamiltonian function given by (10) reduces approximately to the form

$$H = m_0 c^2 + \frac{1}{2m_0} [(\pi_1 - A_1)^2 + (\pi_2 - A_2)^2 + (\pi_3 - A_3)^2] + V. \quad (10')$$

The equations (11) and (12), with H given by (10'), are equivalent to the Newtonian differential equations of motion (1'). Here again the constant term $m_0 c^2$ is of no effect, and it is ordinarily omitted in writing the Newtonian form of the function H . The Newtonian forms of the functions H and L satisfy the identity (13), whether or not the constant terms $m_0 c^2$ and $-m_0 c^2$ are included.

V. STATIC FIELDS OF FORCE: THE ENERGY INTEGRAL; NATURAL FAMILIES OF TRAJECTORIES

By equations (11) and (12), we have the relation

$$\begin{aligned} \frac{dH}{dt} &= \frac{\partial H}{\partial t} + \sum_{n=1}^3 \left[\frac{\partial H}{\partial x_n} \dot{x}_n + \frac{\partial H}{\partial \pi_n} \dot{\pi}_n \right] \\ &= \frac{\partial H}{\partial t} + \sum_{n=1}^3 \left[\frac{\partial H}{\partial x_n} \frac{\partial H}{\partial \pi_n} - \frac{\partial H}{\partial \pi_n} \frac{\partial H}{\partial x_n} \right] = \frac{\partial H}{\partial t}. \end{aligned} \quad (14)$$

In particular, if no one of the functions V , A_1 , A_2 , A_3 involves the time explicitly, we have $dH/dt = 0$, so that the value of H remains constant during the motion of the particle. That is, under the condition stated we have

$$m_0 c^2 [1 - v^2 c^{-2}]^{-1/2} + V(x_1, x_2, x_3) = \text{constant}. \quad (15)$$

In the Newtonian case equation (15) reduces approximately to the form

$$m_0 c^2 + \frac{m_0}{2} v^2 + V(x_1, x_2, x_3) = \text{constant},$$

which is equivalent to the equation

$$\frac{m_0}{2} v^2 + V(x_1, x_2, x_3) = \text{constant}. \quad (15')$$

It is well known that this equation is a consequence of the Newtonian differential equations of motion.

The left-hand member of equation (15') is the energy of the particle in

Newtonian dynamics, the first and second terms being the kinetic energy and the potential energy, respectively. The equation itself is called the energy integral.⁷ Similarly, we call (15) the energy integral in relativistic dynamics, and we call the expression

$$m_0c^2[1 - v^2c^{-2}]^{-1/2} + V$$

the *relativistic energy*. This energy is the sum of three parts: the *proper energy* m_0c^2 , the *relativistic kinetic energy*

$$m_0c^2[1 - v^2c^{-2}]^{-1/2} - m_0c^2,$$

and the *potential energy* V .

The totality of possible trajectories of a particle in a static field of force forms a five-parameter family. We now see that if the field of force is static and of the kind we are considering now, the five-parameter family of curves consists of ∞^1 four-parameter subfamilies, each of which corresponds to a different value of the energy of the particle. Each of these four-parameter subfamilies is called a natural family of trajectories. We proceed to derive the differential equations defining a natural family.

If the constant in the right-hand member of equation (15) is denoted by the symbol E , we have the relation

$$\dot{x}_1[1 + \dot{x}_2'^2 + \dot{x}_3'^2]^{1/2} = c[1 - m_0^2c^4(E - V)^{-2}]^{1/2}, \quad (16)$$

where

$$\dot{x}_2' = dx_2/dx_1, \quad \dot{x}_3' = dx_3/dx_1.$$

Hence,

$$dt = c^{-1}[1 + \dot{x}_2'^2 + \dot{x}_3'^2]^{1/2}[1 - m_0^2c^4(E - V)^{-2}]^{-1/2} dx_1.$$

From this, and the two equations

$$\frac{d}{dt} \frac{m_0 \dot{x}_2}{(1 - v^2c^{-2})^{1/2}} = -\frac{\partial V}{\partial x_2} + \dot{x}_3 \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right] - \dot{x}_1 \left[\frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2} \right],$$

$$\frac{d}{dt} \frac{m_0 \dot{x}_3}{(1 - v^2c^{-2})^{1/2}} = -\frac{\partial V}{\partial x_3} + \dot{x}_1 \left[\frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1} \right] - \dot{x}_2 \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right],$$

it follows that we have the following system of differential equations defining the natural family of trajectories corresponding to the total energy E :

⁷ In the theory of differential equations, an equation relating the unknowns involved in a system of differential equations, their derivatives of orders less than the highest orders appearing in the system, the independent variable, and one or more arbitrary constants, is called an integral of the system of differential equations.

$$\begin{aligned}
& [1 + x_2'^2 + x_3'^2]^{-1/2} \frac{d}{dx_1} \left(x_2' \left[\frac{(E - V)^2 - m_0^2 c^4}{1 + x_2'^2 + x_3'^2} \right]^{1/2} \right) \\
& \quad = \frac{\partial}{\partial x_2} [(E - V)^2 - m_0^2 c^4]^{1/2} \\
& \quad + c [1 + x_2'^2 + x_3'^2]^{-1/2} \left(x_3' \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right] - \left[\frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2} \right] \right), \\
& [1 + x_2'^2 + x_3'^2]^{-1/2} \frac{d}{dx_1} \left(x_3' \left[\frac{(E - V)^2 - m_0^2 c^4}{1 + x_2'^2 + x_3'^2} \right]^{1/2} \right) \\
& \quad = \frac{\partial}{\partial x_3} [(E - V)^2 - m_0^2 c^4]^{1/2} \\
& \quad + c [1 + x_2'^2 + x_3'^2]^{-1/2} \left(\left[\frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1} \right] - x_2' \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right] \right). \tag{17}
\end{aligned}$$

The equations which correspond to (17) in the Newtonian case are most readily obtained by going back to the Newtonian differential equations of motion and employing the integral

$$m_0 v^2 / 2 + V = E.$$

An easy calculation, which is entirely parallel to the foregoing, gives us the following system of equations:

$$\begin{aligned}
& [1 + x_2'^2 + x_3'^2]^{-1/2} \frac{d}{dx_1} \left(x_2' \left[\frac{E - V}{1 + x_2'^2 + x_3'^2} \right]^{1/2} \right) = \frac{\partial}{\partial x_2} (E - V)^{1/2} \\
& \quad + [2m_0(1 + x_2'^2 + x_3'^2)]^{-1/2} \left(x_3' \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right] - \left[\frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2} \right] \right), \\
& [1 + x_2'^2 + x_3'^2]^{-1/2} \frac{d}{dx_1} \left(x_3' \left[\frac{E - V}{1 + x_2'^2 + x_3'^2} \right]^{1/2} \right) = \frac{\partial}{\partial x_3} (E - V)^{1/2} \\
& \quad + [2m_0(1 + x_2'^2 + x_3'^2)]^{-1/2} \left(\left[\frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1} \right] - x_2' \left[\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \right] \right). \tag{17'}
\end{aligned}$$

On comparing the systems of equations (17) and (17'), we get the following useful theorem.

If the constants E , E^* , m_0 , m_0^* , k , and the functions (of x_1, x_2, x_3) V , A_1 , A_2 , A_3 , V^* , A_1^* , A_2^* , A_3^* are such that we have identically

$$\begin{aligned}
(E - V)^2 - m_0^2 c^4 &= k^2 (E^* - V^*), \\
\frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} &= \frac{k}{c(2m_0^*)^{1/2}} \left[\frac{\partial A_3^*}{\partial x_2} - \frac{\partial A_2^*}{\partial x_3} \right],
\end{aligned}$$

$$\frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2} = \frac{k}{c(2m_0^*)^{1/2}} \left[\frac{\partial A_2^*}{\partial x_1} - \frac{\partial A_1^*}{\partial x_2} \right],$$

$$\frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1} = \frac{k}{c(2m_0^*)^{1/2}} \left[\frac{\partial A_1^*}{\partial x_3} - \frac{\partial A_3^*}{\partial x_1} \right],$$

the natural family of trajectories of a relativistic particle⁸ (of rest-mass m_0) moving with relativistic total energy E in the field of force derived from the functions V, A_1, A_2, A_3 is identical with the natural family of trajectories of a Newtonian particle (of mass m_0^*) moving with Newtonian energy E^* in the field of force derived from the functions V^*, A_1^*, A_2^*, A_3^* .

In particular, the conditions of the theorem are satisfied if

$$k = c(2m_0)^{1/2}, \quad E^* = c^{-2}(2m_0)^{-1}(E^2 - m_0^2c^4), \quad m_0^* = m_0,$$

$$V = V^* = 0, \quad A_1^* = A_1, \quad A_2^* = A_2, \quad A_3^* = A_3.$$

Hence, we have the corollary:

In the case of an electrified particle moving in any static magnetic field the natural family of trajectories corresponding to any value of the energy given by relativistic (Newtonian) dynamics is identical with the natural family of trajectories corresponding to a certain other value of the energy given by Newtonian (relativistic) dynamics.

The equation

$$E^* = c^{-2}(2m_0)^{-1}(E^2 - m_0^2c^4)$$

establishes a one-to-one correspondence between the physically significant ($E \geq m_0c^2$ and $E^* \geq 0$) values of the relativistic energy E and the Newtonian energy E^* . From this fact and the preceding corollary we get the following further result:

In the case of an electrified particle moving in any static magnetic field the total five-parameter family of trajectories given by relativistic dynamics is identical with that given by Newtonian dynamics.

Of course, these peculiar properties of motion of an electrified particle moving in a static magnetic field are explained physically by the fact that the magnetic forces do no work, so that the speed of the particle, and consequently also its mass, remain constant during the motion.

VI. SOME FORMULAE FROM THE CALCULUS OF VARIATIONS

This section is devoted to the derivation of some formulae from the Calculus of Variations which will be needed in the further discussion of the

⁸ I.e. a particle obeying the laws of relativistic dynamics.

dynamics of a particle. All constants, variables, and functions considered here are understood to be real.⁹

Let $F(t, x, y, z, p, q, r)$ be a function of the seven arguments indicated,¹⁰ which, together with all of its partial derivatives of the first three orders, is continuous in a region R defined as follows:

$$\begin{aligned} a_1 &< t < a_2, \\ b_1 &< x < b_2, \\ R: \quad c_1 &< y < c_2, \\ d_1 &< z < d_2, \\ p, q, \text{ and } r &\text{ unrestricted,} \end{aligned}$$

the a 's, b 's, c 's, and d 's, being constants.

Let $x(t)$, $y(t)$, $z(t)$, $\varphi(t)$, $\psi(t)$, and $\omega(t)$ be continuous functions with continuous first derivatives, and let ϵ , η , and θ be parameters, independent of t , such that we have the relations

$$\begin{aligned} b_1 &< x(t) + \epsilon\varphi(t) < b_2, \\ c_1 &< y(t) + \eta\psi(t) < c_2, \quad (a_1 < t < a_2). \\ d_1 &< z(t) + \theta\omega(t) < d_2, \end{aligned}$$

Let T_1 and T_2 be constants, and let t_1 and t_2 be parameters, such that

$$a_1 < T_1 + t_1 < T_2 + t_2 < a_2.$$

We now consider the integral

$$\begin{aligned} I(\epsilon, \eta, \theta, t_1, t_2) \\ = \int_{T_1+t_1}^{T_2+t_2} F(t, x + \epsilon\varphi, y + \eta\psi, z + \theta\omega, x' + \epsilon\varphi', y' + \eta\psi', z' + \theta\omega') dt. \end{aligned}$$

It can be shown without difficulty that the integral exists and is a differentiable function of ϵ , η , θ , t_1 , t_2 . We are interested in formulae giving the values of $\partial I/\partial\epsilon$, $\partial I/\partial\eta$, $\partial I/\partial\theta$, $\partial I/\partial t_1$, $\partial I/\partial t_2$ at the point $\epsilon = \eta = \theta = t_1 = t_2 = 0$.

⁹ Since this section is purely mathematical, the constants, variables, and functions do not necessarily have any special physical significance.

¹⁰ We treat the case of a function of seven arguments in order to fix the ideas, and because this is a case we shall meet in Section VII. However, the discussion applies essentially to other cases as well. In particular, in Section VII we shall also deal with a case in which F has only five arguments, z and r being absent.

By a well known theorem concerning the differentiation of definite integrals with respect to parameters,¹¹ we have

$$\frac{\partial I}{\partial \epsilon} = \int_{T_1+t_1}^{T_2+t_2} \left[\varphi \frac{\partial}{\partial(x+\epsilon\varphi)} + \varphi' \frac{\partial}{\partial(x'+\epsilon\varphi')} \right] F(t, x + \epsilon\varphi, \dots, z' + \theta\omega') dt,$$

$$\frac{\partial I}{\partial t_1} = -F[T_1 + t_1, x(T_1 + t_1) + \epsilon\varphi(T_1 + t_1), \dots, z'(T_1 + t_1) + \theta\omega'(T_1 + t_1)],$$

$$\frac{\partial I}{\partial t_2} = F[T_2 + t_2, x(T_2 + t_2) + \epsilon\varphi(T_2 + t_2), \dots, z'(T_2 + t_2) + \theta\omega'(T_2 + t_2)].$$

The formulae for $\partial I/\partial \eta$ and $\partial I/\partial \theta$ are similar to that for $\partial I/\partial \epsilon$, and need not be written down.

In particular, if $[\partial I/\partial \epsilon]_0$, etc. denote the values of the derivatives at the point $\epsilon = \eta = \theta = t_1 = t_2 = 0$, we have

$$\begin{aligned} \left[\frac{\partial I}{\partial \epsilon} \right]_0 &= \int_{T_1}^{T_2} \left[\varphi \frac{\partial}{\partial x} + \varphi' \frac{\partial}{\partial x'} \right] F(t, x, \dots, z') dt, \\ \left[\frac{\partial I}{\partial \eta} \right]_0 &= \int_{T_1}^{T_2} \left[\psi \frac{\partial}{\partial y} + \psi' \frac{\partial}{\partial y'} \right] F(t, x, \dots, z') dt, \\ \left[\frac{\partial I}{\partial \theta} \right]_0 &= \int_{T_1}^{T_2} \left[\omega \frac{\partial}{\partial z} + \omega' \frac{\partial}{\partial z'} \right] F(t, x, \dots, z') dt, \\ \left[\frac{\partial I}{\partial t_1} \right]_0 &= -F[T_1, x(T_1), \dots, z'(T_1)], \\ \left[\frac{\partial I}{\partial t_2} \right]_0 &= F[T_2, x(T_2), \dots, z'(T_2)]. \end{aligned} \quad (18)$$

The first three of equations (18) can be transformed to advantage, as follows. Integrating by parts, we obtain the formula

$$\begin{aligned} \int_{T_1}^{T_2} \varphi' \frac{\partial}{\partial x'} F(t, x, \dots, z') dt &= \left[\varphi \frac{\partial}{\partial x'} F(t, x, \dots, z') \right]_{T_1}^{T_2} \\ &\quad - \int_{T_1}^{T_2} \varphi \frac{d}{dt} \frac{\partial}{\partial x'} F(t, x, \dots, z') dt, \end{aligned}$$

and similar formulae for the integrals

$$\int_{T_1}^{T_2} \psi' \frac{\partial}{\partial y'} F(t, x, \dots, z') dt$$

and

$$\int_{T_1}^{T_2} \omega' \frac{\partial}{\partial z'} F(t, x, \dots, z') dt.$$

¹¹ The theorem is given, often in the form of two separate theorems, in most works on Advanced Calculus and the Theory of Functions of Real Variables. See the bibliography.

It follows, therefore, that we have

$$\begin{aligned} \left[\frac{\partial I}{\partial \epsilon} \right]_0 &= \left[\varphi \frac{\partial}{\partial x'} F(t, x, \dots, z') \right]_{T_1}^{T_2} \\ &\quad + \int_{T_1}^{T_2} \varphi(t) \left[\frac{\partial}{\partial x} - \frac{d}{dt} \frac{\partial}{\partial x'} \right] F(t, x, \dots, z') dt, \\ \left[\frac{\partial I}{\partial \eta} \right]_0 &= \left[\psi \frac{\partial}{\partial y'} F(t, x, \dots, z') \right]_{T_1}^{T_2} \\ &\quad + \int_{T_1}^{T_2} \psi(t) \left[\frac{\partial}{\partial y} - \frac{d}{dt} \frac{\partial}{\partial y'} \right] F(t, x, \dots, z') dt, \quad (19) \\ \left[\frac{\partial I}{\partial \theta} \right]_0 &= \left[\omega \frac{\partial}{\partial z'} F(t, x, \dots, z') \right]_{T_1}^{T_2} \\ &\quad + \int_{T_1}^{T_2} \omega(t) \left[\frac{\partial}{\partial z} - \frac{d}{dt} \frac{\partial}{\partial z'} \right] F(t, x, \dots, z') dt. \end{aligned}$$

An important special case is that in which t_1 and t_2 are zero (so that the limits of integration are fixed), and

$$\varphi(T_1) = \varphi(T_2) = \psi(T_1) = \psi(T_2) = \omega(T_1) = \omega(T_2) = 0.$$

In this case we have in general

$$\begin{aligned} I(\epsilon, \eta, \theta, 0, 0) - I(0, 0, 0, 0, 0) &= \epsilon \int_{T_1}^{T_2} \varphi(t) \left[\frac{\partial F}{\partial x} - \frac{d}{dt} \frac{\partial F}{\partial x'} \right] dt \\ &\quad + \eta \int_{T_1}^{T_2} \psi(t) \left[\frac{\partial F}{\partial y} - \frac{d}{dt} \frac{\partial F}{\partial y'} \right] dt + \theta \int_{T_1}^{T_2} \omega(t) \left[\frac{\partial F}{\partial z} - \frac{d}{dt} \frac{\partial F}{\partial z'} \right] dt \\ &\quad + o(\epsilon, \eta, \theta), \end{aligned}$$

where $o(\epsilon, \eta, \theta)$ denotes a term, the exact form of which is unimportant, which is such that the expression

$$\frac{o(\epsilon, \eta, \theta)}{|\epsilon| + |\eta| + |\theta|}$$

approaches the limit zero as ϵ , η , and θ tend simultaneously toward zero.

In particular, if the functions $x(t)$, $y(t)$, $z(t)$ satisfy the system of differential equations

$$\frac{d}{dt} \frac{\partial F}{\partial x'} - \frac{\partial F}{\partial x} = 0, \quad \frac{d}{dt} \frac{\partial F}{\partial y'} - \frac{\partial F}{\partial y} = 0, \quad \frac{d}{dt} \frac{\partial F}{\partial z'} - \frac{\partial F}{\partial z} = 0, \quad (20)$$

we have (for all choices of the functions φ , ψ , ω subject to the conditions stated)

$$I(\epsilon, \eta, \theta, 0, 0) - I(0, 0, 0, 0, 0) = o(\epsilon, \eta, \theta). \quad (21)$$

Also, it can be shown without difficulty that in order that we have (21), for all such choices of φ, ψ, ω , it is necessary that x, y , and z , satisfy the equations (20).*

The last result can be stated in the following summary, and not quite explicit, form: If, and only if, the functions $x(t), y(t), z(t)$ satisfy equations (20), the integral

$$\int_{T_1}^{T_2} F(t, x, y, z, x', y', z') dt \quad (22)$$

is stationary with respect to infinitesimal variations of the functions $x(t), y(t), z(t)$ which leave the terminal values unaltered.

The problem of finding functions which render the values of definite integrals stationary is the chief subject of the Calculus of Variations.

The equations (20) are called the Eulerian equations of the Calculus of Variations problem of making the value of the integral (22) stationary, or, as we usually say, of maximizing or minimizing the integral.

VII. HAMILTON'S PRINCIPLE AND THE PRINCIPLE OF LEAST ACTION

We immediately recognize equations (6) as the Eulerian equations of a problem in the Calculus of Variations. Thus we have the following principle (*Hamilton's principle*):

The particle moves, under forces of the type (4), so that the value of the integral

$$\int_{t_1}^{t_2} L dt,$$

with t_1 and t_2 held fixed, is stationary with respect to infinitesimal variations of the functions $x_n(t)$ which leave the initial and final points unaltered.

The precise meaning of this is determined by the discussion given in Section VI.

Hamilton's principle leads to the relativistic or Newtonian differential equations of motion, according as we use in it the function L given by (5) or by (5').

A little inspection suffices to show that the system of equations (17) is also the system of Eulerian equations of a problem in the Calculus of

* In brief, suppose that $\frac{d}{dt} \frac{\partial F}{\partial x'} - \frac{\partial F}{\partial x}$ were not zero for some value of t . Then if we should choose a function $\varphi(t)$ which was (say) positive in the neighborhood of that value, and zero elsewhere, the integral

$$\int_{T_1}^{T_2} \varphi(t) \left[\frac{\partial F}{\partial x} - \frac{d}{dt} \frac{\partial F}{\partial x'} \right] dt$$

would have a value other than zero. We shall not give the actual proof here; it is to be found in the works on the Calculus of Variations cited in the bibliography.

Variations. Thus we get the so-called *principle of least action*, which can be stated as follows:

The particle moves, in a static field of force of the type (4), and with the prescribed total energy E , in such a curve that the value of the integral

$$\int_{(x_1)_1}^{(x_1)_2} ([1 + x_2'^2 + x_3'^2]^{1/2} [(E - V)^2 c^{-2} - m_0^2 c^2]^{1/2} + A_1 + A_2 x_2' + A_3 x_3') dx_1,$$

with the limits of integration held fixed, is stationary with respect to infinitesimal variations of the trajectory which leave the end points unaltered.

We have a precisely similar principle in Newtonian dynamics, but here the integral in question is

$$\int_{(x_1)_1}^{(x_1)_2} ([1 + x_2'^2 + x_3'^2]^{1/2} [2m_0(E - V)]^{1/2} + A_1 + A_2 x_2' + A_3 x_3') dx_1.$$

The last two integrals can be written more symmetrically, but not quite so explicitly, as follows:

$$\int_{P_1}^{P_2} \left([(E - V)^2 c^{-2} - m_0^2 c^2]^{1/2} + A_1 \frac{dx_1}{ds} + A_2 \frac{dx_2}{ds} + A_3 \frac{dx_3}{ds} \right) ds,$$

$$\int_{P_1}^{P_2} \left([2m_0(E - V)]^{1/2} + A_1 \frac{dx_1}{ds} + A_2 \frac{dx_2}{ds} + A_3 \frac{dx_3}{ds} \right) ds,$$

where P_1 and P_2 denote the end points of the trajectory, and $ds^2 = dx_1^2 + dx_2^2 + dx_3^2$.

VIII. THE HAMILTON-JACOBI THEORY

Let us write

$$W = \int_{t_1}^{t_2} L[x_1(t), x_2(t), x_3(t), x_1'(t), x_2'(t), x_3'(t), t] dt. \quad (23)$$

We have already studied the variation of W when t_1 and t_2 are held fixed, and the functions $x_n(t)$ are varied in such a way that the terminal values are unaltered; and we have shown that under these circumstances the variation of W vanishes, to the first order of small quantities, in the natural motion.¹² In the following we shall study the variation of W under some other conditions.

Specifically, we shall study the quantity ΔW defined by equation (23) and the equation

$$W + \Delta W = \int_{t_1 + \Delta t_1}^{t_2 + \Delta t_2} L[x_1(t) + \xi_1(t), \dots, x_3(t) + \xi_3(t), t] dt,$$

¹² I.e. a motion satisfying equations (1).

where the functions $x_n(t)$ represent a natural motion, the $\xi_n(t)$ are small functions, and Δt_1 and Δt_2 are small parameters.

It follows from the results of Section VI that we have (to within terms of the second order in small quantities)¹³

$$\begin{aligned} \Delta W &= \Delta t_2 L[x_1(t_2), \dots, x_3'(t_2), t_2] \\ &\quad - \Delta t_1 L[x_1(t_1), \dots, x_3'(t_1), t_1] \\ &\quad + \sum_{n=1}^3 \left[\frac{\partial L}{\partial x_n'} \right]_{t=t_2} \xi_n(t_2) - \sum_{n=1}^3 \left[\frac{\partial L}{\partial x_n'} \right]_{t=t_1} \xi_n(t_1) \\ &= \Delta t_2 L[x_1(t_2), \dots, x_3'(t_2), t_2] \\ &\quad - \Delta t_1 L[x_1(t_1), \dots, x_3'(t_1), t_1] \\ &\quad + \sum_{n=1}^3 [\pi_n(t_2)\xi_n(t_2) - \pi_n(t_1)\xi_n(t_1)]. \end{aligned}$$

Let us write

$$(\Delta x_n)_2 = x_n(t_2 + \Delta t_2) + \xi_n(t_2 + \Delta t_2) - x_n(t_2) = \xi_n(t_2) + x_n'(t_2) \Delta t_2,$$

$$(\Delta x_n)_1 = x_n(t_1 + \Delta t_1) + \xi_n(t_1 + \Delta t_1) - x_n(t_1) = \xi_n(t_1) + x_n'(t_1) \Delta t_1,$$

so that $(\Delta x_1)_2$, $(\Delta x_2)_2$, $(\Delta x_3)_2$ are the coordinate differences of the terminal points of the varied and unvaried curves, and similarly $(\Delta x_1)_1$, $(\Delta x_2)_1$, $(\Delta x_3)_1$ are the coordinate differences of the initial points. Then we have the formula

$$\begin{aligned} \Delta W &= \left(L[x_1(t_2), \dots] - \sum_{n=1}^3 \pi_n(t_2) x_n'(t_2) \right) \Delta t_2 \\ &\quad - \left(L[x_1(t_1), \dots] - \sum_{n=1}^3 \pi_n(t_1) x_n'(t_1) \right) \Delta t_1 \\ &\quad + \sum_{n=1}^3 [\pi_n(t_2)(\Delta x_n)_2 - \pi_n(t_1)(\Delta x_n)_1], \end{aligned}$$

which, by equation (13), can be written in the form

$$\begin{aligned} \Delta W &= -H[x_1(t_2), \dots] \Delta t_2 + H[x_1(t_1), \dots] \Delta t_1 \\ &\quad + \sum_{n=1}^3 [\pi_n(t_2)(\Delta x_n)_2 - \pi_n(t_1)(\Delta x_n)_1]. \quad (24) \end{aligned}$$

Now, the integration in (23) being taken over a natural motion of the particle, the value of W depends upon the initial instant, the initial coordi-

¹³ This is also the sense in which the following equations are to be understood.

nates, the initial components of velocity, and the final instant. It is necessary now to consider W as depending upon the following equivalent set of eight variables: the initial and final instants t_1 and t_2 , the coordinates (x_{11}, x_{21}, x_{31}) of the initial point, and the coordinates (x_{12}, x_{22}, x_{32}) of the final point. Regarding W in this manner, we at once obtain the following relations from equation (24)

$$\frac{\partial W}{\partial t_2} = -H_2, \quad \frac{\partial W}{\partial x_{n2}} = \pi_{n2}, \quad (25)$$

$$\frac{\partial W}{\partial t_1} = H_1, \quad \frac{\partial W}{\partial x_{n1}} = -\pi_{n1}, \quad (26)$$

where H_2 denotes $H[x_1(t_2), \dots, \pi_1(t_2), \dots, t_2]$ and H_1 denotes $H[x_1(t_1), \dots, \pi_1(t_1), \dots, t_1]$.

Let us now consider the partial differential equation

$$\frac{\partial W}{\partial t} + H(x_1, x_2, x_3, \partial W/\partial x_1, \partial W/\partial x_2, \partial W/\partial x_3, t) = 0. \quad (27)$$

The preceding work shows that the function W we have been considering (with $x_{11}, x_{21}, x_{31}, t_1$ regarded as parameters, and with the symbols $x_{12}, x_{22}, x_{32}, t_2$ replaced by x_1, x_2, x_3, t respectively) is a *particular* solution of this equation. We shall show that the *complete* solution of this equation possesses remarkable properties in connection with dynamical problems.

The complete solution of equation (27) is a function of x_1, x_2, x_3, t , and of four arbitrary constants, of which one is merely additive, and can be neglected for our purposes. Let the solution be written

$$W = W(x_1, x_2, x_3, t, \alpha_1, \alpha_2, \alpha_3),$$

where the α 's are the three essential arbitrary constants.

We write the equations

$$\frac{\partial W}{\partial \alpha_n} = \beta_n, \quad (28)$$

where the β 's are further arbitrary constants. These equations implicitly determine the α 's as functions of t and the six arbitrary constants α_1, \dots, β_3 .

We also write the equations

$$\frac{\partial W}{\partial x_n} = \pi_n, \quad (29)$$

These equations determine three functions π_n of the x 's, the α 's, and t . In virtue of equations (28), the π 's are ultimately functions of t , the α 's, and the β 's.

There is no reason to foresee *a priori* that the functions $x_1(t, \alpha_1, \dots, \beta_3), \dots, \pi_3(t, \alpha_1, \dots, \beta_3)$ determined in this way, by means of the complete solution of equation (27), satisfy the differential equations of motion (11) and (12). Nevertheless, they actually do satisfy those equations, as we proceed to show.

By equations (28), we have the relations

$$0 = \frac{d\beta_n}{dt} = \frac{\partial^2 W}{\partial \alpha_n \partial t} + \sum_{m=1}^3 \frac{\partial^2 W}{\partial \alpha_n \partial x_m} \dot{x}_m. \quad (30)$$

On the other hand, by (27) and (29), we have¹⁴

$$\begin{aligned} 0 &= \frac{\partial}{\partial \alpha_n} \left[\frac{\partial W}{\partial t} + H(x_1, x_2, x_3, \pi_1, \pi_2, \pi_3, t) \right] \\ &= \frac{\partial^2 W}{\partial \alpha_n \partial t} + \sum_{m=1}^3 \frac{\partial H}{\partial \pi_m} \frac{\partial \pi_m}{\partial \alpha_n} = \frac{\partial^2 W}{\partial \alpha_n \partial t} + \sum_{m=1}^3 \frac{\partial H}{\partial \pi_m} \frac{\partial^2 W}{\partial \alpha_n \partial x_m}. \end{aligned} \quad (31)$$

The determinant

$$\begin{vmatrix} \frac{\partial^2 W}{\partial \alpha_1 \partial x_1} & \cdots & \frac{\partial^2 W}{\partial \alpha_1 \partial x_3} \\ \dots & \dots & \dots \\ \frac{\partial^2 W}{\partial \alpha_3 \partial x_1} & \cdots & \frac{\partial^2 W}{\partial \alpha_3 \partial x_3} \end{vmatrix}$$

is not zero. For if it were, we would have a relation of the form

$$\Phi[\partial W / \partial x_1, \partial W / \partial x_2, \partial W / \partial x_3, x_1, x_2, x_3, t] = 0, \quad (32)$$

independent of the α 's. Now equation (32) is obviously distinct from (27), since it does not involve $\partial W / \partial t$. Hence, the vanishing of the determinant would imply that the function $W(x_1, x_2, x_3, t, \alpha_1, \alpha_2, \alpha_3)$ satisfies two distinct partial differential equations of the first order. This, however, is impossible when W is the complete solution of (27); for an essential part of the concept of the complete solution of a differential equation is that the elimination of the arbitrary constants, from the solution and the equations obtained by differentiation, shall result in the given differential equation and no other.

It follows, therefore, from (30) and (31) that

$$\dot{x}_m = \frac{\partial H}{\partial \pi_m}.$$

We also have, by (29),

$$\dot{\pi}_n = \frac{\partial^2 W}{\partial x_n \partial t} + \sum_{m=1}^3 \frac{\partial^2 W}{\partial x_m \partial x_n} \dot{x}_m = \frac{\partial^2 W}{\partial x_n \partial t} + \sum_{m=1}^3 \frac{\partial^2 W}{\partial x_m \partial x_n} \frac{\partial H}{\partial \pi_m}. \quad (33)$$

¹⁴ Since the function $W(x_1, x_2, x_3, t, \alpha_1, \alpha_2, \alpha_3)$ satisfies equation (27) *identically* in the x 's, t , and the α 's. This remark applies also in the case of equation (34).

On the other hand, we have

$$0 = \frac{\partial}{\partial x_n} \left[\frac{\partial W}{\partial t} + H \right] = \frac{\partial^2 W}{\partial x_n \partial t} + \frac{\partial H}{\partial x_n} + \sum_{m=1}^3 \frac{\partial H}{\partial \pi_m} \frac{\partial^2 W}{\partial x_m \partial x_n}. \quad (34)$$

By (33) and (34), we have the second set of canonical equations

$$\dot{\pi}_n = -\frac{\partial H}{\partial x_n}.$$

This completes the demonstration.

If H does not involve the time explicitly, we can write

$$W = S - Et, \quad (35)$$

where E is an arbitrary parameter, and S is a solution of the differential equation

$$H[x_1, x_2, x_3, \partial S/\partial x_1, \partial S/\partial x_2, \partial S/\partial x_3] = E. \quad (36)$$

The complete solution of (36) contains three arbitrary constants (besides the parameter E), of which one is merely additive, and can be neglected. It is easily seen that the solution of the canonical equations determined in the way described above, using the function W given by (35), and treating E as one of the α 's, represents a motion of the particle with the total energy E .

All of this theory holds both for the relativistic case and for the Newtonian case, the only difference being in the forms of the differential equations (27) and (36) in the two cases.

IX. CURVILINEAR COORDINATES

In all of the foregoing we have employed rectangular coordinates, because they afford the simplest and most direct expression of the basic physical facts. However, in the solution of particular problems it is often more convenient to use other systems of coordinates. For this reason, we shall now formulate the more important equations in terms of general curvilinear coordinates. In this work, as in all work with general coordinate systems, we shall encounter concepts and relations which can be handled most perspicuously by means of the modern tensor calculus. Actually, the amount of tensor calculus we shall use is very slight, and no extended preliminary discussion is necessary in order to make the formulae intelligible. It will suffice to give occasional explanations of the notation, and of some of the concepts, as we proceed. Further information is to be found in the works cited in the bibliography.

First consider the Lagrangian equations, which, as we have seen, are merely the Eulerian equations which follow from Hamilton's principle.

Now Hamilton's principle expresses a fact concerning the motion of a particle which is, by its very nature, independent of the choice of coordinates. Hence, the Lagrangian equations (6) hold in any coordinate system. However, the form of the function L depends upon the particular coordinate system, and we must discuss the change of the form of the function resulting from a transformation of the coordinate system.

In accordance with the common practice in the tensor calculus, we shall now denote the coordinates by the symbols x^1, x^2, x^3 , instead of by the symbols x_1, x_2, x_3 .

In rectangular coordinates the differential distance ds between the points (x^1, x^2, x^3) and $(x^1 + dx^1, x^2 + dx^2, x^3 + dx^3)$ is given by the simple formula

$$ds^2 = dx^1{}^2 + dx^2{}^2 + dx^3{}^2,$$

but this is highly special; in general coordinates we have

$$ds^2 = \sum_{m=1}^3 \sum_{n=1}^3 g_{mn}(x^1, x^2, x^3) dx^m dx^n, \quad (37)$$

where the g 's are functions which depend upon the particular coordinate system under consideration. It is understood that $g_{mn} = g_{nm}$. Henceforth, we shall write (37) in the form

$$ds^2 = g_{mn}(x^1, x^2, x^3) dx^m dx^n, \quad (38)$$

and we shall observe this general rule throughout: *When the same literal index occurs twice in a term, once as a subscript and once as a superscript, that term is understood to be summed for the three values of the index.*

We now have the result

$$v^2 = [ds/dt]^2 = g_{mn}(x^1, x^2, x^3) \dot{x}^m \dot{x}^n,$$

and

$$m_0 c^2 (1 - v^2 c^{-2})^{1/2} = m_0 c^2 [1 - c^{-2} g_{mn} \dot{x}^m \dot{x}^n]^{1/2}.$$

The function $V(x^1, x^2, x^3, t)$ is a scalar. That is to say, when the coordinate system is changed, the first three arguments of the function are replaced by their expressions in terms of the new coordinates, and so we obtain a function which is of a new analytical form, but which has the same value as the original function at each point of space.

Now we consider the expression

$$A_1 \dot{x}^1 + A_2 \dot{x}^2 + A_3 \dot{x}^3.$$

In rectangular coordinates this is the scalar product of the vectors (A_1, A_2, A_3) and $(\dot{x}^1, \dot{x}^2, \dot{x}^3)$. The expression retains its form and interpretation

under changes of the coordinate system, provided (as the notation implies) (A_1, A_2, A_3) is treated as a covariant vector.¹⁵

With these understandings as to the significance of the symbolism, we can now write down the following general expressions for the Lagrangian function L in the relativistic and Newtonian cases, respectively,

$$L = -m_0 c^2 [1 - c^{-2} g_{mn} \dot{x}^m \dot{x}^n]^{1/2} - V + A_m \dot{x}^m,$$

$$L = -m_0 c^2 + \frac{m_0}{2} g_{mn} \dot{x}^m \dot{x}^n - V + A_m \dot{x}^m.$$

These hold for any coordinate system; and from the appropriate one of these, and the Lagrangian equations

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{x}^n} - \frac{\partial L}{\partial x^n} = 0,$$

we obtain the relativistic or Newtonian differential equations of motion in any coordinates.

Now let us consider the Hamiltonian canonical equations.

We have already agreed to consider (A_1, A_2, A_3) as a covariant vector. We now make the same convention in regard to (π_1, π_2, π_3) . Then it readily follows that the equations

$$\frac{\partial L}{\partial \dot{x}^n} = \pi_n \quad (40)$$

¹⁵ Suppose that with a point P (which may be either a special point or a typical point), and with each coordinate system, we have associated an ordered triple of numbers.

If the triples of number (a_1, a_2, a_3) and (a_1', a_2', a_3') associated, respectively, with any two coordinate systems (x^1, x^2, x^3) and (x^1', x^2', x^3') satisfy the relations

$$a_{m'} = \frac{\partial x^n}{\partial x^{m'}} a_n,$$

the numbers (a_1, a_2, a_3) are said to be the components of a covariant vector in the coordinate system (x^1, x^2, x^3) . (It is understood, of course, that the partial derivatives are evaluated at the point P .)

On the other hand, if the triples of numbers (a^1, a^2, a^3) and $(a^{1'}, a^{2'}, a^{3'})$ associated with the typical coordinate systems (x^1, x^2, x^3) and $(x^{1'}, x^{2'}, x^{3'})$ satisfy the relations

$$a^{m'} = \frac{\partial x^{m'}}{\partial x^n} a^n,$$

the numbers (a^1, a^2, a^3) are said to be the components of a contravariant vector in the coordinate system (x^1, x^2, x^3) .

These concepts agree only in part with the ones used in the elementary theory of vectors. From our present standpoint, the only vectors used in the elementary theories are those which are defined with reference to rectangular coordinate systems. When other coordinate systems are used (e.g. cylindrical coordinates), the vectors, defined in terms of rectangular coordinates, are merely resolved along the tangents to the coordinate curves. The components obtained in this way are not the same as the components considered in the tensor calculus, which we are using here.

are tensor equations; and since they hold when the coordinates are rectangular, they hold for all coordinate systems.¹⁶

We let g^{mn} denote g^{-1} times the cofactor of the element g_{mn} in the determinant

$$g = \begin{vmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{vmatrix}.$$

Now we write

$$H = c[m_0^2 c^2 + g^{mn}(\pi_m - A_m)(\pi_n - A_n)]^{1/2} + V \quad (41)$$

for the relativistic case, and

$$H = m_0 c^2 + (2m_0)^{-1} g^{mn}(\pi_m - A_m)(\pi_n - A_n) + V \quad (41')$$

for the Newtonian case. We see that these expressions specialize into the ones given earlier for the Hamiltonian function when the coordinates are rectangular.

H , L , and $\pi_n \dot{x}^n$ are all scalars. Consequently, the equation

$$H + L = \pi_n \dot{x}^n \quad (42)$$

is a tensor relation; and since it holds when the coordinates are rectangular, it holds for all coordinate systems.

The Lagrangian equations can be written in the form

$$\dot{\pi}_n = \frac{\partial L}{\partial x^n}. \quad (43)$$

Let us consider the variation of the function L resulting from small variations of the x 's and \dot{x} 's. By (40) and (43), we have the relation

$$\begin{aligned} \delta L &= \frac{\partial L}{\partial x^n} \delta x^n + \frac{\partial L}{\partial \dot{x}^n} \delta \dot{x}^n \\ &= \dot{\pi}_n \delta x^n + \pi_n \delta \dot{x}^n \\ &= \delta(\pi_n \dot{x}^n) + (\dot{\pi}_n \delta x^n - \dot{x}^n \delta \pi_n). \end{aligned} \quad (44)$$

It follows from (42) and (44) that the variation of H resulting from small variations of the x 's and the π 's is given by the formula

$$\delta H = \dot{x}^n \delta \pi_n - \dot{\pi}_n \delta x^n.$$

¹⁶ The argument is explained in detail in the works on the tensor calculus cited in the bibliography.

From this it follows that we have the Hamiltonian canonical equations

$$\dot{x}^n = \frac{\partial H}{\partial \pi_n}, \quad \dot{\pi}_n = -\frac{\partial H}{\partial x^n},$$

in any coordinate system.

We have already seen how to state Hamilton's principle in terms of general coordinates.

In the relativistic case the principle of least action takes the form: *The particle moves, in a static field of force of the type (4), and with the prescribed total energy E, in such a curve that the value of the integral*

$$\int_{(x^1)_1}^{(x^1)_2} \left(\left[g_{mn} \frac{dx^m}{dx^1} \frac{dx^n}{dx^1} \right]^{1/2} [(E - V)^2 c^{-2} - m_0^2 c^2]^{1/2} + A_m \frac{dx^m}{dx^1} \right) dx^1,$$

with the limits of integration held fixed, is stationary with respect to infinitesimal variations of the trajectory which leave the end points unaltered. The corresponding form of the principle for the Newtonian case is obvious.

We are now in a position to dispose very quickly of the problem of formulating the Hamilton-Jacobi theory in terms of general curvilinear coordinates.

The general form of the Hamiltonian function being given by (41) (for the relativistic case) or (41') (for the Newtonian case), we can at once write down the partial differential equation

$$\frac{\partial W}{\partial t} + H(x^1, x^2, x^3, \partial W/\partial x^1, \partial W/\partial x^2, \partial W/\partial x^3, t) = 0. \quad (45)$$

Let

$$W = W(x^1, x^2, x^3, t, \alpha^1, \alpha^2, \alpha^3)$$

represent the complete solution of (45), without the irrelevant additive constant of integration.

Our chief problem is that of proving that the functions $x^n(t, \alpha^1, \alpha^2, \alpha^3, \beta_1, \beta_2, \beta_3)$, $\pi_n(t, \alpha^1, \alpha^2, \alpha^3, \beta_1, \beta_2, \beta_3)$ determined by the equations

$$\frac{\partial W}{\partial \alpha^n} = \beta_n, \quad \frac{\partial W}{\partial x^n} = \pi_n,$$

where the β 's are further arbitrary constants, satisfy the canonical equations

$$\dot{x}^n = \frac{\partial H}{\partial \pi_n}, \quad \dot{\pi}_n = -\frac{\partial H}{\partial x^n}.$$

Now, referring to the proof given in Section VIII for the special case of rectangular coordinates, we see at once that nothing in the proof depends

upon the special forms which the Hamiltonian function and equation (45) assume in those coordinates. Hence the proof already given applies immediately to the present general case.

Similar remarks apply also to the case in which H does not involve the time explicitly, and in which we write

$$H = S - Et,$$

where S is the complete solution (without the additive arbitrary constant) of the equation

$$H(x^1, x^2, x^3, \partial S/\partial x^1, \partial S/\partial x^2, \partial S/\partial x^3) = E.$$

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CHAPTER I

Quartz Crystal Applications

By W. P. MASON

1.1. INTRODUCTION—PURPOSE OF SERIES

THIS paper is the first one of a series of papers dealing with quartz crystals, their applications in oscillators, filters, and transducers, and the methods of producing them from the natural crystal. This series was prepared first to make available to the Western Electric Co. and other manufacturers of quartz crystals some of the specialized knowledge on these subjects that has been acquired at the Bell Telephone Laboratories. Sufficient interest has been expressed in this series to make it desirable to publish them in serial form.

This first paper in the series is a general introductory paper covering the application of crystals to oscillators, filters and transducers. An appendix is given which discusses the elastic and electric relations in crystals and gives recent measurements of the elastic constants, their temperature coefficients, and the piezoelectric constants of quartz. This paper is followed by more detailed papers by Messrs. Bond, Willard, Sykes, McSkimin, and Fair which give consideration to quartz crystallography; determination of orientation by optical methods, X-ray methods, and etching methods; the imperfections occurring in quartz crystals; modes of motion and their calculation; the dimensioning of crystals to avoid undesirable resonances; and the use of crystals in oscillators.

1.2 EARLY HISTORY OF PIEZOELECTRICITY AND ITS APPLICATIONS

The direct piezoelectric effect was discovered by the brothers Curie in 1880. They measured the effect first for a quartz crystal by putting a weight on the surface and measuring the charge appearing on the surface, the magnitude of which was proportional to the applied weight. A simple model for demonstrating this effect can be made by using a large piece of Rochelle salt cut with its length 45° from the Y and Z crystallographic axes and placing tinfoil electrodes normal to the X axis. If these electrodes are connected to a neon lamp, and the crystal is compressed by hitting it with a hammer, a charge is generated on the surface and a voltage applied to the lamp sufficient to break it down. In fact as much as 2000 volts can be generated by striking the crystal hard.

The converse piezoelectric effect was predicted in 1881 by the French physicist Lippmann on the basis of the principle of conservation of electricity. It was verified in the same year by the brothers Curie. In this effect a crystal is strained when a voltage is applied to it. The effect can be demonstrated by a model which consists of two thin pieces of Rochelle salt poled so that one expands when the voltage is applied and the other contracts. The result is—as in a bimetallic thermostat—the crystal bends. For crystals 10 mil inches thick and 4 inches long, a ninety-volt battery applied causes a displacement of a quarter of an inch or more of the end of the unit. Reversing the voltage reverses the direction of the displacement. The Curies constructed a bimorph unit of this type out of quartz and used it practically to measure voltage by measuring the displacement of the end of the crystal. By connecting the leads of an electrometer to the terminals, they could measure force applied by measuring the amount of charge generated at the terminals.

Outside of this use which was quite minor, the piezoelectric effect remained a scientific curiosity until the war of 1914–1918. It did inspire, however, considerable scientific speculation. Lord Kelvin in 1893 proposed a model for explaining the piezoelectricity of quartz and was able to calculate approximately the value of the piezoelectric constant. This model is discussed briefly in the next section. He also constructed and demonstrated a “piezoelectric pile” made from small spheres of zinc and copper, to illustrate the effect. At about the same time (1890–1892) Voigt published a series of papers followed by a book “Lehrbuch der Kristall Physik” (1910) in which the stresses, strains, fields and polarizations of piezoelectric crystals are related in mathematical form. These mathematical expressions (which are discussed further in the appendix) form a basis for the development of the properties of oriented crystals as discussed in section 1.5.

During the war of 1914–1918, Professor Langevin in Paris was requested by the French Government to devise some way of detecting submarines by acoustic waves they produce in water. After trying several devices he finally found that piezoelectric quartz plates could be used for that purpose. His device, which is shown in Fig. 1.1, consisted essentially of a mosaic of quartz which has the property that when a voltage is applied the crystal will expand and send out a longitudinal wave. Similarly, if a wave strikes it, the wave will set the quartz in vibration and generate a voltage which can be detected by vacuum tube devices. Langevin did not get his device perfected till after the war so it was not used at that time to detect submarines. Similar devices have, however, been used in this war. Langevin’s original apparatus was used extensively as a sonic depth finder. In this use a pulse is generated which is recorded directly on a moving record and

is also sent out into the ocean. It strikes the bottom and is reflected back causing another mark to appear on the record. Knowing the difference in time and the velocity of sound in sea water, the distance to the bottom can be measured. A typical record is shown in Fig. 1.2. The top record shows the contour of the sea bottom while the second record shows the reflections from a school of fish.

At about the same time, Nicolson at Bell Telephone Laboratories was experimenting with Rochelle salt, another piezoelectric material having a

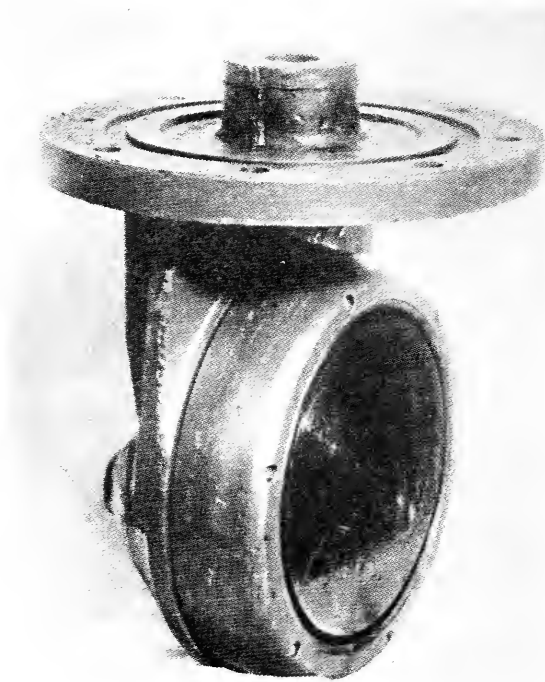


Fig. 1.1—Ultrasonic transmitting apparatus

much larger piezoelectric effect than quartz. He constructed and demonstrated loud speakers, microphones, and phonograph pick-ups using Rochelle salt.¹ He was also the first one to control an oscillator by means of a crystal—in this case Rochelle salt—and has the primary crystal oscillator patent.² Nicolson's circuit is shown in Fig. 1.3. The crystal is effectively in a path between the resonating coil in the output and the grid, since the electrode

¹ "The Piezoelectric Effect in the Composite Rochelle Salt Crystal"—A. M. Nicolson, *Proc. A. I. E. E.* 1919, 38, 1315.

² See Patent 2,212,845 filed April 10, 1918; issued Aug. 27, 1940.

3 is in the direction of the smallest piezoelectric effect in Rochelle salt and contributes little to the action. If terminal one to the tapped coil is at the top of the coil, the circuit although employing a three electrode crystal connection, effectively reduces to *B* in which the crystal is in the feedback path from plate to grid. On the other hand, if the tap is effectively at the bottom of the coil, the crystal is between grid and ground and feedback occurs through a distributed capacity from plate to grid. Both of these

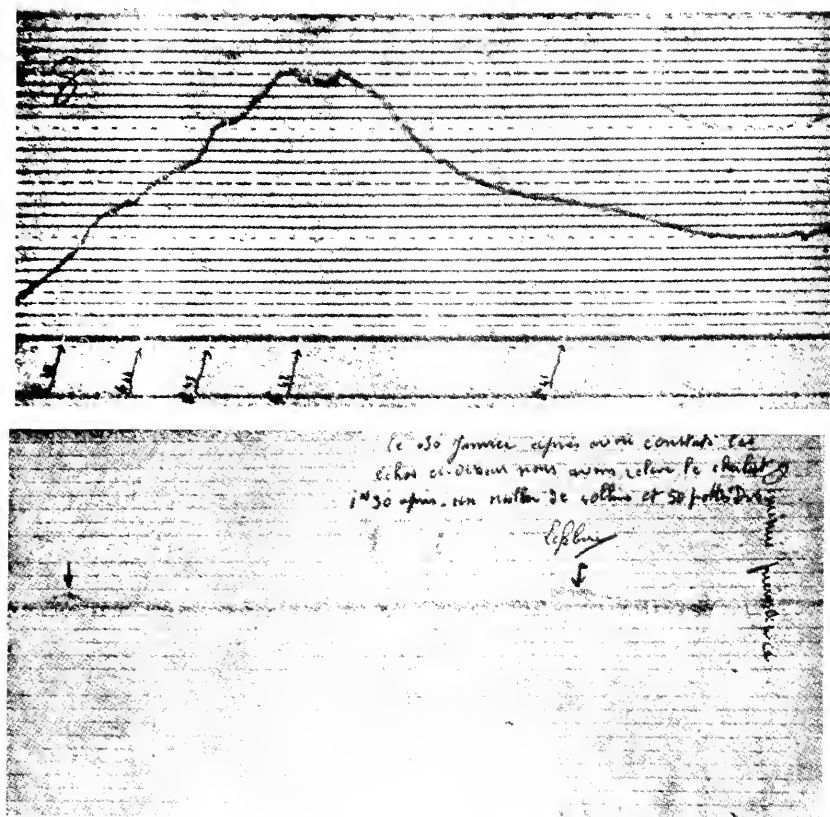


Fig. 1.2—Ocean contour curves

circuits *B* and *C* are widely used in oscillators of Pierce. Prof. G. W. Pierce published a circuit similar to circuit *B*, having a two electrode quartz crystal connected between grid and plate.³

In 1921, Professor Cady at Wesleyan University first showed⁴ that quartz

³"Piezoelectric Crystal Resonators and Crystal Oscillators Applied to the Precision Calibration of Wave Meters." G. W. Pierce, *Amer. Acad. of Arts and Sciences*, Oct. 1923, 81-106.

⁴"The Piezoelectric Resonator" W. G. Cady, *Proc. I. R. E.* 1922, 10 83.

crystals could be used to control oscillators and that much more stable oscillators could be obtained in this fashion. These were later applied to controlling the frequency of broadcasting stations and radio transmitters in general and about 1925 Mr. W. A. Marrison applied them to obtain a very constant frequency and time standard, which is now used considerably by the Bell System, by radio broadcasting systems, and by power companies. The oscillators were subsequently improved by using crystals with small temperature coefficients as described in Section V. At the present time

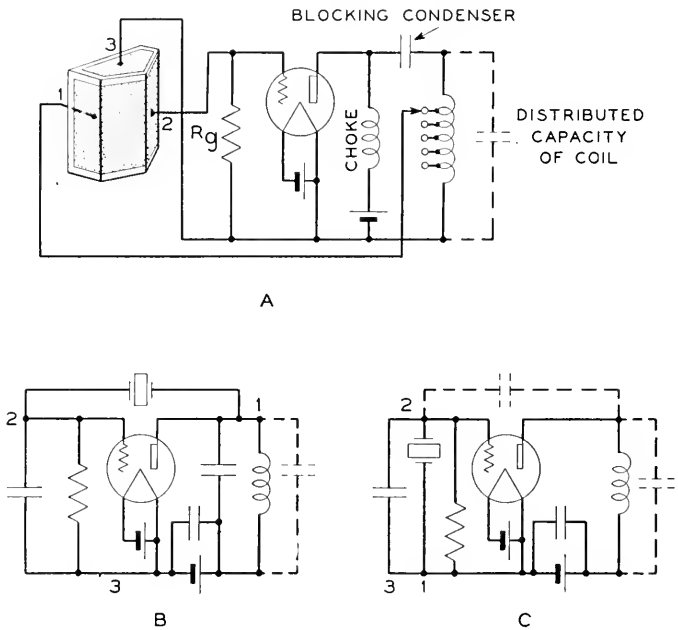


Fig. 1.3—Nicolson's oscillator circuit

crystal controlled oscillators are used very widely in radio military and commercial applications.

Another large use for quartz crystals is their use in providing very selective filters. Probably the first use of a crystal to select a narrow frequency range was made by Cady.⁴ Using the very sharp maximum in current through a crystal at its resonant frequency, Cady proposed the use of such a crystal as a wave standard. This is equivalent to the use of a crystal as a tuned circuit. By incorporating a crystal in a three-winding transformer and balancing out the static capacity of the crystal by an auxiliary condenser, W. A. Marrison⁵ improved the selecting ability of a crystal used

⁵ Patent 1,994,658, filed June 7, 1927, issued March 19, 1935.

as a narrow band filter. At about the same time, L. Espenschied,⁶ taking advantage of the knowledge of the equivalent electrical circuit of a crystal given previously by Van Dyke,⁷ showed how to combine other electrical elements with crystals in ladder form to obtain band-pass filters. It was not, however, until the crystals were combined with auxiliary coils and condensers into the form of resistance compensated lattice type networks⁸ that much progress was made in achieving the wide pass-band characteristics necessary for telephone and radio communication. Such filters have provided very selective devices which are able to separate one band of speech frequencies from another band different by only a small frequency percentage from the desired band. This property makes it possible to space channels close together with only a small frequency separation up to a high frequency, and such filters have had a wide use in the high-frequency carrier systems, and in the coaxial system which transmits more than 480 conversions over one pair of conductors. In radio systems such filters have been used extensively in separating one side band from the other in single side-band systems.

In conclusion we can say, that the science of piezoelectricity was born about 62 years ago, lay dormant for nearly 40 years, but during the last 25 years has advanced at such a rate that it can be regarded as one of the foundation stones of the whole communication art.

1.3. THEORY OF PIEZOELECTRIC MATERIALS

Piezoelectric crystals are of interest in communication circuits because they possess three properties. These properties are: (1) the piezoelectric effect provides a coupling between the electrical circuit and the mechanical properties of the crystal; (2) the internal dissipation of most crystals and particularly quartz crystals is very low, and the density and elastic constants of the crystals are very uniform, so that a crystal cut at a given orientation always has the same frequency constant; and (3), at specified orientations crystals can be cut which have advantageous mechanical properties such as a small change in frequency with a change in temperature, or a freedom from secondary modes of motion. It is the purpose of this section to discuss the first property, the coupling between the electrical and mechanical properties of the crystal.

The piezoelectricity of quartz and other materials is due to the fact that

⁶ Patent 1,795,204, filed Jan. 3, 1927, issued August 8, 1933.

⁷ K. S. Van Dyke; Abstract 52, *Phys. Rev.* June 1925; *Proc. I. R. E.* June 1928.

⁸ See "Electrical Wave Filters Employing Quartz Crystals as Elements," W. P. Mason, *B. S. T. J.*, Vol. XIII, p. 405, July 1934; "Resistance Compensated Band Pass Crystal Filters for Unbalanced Circuits," *B. S. T. J.*, Vol. XVI, p. 423, Oct. 1937; "The Evolution of the Crystal Wave Filter," O. E. Buckley, *Jour. App. Phys.*, Oct. 1936; and Patents 1,921,035; 1,967,249; 1,967,250; 1,969,571; 1,974,081; 2,045,991; 2,094,044.

a pressure which deforms the crystal lattice causes a separation of the centers of gravity of the positive and negative charges thus generating a dipole moment (product of the value of the charges by their separation) in each molecule. How this separation can cause a coupling to an electrical circuit is illustrated by Fig. 1.4 which shows a crystal with metal electrodes normal to the direction of charge separation. If we short-circuit these electrodes and apply a stress which causes the centers of gravity of the charges to separate, free negative charges in the wire will be drawn toward the electrode in the direction of positive charge separation, and free positive charges in the wire will be drawn to the electrode in the direction of negative charge displacement until the crystal appears to be electrically neutral by any test conducted outside the crystal. When the stress is released the charges in the wire will flow back to their normal position. If, during the process, we connect an oscillograph in the short-circuited wire, there will be a pulse of current in one direction when the stress is applied and a pulse in the oppo-

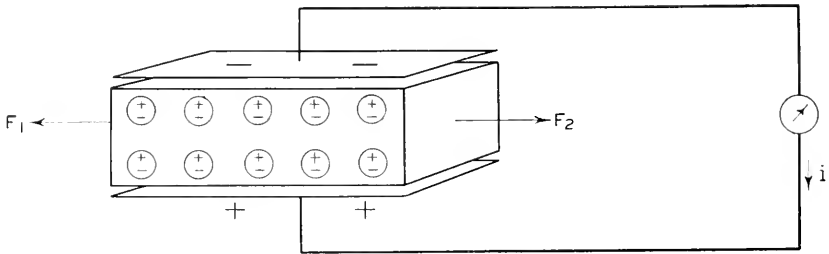


Fig. 1.4—Method for transforming mechanical energy into electrical energy in a crystal

site direction when the stress is released. By putting a resistance in the connecting wire and applying a sinusoidal stress to the crystal, an alternating current will flow through the load and consequently mechanical power will be changed into electrical power. Using the converse effect, a source of alternating voltage in the electrical circuit will produce an alternating stress in the crystal, and if this is working against a mechanical load, the electrical energy will be changed into mechanical energy.

To apply this concept to quartz let us consider Fig. 1.5, which represents the approximate arrangement of molecules in a quartz molecule. Lord Kelvin's explanation of the piezoelectricity of quartz is the following:

"The diagram (Fig. 1.5A) shows a crystalline molecule surrounded by six nearest neighbors in a plane perpendicular to the optic axis of a quartz crystal. Each silicon atom is represented by + (plus) and each oxygen double atom - (minus). The constituents of each cluster must be supposed to be held together in stable equilibrium in virtue of their chemical affinities. The different clusters, or crystalline molecules, must be supposed to be relatively mobile before taking

positions in the formation of a crystal. But we must suppose, or we may suppose, the mutual forces of attraction (or chemical affinity), between the silicon of one crystalline molecule and the oxygen of a neighboring crystalline molecule, to be influential in determining the orientation of each crystalline molecule, and in causing disturbance in the relative positions of the atoms of each molecule, when the crystal is strained by force applied from without.

“Imagine now each double atom of oxygen to be a small negatively electrified particle, and each atom of silicon to be a particle electrified with an equal quantity of positive electricity. Suppose now such pressures, positive and negative, to be applied to the surface of a portion of crystal as shall produce a simple elongation in the direction perpendicular to one of the three sets of rows. This strain is indicated by the arrow heads in Fig. 1.5A and is realized to an exaggerated extent in Fig. 1.5B.

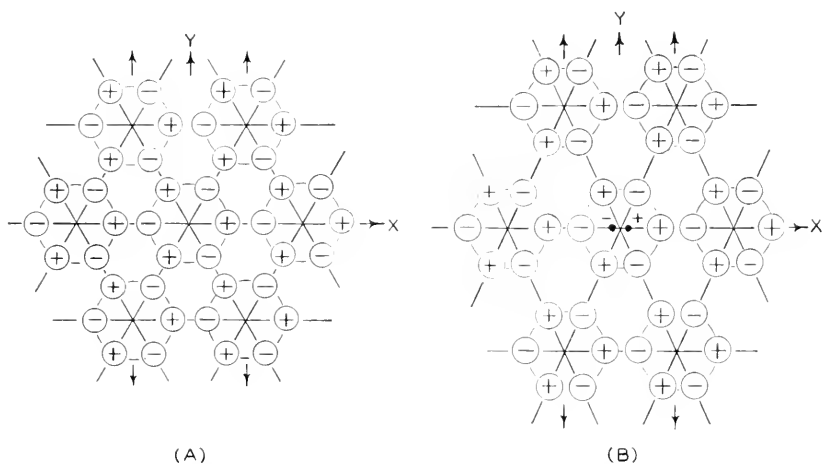


Fig. 1.5—Kelvin's model of quartz molecules

“This second diagram shows all the atoms and the centers of all the crystalline molecules in the positions to which they are brought by the strain. Both diagrams are drawn on the supposition that the stiffness of the relative configuration of atoms of each molecule is slight enough to allow the mutual attractions between the positive atoms and the negative atoms of neighboring molecules to keep them in line through the centers of the molecules, as Fig. 1.5A shows for the undisturbed condition of the systems, and Fig. 1.5B for the system subjected to the supposed elongation. Hence two of the three diameters through atoms of each crystalline molecule are altered in direction, by the elongation, while the diameter through the third pair of atoms remains unchanged, as is clearly shown by Fig. 1.5B compared to Fig. 1.5A.

“Remark, first that the rows of atoms, in lines through the centers of the crystalline molecules, perpendicular to the direction of the strain, are shifted to parallel positions with distances between the atoms in them unchanged. Hence the atoms in these rows contributed nothing to the electrical effect. But in parallel to these rows, on each side of the center of each molecule, we find two pairs of atoms whose distances are diminished.

“This produces an electrical effect which, for great distances from the molecule, is calculated by the same formula as the magnetic effect of an infinitesimal bar magnet whose magnetic moment is numerically equal to the product of the quantity of electricity of a single atom into the sum of the diminutions of the two distances between the atoms of the two pairs under consideration. Hence, denoting by N the number of crystalline molecules per unit bulk of the crystal; by b the radius of the circle of each crystalline molecule; by q the quantity of electricity of each of the six atoms or double atoms, whether positive or negative; by θ the change of direction of each of the two diameters through atoms which experience change of direction; and by μ the electric moment developed per unit volume of the crystal, by the strain which we have been considering and which is shown in Fig. 1.5B; we have

$$\mu = N q 4 b \theta \cos 30^\circ = 2\sqrt{3} N b q \theta \quad (1.1)''$$

Kelvin's model shows some of the symmetry properties of quartz. The axis marked X is the X or electrical axis of the crystal. The Z or optic axis is normal to the plane of the paper. The Y or mechanical axis is the axis

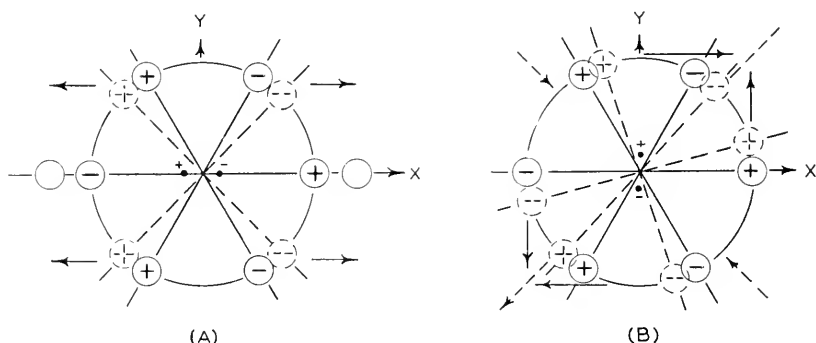


Fig. 1.6—Longitudinal and shear strains applied to a quartz molecule

along which the stress is applied. It is obvious that if we rotate the direction of the applied stress by 120° , a similar separation of charges at right angles to the stress will occur. There are then three electrical axes and three mechanical axes so that the optic axis can be regarded as an axis of threefold symmetry for the crystal.

As can be shown from an extension of Kelvin's model there are two other types of stresses that will produce a charge separation normal to the axis. Suppose that we stress the crystal along the X or electrical axis as shown by Fig. 1.6A. Applying the same reasoning as before, we see that the apex molecules are separated farther apart without changing the separation between the other molecules. This results in a separation of the centers of gravity of the positive and negative charges, with the negative charges moving toward the left and the positive charges moving toward the right. The separation is still along the electric axis, but is in the opposite direction

to that caused by a stress along the Y axes. A detailed analysis shows that the value of the electrical separation moment (dipole moment) for a stress along either axis is the same value but the sign is reversed. A longitudinal stress then can only produce a charge moment along the X or electrical axis which is the origin of the name electrical axis.

If, however, we introduce a different kind of stress known as a shearing stress, a separation of centers of charges can occur along the mechanical or Y axis of the crystal. A simple shear stress is one in which forces act normal to the direction of space separation rather than along it as shown, for example, by the two opposed arrows normal to the mechanical axis in Fig. 1.6B. Such a shear does not occur in nature, but rather a pure shear which consists of two simple shears which are directed in such a way as to produce no rotation of the molecule as a whole about its axis. If we resolve these force components along directions 45° from the crystal axes, a pure shear is equivalent to an extensional stress along one 45° axis and a compressional stress along the other 45° axis. Such a stress would cause the charges to be displaced from their normal position, as shown in the figure. This causes the center of positive charge to be displaced downward along the mechanical or Y axis of the crystal while the center of negative charge is displaced upward along the mechanical axis.

These three relations can be written in the form

$$P_x = -d_{11}X_x + d_{11}Y_y; \quad P_y = 2d_{11}X_y \quad (1.2)$$

where P_x is the polarization or charge per unit area developed on an electrode surface normal to the X axis due to the applied longitudinal stresses X_x and Y_y , while P_y is the polarization normal to the Y axis caused by the shearing stress X_y . d_{11} is the piezoelectric constant and equations (1.2) show that the magnitudes of all these effects are closely related. In addition to these three major piezoelectric effects, quartz has two smaller effects which, since they are connected with the distribution of molecules in the YZ and XZ planes, cannot be demonstrated by the figures given previously. The complete piezoelectric relations are then

$$P_x = -d_{11}X_x + d_{11}Y_y - d_{14}Y_z; \quad P_y = d_{14}Z_x + 2d_{11}X_y \quad (1.3)$$

where Y_z and Z_x are respectively similar shearing stresses exerted in the YZ and ZX planes respectively. The best values for the d_{11} and d_{14} constants are respectively

$$d_{11} = -6.76 \times 10^{-8} \frac{\text{e.s.u.}}{\text{dyne}}; \quad d_{14} = 2.56 \times 10^{-8} \frac{\text{e.s.u.}}{\text{dyne}} \quad (1.4)$$

as obtained by recent measurements for a number of X cut and rotated X -cut crystals discussed in appendix A.

Quartz is not the only type of crystal which is piezoelectric. In fact there are hundreds of crystals that exhibit this property. Whether a crystal is piezoelectric or not and the relation between the stresses and charge displacements depend on the symmetry of the crystal. Whenever there is a center of symmetry; that is, when the properties of the crystal are the same in both directions along any line, no piezoelectric effect can occur. This is illustrated by the simple arrangement of atoms shown by Fig. 1.7. It is obvious that no symmetrical application of forces can separate the center of gravity of the charges and hence such a crystal will not be

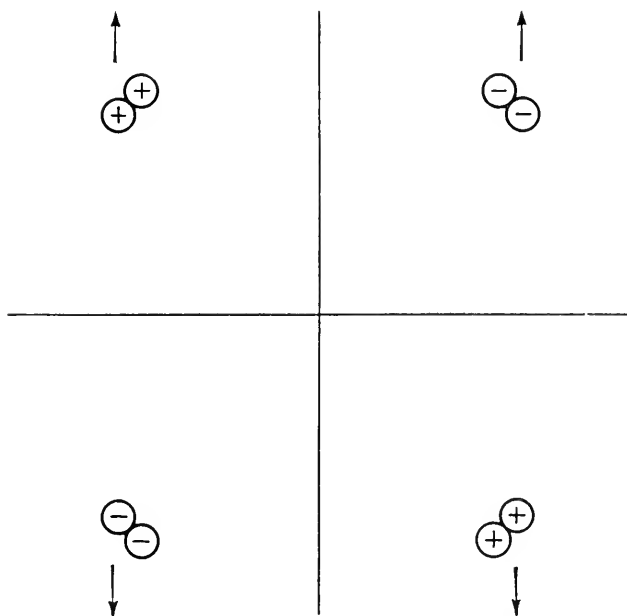


Fig. 1.7—Crystal with a center of symmetry

piezoelectric. Crystals can be classified into 32 possible classes on the basis of the symmetry they exhibit; and of these 32 classes, 20 are piezoelectric and 12 are not. As illustrated by the model for quartz, the response to different types of force depends solely on the type of symmetry existing in the crystal.

1.4. ELECTRICAL IMPEDANCE AND LOW DISSIPATION IN CRYSTALS

The first crystal used by Cady in controlling oscillators, was a crystal cut with its major faces perpendicular to the X or electrical axis and with its length along the Y or mechanical axis. Referring to Fig. 1.5B, we see that a stretch along the Y axis will produce a charge displacement along the E

or X axis. Conversely, a voltage applied along the X axis will produce a charge displacement and consequently a mechanical stress along the Y axis which will set up a longitudinal wave along the mechanical axis. As shown by Fig. 1.8, the type of motion resulting when the crystal is free to move on the ends is one in which the center is stationary and the ends move in and out. The crystal can then be clamped at its center or mounted from leads soldered to electrodes deposited on the surface.

In using a crystal in an electrical circuit it is desirable to have an electrical equivalent circuit which will represent the electrical impedance as measured from the terminals of the crystal. Such a circuit⁹ is shown in Fig. 1.8. In

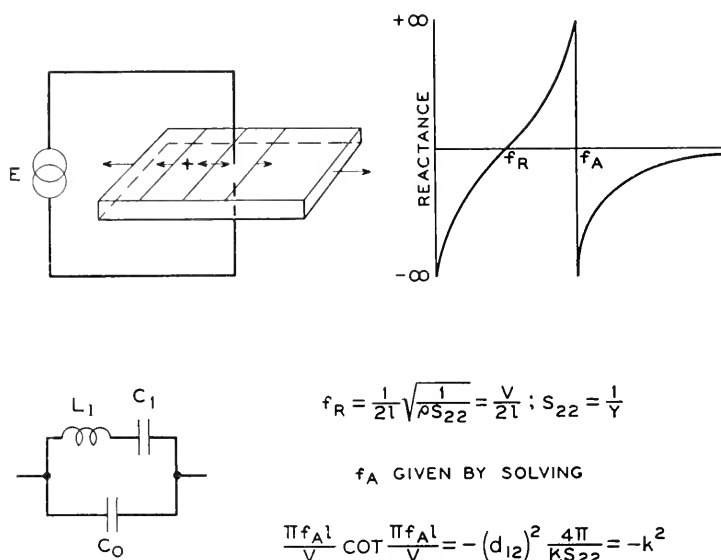


Fig. 1.8—Longitudinally vibrating crystal and electrical equivalent circuit

this representation C_0 is the static capacity of the crystal which would be measured if the crystal were held from moving. C_1 is the stiffness of the crystal transformed into electrical terms through the piezoelectric effect of the crystal, while L_1 is the effective mass of the crystal also transformed into electrical terms. The resonant frequency of the crystal is determined by the Young's modulus and density of the bar according to the usual formula:

$$f_R = \frac{1}{2l} \sqrt{\frac{Y_0}{\rho}} \tag{1.5}$$

⁹ Circuits of this type for representing the electrical impedance of a crystal were first derived by Van Dyke; see reference (7). The method of deriving them from Voigt's equations is discussed in the appendix.

where Y_0 is the value of Young's modulus along the bar, ρ the density, and l the length of the bar.

A significant feature of the equivalent circuit is that there is always a definite ratio between C_0 and C_1 for a given crystal cut. This is really a measure of the ratio of electrical to mechanical energy stored in the crystal under an applied constant voltage. The reactance characteristic of the network is shown by Fig. 1.8 as a function of frequency. The reactance starts out as a negative reactance at low frequencies, becomes zero at the resonant frequency f_R , becomes positive and very large at the anti-resonant frequency f_A , then again becomes a negative reactance. Due to the high ratio of C_0 to C_1 existing in a crystal the separation between f_A and f_R becomes very small. For example, for an AT crystal this ratio is around 200 and the separation of f_A from f_R is only a quarter of a per cent in frequency. Since it can be shown that an oscillator will only oscillate on the positive reactance part of the crystal characteristic, the narrow separation between resonant and anti-resonant frequencies explains why a crystal can act as such a good stabilizer for an oscillator. As long as the crystal resonance itself does not change with temperature or other conditions, the very sharp reactance frequency characteristic will not allow the oscillator frequency to change much with a change in oscillator voltage, tube conditions, or any other changes which are likely to cause a change in frequency for a coil and condenser controlled oscillator.

Strictly speaking, a resistance should be added in series with the inductance L_1 to represent the internal losses in the crystal, the loss of energy at the clamping points and the loss of energy due to setting up of air waves by the crystal motion. However, the value of this resistance and the amount of energy lost is very small in a crystal compared to what the losses are in purely electrical elements. A demonstration which shows this effect and shows that most of the losses of a well mounted longitudinally vibrating crystal are acoustic losses caused by setting up air waves in the vicinity of the crystal, can be made by using two oscillators, one a fixed oscillator and the other one controlled by a resonant circuit or a crystal. The fixed oscillator may be set at 99 kilocycles and the crystal oscillator controlled by a 100-kc crystal. The two will beat together giving the 1000-cycle note. When the battery is taken off the crystal oscillator, it continues to oscillate till the energy built up in the crystal is dissipated in the internal dissipation of the crystal. A good electrical circuit which has a ratio of reactance to resistance, or Q of the coil of 300 dies down almost instantaneously. For a crystal mounted in air it takes about half a second to become inaudible. This corresponds to a Q of 30,000 where Q is defined as the ratio of the reactance of the coil L_1 of Fig. 1.8 to the resistance. For a crystal mounted in a vacuum a much higher Q is obtained due to the elimination of the loss of energy by acoustic radiation. For such a crystal it takes eight

seconds to die down which corresponds to a Q of 330,000, which is about 1000 times as great as that for a good electrical circuit.

1.5. MODES OF MOTION AND CRYSTAL ORIENTATION TO PRODUCE LOW TEMPERATURE COEFFICIENT CRYSTALS

As mentioned previously the first crystal cut used in oscillators was a longitudinal vibration along the Y or mechanical axis excited by a field applied

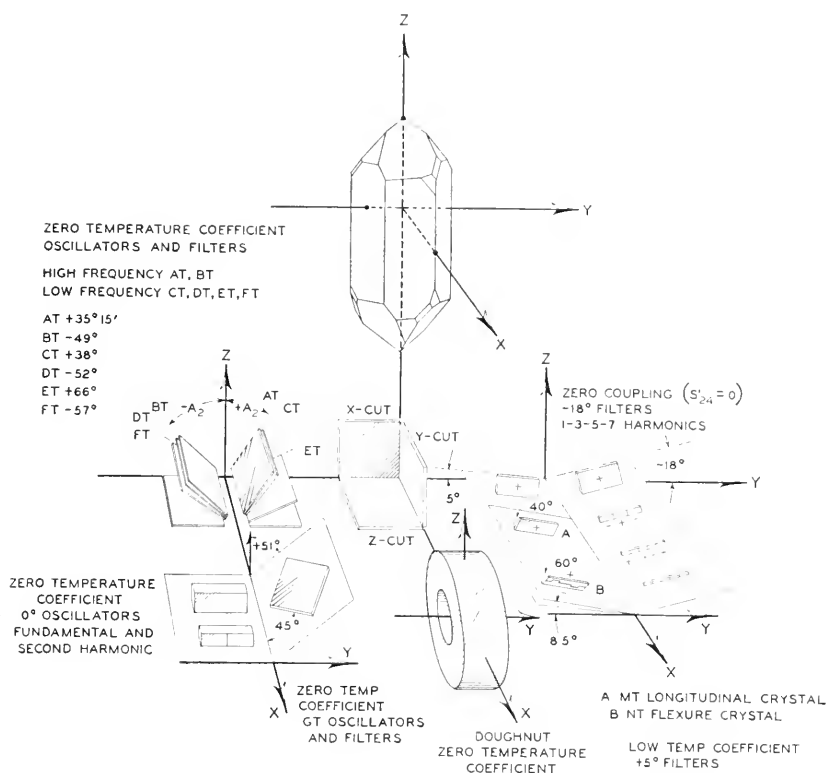


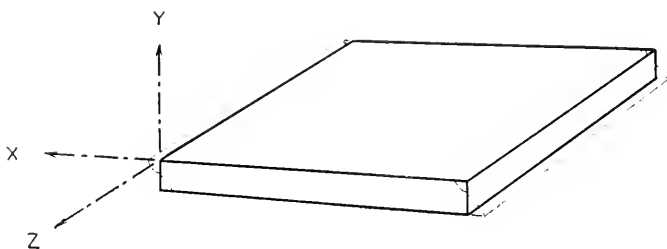
Fig. 1.9—Oriented quartz crystal cuts in relation to the natural crystal

along the electrical or X axis. This mode gives a good resonance free from other modes and a modification of it is now used in crystal filters. This modification, as shown by Fig. 1.9, (-18.5° filter crystal) consists in rotating the direction of the length by 18.5° from the Y or mechanical axis, about the X or electrical axis. As described previously¹⁰, the effect of this rotation is to eliminate the coupling between the desired longitudinal mode and the undesired face shear mode, thus simplifying the motion and eliminating an

¹⁰ "Electrical Wave Filters Employing Quartz Crystals as Elements," W. P. Mason, *B. S. T. J.*, Vol. XIII, p. 405 July 1934 or patent 2,173,589.

undesired resonance. However, to get a reasonably high frequency out of a length vibrating type of cut requires too small a length to be practical.

It was not long before crystal oscillators were controlled by thickness vibrating crystals whose frequencies were determined by the thickness of the crystals or by their smallest dimension. Referring to Fig. 1.6A, we see that the same X cut type of crystal will generate a vibration along the electrical or X axis when a field is applied along this axis. Since the thickness dimension can be made very small, a high frequency is obtainable. However, when the smallest dimension is used to control the frequency, a difficulty arises not present when the largest dimension is used to control the frequency, namely, that harmonics and overtone modes of all the lower frequency types of motion produce frequencies near the frequency of the thickness mode and it is difficult to pick out the desired mode. This was



$$\delta X = A \cos \frac{n\pi Y}{a} \cos 2n\pi f t$$

$$f = \frac{n}{2t} \sqrt{\frac{c_{66}}{\rho}}; \quad n=1, 3, 5; \quad c_{66} = \frac{c_{11} - c_{12}}{2}$$

Fig. 1.10—High frequency shear mode of motion

especially true for the thickness vibrating X cut crystal and led to its abandonment in favor of Y cut crystals vibrating in shear.

As seen from Fig. 1.6B, when a voltage is applied along the Y or mechanical axis, a shear vibration is produced which tends to change a square into a rhombus. For a large plate in which the edge dimensions are large compared to the thickness, the motion occurs as shown by Fig. 1.10. For such a plate the motion is perpendicular to the thickness, which is the direction of transmission of the wave, and hence a shear wave is sometimes called a transverse wave. The frequency of such a wave can be shown to be

$$f = \frac{1}{2t} \sqrt{\frac{c_{66}}{\rho}} \quad (1.6)$$

where t is the thickness of the plate, c_{66} is the shear stiffness constant and ρ the density. The use of Y cut plates considerably improved the per-

formance of oscillators since the plates do not have as many secondary modes of motion as do the X plates. They have, however, one drawback. The frequency increases about 86 parts in a million for every degree Centigrade increase in temperature. This requires regulating the temperature quite closely.

In order to improve on the performance of the Y cut crystal, investigations were made by Lack, Willard and Fair, Koga, Bechmann, Straubel and others¹¹ on how the properties of such crystals varied as the orientation angle of cutting blanks from the natural crystal was varied. As shown by Fig. 1.9, the crystals investigated all had one edge along the X or electrical axis with the normals making positive and negative angles with the Y axis. All of these crystals will have a component of field along the Y axis, which

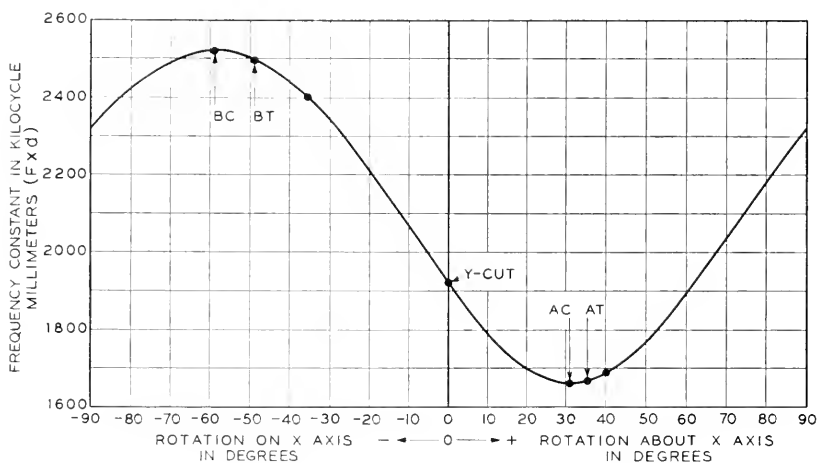


Fig. 1.11—Frequency constant of oriented Y cut crystals

will produce a shearing motion until the angles of cut approach 90 degrees from the Y axis. The smaller the angle, the more strongly will the shear mode be driven. However, advantageous elastic relationships can be obtained by using oriented cuts. As shown by Fig. 1.11, Lack, Willard and Fair found that the frequency constant of a rotated crystal expressed in kilocycle millimeters varied with angle of cut and that there was a minimum frequency at +31 degrees and a maximum at -59 degrees. It was subsequently pointed¹² out that these minimum and maximum points were significant angles in the elastic behavior of the crystal for they were the angles for

¹¹ "Some Improvements in Quartz Crystal Circuit Elements," F. R. Lack, G. W. Willard, I. E. Fair—*B. S. T. J.*, Vol. 13, pp. 453-463, July 1934; R. Bechmann—*HF Techn. u. El. Ak.* 44, 145 (1934); I. Koga—*Rep. of Rad. Res. i. Jap.* 6, 1 (1934); J. Straubel, *Z. tech. Physik.*, 35, 179, 1934.

¹² See patent 2,173,589.

which the high-frequency shear mode had zero coupling with the troublesome low-frequency shear mode system of vibrations. Crystals cut at these angles have a much cleaner frequency spectrum than *Y* cut crystals. Lack, Willard, and Fair also found that the temperature coefficient of frequency varied with angle as shown by Fig. 1.12. Starting from a high positive value for the *Y* cut, the coefficient becomes zero at an angle of $+35^\circ - 15'$ and -49° . The first angle cut is known as the *AT* cut and the second as the *BT* cut. Since the *AT* angle is nearer the *Y* cut, the piezo-electric constant is larger and it is more strongly driven than the *BT*. On the other

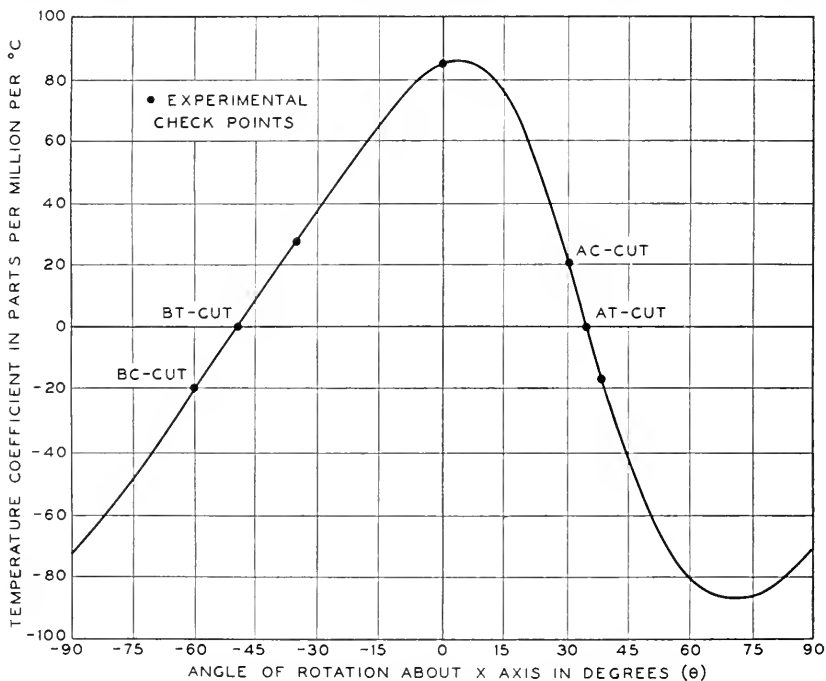


Fig. 1.12—Temperature coefficients of oriented *Y* cut crystals

hand, the *BT* has a higher frequency for the same thickness. Both crystals are near enough to the *AC* and *BC* cuts so that the systems of low-frequency shear modes are rather weakly driven. On the other hand, the shear mode of both crystals is rather strongly coupled to flexure modes of motion, as will be discussed by Mr. Sykes in a later chapter, and the crystal has to be exactly dimensioned in order that the flexure frequencies and other disturbing frequencies will not coincide with the desired shear mode.

Other oriented shear crystals for lower frequency work are the *CT* and *DT* crystals investigated by Willard and Hight. They are related to the *AT* and *BT* crystals as shown by Fig. 1.13. The plate on the right shows the

motion of an *AT* plate. If we were to increase the thickness dimension until the plate was nearly square, the *AT* motion would correspond to a face shear mode which should be controlled by the same elastic constants as the *AT* motion. At the same time in order to drive the crystal efficiently we could decrease the width until it became the thickness. This procedure would be the same as cutting a crystal at right angles to the *AT* and would suggest that by so doing we should obtain a low-frequency shear crystal with a low coefficient. Actually, Willard and Hight found that a crystal

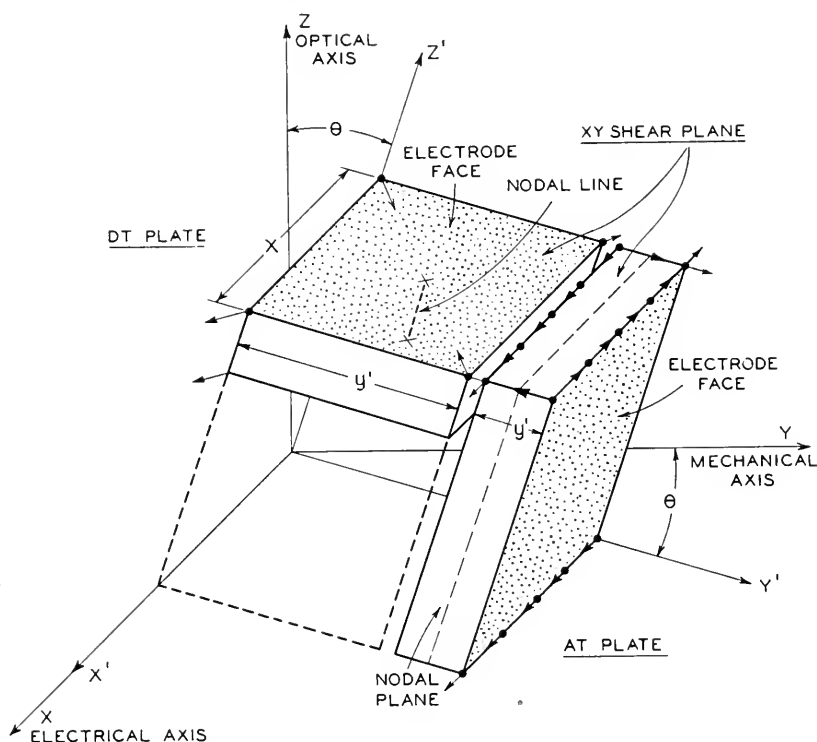


Fig. 1.13—Relation of *AT* and *DT* low temperature coefficient crystals

at -52° or 87° from the *AT* would give a low coefficient. This crystal was called the *DT*. Similarly, a crystal cut at $+38^\circ$ or 87° from the *BT* would also give a low coefficient and this has been called the *CT*. It can be shown that a component of the voltage applied along the mechanical axis will drive the shearing type of motion. The *CT* is larger for the same frequency and more strongly driven than the *DT*. It is extensively used in controlling oscillators in the frequency range from 200 to 500 kilocycles.

Quite a few other crystal cuts have been discovered as shown by Fig. 1.9.

Another important cut is the GT ,¹³ which has a very constant frequency over a wide temperature range. As shown by Fig. 1.14, all zero temperature coefficient crystals are zero coefficient at one temperature only and usually vary in a square law curve about this temperature. The GT crystal represented an attempt to get a crystal in which the frequency remained constant over a wide temperature range. As can be seen from the figure, when properly adjusted this aim is attained, for the frequency does not vary more than one part in a million over a 100-degree Centigrade range of temperature.

This crystal makes use of the fact that a face shear vibration can be resolved into two longitudinal vibrations coupled together. As shown by

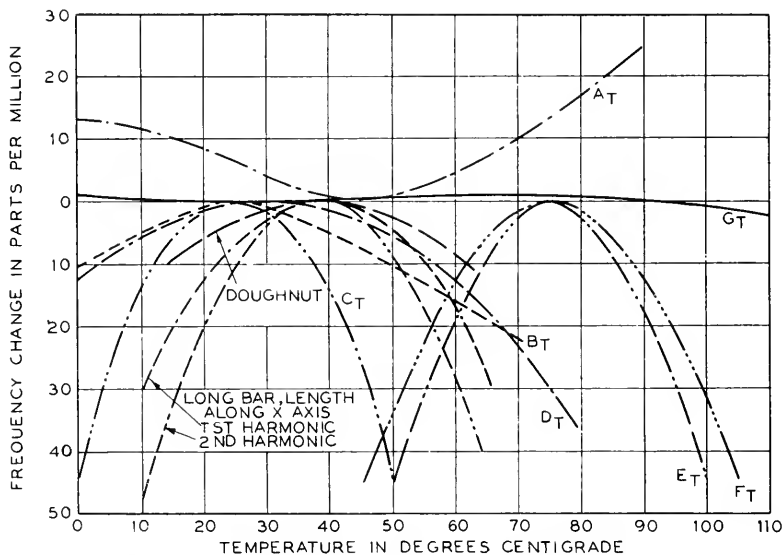


Fig. 1.14—Temperature frequency characteristics of a number of low temperature coefficient crystals

Fig. 1.15, if we cut a crystal at an angle of 45 degrees from that of a shear vibrating crystal, an expansion occurs along one axis and a contraction along the other indicating that a face shear can be resolved into two longitudinal modes that are coupled together. Now since it can be shown that all pure longitudinal modes for blanks cut in all possible directions in a quartz crystal will have zero or negative temperature coefficients,¹⁴ it follows that if we have a shear vibrating crystal with a positive coefficient, that

¹³ "A New Quartz Crystal Plate, Designated the GT , Which Produces a Very Constant Frequency Over A Wide Temperature Range," W. P. Mason, *Proc. I. R. E.*, Vol., 28, pp. 220-223, May 1940

¹⁴ This can be proved as discussed in the appendix by combining the Voigt expressions for the elastic relations in a crystal with the measured temperature coefficients of the six elastic constants.

coefficient must have been caused by the coupling between the two modes. As a result of this observation it follows that if we have a shear vibrating crystal with a positive temperature coefficient and cut another crystal at 45 degrees from this crystal, the strong coupled mode which corresponds to the shear vibration will also have a positive temperature coefficient. As we grind down on the side, the two modes become farther apart in frequency and less closely coupled. Then, since they both will have a negative coefficient if separated far enough, it follows that for some ratio of axes, one of the modes will have a zero coefficient. This was tested out for a series of orientations near the *CT* and *DT* with the results shown in Fig. 1.16. Positive angle crystals had zero coefficients at ratios of axes varying from 1 to .855

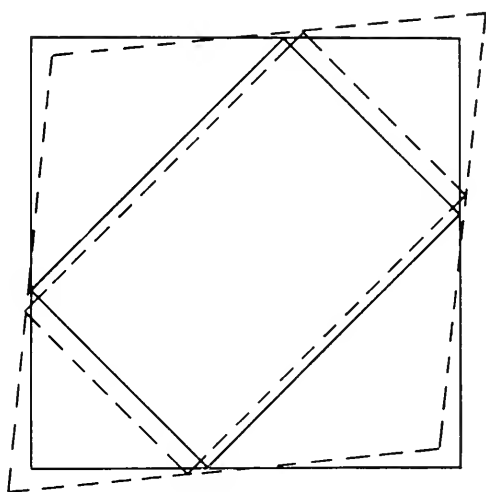


Fig. 1.15—Relation between a face shear mode and two coupled longitudinal modes

depending on the angle while negative angle crystals had zero coefficients at ratios from .64 to 1.0. For positive angle crystals it was the higher frequency mode that was the stronger and could be given the zero coefficient, while for the negative angle crystals it was the lower frequency mode that was the stronger and corresponded to the face shear mode.

Several of the positive angle crystals were measured over a temperature range with the results shown by Fig. 1.17. For angles above $51^{\circ}\text{-}30'$ the curvature was positive, while for angles below $51^{\circ}\text{-}30'$ the curvature was negative. Right at $51^{\circ}\text{-}30'$ the large square law curvature term disappeared and the frequency was constant to one part in a million over a 100-degree Centigrade range centered at 50°C . as shown by Fig. 1.18. Some further experiments showed that this flat range could be moved around a bit by

changing the angle of cut and the ratio of axes simultaneously. To go from -25°C. to $+75^{\circ}\text{C.}$ with a mid-range at 25°C. , a crystal cut at $51^{\circ}-7.5'$

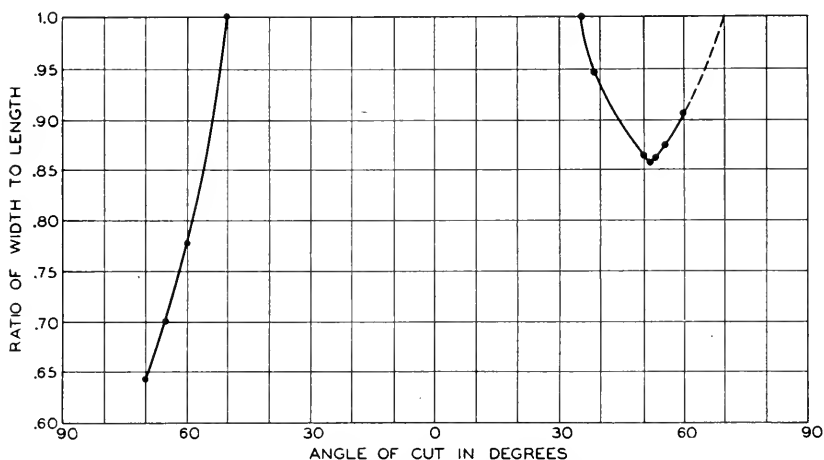


Fig. 1.16.—Relation between angle of cut and ratio of width to length for zero temperature coefficient for G type crystals

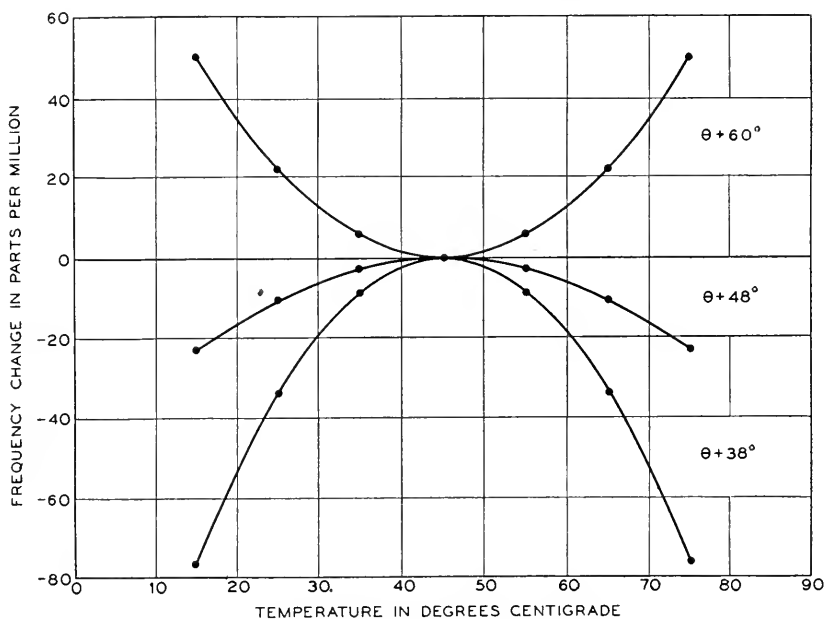


Fig. 1.17—Temperature frequency relations for various angles for G type crystals with a ratio of axes of 0.859 is required. The GT crystal has been used quite extensively in frequency and time standards and in filters meeting rigid phase requirements.

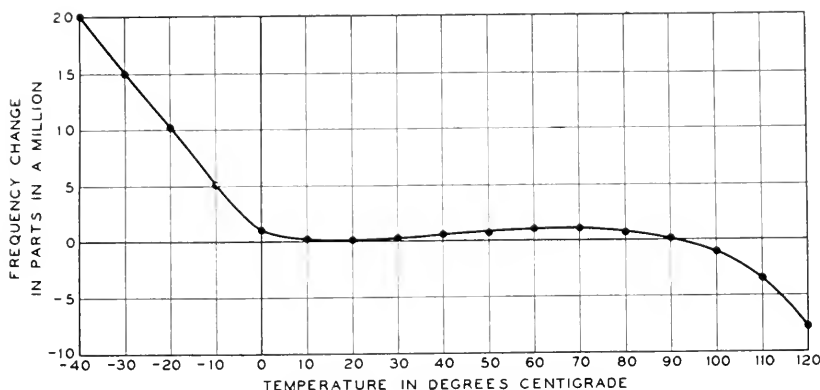


Fig. 1.18—Temperature frequency characteristic for GT crystal

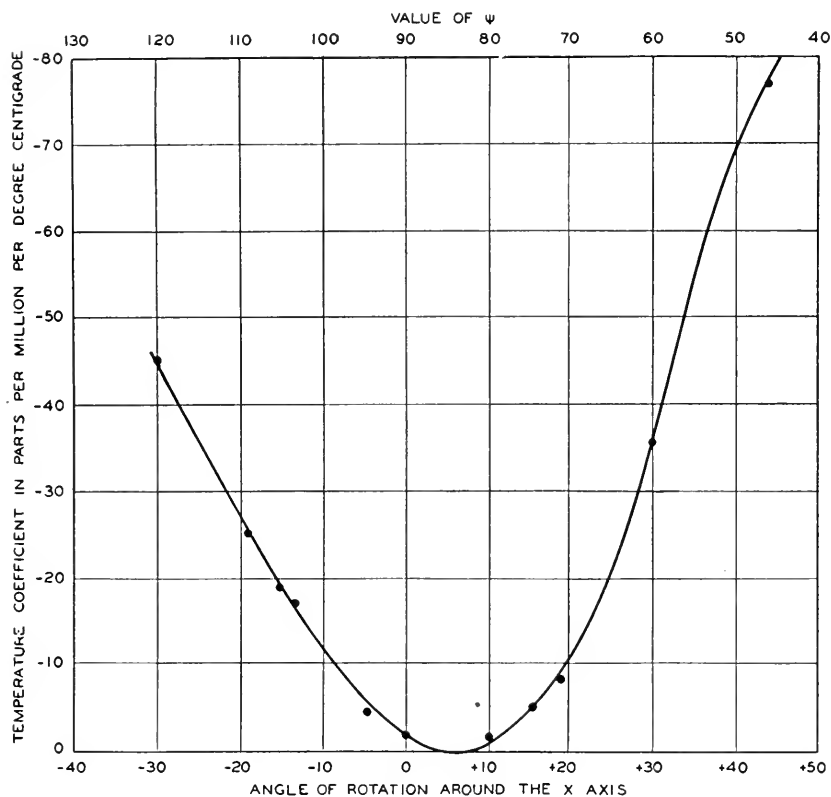


Fig. 1.19—Temperature coefficients of long thin rotated X cut crystals. Angle of rotation measured between length and Y axis. Dots are measured points. Solid line calculated from temperature coefficients evaluated in the appendix.

Two other cuts not previously described are shown also by Fig. 1.9. They are the *MT* low coefficient longitudinally vibrating crystal and the *NT* low coefficient flexurally vibrating crystal. Both of these are related to the $+5^\circ X$ cut crystal of Fig. 1.9. As shown by Fig. 1.19 a long thin $5^\circ X$ cut crystal is the best length direction for an X cut crystal to obtain a low-temperature coefficient. Figure 1.19 plots the temperature coefficients for long thin oriented X cut crystals, and this data is used in the appendix to derive the temperature coefficients of the six elastic constants. However, as the width of the crystal is increased the temperature coefficient becomes highly negative as shown by Fig. 1.20.

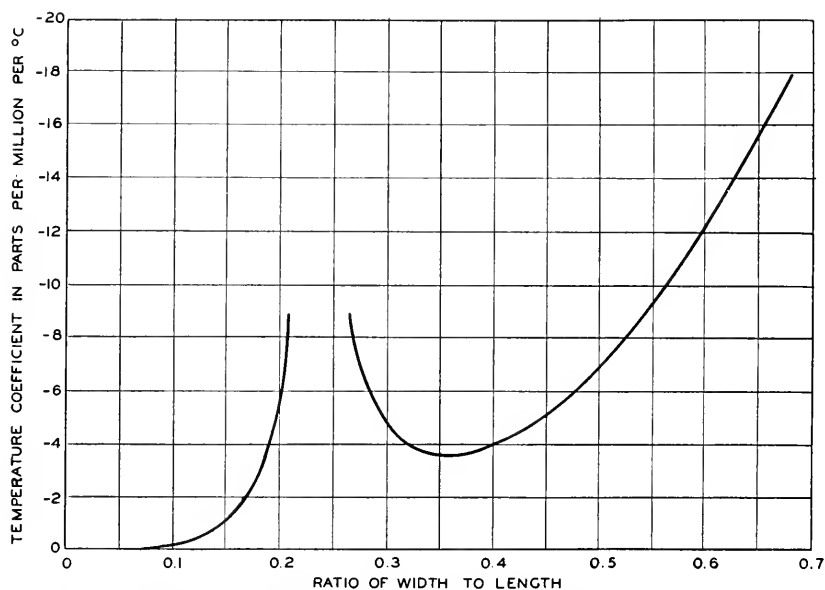


Fig. 1.20—Temperature coefficient of a $+5^\circ X$ cut crystal ($\varphi = 0^\circ$; $\theta = 90^\circ$; $\psi = 85^\circ$) as a function of the ratio of width to length. Ratio of thickness to length = 0.05.

This change of coefficient occurs due to the fact that as the crystal width is increased, the face shear mode of motion becomes more strongly excited and contributes to the elastic constant. Then since the temperature coefficient of the shear elastic constant is highly negative for this orientation the temperature coefficient of the $+5^\circ X$ cut crystal becomes more highly negative as the width is increased.

The *MT* longitudinally vibrating crystal employs a rotation of the plane of the crystal cut about the Y' or length axis. The effect of this rotation is to change the temperature coefficient of the shear mode from highly negative to nearly zero. The result is that the temperature coefficient becomes

very low and nearly independent of the width length ratio. The *NT* low coefficient flexurally vibrating crystal is similar to the *MT* but requires a somewhat higher rotation about the I' axis to produce a low coefficient.

The *MT* crystal has been used in narrow band filters such as pilot channel filters of the cable carrier system and in oscillators having frequencies between 50 kilocycles and 100 kilocycles. The *NT* flexure crystal is capable of producing frequencies as low as 4 kilocycles, and can be used to produce filters and control oscillators in the frequency range from 4 kilocycles to 50 kilocycles. Crystals of this type have been used with the Western Electric frequency modulation broadcast transmitter.¹⁵ Operating in the region of 5 kilocycles, they maintain the frequency of the transmitter to $\pm .0025$ per cent without temperature regulation. These two crystals will be described in more detail in a subsequent paper.

APPENDIX A

VOIGT'S ELASTIC AND PIEZOELECTRIC RELATIONS AND THEIR APPLICATION TO THE DETERMINATION OF LOW TEMPERATURE COEFFICIENT CRYSTALS

A.1 MATHEMATICAL EXPRESSIONS FOR PIEZOELECTRIC RELATIONS

As mentioned in the historical introduction, Voigt formulated a mathematical relation between the stresses, strains, polarizations, and electric fields existing in a crystal. For a general crystal devoid of symmetry these relations take the form

$$\begin{aligned}
 -x_x &= s_{11}^E X_x + s_{12}^E Y_y + s_{13}^E Z_z + s_{14}^E Y_z + s_{15}^E Z_x \\
 &\quad + s_{16}^E X_y - d_{11} E_x - d_{21} E_y - d_{31} E_z \\
 -y_y &= s_{21}^E X_x + s_{22}^E Y_y + s_{23}^E Z_z + s_{24}^E Y_z + s_{25}^E Z_x \\
 &\quad + s_{26}^E X_y - d_{12} E_x - d_{22} E_y - d_{32} E_z \\
 -z_z &= s_{31}^E X_x + s_{32}^E Y_y + s_{33}^E Z_z + s_{34}^E Y_z + s_{35}^E Z_x \\
 &\quad + s_{36}^E X_y - d_{13} E_x - d_{23} E_y - d_{33} E_z \\
 -y_z &= s_{41}^E X_x + s_{42}^E Y_y + s_{43}^E Z_z + s_{44}^E Y_z + s_{45}^E Z_x \\
 &\quad + s_{46}^E X_y - d_{14} E_x - d_{24} E_y - d_{34} E_z
 \end{aligned}
 \tag{A.1}$$

¹⁵ "A New Broadcast Transmitter Circuit Design for Frequency Modulation," J. F. Morrison, *Proc. I. R. E.*, Vol. 28, No. 10, Oct. 1940, pp. 444-449.

Equation (A.5) is not the only way of relating the elastic and electric quantities. For example if we substitute the values of the fields of the last three equations of (A.6) in the first six equations, we can write

$$\begin{aligned}
 -x_x &= s_{11}^Q X_x + s_{12}^Q Y_y + s_{13} Z_z + s_{14}^Q Y_z - g_{11} Q_x \\
 -y_y &= s_{12}^Q X_x + s_{11}^Q Y_y + s_{13} Z_z - s_{14}^Q Y_z + g_{11} Q_x \\
 -z_z &= s_{13} X_x + s_{13} Y_y + s_{33} Z_z \\
 -y_z &= s_{14}^Q X_x - s_{14}^Q Y_y + s_{44}^Q Y_z - g_{14} Q_x \\
 -z_x &= s_{44}^Q Z_z + 2s_{14}^Q X_x + g_{14} Q_y \\
 -x_y &= 2s_{14}^Q Z_z + 2(s_{11}^Q - s_{12}^Q) X_x + 2g_{11} Q_y \\
 E_x &= \frac{4\pi}{K_1^F} Q_x + g_{11} X_x - g_{11} Y_y + g_{14} Y_z \\
 E_y &= \frac{4\pi}{K_1^F} Q_y - g_{14} Z_z - 2g_{11} X_x \\
 E_z &= \frac{4\pi}{K_3} Q_z
 \end{aligned} \tag{A.7}$$

where

$$\begin{aligned}
 s_{11}^Q &= s_{11}^E - \frac{4\pi d_{11}^2}{K_1^F}; & s_{12}^Q &= s_{12}^E + \frac{4\pi d_{11}^2}{K_1^F}; & s_{14}^Q &= s_{14}^E - \frac{4\pi d_{11} d_{14}}{K_1^F} \\
 s_{44}^Q &= s_{44}^E - \frac{4\pi d_{14}^2}{K_1^F}; & g_{11} &= \frac{4\pi d_{11}}{K_1^F}; & g_{14} &= \frac{4\pi d_{14}}{K_1^F}
 \end{aligned}$$

The superscript Q is added to show that these are the elastic compliances that will be measured when the free charge on the surface is zero. These elastic constants are the ones measured when an unplated crystal is put in an airgap holder with a large air-gap since then no charge can flow to the surface of the crystal. The difference between the zero field and zero charge elastic constants for quartz is less than 1 per cent. For rochelle salt, however, they may differ by a factor of 4. For rochelle salt the principal piezoelectric constant d_{14} and the "free" dielectric constant K_1^F vary widely in value and phase angle with variations in temperature and frequency, whereas the piezoelectric constant g_{14} which is proportional to the ratio of these two is nearly a constant for all frequencies and temperatures, so that the formulation of equation (A.7) is more advantageous than that of equation (A.6). For quartz, however, both forms are reasonably constant. Furthermore the elastic constants of equation (A.6) are those for a plated crystal which are usually the ones of interest for a crystal employed in an oscillator or filter. Hence this formulation has been used in this appendix.

Both the formulation of (A.6) and (A.7) can be expressed in terms of the strains rather than the stresses. Since these are useful forms and are used later in this appendix, they are given below. Equations (A.8) are obtained directly from equations (A.6) by solving them simultaneously to replace the strain by the stress, while equations (A.10) are obtained in the same way from equations (A.7).

$$\begin{aligned}
 -X_x &= c_{11}^E x_x + c_{12}^E y_y + c_{13} z_z + c_{14}^E y_z - e_{11} E_x \\
 -Y_y &= c_{12}^E x_x + c_{11}^E y_y + c_{13} z_z - c_{14}^E y_z + e_{11} E_x \\
 -Z_z &= c_{13} x_x + c_{13} y_y + c_{33} z_z \\
 -Y_z &= c_{14}^E x_x - c_{14}^E y_y + c_{44}^E y_z - e_{14} E_x \\
 -Z_x &= c_{44}^E z_x + c_{11}^E x_y + c_{14} E_y \\
 -X_y &= c_{14}^E z_x + \left(\frac{c_{11}^E}{2} - \frac{c_{12}^E}{2} \right) x_y + e_{11} E_y
 \end{aligned} \tag{A.8}$$

$$Q_x = \frac{E_x}{4\pi} + P_x = \frac{E_x K_1^C}{4\pi} + e_{11} x_x - e_{11} y_y + e_{14} y_z$$

$$Q_y = \frac{E_y}{4\pi} + P_y = \frac{E_y K_1^C}{4\pi} - e_{14} z_x - e_{11} x_y$$

$$Q_z = \frac{E_z}{4\pi} + P_z = \frac{E_z K_3}{4\pi}$$

where the relations for the elastic constants are

$$\begin{aligned}
 2c_{11}^E &= \frac{s_{33}^E}{\alpha} + \frac{s_{44}^E}{\beta}; & 2c_{12}^E &= \frac{s_{33}^E}{\alpha} - \frac{s_{44}^E}{\beta}; & c_{13} &= \frac{-s_{13}}{\alpha}; \\
 c_{14}^E &= \frac{-s_{14}}{\beta}; & c_{33} &= \frac{s_{11}^E + s_{12}^E}{\alpha}; & c_{44}^E &= \frac{s_{11}^E - s_{12}^E}{\beta}; \\
 c_{66}^E &= \frac{c_{11}^E - c_{12}^E}{2} = \frac{s_{44}^E}{2\beta}; & \alpha &= s_{33}(s_{11}^E + s_{12}^E) - 2s_{13}^2; \\
 \beta &= s_{44}(s_{11}^E - s_{12}^E) - 2s_{14}^{E2}.
 \end{aligned}$$

Conversely we can also write the useful relation

$$\begin{aligned}
 2s_{11}^E &= \frac{c_{33}^E}{\alpha'} + \frac{c_{44}^E}{\beta'}; & 2s_{12}^E &= \frac{c_{33}^E}{\alpha'} - \frac{c_{44}^E}{\beta'}; \\
 s_{13} &= \frac{-c_{13}}{\alpha'}; & s_{14} &= \frac{-c_{14}^E}{\beta'}; & s_{33} &= \frac{c_{11}^E + c_{12}^E}{\alpha'}; \\
 s_{44}^E &= \frac{c_{11}^E - c_{12}^E}{\beta'}; & s_{66}^E &= 2(s_{11}^E - s_{12}^E) = \frac{2c_{44}^E}{\beta'}; \\
 \alpha' &= c_{33}(c_{11}^E + c_{12}^E) - 2c_{13}^2; & \beta' &= c_{44}^E(c_{11}^E - c_{12}^E) - 2c_{14}^{E2}.
 \end{aligned}$$

For the piezoelectric constants

$$e_{11} = d_{11}(c_{11}^E - c_{12}^E) + d_{14}c_{14}^E; \quad e_{14} = 2d_{11}c_{14}^E + d_{14}c_{44}^E;$$

and conversely

$$-d_{11} = c_{11}(s_{11}^E - s_{12}^E) + e_{14}s_{14}^E; \quad -d_{14} = 2e_{11}s_{14}^E + e_{14}s_{44}^E.$$

The dielectric constant K_1^C denotes the clamped dielectric constant, i.e., the constant measured when the crystal is free from strain. This is related to the free dielectric constant K_1^F by the equation

$$K_1^C = K_1^F - 4\pi[d_{14}e_{14} + 2d_{11}e_{11}]. \quad (\text{A.9})$$

In a similar way if we solve equations (A.7) simultaneously, for the stresses in terms of the strains, we have

$$\begin{aligned} -X_x &= c_{11}^Q x_x + c_{12}^Q y_y + c_{13}z_z + c_{14}^Q y_z - f_{11}Q_x; \\ -Y_y &= c_{12}^Q x_x + c_{11}^Q y_y + c_{13}z_z - c_{14}^Q y_z + f_{11}Q_x; \\ -Z_z &= c_{13}x_x + c_{13}y_y + c_{33}z_z; \\ -Y_z &= c_{14}^Q x_x - c_{14}^Q y_y + c_{44}^Q y_z - f_{14}Q_x; \\ -Z_x &= c_{44}^Q z_x + c_{14}^Q x_y + f_{14}Q_y; \\ -X_y &= c_{14}^Q z_x + \left(\frac{c_{11}^Q - c_{12}^Q}{2} \right) x_y + f_{11}Q_y; \\ E_x &= \frac{4\pi}{K_1^C} Q_x - f_{11}x_x + f_{11}y_y - f_{14}y_z; \\ E_y &= \frac{4\pi}{K_1^C} Q_y + f_{14}z_z + f_{11}x_y; \\ E_z &= \frac{4\pi}{K_3} Q_z. \end{aligned} \quad (\text{A.10})$$

where the c^Q constants are related to the s^Q constants as in equation (A.8). The piezoelectric relations are

$$f_{11} = g_{11}(c_{11}^Q - c_{12}^Q) + g_{14}c_{14}^Q; \quad f_{14} = 2g_{11}c_{14}^Q + g_{14}c_{44}^Q;$$

or conversely

$$-g_{11} = f_{11}(s_{11}^Q - s_{12}^Q) + e_{14}s_{14}^Q; \quad -g_{14} = 2f_{11}s_{14}^Q + f_{14}s_{44}^Q;$$

while the dielectric relation between the free and clamped crystal

$$\frac{4\pi}{K_1^F} = \frac{4\pi}{K_1^C} - (g_{14}f_{14} + 2g_{11}f_{11}). \quad (\text{A.11})$$

Equations (A.10) might also have been obtained directly from equations (A.8) by substituting the charges from the last three equations in terms of the fields. This substitution yields the additional relations

$$\begin{aligned}
 c_{11}^Q &= c_{11}^E + \frac{4\pi e_{11}^2}{K_1^C}; & c_{12}^Q &= c_{12}^E - \frac{4\pi e_{11}^2}{K_1^C}; & c_{13}^Q &= c_{13}^E; \\
 c_{14}^Q &= c_{14}^E + \frac{4\pi e_{11} e_{14}}{K_1^C}; & c_{33}^Q &= c_{33}^E; \\
 c_{44}^Q &= c_{44}^E + \frac{4\pi e_{14}^2}{K_1^C}; & c_{66}^Q &= \frac{c_{11}^Q - c_{12}^Q}{2} = \frac{c_{11}^E - c_{12}^E + \frac{8\pi e_{11}^2}{K_1^C}}{2}; \\
 f_{11} &= \frac{4\pi}{K_1^C} e_{11}; & f_{14} &= \frac{4\pi}{K_1^C} e_{14}.
 \end{aligned} \tag{A.12}$$

(A.2). VALUES OF THE ELASTIC AND PIEZOELECTRIC CONSTANTS

The first and one of the best determinations of the elastic constants of quartz was made by Voigt. Using static deformations of unplated crystals he determined the elastic constants to be

$$\begin{aligned}
 c_{11} &= 85.1 \times 10^{10} \text{ dynes/cm}^2; & c_{12} &= 6.95 \times 10^{10}; \\
 c_{13} &= 14.1 \times 10^{10}; & c_{14} &= 16.8 \times 10^{10} \\
 c_{33} &= 105.3 \times 10^{10}; & c_{44} &= 57.1 \times 10^{10}; \\
 c_{66} &= \left(\frac{c_{11} - c_{12}}{2} \right) = 39.1 \times 10^{10}
 \end{aligned} \tag{A.13}$$

From these the moduli of compliance can be calculated and are

$$\begin{aligned}
 s_{11} &= 129.8 \times 10^{-14} \text{ cm}^2/\text{dyne}; & s_{12} &= -16.6 \times 10^{-14}; \\
 s_{13} &= -15.2 \times 10^{-14}; & s_{14} &= -43.1 \times 10^{-14}; \\
 s_{33} &= 99.0 \times 10^{-14}; & s_{44} &= 200.5 \times 10^{-14}; \\
 s_{66} &= 2(s_{11} - s_{12}) = 292.8 \times 10^{-14}.
 \end{aligned} \tag{A.14}$$

Whether these are zero field or zero charge constants is not known. If they were measured in a room with high humidity, the polarization produced by strain would soon be annulled by a current flow through the leakage resistance of the adsorbed moisture, and the constants would be c_{ij}^E or s_{ij}^E . On the other hand if the displacements were measured in a very dry room, the leakage resistance is very small and it may take hours to annul the polarization through a leakage current flow. In that case the constants measured

would be c_{ij}^Q or s_{ij}^Q . In any case the difference was probably less than the accuracy of measurement.

Later measurements by Perrier and Mandrot for two of the constants s_{11} and s_{33} give the values

$$s_{11} = 127.3 \times 10^{-14}; \quad s_{33} = 97 \times 10^{-14} \quad (\text{A.15})$$

By using the measured resonance frequencies of known modes of motion, the uncertainty of the type of elastic constant can be removed, for the alternations occur so fast that the leakage resistance has little effect. If a crystal is lightly plated, it is shown in the next section that the resonant frequency of a length vibrating bar will be determined by the zero field elastic constants s_{ij}^E . On the other hand if an unplated crystal is measured in an air gap holder with a large air gap it has been shown that¹ the frequency measured will be determined by the zero charge elastic constants s_{ij}^Q or c_{ij}^Q . A careful measurement of the elastic constants of quartz has recently been made by Atanasoff and Hart². Using thickness modes for

¹ The resonances of length vibrating crystals have been discussed by Cady, "The Piezoelectric Resonator and The Effect of Electrode Spacing on Frequency," *Physics*, Vol. 7, No. 7, July 1936, pages 237-259; and by the writer, "Dynamic Measurement of The Constants of Rochelle Salt," *Phys. Rev.*, Vol. 55, pages 775-789, April 15, 1939; while the resonances of thickness vibrating crystals have been discussed by Cady (above paper) and Lawson "The Vibration of Piezoelectric Plates," *Phys. Rev.*, Vol. 62, July 1, 1942, pp. 71-76. For a length vibrating crystal Cady shows that the resonant frequency for no air gap (plated crystal) is controlled by the constant $1/s_{11}^E$. For a crystal with a large air gap, the frequency is controlled by the constant.

$$1/s_{11}^E + 4\pi d_{11}^2/K_1^F s_{11}^{E2} = 1/s_{11}^Q.$$

Starting with equations of the form (A.10), the writer showed that the frequency of a bar in an air gap holder would be controlled by the constant $1/s_{11}^Q$, while the frequency of a plated crystal is determined by

$$s_{11}^Q / \left(1 - \frac{d_{11}^2 4\pi}{K_1^C s_{11}^Q} \right) = s_{11}^E.$$

For a thickness vibrating crystal for which the field is applied in the direction of wave propagation, Cady and Lawson find that the resonant frequency is controlled by the elastic constant

$$c^* = c_{11}^E + \frac{4\pi e_{11}^2}{K_1^C} \left[1 - \frac{8}{\pi^2 \left[1 + K_1^C \left(\frac{D}{t} - 1 \right) \right]} \right]$$

where D is the total separation between electrodes and t the thickness of the crystal. When the separation is infinite, the controlling elastic constant is $c_{11}^E + 4\pi e_{11}^2/K_1^C$ which, from equation (A.12) is c_{11}^Q . When the air gap is zero or $D = t$, the controlling constant is

$$c_{11}^E + \frac{4\pi e_{11}^2}{K_1^C} \left(1 - \frac{8}{\pi^2} \right)$$

which, for all practical purposes, can be taken as c_{11}^E for quartz.

² "Dynamical Determination of the Elastic Constants and their Temperature Coefficients for Quartz," *Phys. Rev.*, Vol. 59, No. 1 (85-96), Jan. 1, 1941.

relatively thick pieces of quartz, and determining the asymptotic value for high order harmonics, they obtained the elastic constants

$$\begin{aligned} c_{11} &= 87.55 \times 10^{10} \text{ dynes/cm}^2; & c_{12} &= 6.07 \times 10^{10}; & c_{13} &= 13.3 \times 10^{10}; \\ c_{14} &= -c_{24} = 17.25 \times 10^{10}; & c_{33} &= 106.8 \times 10^{10}; & c_{44} &= 57.19 \times 10^{10}. \end{aligned} \quad (\text{A.16})$$

In addition they came to the conclusion that c_{56} had a value of 18.4×10^{10} , which was different from the value of c_{14} as required by theory. Their measurements were made with high harmonics in air gap holders so that the values measured should determine the c_{ij}^Q constant. To explain the discrepancy found, Lawson³ has suggested that the c_{ij}^Q constants

$$c_{ij}^Q = c_{ij}^E + 4\pi e_{1i} e_{1j} / K_1^E \quad (\text{A.17})$$

do not obey the same symmetry relations as the c_{ij}^E constants. This suggestion does not seem to be borne out by equations (A.10), from which the symmetry relations of the c_{ij}^Q constants can be determined. If we start with a generalized form of these equations applicable to any crystal and apply the symmetry relations for quartz, we find that it is still necessary to satisfy the symmetry relations between the constants found previously and in particular

$$c_{56}^Q = c_{14}^Q \quad (\text{A.18})$$

In order to investigate this matter further, and to obtain more reliable values of the elastic constants, an analysis has been made of a number of measurements previously obtained for oriented crystals. In particular two families of oriented crystals were investigated. One family was a set of oriented X cut crystals vibrating longitudinally. They were cut with their major faces normal to the X axis and with their lengths at angles A_2 of from $+43^\circ$ to -79° with respect to the Y or mechanical axis. They were oriented similarly to the $+5^\circ$ and -18.5° filter crystals shown by Fig. 1.9. When these crystals are 7 to 10 times as long as they are wide or thick it has been shown previously⁴ that their length resonances are determined very accurately by the equation

$$f_R = \frac{1}{2\ell_y} \sqrt{\frac{1}{\rho s_{22}^E}} \quad (\text{A.19})$$

where ℓ_y is the length of the crystal, ρ the density and s_{22}^E , the inverse of Young's Modulus along the length for a plated crystal. This is related to the angle of cut A_2 by the equation

$$\begin{aligned} s_{22}^E &= s_{11}^E \cos^4 A_2 + s_{33}^E \sin^4 A_2 + 2s_{14}^E \cos^3 A_2 \sin A_2 \\ &\quad + (2s_{13} + s_{44}^E) \sin^2 A_2 \cos^2 A_2 \end{aligned} \quad (\text{A.20})$$

³ A. W. Lawson, *Phys. Rev.*, 59, 838 (1941).

⁴ "Electrical Wave Filters Employing Quartz Crystals as Elements." W. P. Mason, *B. S. T. J.*, Vol. XIII, pp. 405-452, July 1934. See Figs. 25, 31 and 32.

Since the resonant frequency of the plated crystal was measured, it was the zero potential elastic constant that was determined. These crystals were lightly plated with aluminum and it had been previously shown that the added plating would affect the frequency by considerably less than 0.1 per cent. The crystal orientations, their dimensions, the frequency constants and the values of s_{22}^E , are shown by Table I.

These measured variations satisfy equation (A.20) for the variation of s_{22}^E with angle very well if we take

$$\begin{aligned} s_{11}^E &= 127.9 \times 10^{-14} \text{ cm}^2/\text{dyne}; & s_{33} &= 95.6 \times 10^{-14}; \\ s_{14}^E &= -44.6 \times 10^{-14}; \\ s_{44}^E + 2s_{13} &= 175.8 \times 10^{-14}. \end{aligned} \quad (\text{A.21})$$

TABLE I

Angle of Cut, A_2	Dimension, mm			Resonant Frequency 25°C	Frequency Constant KC cms	Value of s_{22}^E
	Length	Width	Thickness			
-79.5°	24.03	2.50	.502	130,700	314.1	$95.6 \times 10^{-14} \text{ cm}^2/\text{dyne}$
-18.5°	20.00	2.50	.502	127,710	255.4	
-13.14°	19.99	2.97	.505	128,390	256.8	
-12.33	19.98	2.95	.500	128,590	257.0	
-5.6	20.02	2.92	.500	132,130	264.5	
-1.4	20.03	3.02	.502	134,050	269.2	
-.9°	19.97	2.99	.502	135,240	270.5	
+ .36°	20.03	3.03	.508	135,890	272.0	
+ .54	19.96	2.98	.506	135,920	272.1	
+ 1.44	20.02	2.98	.505	136,890	274.0	
+ 2.61	19.97	3.00	.505	138,400	276.5	
+ 4.05	19.95	2.97	.510	139,900	279.0	
+11.8	19.11	3.01	.500	154,600	295.4	
+18.0	20.02	2.95	.500	155,380	311.1	
+42.6	20.00	2.95	.500	174,750	349.5	

This gives three of the constants directly, and a relation between two more. To obtain the remaining constants and to test out the hypothesis that there are seven elastic constants rather than six, use has been made of measurements made for thickness vibrating shear crystals obtained by rotating one edge about the X axis. These are the AT and BT series shown by Fig. 1.9. As shown by a former paper⁵, the frequency of such crystals depends on the edge dimensions as well as the thickness dimensions. However, as the edge dimensions become large compared to the thickness dimension the principal frequency approaches an asymptotic value which is taken as that for the infinite plate. For the AT , BT and Y cut crystals these asymptotic values have been determined to have the values shown by Table II.

⁵ "Low Temperature Coefficient Quartz Crystals," *B. S. T. J.*, Vol. XIX, pp. 74-93, Jan. 1940. See Fig. 5.

If we make the assumption that there are seven elastic constants and c_{56}^E differs from c_{14}^E , the frequency of this series of crystals will be⁵

$$f = \frac{1}{2l} \sqrt{\frac{c_{66}^E}{\rho}} \quad \text{where } c_{66}^E = c_{66}^E \cos^2 A_2 + c_{44}^E \sin^2 A_2 - c_{56}^E \sin 2A_2 \quad (\text{A.22})$$

The determination for the Y cut gives directly

$$c_{66}^E = 40.5 \times 10^{10} \text{ dynes per square cm.} \quad (\text{A.23})$$

The other two cuts give the values

$$c_{56}^E = 18.2 \times 10^{10}; \quad c_{44}^E = 58.65 \times 10^{10} \quad (\text{A.24})$$

To test out the hypothesis that c_{56}^E differs from c_{14}^E or s_{56}^E from $2s_{14}^E$ we can make use of equation (A.8) writing c_{56}^E in place of c_{14}^E . Then solving these equations simultaneously we find

$$s_{44}^E = \frac{c_{66}^E}{(c_{44}^E c_{66}^E - c_{56}^E{}^2)}; \quad s_{56}^E = \frac{-c_{56}^E}{(c_{44}^E c_{66}^E - c_{56}^E{}^2)}; \quad s_{66}^E = \frac{c_{44}^E}{(c_{44}^E c_{66}^E - c_{56}^E{}^2)} \quad (\text{A.25})$$

TABLE II

Crystal	Angle of Cut A_2	Asymptotic Frequency constant KC mms	Value of c_{66}^E
AT	+35° 15'	1661.5	29.39×10^{10} dynes/cm ²
Y Cut	0	1954	40.50
BT	-49°	2549	68.86

Substituting in the values from (A.23) and (A.24) we find

$$s_{44}^E = 197.8 \times 10^{-14} \text{ cm}^2/\text{dyne}; \quad s_{56}^E = -89.0 \times 10^{-14}; \quad (\text{A.26})$$

$$s_{66}^E = 2(s_{11}^E - s_{12}^E) = 286.5 \times 10^{-14}.$$

Comparing the value of s_{56}^E with $2s_{14}^E$ given in equation (A.21) we see that they are equal within the experimental error, so that these measurements do not indicate that there are seven elastic constants but only the customary six. Using these values all the elastic constants can be evaluated as shown by Table III.

Measurements have also been made to determine accurately the piezoelectric constants. This was done by using the ratios of capacities of two standard rotated X cut crystals for which these ratios have been accurately determined. As shown by section C of this appendix, the ratio of capacities r of a crystal is related to the piezoelectric constant d'_{12} , the elastic constant s_{22}^E , and the free dielectric constant K_1^F by the equation

$$r = \text{ratio of capacities} = \frac{\pi^2}{8} \left(\frac{1 - k^2}{k^2} \right) \quad (\text{A.27})$$

where k the electromechanical coupling is given by

$$k = d'_{12} \sqrt{\frac{4\pi}{K_1^E s_{22}^E}}. \quad (\text{A.28})$$

The two crystal cuts and their constants are given in Table IV. Only the numerical value and not the sign are determined for d'_{12} .

TABLE III

Elastic Compliance Moduli	Elastic Stiffness Moduli
$s_{11}^E = 127.9 \times 10^{-14}$ cm ² /dyne	$c_{11}^E = 86.05 \times 10^{10}$ dynes/cm ²
$s_{12}^E = -15.35$	$c_{12}^E = 5.05$
$s_{13} = -11.0$	$c_{13} = 10.45$
$s_{14}^E = -44.6$	$c_{14}^E = 18.25$
$s_{33} = 95.6$	$c_{33} = 107.1$
$s_{44}^E = 197.8$	$c_{44}^E = 58.65$
$s_{66}^E = 2(s_{11}^E - s_{12}^E) = 286.5$	$c_{66}^E = \frac{c_{11}^E - c_{12}^E}{2} = 40.5$

TABLE IV

Angle of Cut, A_2	Ratio of Capacities	Value of s_{22}^E	Value of K_1^E	Value of d'_{12}
$-18.5^\circ X$ cut	137	144.5	4.58	6.85×10^{-8}
$0^\circ X$ cut	125	127.9	4.58	6.76×10^{-8}

TABLE V

Piezoelectric constant	Value in cgs electrostatic units	Piezoelectric constant	Value in cgs electrostatic units
d_{11}	-6.76×10^{-8}	g_{11}	-18.55×10^{-8}
d_{14}	2.56×10^{-8}	g_{14}	7.02×10^{-8}
e_{11}	-5.01×10^4	f_{11}	-13.85×10^4
e_{14}	$-.97 \times 10^4$	f_{14}	-2.68×10^4

The variation of d'_{12} as a position of angle has been shown to be⁶

$$d'_{12} = -\frac{1}{2}[d_{11}(1 + \cos 2A_2) + d_{14} \sin 2A_2] \quad (\text{A.29})$$

The two values of d'_{12} of table IV are satisfied by

$$d_{11} = -6.76 \times 10^{-8}; \quad d_{14} = +2.56 \times 10^{-8} \quad (\text{A.30})$$

⁶ See "Electrical Wave Filters Employing Quartz Crystals as Elements," W. P. Mason, *B. S. T. J.*, Vol. XIII, 405 (July 1934).

From these values and the elastic constants of Table III we can calculate all the different forms of the piezoelectric constants. These are given in Table V.

(A.3). DERIVATION OF EQUIVALENT CIRCUIT OF CRYSTAL

The electrical impedance and electrical equivalent circuit for a fully plated crystal can be derived from the piezoelectric relations of equation (A.6) taken together with Newton's law of motion

$$F_y = ma = (\rho \, dx \, dy \, dz) \frac{d^2\xi}{dt^2} \tag{A.31}$$

where m is mass of an elementary volume $dx \, dy \, dz$, a the acceleration, and ξ is the displacement of the element in the y direction. If we consider a long thin X cut crystal with its length in the y direction, the piezoelectric relations of interest are

$$\begin{aligned} -y_y &= s_{12}^E X_x + s_{11}^E Y_y + s_{13} Z_z - s_{14}^E Y_z + d_{11} E_x; \\ Q_x &= \frac{E_x K_1^F}{4\pi} - d_{11} X_x + d_{11} Y_y - d_{14} Y_z. \end{aligned} \tag{A.32}$$

For a long thin crystal with its long dimension in the Y direction we can set

$$X_x = Z_z = Y_z = 0 \tag{A.33}$$

This follows since the crystal is free from external forces, and hence these stresses on the edges of the crystal must be zero. On account of the small x and z dimensions, the rate of change of these stresses with x or z will have to be high in order that the stresses shall differ appreciably from zero, and there are no mechanical strains causing a high stress gradient. Then for a long thin bar the piezoelectric equations can be written

$$\begin{aligned} -y_y &= s_{11}^E Y_y + d_{11} E_x; \\ Q_x &= \frac{E_x K_1^F}{4\pi} + d_{11} Y_y. \end{aligned} \tag{A.34}$$

Let us next consider a small cross section of the crystal with a dimension dy along the crystal length. The total force on the section is a resultant of the difference in stresses on the two faces or equal to

$$\ell_w \ell_t [Y_{y_1} - Y_{y_2}] = -\ell_w \ell_t \frac{\partial Y_y}{\partial y} dy = F_y \tag{A.35}$$

where Y_y the stress is considered as a compressional force acting on the faces of the element. By Newton's law of motion (A.31) we have

$$-\ell_w \ell_t dy \frac{\partial Y_y}{\partial y} = \ell_w \ell_t dy \rho \frac{d^2\xi}{dt^2} \quad \text{or} \quad \frac{\partial Y_y}{\partial y} = -\rho \frac{d^2\xi}{dt^2} \tag{A.36}$$

For a completely plated crystal such as we are considering, the potential gradient E_x will be independent of the y direction, since any charge distribution will be equalized with the speed of light which is much higher than the speed of sound in the crystal. Then equation (A.34) when differentiated by y becomes

$$-\frac{\partial Y_y}{\partial y} = -\frac{\partial^2 \xi}{\partial y^2} = s_{11}^E \frac{\partial y_y}{\partial y}. \quad (\text{A.37})$$

Introducing equation (A.36), the equation of motion for a plated crystal becomes

$$\frac{\partial^2 \xi}{\partial y^2} = s_{11}^E \rho \frac{d^2 \xi}{dt^2}. \quad (\text{A.38})$$

For simple harmonic motion the variation of ξ with time can be written in the usual form

$$\xi = \xi e^{j\omega t}, \quad (\text{A.39})$$

so that for simple harmonic motion equation (A.38) becomes

$$\frac{d^2 \xi}{dy^2} - \omega^2 s_{11}^E \rho \xi = \frac{d^2 \xi}{dy^2} - \frac{\omega^2}{v^2} \xi = 0 \quad (\text{A.40})$$

where v the velocity of sound in the plated crystal is given by the formula

$$v^2 = \frac{1}{\rho s_{11}^E}. \quad (\text{A.41})$$

A solution of equation (A.40) with two arbitrary boundary conditions is

$$\xi = A \cos \frac{\omega}{v} y + B \sin \frac{\omega y}{v}. \quad (\text{A.42})$$

To determine the constants A and B , use is made of equation (A.34). Differentiating (A.42)

$$-\frac{\partial \xi}{\partial y} = -y_y = \frac{\omega}{v} \left[A \sin \frac{\omega}{v} y - B \cos \frac{\omega y}{v} \right] = s_{11}^E Y_y + d_{11} E_x. \quad (\text{A.43})$$

When $y = 0$ and $y = \ell$ the bar length

$$Y_y = Y_{y_1} \quad \text{and} \quad Y_y = Y_{y_2} \quad (\text{A.44})$$

provided the crystal is driving a load. For most electrical cases the only load driven is an air load and this is usually very small so that it is customary to set $Y_{y_1} = Y_{y_2} = 0$. Under these conditions

$$-\frac{\omega}{v} B = d_{11} E_x \quad \text{and} \quad \frac{\omega}{v} \left[A \sin \frac{\omega \ell}{v} - B \cos \frac{\omega \ell}{v} \right] = d_{11} E_x. \quad (\text{A.45})$$

Solving these equations for A and B and substituting in (A.43) we have

$$-y_y = d_{11} E_x \left[\tan \frac{\omega \ell}{2v} \sin \frac{\omega y}{v} + \cos \frac{\omega y}{v} \right] = s_{11}^E Y_y + d_{11} E_x$$

or

$$Y_y = -\frac{d_{11} E_x}{s_{11}^E} \left[1 - \frac{\cos \frac{\omega(y - \ell/2)}{v}}{\cos \frac{\omega \ell}{2v}} \right]. \tag{A.46}$$

The electrical impedance measured at the terminals of a plated crystal is then determined by substituting the value of Y_y in the last of equations (A.34) and integrating the charge Q over the whole surface. The current into the crystal is then

$$i = j\omega Q = j\omega \ell_w \int_0^\ell E_x \left[\frac{K_1^F}{4\pi} - \frac{d_{11}^2}{s_{11}^E} \left(1 - \frac{\cos \omega(y - \ell/2)}{\cos \frac{\omega \ell}{2v}} \right) \right] dy$$

$$= j\omega E_x \ell_w \ell \left[\frac{K_1^F}{4\pi} - \frac{d_{11}^2}{s_{11}^E} \left(1 - \frac{\tan \frac{\omega \ell}{2v}}{\frac{\omega \ell}{2v}} \right) \right] \tag{A.47}$$

$$= j\omega E_x \ell \left[\frac{K_1^{LC}}{4\pi} + \frac{d_{11}^2}{s_{11}^E} \frac{\tan \frac{\omega \ell}{2v}}{\frac{\omega \ell}{2v}} \right]$$

where $K_1^{LC} = K_1^F - \frac{4\pi d_{11}^2}{s_{11}^E}$ is called the longitudinally clamped dielectric constant, i.e. the dielectric constant that would be measured if we suppress the longitudinal strain along the y axis but not the other strains. The admittance of the crystal then is

$$\frac{i}{E} = \frac{i}{E_x \ell_t} = \frac{j\omega \ell_w \ell}{\ell_t} \left[\frac{K_1^{LC}}{4\pi} + \frac{d_{11}^2}{s_{11}^E} \frac{\tan \frac{\omega \ell}{2v}}{\frac{\omega \ell}{2v}} \right]. \tag{A.48}$$

This consists of two terms which represent parallel branches in the equivalent circuit. One of these is the capacitance

$$C_0 = \frac{\ell_w \ell K_1^{LC}}{4\pi \ell_t} \text{ cgs units} = \frac{\ell_w \ell K_1^{LC}}{4\pi \ell_t 9 \times 10^{11}} \text{ farads} \tag{A.49}$$

The other branch contains the impedance

$$\frac{-j\ell_t \left[\frac{s_{11}^E}{d_{11}^2} \frac{\omega\ell}{2v} \right]}{\omega\ell_w \ell \left[\frac{\omega\ell}{2v} \tan \frac{\omega\ell}{2v} \right]} \text{ cgs units} = \frac{-j\ell_t s_{11}^E \frac{\omega\ell}{2v} \times 9 \times 10^{11}}{\omega\ell_w \ell d_{11}^2 \tan \frac{\omega\ell}{2v}} \text{ ohms} \quad (\text{A.50})$$

This branch will have a zero impedance or will resonate when the tangent is infinite or when

$$\frac{2\pi f_R \ell}{2v} = \frac{\pi}{2} \text{ or } f_R = \frac{v}{2\ell} = \frac{1}{2\ell\sqrt{\rho s_{11}^E}} \quad (\text{A.51})$$

Hence for a fully plated crystal it is the zero field elastic constant that determines the resonant frequency.

Near this resonant frequency, the impedance of equation (A.50) can be represented by a series capacitance and inductance having the values

$$C_1 = \frac{\ell_w \ell}{\ell_t} \frac{8}{\pi^2} \frac{d_{11}^2}{s_{11}^E \times 9 \times 10^{11}}, \quad I_1 = \frac{\rho s_{11}^{E2} \ell \ell_t \times 9 \times 10^{11}}{8\ell_w d_{11}^2} \quad (\text{A.52})$$

Taking the ratio between C_0 and C_1 we have

$$\frac{C_0}{C_1} = r = \frac{\pi^2 \left(\frac{K_1^{LC} s_{11}^E}{4\pi d_{11}^2} \right)}{8 \left(\frac{4\pi d_{11}^2}{K_1^F s_{11}^E} \right)} = \frac{\pi^2 \left(1 - \frac{4\pi d_{11}^2}{s_{11}^E K_1^F} \right)}{8 \left(\frac{1}{k^2} \right)} = \frac{\pi^2 (1 - k^2)}{8} \quad (\text{A.53})$$

where k the coefficient of electromechanical coupling is equal to

$$k = d_{11} \sqrt{\frac{4\pi}{K_1^F s_{11}^E}} \quad (\text{A.54})$$

These values are used in equations (A.27) and (A.28) to evaluate the piezoelectric constants of quartz.

A.4. USE OF VOIGT'S RELATIONS IN LOCATING REGIONS OF LOW TEMPERATURE COEFFICIENT CRYSTALS FOR SIMPLE MODES OF MOTION

In Section 1.5 of the text, the statement is made that all longitudinally vibrating crystals of quartz have a zero or negative temperature coefficients. This can be proved from Voigt's relations for quartz and a knowledge of the temperature coefficients of the six elastic constants of quartz. Since the same method can be used to locate the regions of low temperature coefficient for other simple modes of motion a short discussion of the method is given here.

The Voigt relations given in equation (A.6) give the values of the piezo-

electric and elastic constants for crystals with their three edge dimensions along the three crystallographic axes. Most low-coefficient crystals, however, are oriented crystals with one or more of their edges lying along directions not parallel to the crystallographic axes. The theory of elasticity, however, provides methods for calculating the values of the constants for rotated axes. If the rotated axes X' , Y' , Z' are related to the crystallographic axes X , Y , and Z by the relation

$$\begin{array}{l} X' \\ Y' \\ Z' \end{array} \begin{array}{c} \left| \begin{array}{ccc} X & Y & Z \\ \hline \ell_1 & m_1 & n_1 \\ \ell_2 & m_2 & n_2 \\ \ell_3 & m_3 & n_3 \end{array} \right. \end{array} \quad (\text{A.55})$$

where ℓ_1, \dots, n_3 are the direction cosines between the axes indicated, the theory of elasticity provided relations between the stresses of the rotated axes and the stresses of the crystallographic axes, between the strains of the rotated axes and the strains of the crystallographic axes, and between the field, polarizations, or charges of the rotated axes and the same quantities for the crystallographic axes. Then if we express⁷ the relation between the stress, strain and fields for the rotated axes, the elastic and piezoelectric constants are determined.

Two shorthand methods are also available for calculating the constants of rotated crystals. One method⁸ is the matrix method which is based upon the fact that relations in (A.6) can be expressed in a matrix equation

$$-\epsilon = s^E X + dE \quad (\text{A.56})$$

where ϵ are the strain components, X the stress components, s^E the elastic compliance matrix, d the piezoelectric matrix and E the field components. By applying the rules of matrix multiplication the s and d matrices can be transformed to rotated axes having the direction cosines of equation (A.57) with respect to the crystallographic axes. The other method is the method of tensor analysis. Equations (A.6) can be expressed in the form⁹

$$-\epsilon_{ij} = s_{ij\alpha\beta}^E X_{\alpha\beta} + d_{ij\nu} E_\nu \quad (\text{A.57})$$

where ϵ_{ij} is the second rank strain tensor, $X_{\alpha\beta}$ the second rank stress tensor, $s_{ij\alpha\beta}^E$ the fourth rank compliance tensor, E_ν the field vector, and $d_{ij\nu}$ the third rank piezoelectric tensor. By employing the geometric rules for tensor

⁷ This method of determining the constants for rotated axes is discussed in a former paper "Dynamic Measurements of the Constants of Rochelle Salt," *Phys. Rev.*, April 15, 1939, Appendix I.

⁸ This method is discussed in a recent paper by W. L. Bond, "The Mathematics of The Physical Properties of Crystals," *B. S. T. J.*, Jan. 1943.

⁹ The tensor method of writing the elastic and piezoelectric relations is discussed by Atanasoff and Hart and by Lawson. See references (2) and (3).

transformation of axes, the components of the rotated tensors are easily calculated and the elastic and piezoelectric constants for rotated crystals determined.

The variation of Young's modulus as a function of orientation was first worked out by Voigt. In terms of the *IRE* angles specifying the orientation of a crystal plate, the *s* compliance modulus (inverse of Young's Modulus) is given by the equation

$$s_{11}^{E'} = s_{11}^E (\cos^2 \theta \cos^2 \psi + \sin^2 \psi)^2 + (2s_{13} + s_{44}^E) \sin^2 \theta \cos^2 \psi \\ \times (\cos^2 \theta \cos^2 \psi + \sin^2 \psi) + s_{33} \sin^4 \theta \cos^4 \psi - 2s_{14}^E \sin \theta \sin \psi \cos \psi \quad (\text{A.58}) \\ \times [3(\cos \varphi \cos \theta \cos \psi - \sin \varphi \sin \psi)^2 - (\sin \varphi \cos \theta \cos \psi - \cos \varphi \sin \psi)^2]$$

As discussed in Chapter II by W. L. Bond,¹⁰ the *IRE* angles are measured as follows: Taking the *X'* axis along the length of the crystal, the *Y'* along the width, and the *Z'* along the thickness, the angle θ is the angle between the *Z* or optic axis and *Z'*. φ is the angle between the projection of the *Z'* axis on the *XY* plane and the *X* axis, while ψ the skew angle is the angle between the length and the tangent to the great circle which contains the *Z* and *Z'* axes and the length of the crystal *X'*. A crystal having its thickness along the *X* axis (*X*-cut crystal) will have the angles

$\theta = 90^\circ$; $\varphi = 0^\circ$; ψ variable but equal to 90° when the length coincides with the *Y* axis. Under these conditions

$$s_{11}^{E'} = s_{11}^E \sin^4 \psi + (2s_{13} + s_{44}^E) \sin^2 \psi \cos^2 \psi \\ + s_{33} \cos^4 \psi - 2s_{14}^E \sin^3 \psi \cos \psi \quad (\text{A.59})$$

This equation has been made use of in evaluating the elastic constants of quartz as shown by equations (A.20). For this equation A_2 was measured from the *Y* axis rather than from the *Z* as in the *IRE* angle and

$$A_2 = \psi - 90^\circ \quad (\text{A.60})$$

Since from equation (A.19) the frequency of a long thin crystal in longitudinal motion is known to be

$$f = \frac{1}{2l} \sqrt{\frac{1}{\rho s_{11}^{E'}}} \quad (\text{A.19})$$

the longitudinal frequency of any oriented crystal can be calculated from equations (A.58) and (A.19).

It is the purpose of this section to show also that the temperature coefficient of the longitudinal frequency of any oriented crystal can be calculated provided we know the temperature coefficient of the six elastic constants of

¹⁰ Methods for Specifying Quartz Crystal Orientation and their Determination by Optical Means," this issue of the *B. S. T. J.*

quartz, and that regions of low temperature coefficient crystals can be located for this and other simple modes of motion for which the frequency can be calculated in terms of the elastic constants.

Differentiating equation (A.19) with respect to t the temperature

$$\frac{df}{dt} = -\frac{1}{2\ell} \sqrt{\frac{1}{\rho s_{11}^{E'}}} \left[+ \frac{d\ell}{dt} + \frac{1}{2} \left[\frac{d\rho}{dt} + \frac{ds_{11}^{E'}}{s_{11}^{E'}} \right] \right] \text{ or} \quad (\text{A.61})$$

$$\frac{df}{f} = T_f = -T_\ell - \frac{1}{2}[T_\rho + T_{s_{11}^{E'}}]$$

where T_α the temperature coefficient of the quantity α is defined as the rate of change of α with temperature divided by the value of α . The temperature coefficient of the length $\ell = X'$ is 7.8 parts per million per degree centigrade along the optic axis, and 14.3 parts per million perpendicular to it. For a general orientation, the temperature coefficient of length varies as

$$T_\ell = 14.3 - 6.5(\sin^2 \theta \cos^2 \psi) \quad (\text{A.62})$$

Since the total mass remains the same when the crystal expands, the temperature coefficient of the density is the negative of the sum of the coefficients of the three axes or

$$T_\rho = -36.4 \quad (\text{A.63})$$

Hence the temperature coefficient of frequency becomes

$$T_f = 3.9 + 6.5 \sin^2 \theta \cos^2 \psi - \frac{1}{2} \left(\frac{ds_{11}^{E'}}{s_{11}^{E'}} \right) \quad (\text{A.64})$$

Differentiating equation (A.58) we have as the temperature coefficient of a general orientation

$$T_f = 3.9 + 6.5 \sin^2 \theta \cos^2 \psi$$

$$\frac{1}{2} \left[\frac{s_{11}^E T_{s_{11}^E} (\cos^2 \theta \cos^2 \psi + \sin^2 \psi)^2 + (2s_{13} T_{s_{13}} + s_{44}^E T_{s_{44}^E}) \times \sin^2 \theta \cos^2 \psi (\cos^2 \theta \cos^2 \psi + \sin^2 \psi) + s_{33} T_{s_{33}} \times \sin^4 \theta \cos^4 \psi - 2s_{14}^E T_{s_{14}^E} \sin \theta \sin \psi \cos \psi \times [3(\cos \varphi \cos \theta \cos \psi - \sin \varphi \sin \psi)^2 - (\sin \varphi \cos \theta \cos \psi + \cos \varphi \sin \psi)^2]}{s_{11}^E (\cos^2 \theta \cos^2 \psi + \sin^2 \psi)^2 + (2s_{13} + s_{44}^E) \sin^2 \theta \cos^2 \psi \times (\cos^2 \theta \cos^2 \psi + \sin^2 \psi) + s_{33} \sin^4 \theta \cos^4 \psi - 2s_{14}^E \sin \theta \sin \psi \cos \psi [3(\cos \varphi \cos \theta \cos \psi - \sin \varphi \sin \psi)^2 - (\sin \varphi \cos \theta \cos \psi + \cos \varphi \sin \psi)^2]} \right] \quad (\text{A.65})$$

Hence since the elastic constants are definitely known, the temperature coefficient of any longitudinally vibrating crystal can be obtained when the separate temperature coefficients are evaluated.

The temperature coefficients appearing in equation (A.65) can all be evaluated from the temperature coefficient angle curves for X cut rotated crystals shown by Fig. 1.19. For an X cut crystal equation (A.65) reduces to

$$T_f = 3.9 + 6.5 \cos^2 \psi - \frac{1}{2} \left[\frac{s_{11}^E T_{s_{11}}^E \sin^4 \psi + (2s_{13} T_{s_{13}} + s_{44}^E T_{s_{44}}^E) \sin^2 \psi \cos^2 \psi + s_{33} T_{s_{33}} \cos^4 \psi - 2s_{14}^E T_{s_{14}}^E \sin^3 \psi \cos \psi}{s_{11}^E \sin^4 \psi + (2s_{13} + s_{44}^E) \sin^2 \psi \cos^2 \psi + s_{33} \cos^4 \psi - 2s_{14}^E \sin^3 \psi \cos \psi} \right] \quad (\text{A.66})$$

The value of $T_{s_{11}}^E$ is obtained directly for $A_2 = 0$ or $\psi = 90^\circ$, for $T_f = -2$ and hence

$$T_{s_{11}}^E = 11.8 \quad (\text{A.67})$$

Taking three other angles and solving for the remaining constants we find

$$T_{s_{14}}^E s_{14}^E = -5310; \quad (2s_{13} T_{s_{13}} + s_{44}^E T_{s_{44}}^E) = 45,130; \quad (\text{A.68})$$

$$T_{s_{33}} s_{33} = 17,400.$$

Inserting the values found for the elastic constants, two temperature coefficients are determined, and one relation is given between the others,

$$T_{s_{14}}^E = +119; \quad T_{s_{33}} = 182; \quad T_{s_{44}}^E - .1112 T_{s_{13}}^E = 228.2 \quad (\text{A.69})$$

The values of (A.68) are sufficient to determine the temperature coefficient of long thin crystals cut at any angle, for inserting these values in (A.65) the temperature coefficient for any oriented crystal in longitudinal vibration is given by

$$T_f = 3.9 + 6.5 \sin^2 \theta \cos^2 \psi - \left[\frac{+755 (\cos^2 \theta \cos^2 \psi + \sin^2 \psi)^2 + 22,565 \sin^2 \theta \cos^2 \psi (\cos^2 \theta \cos^2 \psi + \sin^2 \psi) + 8700 \sin^4 \theta \cos^4 \psi + 5310 \sin \theta \sin \psi \cos \psi [3(\cos \varphi \cos \theta \cos \psi - \sin \varphi \sin \psi)^2 - (\sin \varphi \cos \theta \cos \psi + \cos \varphi \sin \psi)^2]}{127.9 (\cos^2 \theta \cos^2 \psi + \sin^2 \psi)^2 + 175.8 \sin^2 \theta \cos^2 \psi (\cos^2 \theta \cos^2 \psi + \sin^2 \psi) + 95.6 \sin^4 \theta \cos^4 \psi + 89.2 \sin \theta \sin \psi \cos \psi [3(\cos \varphi \cos \theta \cos \psi - \sin \varphi \sin \psi)^2 - (\sin \varphi \cos \theta \cos \psi + \cos \varphi \sin \psi)^2]} \right] \quad (\text{A.70})$$

The only regions of low temperature coefficients are the regions for which the two big middle terms are small which requires that $\theta \rightarrow 0$, or $\psi \rightarrow 90^\circ$.

The first region would be a *Z*-cut crystal with its length somewhere in the *XY* plane and would result in a temperature coefficient of two parts per million negative. Such a crystal is not of much interest since there is no piezoelectric constant for driving it. The other region $\psi \rightarrow 90^\circ$ would also result in the length being near the *XI* crystallographic plane, but would allow the major surface to be made perpendicular to the *X* axis and hence would allow the crystal to be driven piezoelectrically. By allowing ψ to be slightly greater than 90° , the fourth term in the numerator can be made slightly negative and of a value greater than the two positive terms. This results in the $+5^\circ$ *X*-cut crystal having nearly a zero coefficient and this angle is the most favorable one for a low coefficient longitudinal mode of motion. All other directions have a negative temperature coefficient.

The remaining temperature coefficients of the six elastic constants can be evaluated from Fig. 1.12, and equation (A.22). The frequency temperature coefficient can be expressed by the equation:

$$T_f = 3.9 + 6.5 \cos^2 \theta + \frac{1}{2} \left[\frac{c_{66}^E T_{c_{66}^E} \sin^2 \theta + c_{44}^E T_{c_{44}^E} \cos^2 \theta + T_{c_{14}^E} c_{14}^E \sin 2\theta}{c_{66}^E \sin^2 \theta + c_{44}^E \cos^2 \theta + c_{14}^E \sin 2\theta} \right] \quad (\text{A.71})$$

since in terms of the *IRE* angles the series of crystals is given by $\varphi = -90$; $\theta = 90 - A_2$; $\psi = 90^\circ$. Taking the *AT*, *BT*, and *Y*-cut, whose coefficients have accurately been determined, we have

TABLE VI

Crystal Cut	Value of A_2	Value of θ	T_f	$T_{c_{66}^E}$	$c_{66}^{E'}$
<i>AT</i>	$+35.25^\circ$	54.75°	0	-12.0	29.39×10^{10} dynes/cm ²
<i>Y</i>	0	90	+86	164.2	40.50
<i>BT</i>	-49	139 or -41	0	-15.2	68.86

From these data and equation (A.71), the three temperature coefficients can be evaluated as

$$T_{c_{66}^E} = 164.2; \quad T_{c_{44}^E} = 165.7; \quad T_{c_{14}^E} = +90.2 \quad (\text{A.72})$$

To convert these into compliance temperature coefficients we have to make use of the relations of equations (A.8)

$$s_{66}^E = 2(s_{11}^E - s_{12}^E) = \frac{c_{44}^E}{c_{44}^E c_{66}^E - c_{14}^{E2}}; \quad s_{14}^E = \frac{-c_{14}^E}{2(c_{44}^E c_{66}^E - c_{14}^{E2});}$$

$$s_{44}^E = \frac{c_{66}^E}{c_{44}^E c_{66}^E - c_{14}^{E2}}.$$

Differentiating these with respect to t , we have

$$\begin{aligned}
 T_{s_{66}}^E &= T_{c_{44}}^E - \left[\frac{C_{44}^E C_{66}^E}{C_{44}^E C_{66}^E - C_{14}^E} (T_{c_{44}}^E + T_{c_{66}}^E) \right] + \frac{2C_{14}^{E^2}}{C_{44}^E C_{66}^E - C_{14}^E} T_{c_{14}}^E \\
 &= \frac{S_{11}^E}{S_{11}^E - S_{12}^E} T_{s_{11}}^E - \frac{S_{12}^E}{S_{11}^E - S_{12}^E} T_{s_{12}}^E \\
 T_{s_{14}}^E &= T_{c_{14}}^E - \left[\frac{C_{44}^E C_{66}^E}{C_{44}^E C_{66}^E - C_{14}^E} (T_{c_{44}}^E + T_{c_{66}}^E) \right] + \frac{2C_{14}^{E^2}}{C_{44}^E C_{66}^E - C_{14}^E} T_{c_{14}}^E \\
 T_{s_{44}}^E &= T_{c_{66}}^E - \left[\frac{C_{44}^E C_{66}^E}{C_{44}^E C_{66}^E - C_{14}^E} (T_{c_{44}}^E + T_{c_{66}}^E) \right] + \frac{2C_{14}^{E^2}}{C_{44}^E C_{66}^E - C_{14}^E} T_{c_{14}}^E
 \end{aligned} \tag{A.73}$$

TABLE VII

Temperature Coefficient	Present Determination	Previous Determination	Bechmann
$T_{s_{11}}^E$	+11.8	+12	+11.5
$T_{s_{12}}^E$	-1352	-1265	-1125
$T_{s_{13}}^E$	-294.8	-238	-148
$T_{s_{14}}^E$	+120	+123	+113
$T_{s_{33}}^E$	+182	+213	+180
$T_{s_{44}}^E$	+195.4	+189	+175
$T_{s_{66}}^E$	-134.2	-133.5	-119

TABLE VIII

Temperature Coefficient	Present Determination	Previous Determination	Atanasoff & Hart	Bechmann	Koga
$T_{c_{11}}^E$	-46.5	-54	-49.7	-48	-61.1
$T_{c_{12}}^E$	-3300	-2350	-3000	-2115	—
$T_{c_{13}}^E$	-697	-687	-580	-530	—
$T_{c_{14}}^E$	+90.2	+96	+107	+82	+110
$T_{c_{33}}^E$	-204.5	-251	-213	-208	—
$T_{c_{44}}^E$	-165.7	-160	-169	-151	-199
$T_{c_{66}}^E$	+164.2	+161	+170.1	+144	+199

Inserting the numerical values for the elastic constants and the temperature coefficients we have

$$\begin{aligned}
 T_{s_{66}}^E &= .883T_{s_{11}}^E + .1071T_{s_{12}}^E = -134.5; & T_{s_{14}}^E &= 121.4; \\
 T_{s_{44}}^E &= 195.4
 \end{aligned} \tag{A.74}$$

The value of $T_{s_1^E}$ provides a check on the accuracy of measurement since it has been measured in two ways. The agreement is within about 2 per cent which shows the probable accuracy of the measurement. Combining the coefficients of (A.69) with those given by equation (A.74), the complete temperature coefficients are given in Table VII together with previous determinations^{11,12}. The present determination differs from a previous determination by the writer due to the use of the elastic constants found here rather than Voigt's constants.

The temperature coefficients of the c_{ij}^E elastic constants are easily obtained from the s_{ij}^E constants by employing the relations of equation (A.8). These result in the temperature coefficient values for the c constants given in Table VIII.

By using the elastic constant data, the temperature coefficient data, and the equations of transformation for rotated axes it is possible to calculate the frequency and temperature coefficient of any simple mode for any orientation. Examples are given for a face shear mode and a thickness shear mode in a previous paper "Low Temperature Coefficient Quartz Crystals."¹³ This paper shows contour maps for low temperature coefficient crystals of these types.

¹¹ The first determination of the temperature coefficients of the writer was given in a paper "Electrical Wave Filters Employing Quartz Crystals As Elements," *B. S. T. J.*, July 1934, p. 446. A redetermination using better temperature coefficient data was given in a paper "Low Temperature Coefficient Quartz Crystals," *B. S. T. J.*, Jan. 1940. The present determination uses the same temperature coefficient data but slightly different elastic constants which results in slight changes in the temperature coefficients.

¹² A partial determination of the coefficients was made by Koga, Rep. Rad. Research, Japan 6, 1 (1934). Other complete determinations are R. Bechmann, *Hoch:tech. U. Elek. Akus.* 44,145 (1934) and Atanasoff and Hart, *Phys. Rev.*, Vol. 59, No. 1, Jan. 1, 1941, pp. 85, 96.

¹³ *B. S. T. J.*, Vol. XIX, 74 (Jan. 1940).

CHAPTER II

Methods For Specifying Quartz Crystal Orientation and Their Determination by Optical Means

By W. L. BOND

2.1 QUARTZ AND ITS AXES

The chemist describes quartz as silicon dioxide, SiO_2 , crystallized in hard, brittle, glass-like, six sided prisms, often with pyramidal terminations; melting point 1750° Centigrade, density 2.65, hardness on Moh's scale 7. It transforms from alpha to beta quartz at 573°C under atmospheric pressure. Under stress it transforms at lower temperatures. Alpha quartz is insoluble in ordinary acids but soluble in hydrofluoric acid; and in hot alkalis.

At first glance we might say that it had hexagonal symmetry but if we etch two adjacent pyramid faces we find that the microscopic etch pits are of different shape, hence the faces cannot be equivalent. It has three axes of two-fold symmetry and one axis of three-fold symmetry. Let us also remark that it does *not* have a center of symmetry or a six-fold axis. Figure 2.1 shows us that the three two-fold axes are perpendicular to the three-fold axis and are 120° apart. If they were not like this, they would not be self-consistent.

As we examine more and more quartz crystals we find that there is a tendency for pyramid faces to be alternately large and small, the larger faces being brighter than the smaller faces. Also the etch pits of *alternate* faces are similar. (The etch pit study is a powerful tool in determining crystal symmetry.) Further, two other "kinds" of faces are quite commonly found. If we draw such a crystal as though equivalent faces were of equal size we get such a picture as Fig. 2.2. It is an idealized figure used to illustrate the symmetry of quartz. The prism faces are marked *m*, the six faces marked *r* "constitute the primary rhombohedron"—the ones we called the large bright pyramid faces. The crystallographer thinks of these six faces as pieces of the faces of a rhombohedron. (A crystallographer's rhombohedron is like a cube stood on one corner, then the opposite corner pushed in a little towards the other, or pulled away from it. He thinks of it always as standing on this corner, as Fig. 2.3.) The *z* faces constitute a second rhombohedron—the secondary rhombohedron or minor pyramid faces. The *s* and *x* faces illustrate a further property of quartz. Figure 2.3 differs from its mirror image so that we

might expect to find two kinds of quartz that are related to each other as one's right hand is related to his left. We do find them and call them right-hand quartz and left-hand quartz respectively. They are illustrated in Fig. 2.4. These conventional figures are shown in many texts but no one has seen such perfect quartz crystals. They are drawn possessing just these faces and no others merely to illustrate the symmetry of quartz and its occurrence in right-handed and left-handed forms.

These figures are also useful in defining how a blank shall be cut from one kind of quartz. It is found that if a crystal be compressed with forces

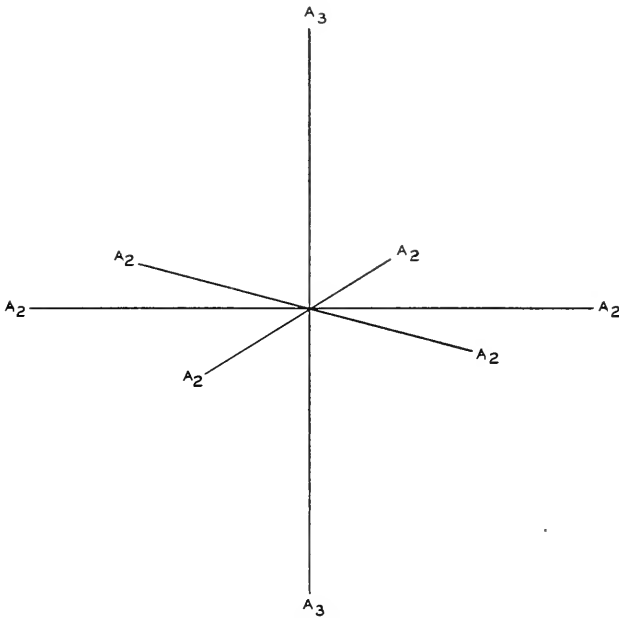


Fig. 2.1—Hexagonal axis system

parallel to a pair of sides of the hexagon an electric polarization takes place in the direction of the forces. The edge "modified" by the presence of s and x faces becomes negative. If we allow these charges to leak off and then suddenly release the mechanical forces the "modified" edge becomes positively charged as the crystal expands. This is true for both right-hand and left-hand crystals.

Let us now talk about right-hand quartz. Since expansion is considered as a positive strain (contraction as negative) it is decided to take the positive end of the electric axis as pointing towards the modified edge. This gives us a positive charge at the positive end of the electric axis when a positive stress (tension) is applied along this axis. This positive direc-

tion of an electric axis is taken as the positive x axis of a right-hand xyz rectangular coordinate system. The z axis is taken along the axis of the hexagonal prism, and since the x axis is an axis of two-fold symmetry we

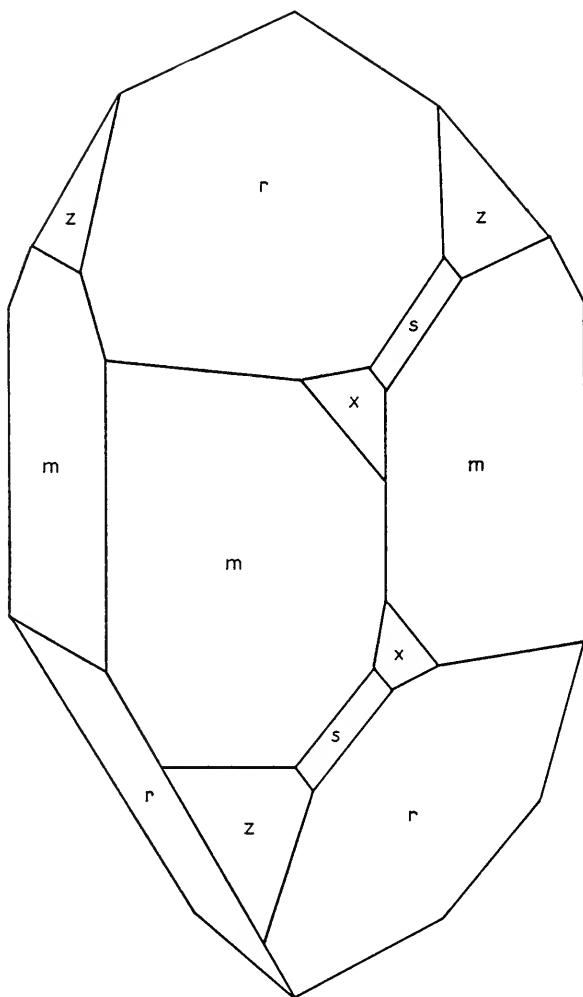


Fig. 2.2—An idealized quartz crystal

can take either end of the prism as the direction of $+z$. We then choose y to form a right-handed coordinate system. (In a right-handed system if a right-handed screw turns about the z axis in the sense x to y it would ad-

vance in the positive z direction.) The y axis will always lie directly under a major rhombohedral face.

We could define the x , y and z axes for a left-hand crystal as forming a left-hand system. Though this is a useful conception in mathematical

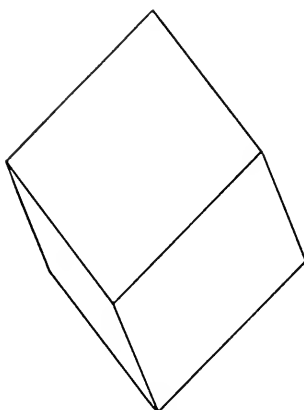


Fig. 2.3—A rhombohedron

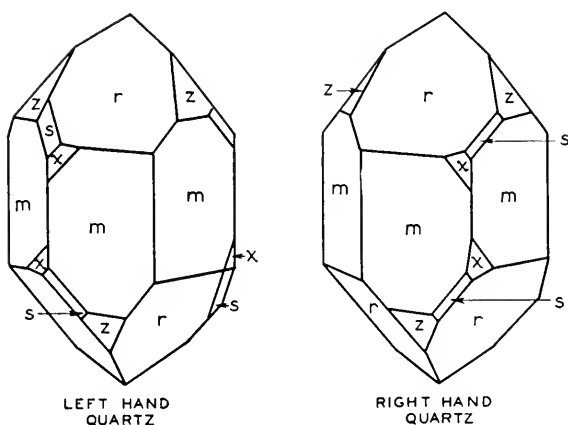


Fig. 2.4

studies, we can dodge this “double standard” by a simple device. For use as a crystal circuit element, left-hand quartz can be used just as well as right-hand quartz. In designing such an element it suffices to think always in terms of right-hand quartz and issue specifications for this kind only, using always right-hand coordinate systems. If now for left-hand

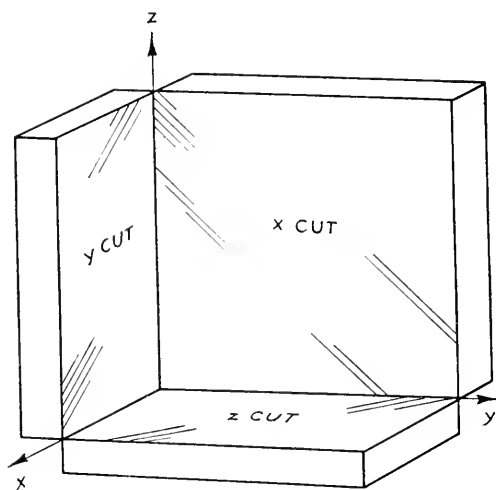


Fig. 2.5—Simple crystal cuts

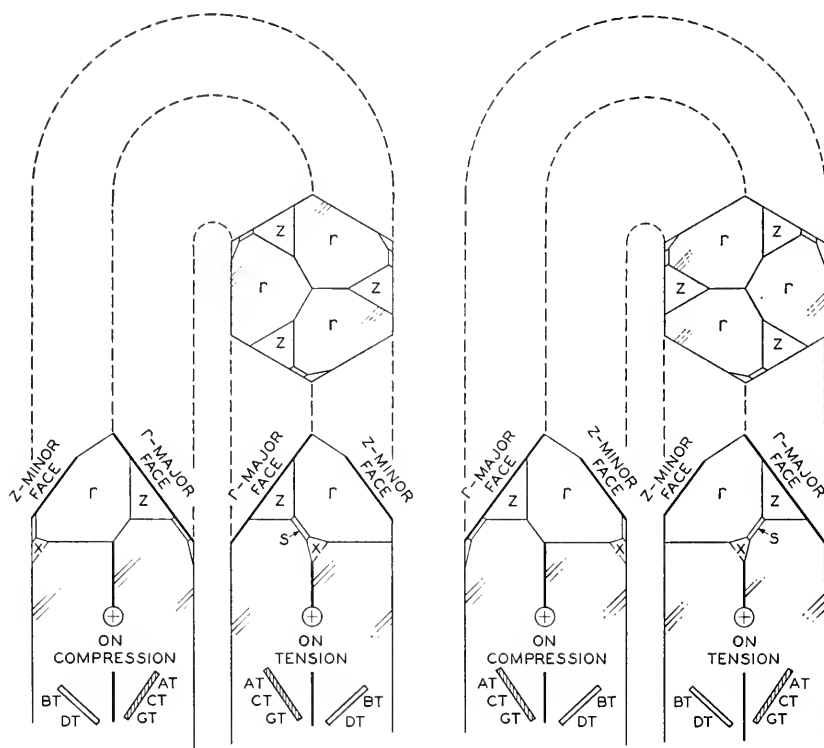


Fig. 2.6—Simply rotated cuts

crystals we mark the negative end of the electric axis as positive we can treat it exactly as though it were a right-handed crystal.

The first plates used were x and y piezoids (squeezing solids). For these simply described cuts one does not need to know the quartz "handedness." These crystals had large frequency temperature coefficients. But when Lack, Willard and Fair brought out the low temperature coefficient AT plate, its more complicated orientation required the right-left differentiation. The AT, the subsequent BT, CT, DT, etc., were thought of as y -cuts rotated through various angles about the edge that coincided with x . For example, the AT was a $+35\frac{1}{4}^\circ$ cut, or was a y plate rotated $35\frac{1}{4}^\circ$ about x ; the BT was a -49° cut. Their orientations are illustrated in Fig. 2.6.

As more complicated orientations were designed to give even better temperature coefficients at extreme frequencies the description became more difficult, requiring the specification of two or three angles. Many schemes for specification have been devised but the Institute of Radio Engineers is recommending the adoption of a system we shall call the I.R.E. system.

The crystal designer has the problem: "How shall I orient the length, width and thickness of a piezoid with respect to the x , y and z axes so as to give the required electrical properties? He thinks in terms of fixed x , y and z axes, variable piezoid edge directions. The crystal cutter has the converse problem. "How shall I orient the x , y and z axes of the crystal so that fixed saws will give the required surfaces?" For this reason the most convenient orientation angles from the designer's viewpoint may not be the simplest from the cutter's viewpoint. Also the translation from one set to the other may not be simple.

The early methods of orientation specification were somewhat chaotic. There was no overall plan of what angles were to be specified and from what axes they were to be measured. Each group of crystals was a law unto itself.

THE I.R.E. ORIENTATION ANGLES

The relations between the x , y and z axes of the crystal and the length, width and thickness of the piezoid are given in Fig. 2.7.

The position of Fig. 2.7 may be considered as a result of turning the piezoid through the successive angles ϕ , θ , ψ starting from an initial position length parallel to x , width parallel to y and thickness parallel to z as in Fig. 2.8. First the crystal is turned through angle ϕ about z in the direction shown in Fig. 2.7. Then it is lowered through angle θ about an axis parallel to the width direction, again in the direction shown in Fig. 2.7. Finally it is skewed through an angle ψ about an axis parallel with the thickness direction in the sense shown in Fig. 2.7.

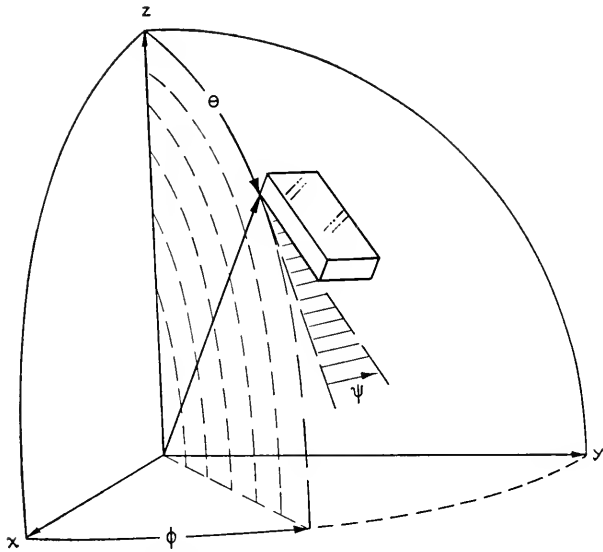


Fig. 2.7—The I.R.E. orientation angles

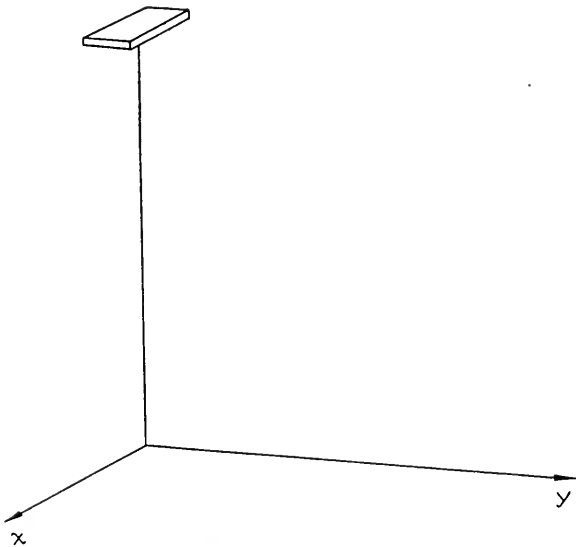


Fig. 2.8—The initial position 0, 0, 0 for the I.R.E. angles

THE I.R.E. ANGLES FOR A FEW STANDARD PIEZONDS

Name	ϕ	θ	ψ
z	0	0	0
x	0	90	90
-18° Filter	0	90	108
+5° “	0	90	85
y	90	90	90
AT	-90	54 ³ ₄	90
BT	-90	-41	90
CT	-90	52	90
GT	-90	38° 52'	±45°
MT	6° 40'	50° 28'	79° 36'
NT	9° 25'	40° 40'	77° 40'

2.2 ORIENTATION BY NATURAL FACES

With well faced material one can do an accurate job of orienting without X-rays if he knows the faces of quartz thoroughly.

The quartz rhombohedral faces are highly perfect and polished, the major often more so than the minor. With two such faces a device like that illustrated in Fig. 2.9 could be used to give an orientation accurate to a minute or two. An adjustable base, symbolized here as a ball and socket, is adjusted so that the eye centers the lamp filament image on the cross hairs, first for one face, and then, turning the base about on the reference table it is adjusted for another face. When the images all pass through center as the base is turned on the table the optic axis is perpendicular to the table. When any one image is centered, the electric axis is perpendicular to the plane of the paper. This with the already mentioned fact that AT plates are cut near a minor face and BT's near a major, allows us to cut the crystal accurately.

Although the rhombohedral faces are highly perfect the prism faces never are. On the prism face, true prism faces that are very short in the z direction alternate with short rhombohedral faces to give the general contour a slant. These "steps" give the face a striped look. The stripes are known as growth lines or striations. They are parallel to x and can be used to find x to a degree or so. If we sight on striations on two adjacent faces we can locate the optic axis to nearly the same accuracy since the optic axis is perpendicular to the striations on all faces.

There are several indications that help us find, from the prism, where the major rhombohedron would be in the absence of such faces. Some crystals grow in the form shown in Fig. 2.10. They are symmetrically doubly terminated and a very narrow prism is found under the major rhombohedron, a wide face under the minor. Hence given a portion like that enclosed in the dotted line we could deduce the complete orientation.

Some crystals grew out at right angles to a wall and because they grew

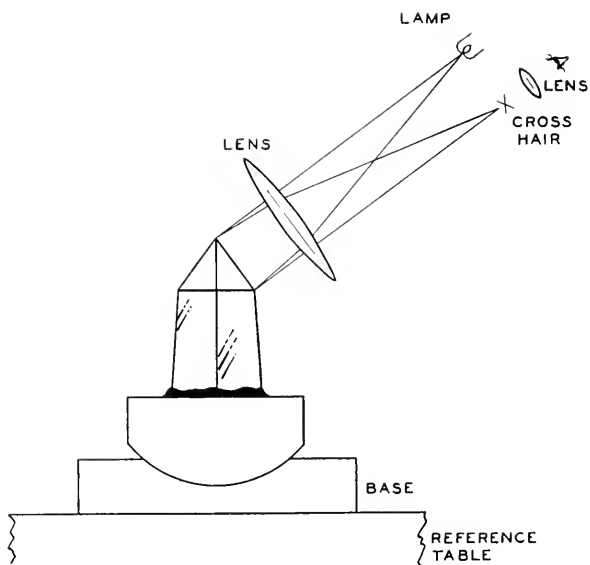


Fig. 2.9—Optical orientation by reflection of light from faces

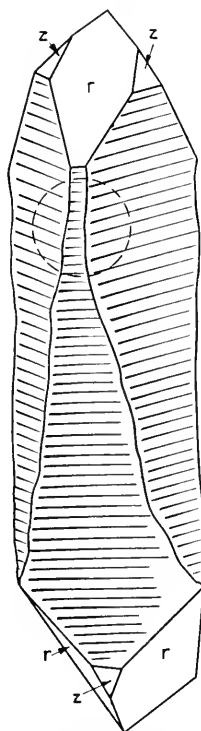


Fig. 2.10—A type of quartz growth

along a z axis in one direction only, the x axis does not appear to be one of two-fold symmetry. Such a crystal is illustrated in Fig. 2.11. Here the prism faces under a major rhombohedron are tapered and bright, the prism faces under a minor are relatively parallel sided and very dull. The bright prism faces are much more nearly parallel to the optic axis than the dull ones. Again, given a portion of the prism we can deduce the orientation.

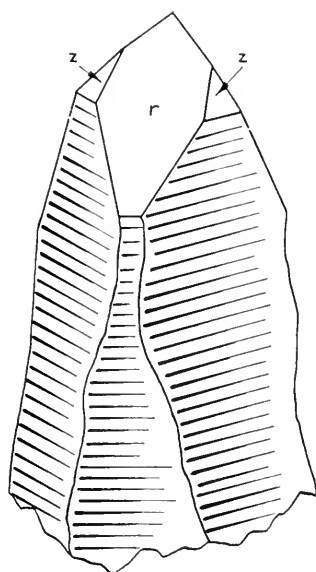


Fig. 2.11—Another type of quartz growth

2.3 FLAT LAY CUTTING

Flat lay cutting takes advantage of the fact that, although tapering quartz prisms have their faces non-parallel to the z axis the prism faces are parallel to the x axis. A crystal is cemented prism face down, to a mounting plate. The mounting plate is tilted and turned on a base plate to render the optic axis parallel to the long edge of the base plate. This is done in a conoscope. Now the edges of the base plate are the x , y , z axes of the crystal.

The crystal can now be cut directly into wafers for dicing into AT's, BT's etc. by mounting on an angle bracket as shown in Fig. 2.13 or cut into X sections from which AT or BT bars shall be made by merely sawing down the length. Again z sections can be cut by cross cutting. Good z sections can be made in this way in the total absence of faces. These sections can

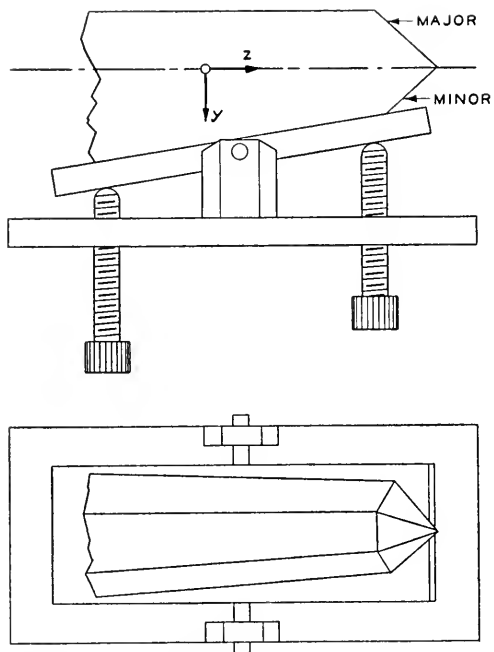


Fig. 2.12—Optical adjustment for the sawing of Z sections or direct crystal blank slabs

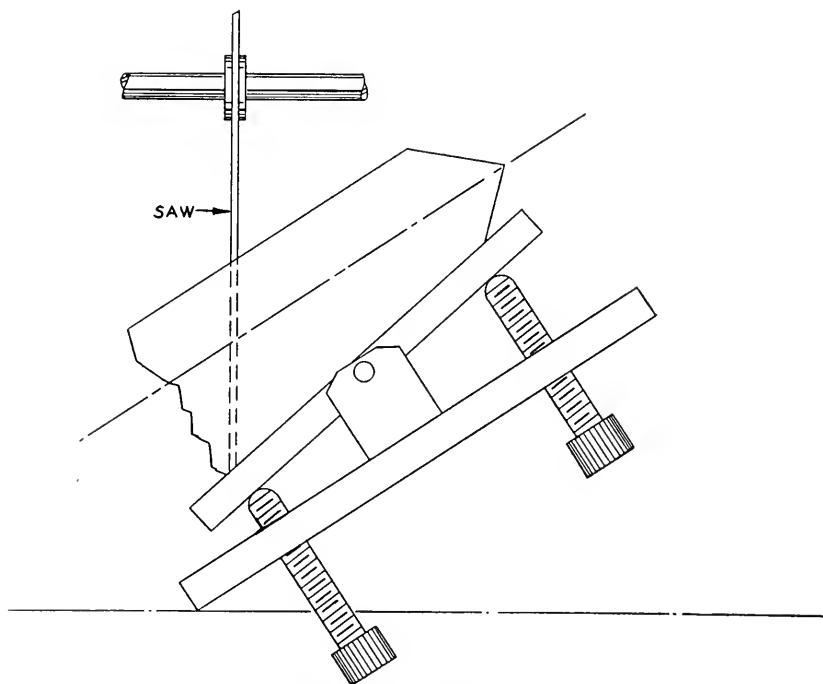


Fig. 2.13—Direct sawing of the slabs

then have their x axes determined by etching and X-rays and cut up by the Z section cutting method.

By turning the base plate on the angle bracket and dicing the wafers at an angle any orientation can be obtained.

2.4 Z SECTION OR VERTICAL CUTTING

Having a true Z basal section it is first marked for the $+x$ axis. The simplest procedure is to use the star mark; for right-hand quartz (R.H.Q.)

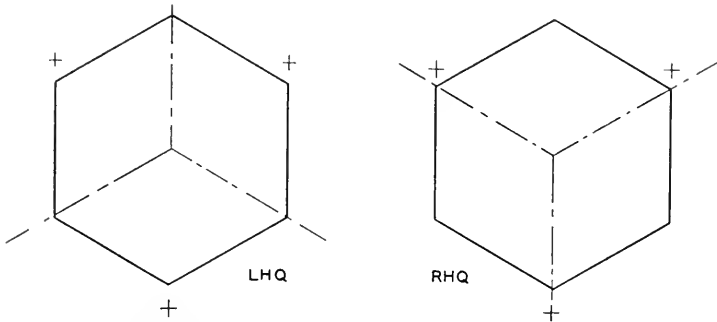


Fig. 2.14—Marking the "sense" of righthand and lefthand sections

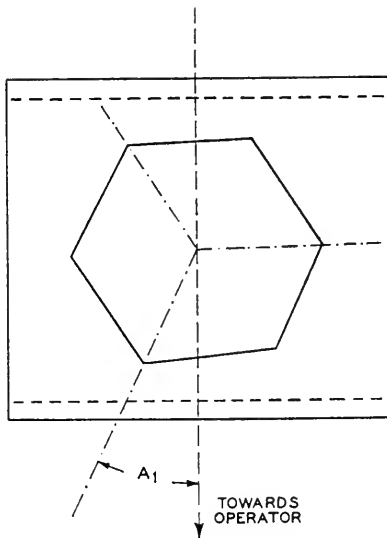


Fig. 2.15—Making the rotations A_1

the rays should point toward the plus electric axis, for left-hand quartz the rays should point towards the negative electric axis.

The section is now placed on the carriage plate, one ray pointing towards the operator (which ray is decided on the basis of the economy of quartz).

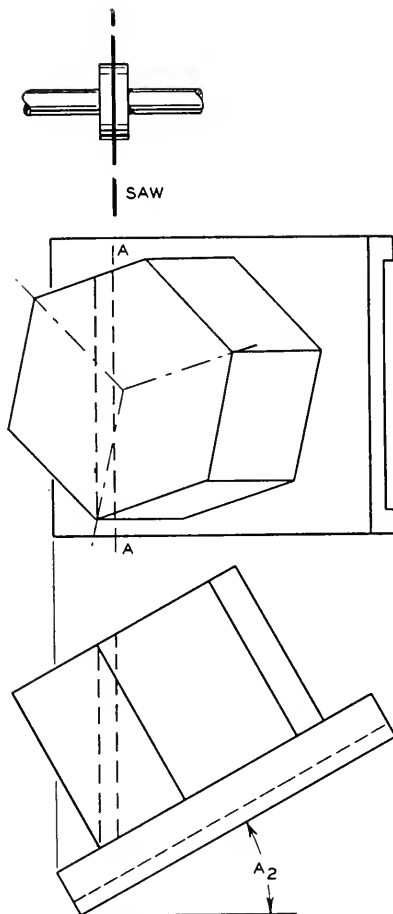


Fig. 2.16—The rotation A_2

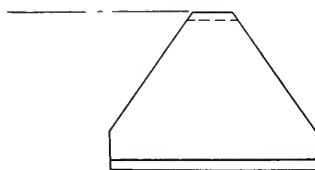


Fig. 2.17—The slab after the rotations A_1 and A_2

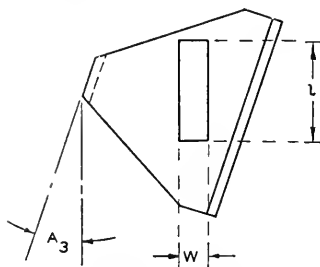


Fig. 2.18—Making the A_3 rotation

The section is then rotated clockwise on its base, through angle A_1 as in Fig. 2.15 and cemented in this position.

The carriage plate is then transferred to a diamond saw angle bracket of tilt A_2 , as in Fig. 2.16, and the crystal is sawed into slices slightly thicker than the required final thickness t .

The operator turns these slices down flat on the table of a dicing saw as in Fig. 2.17 by rotating the slices 90° clockwise about the axis AA , then turns the slice through angle A_3 as in Fig. 18 and makes a cut. The plate is finished as shown in Fig. 2.18.

Since the angle bracket is not reversible, negative A_2 angles are cut by adding $\pm 180^\circ$ to A_1 and reversing the sign of A_3 .

THE A ANGLES FOR SOME STANDARD PLATES

Cut	A_1	A_2	A_3
x	90°	0	0
y	0	0	0
z	0 or 90°	90°	0 or 90°
-18	90°	0	$+18^\circ$
$+5$	90°	0	-5
AT	0	$35\frac{1}{2}$	0
BT	180°	$+49^\circ$	0
CT	0	38°	0
DT	180°	52°	0
GT	0	$51^\circ 7'$	$\pm 45^\circ$
MT	$96^\circ 40'$	$39^\circ 32'$	$-10^\circ 24'$
NT	$99^\circ 25'$	$49^\circ 20'$	$-12^\circ 20'$

2.5 THE RELATION BETWEEN THE I.R.E. ANGLES $\Phi\theta\psi$ AND THE Z SECTION ANGLES A_1, A_2, A_3

It can be shown that:

$$A_1 = 90 + \phi$$

$$A_2 = 90 - \theta$$

$$A_3 = -90 + \psi$$

2.6 POLARIZED LIGHT AS APPLIED TO CRYSTALS

Light consists of electromagnetic "vibrations." The vibrations are perpendicular to the direction of propagation but ordinarily helter-skelter in all directions perpendicular to the propagation. The color of the light is determined by the vibration frequency, blue vibrating more rapidly than red. In a vacuum, light travels at 186,000 miles per second (3×10^{10} cms per second) all colors at the same velocity. On entering a transparent medium the velocity is reduced, ordinarily blue being slowed more than red. The frequencies are unaltered on entering the medium.

Light traveling through a uniaxial crystal in the direction of Fig. 2.19 breaks up into two components that travel at different velocities. For one

of these components the vibration is all in the plane of poz , of the other the vibration is all perpendicular to the plane of poz .

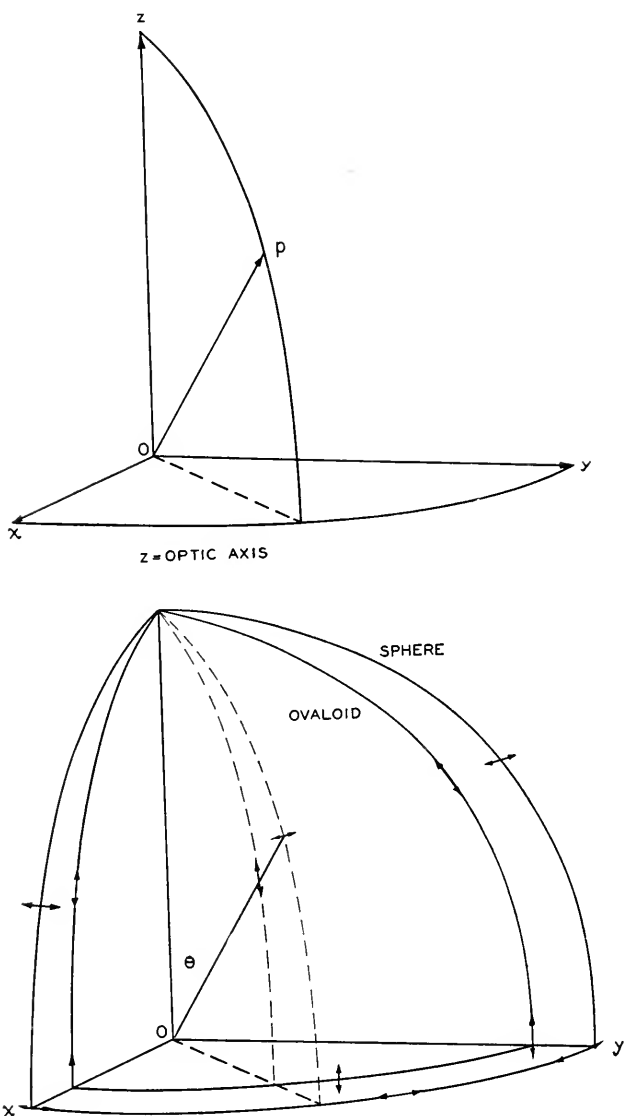


Fig. 2.19—The velocities of light in a uniaxial crystal

A plot of the propagation velocities for all directions is a surface of two sheets, one octant of which is shown in Fig. 2.19. One sheet is a sphere;

the other sheet, which is an ovaloid of revolution, touches the sphere at the two points where the double sheet is pierced by the optic axis. Of the two rays traveling along one line, the one with a velocity corresponding to the sphere is called the ordinary ray; the one with a velocity corresponding to the ovaloid is called the extraordinary ray. For quartz the ovaloid is prolate and lies inside the sphere. For tourmaline the ovaloid is oblate and lies outside the sphere. The small arrows show the direction of vibration. Each of the components is said to be polarized since for each all the vibration is in one direction.

Since both sheets are surfaces of revolution with the optic axis as the axis of revolution, we can never tell the x axis from the y axis by optical means.* Only the z axis is a unique direction and can be determined optically. If this figure is taken to represent the case for blue light there will be a slightly larger but similar figure for red light since, in the crystal, red light travels faster than blue light.

Some kinds of crystals have velocity plots for which the double sheet surfaces touch at four points. Hence they have two optic axes and are called biaxial. All hexagonal, rhombohedral and tetragonal crystals are uniaxial, all others except the isometric ones are biaxial. Rochelle Salt is biaxial.

2.7 POLARIZERS AND ANALYZERS

In the Nicol prism means were found to eliminate the ordinary ray; the other is transmitted as polarized light. That is, ordinary light of any or all colors upon passing through a Nicol prism emerges as plane polarized light with no change in color.

Transparent colored media appear colored because they absorb some colors of light more than other colors. In colored crystals the two rays themselves often differ in their color absorption so that the crystal as viewed by means of the ordinary ray seems to be of a different color than as viewed by the extraordinary ray. Quinine iodo-disulfate, or Herapathite, absorbs most visible colors of one ray almost completely; transmits about 60% of the visible colors in the other ray. Hence light emerging from this crystal is almost completely polarized. In the commercial product called "polaroid", myriads of such crystals, microscopic in size, are contained in a celluloid-like sheet and oriented by stretching the sheet. This material now replaces Nicol prisms for all but the most exacting uses.

If we put two identical polaroid sheets together with their transmission vibration directions parallel as in Fig. 2.20 we can see through them but if their transmission vibration directions are at right angles we cannot see

* Methods depending on etch pits are excluded. They are optical only in the sense that observing natural faces is optical.

through them because the second sheet can transmit none of the vibrations transmitted by the first sheet. As we rotate the second sheet back from complete extinction to "best transmission" the transmitted light increases sinusoidally. In any such arrangement as Fig. 2.20 the first sheet is called the polarizer, the second is called the analyzer. The name analyzer is chosen because light that can be extinguished by means of a suitably rotated analyzer must be plane polarized, and it must be vibrating at right angles to the transmission vibration direction of the analyzer when set for extinction. The transmission vibration direction of a polaroid plate will hereafter be called its vibration axis.

Let us go back to Fig. 2.19 and cut out from around the point p , the small tangential crystal plate shown magnified in Fig. 2.21. Here p is the direction of propagation as before, and z is parallel to the optic axis. Also s which is

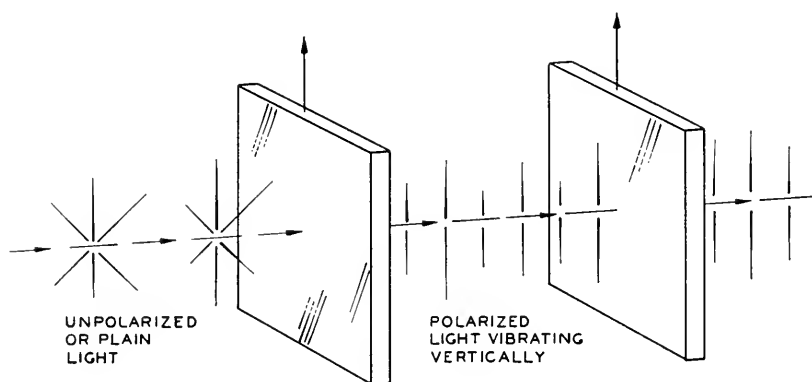


Fig. 2.20—Light polarization

in the plane of p and z , is the direction of slow vibration while f which is perpendicular to this plane is the direction of fast vibration. The vibration frequency is really the same for both. "Slow vibration" means "vibration direction for slow transmission." All directions of propagation that have this vibration axis have the same velocity.

In Fig. 2.22 we have placed this plate between "crossed polaroids"—that is polaroids set for extinction. The slow direction makes an angle α with the polarizer vibration axis. When this vertical-polarized ray of intensity I enters the crystal it breaks up into components, one of intensity:

$$I \cos^2 \alpha \text{ vibrates along } s \quad (2.1)$$

and one of intensity

$$I \sin^2 \alpha \text{ vibrates along } f \quad (2.2)$$

as illustrated in Fig. 2.23.

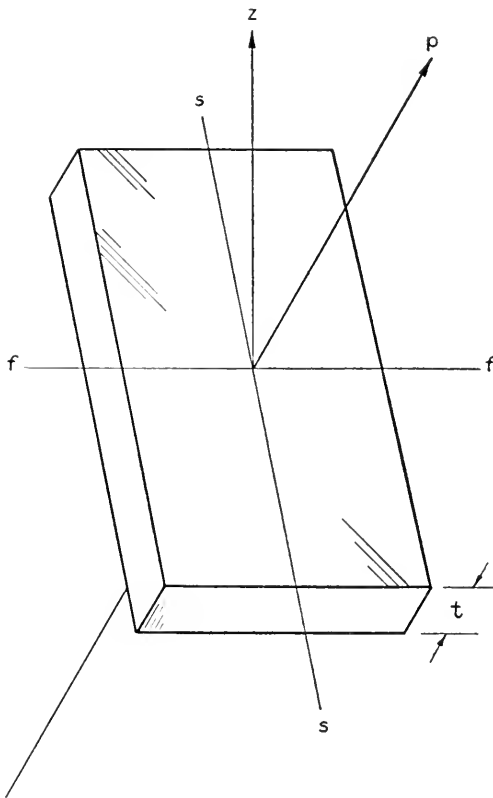


Fig. 2.21—Light breaks into components in the crystal

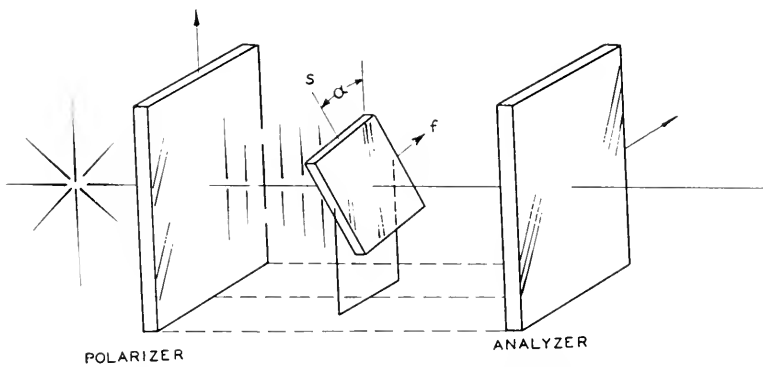


Fig. 2.22—Transmission when a crystal is placed askew between crossed polarizers

If $\alpha = 0$ the fast component reduces to zero and the slow component goes through the crystal unchanged hence emerging plane polarized. It can

then be extinguished by the analyzer. If $\alpha = 90^\circ$ the slow component reduces to zero and the fast one goes through unchanged and again can be extinguished by the analyzer. This effect can be used to check crystal orientations. Such an instrument fitted with a divided circle used to measure α is called a stauroscope. The stauroscope often uses a special analyzer capable of better determination of extinction setting.

If α is not 0 or 90° two components traverse the crystal and recombine at the boundary. These two components are at right angles to each other; they are of unequal intensities, and they differ in phase because they traveled at different speeds.

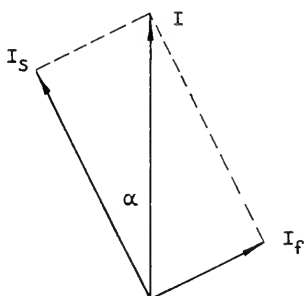


Fig. 2.23—The intensity of the two components from Fig. 22

Now v_s and v_f have the same frequency F so that in unit time each makes F wave-lengths. This requires that the slow ray have F wave-lengths in a distance v_s and hence that each wave have a length:

$$\lambda_s = \frac{v_s}{F} \quad (2.3)$$

Similarly

$$\lambda_f = \frac{v_f}{F} \quad (2.3')$$

In a distance t there are $\frac{t}{\lambda_f}$ fast waves and $\frac{t}{\lambda_s}$ slow ones. Let us say that there are N more fast waves than slow ones in the distance t . Consequently $N = \frac{t}{\lambda_f} - \frac{t}{\lambda_s}$ which, from (2.3) and (2.3') may be written:

$$N = \frac{tF}{v_f} - \frac{tF}{v_s} \quad (2.4)$$

All the data on light are given in terms of wave-lengths in a vacuum, not in terms of frequency, so we will assume that in a vacuum the wave-length

of this light is λ , and as in a vacuum its velocity is $V (= 3 \times 10^{10}$ cms per second) an equation similar to (2.3) would tell us that $\lambda = \frac{V}{F}$ and hence that:

$$F = \frac{V}{\lambda} \quad (2.5)$$

With (2.5) we can rewrite (2.4) as

$$N = \frac{t}{\lambda} \left(\frac{V}{v_f} - \frac{V}{v_s} \right) \quad (2.6)$$

The ratio of the velocity in a vacuum to the velocity in a medium is called the refractive index of the medium commonly given the symbol n . For most transparent materials n is between 1.3 and 1.8.

We write these refractive indices as

$$\frac{V}{v_f} = n_f \quad \text{and} \quad \frac{V}{v_s} = n_s \quad \text{respectively.}$$

Now (2.4) becomes:

$$N = \frac{t}{\lambda} (n_f - n_s) \quad (2.7)$$

After passing through the crystal plate of thickness t , Fig. 2.21, the two light components recombine. They are polarized at right angles each to each; they are of unequal intensities, and they differ in phase by N wavelengths as given by equation (2.7).

If the crystal were vanishingly thin the two components that recombine would be effectively in step or in phase. In Fig. 2.24 we have plotted vibration amplitude against time for these two components. They are separated for clarity. In the upper curve the slow vibration is shown as vertical, in the center curve the fast one is shown as horizontal. In the lower curve corresponding points have been added vectorially. From actual construction we see that in the resultant curve the vibration is always parallel to the line AA' . Hence it is plane polarized and can be extinguished by means of an analyzer.

Let us now consider the case of a thicker plate for which the slow wave gets a quarter-wave-length behind the faster one. This case is plotted in Fig. 2.25 in the same way that the previous case was plotted in Fig. 2.24. It turns out to be a space curve like a slightly flattened corkscrew. Viewed along the axis it looks like an ellipse, as shown to the right of the space curve. If the slow ray had lost but a little with respect to the fast ray, we would have gotten a very flat ellipse. If the two components had had the

same amplitude with the quarter wave phase difference the end view in Fig. 2.25 would have been a true circle. Now since the vibration, in these cases, is not all in one plane, the light cannot be extinguished by an analyzer; it is not plane polarized light. In the one case it is called "elliptically polarized" light and in the other, "circularly polarized" light. If the slow ray loses an integral number of wave-lengths, it makes no difference; only frac-

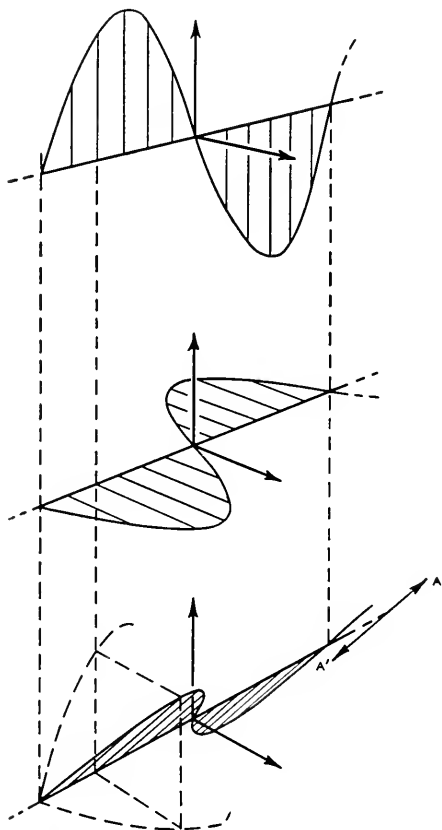


Fig. 2.24—The recombination of the light components after passing through a thin crystal

tions of wave-lengths count, except that if several wave-lengths are present a thickness that is right to give an integral number of wave-lengths for one color may give an integer plus a fraction for some other color. If the thickness is fairly small, this may cause spectral colors from white light. For thick plates the wave-lengths so overlap that the field appears colorless but dark or white according to the value of the angle α ; i.e., if α is zero or

90° the field is dark; if $\alpha \neq 0$ or 90° the field is bright. In Fig. 2.26 we illustrate how, for one color of light the polarization starts out as plane at the

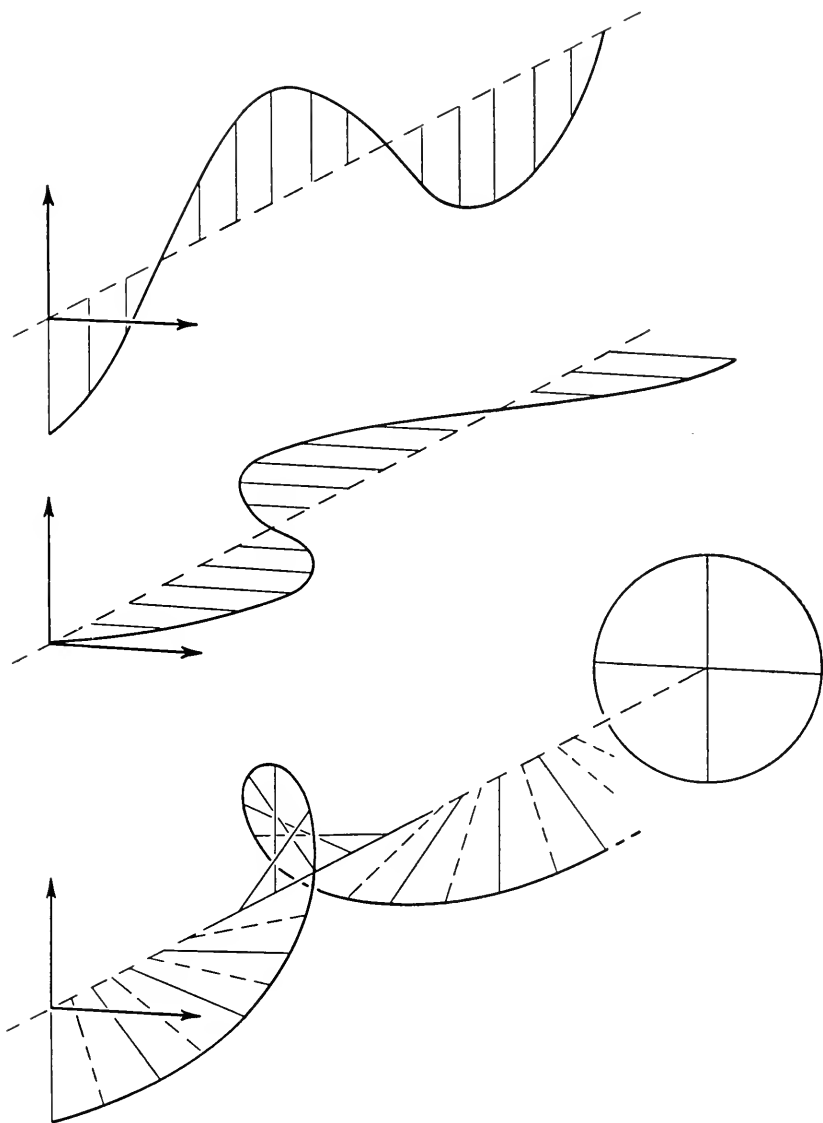


Fig. 2.25—Recombination more generally

crystal boundary, passes through elliptical to circular polarization, then flattens out the other way through elliptical to plane polarization at a distance

in the crystal corresponding to the slow wave being one wave-length behind the fast one.

In Fig. 2.27 we show two AT plates resting on a reference surface. In the first crystal the propagation is perpendicular to x , in the second crystal it is

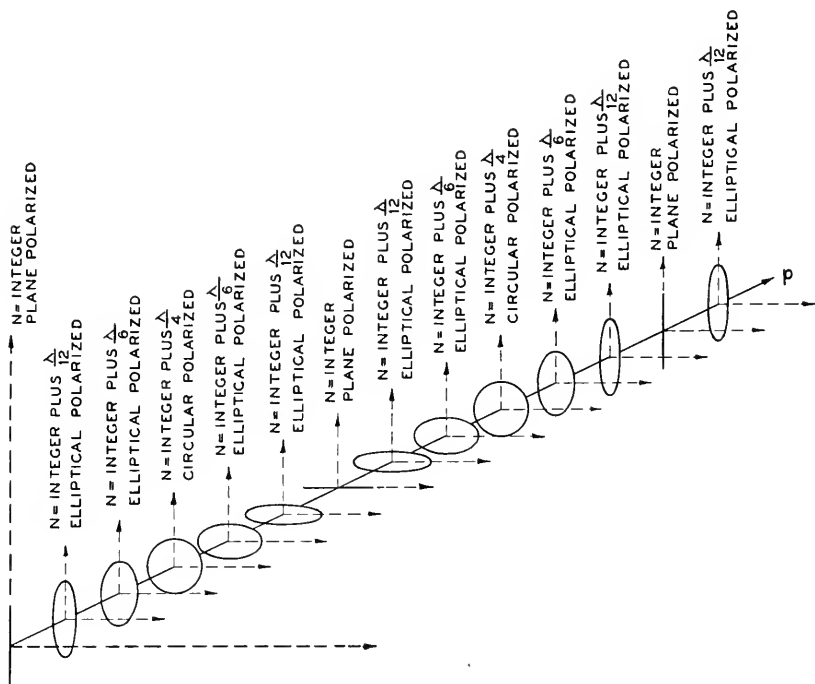


Fig. 2.26—How the kind of polarization changes with crystal thickness

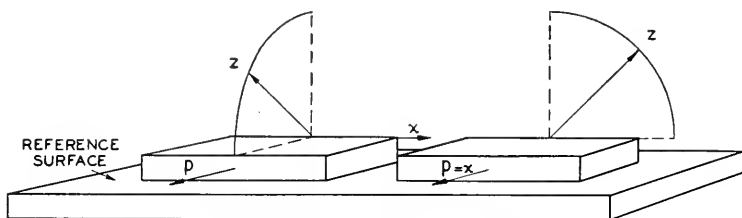


Fig. 2.27—The normoscope principle

along x . If the reference surface is the reference table of a simple stauroscope the edge of the first crystal will appear dark because $\alpha = 0^\circ$ or 90° ; the edge of the second crystal will appear bright because α is not 0° or 90° . Actually this α for an AT plate can be $\pm 35^\circ \pm$ any multiple of 90° because we don't know whether z stands out to the right or to the left. Hence the

reading might be, for instance, -35° , $+35^\circ$, $+55^\circ$, $+125^\circ$, etc. This is the principle of the *normascope* used to identify the x direction for crystal adjustment.

Let us study these relative phase shifts at different angles near the optic axis. Now quartz has an optical complication beyond that just described—it rotates the plane of polarization of plane polarized light traveling along the optic axis. This complicates our present attempt to build up a background sufficient for an understanding of the conoscope. But the conoscope finds the optic axis for other crystals that do not rotate the plane of polarization, tourmaline for example; so we will ignore this rotation, to be

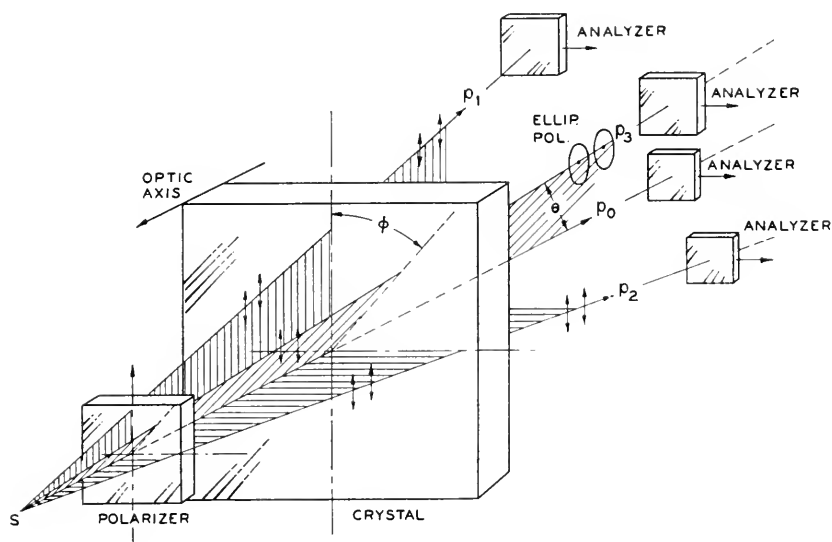


Fig. 2.28—How the polarization changes with propagation direction in a crystal plate

gin with, in order to arrive quickly at some useful conclusions. We will later explain how optical rotation modifies these conclusions.

Consider then the crystal z section shown in Fig. 2.28. A source s sends monochromatic light through the polarizer which passes only vertical vibrations. We will assume that the light passes in and out of the crystal without a deviation of path. Since the vibration is in the plane of z and p_1 (its direction of propagation) the ray does not break up inside the crystal but is propagated as plane polarized light, unchanged. An analyzer set for vertical extinction could then extinguish this ray.

This is true for propagation from s anywhere in this vertical plane. Also since the vibration is perpendicular to the plane of z and p_2 the ray p_2 does not break up inside the crystal but passes through and out un-

changed. All rays from s in the horizontal plane emerge plane polarized and can be extinguished by an analyzer set for vertical extinction. The ray p_0 is in both these planes so it can be similarly extinguished.

With the ray p_3 the situation is different. Here the vibration is not in the $z p_3$ plane so the ray breaks up inside the crystal into two components which travel with different velocities and recombine in or out of phase to give the various degrees of elliptical polarization (including plane and circular). Hence, an eye looking back along p_3 , through an analyzer set for vertical extinction, will see light or dark depending on the phase shift N . Now this phase shift for a given thickness of plate is zero along p_0 but increases as θ increases (without changing ϕ ; see Fig. 2.28), passing through one integral

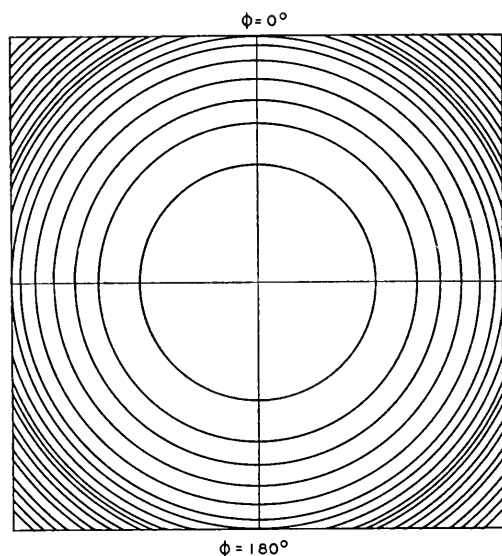


Fig. 2.29—A plot of phase as a function of ϕ and θ

value after another. Therefore, as we allow θ to increase, the eye should see alternate dark and bright regions. Moreover, since the crystal is optically symmetric about z , if ϕ is changed without changing θ , the apparent brightness will not change (except that if $\phi = 0, 90^\circ, 180^\circ$ or 270° the field is dark as we previously explained). Consequently, if we could see along all directions at once we would see a pattern of concentric dark rings on a dark cross as shown in Fig. 2.29.

But we *can* see along all these directions at once if we employ a properly placed lens for a lens can converge all these rays to one point where an eye can be placed for viewing.

Thus an eye at e , Fig. 2.30, will see, in the direction $e p_0'$, the ray that

started along $s p_0$. It will see along $e p_1'$ the ray that started along $s p_1'$. Every point on the lens will have associated with it a different direction in the crystal. Therefore the eye will see a pattern like that of Fig. 2.29. This is the principle of the conoscope. In the conoscope (the name means "conical viewing") the source s is replaced by the image of a source, the image being cast by a lens; see Fig. 2.31. Thus by the use of two similar lenses we get twice as much working space as one lens would give.

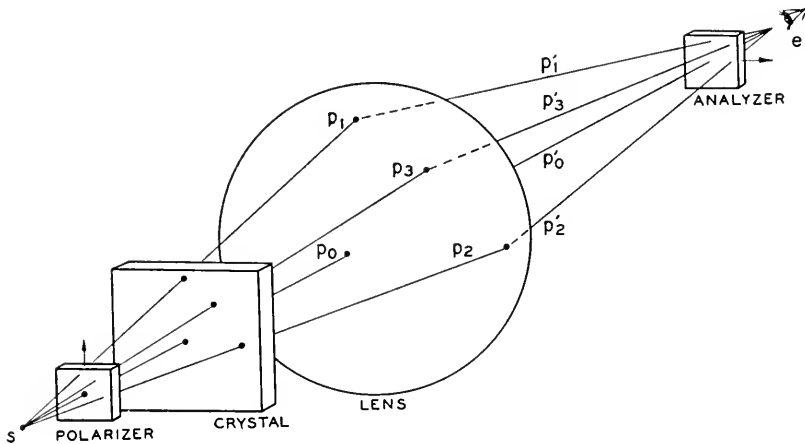


Fig. 2.30—The principle of the conoscope

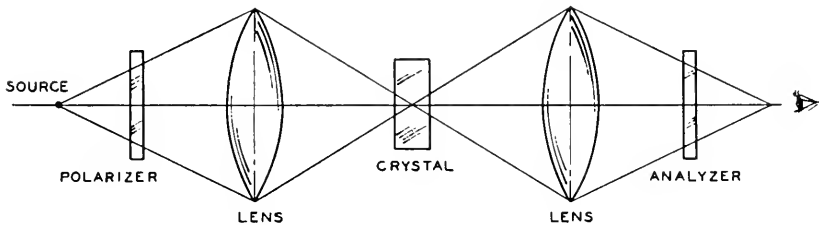


Fig. 2.31—A practical conoscope

Figure 2.32 shows a cross-section of the Western Electric conoscope. The graduated dial shaft goes out through the bottom of the tank to give more working room—older instruments had the shaft overhead and it was in the way. The light source is a mercury arc lamp with filters to isolate the 5461A line. The lenses have a converging power corresponding to $f:0.6$. The focus is not changed by changes in the refraction of the oil—in fact, the focus is the same with no liquid in the tank as when filled with liquid. This is of some interest for those who might wish to use the instrument for Rochelle salt and accordingly use a fluid of refractive index about 1.495

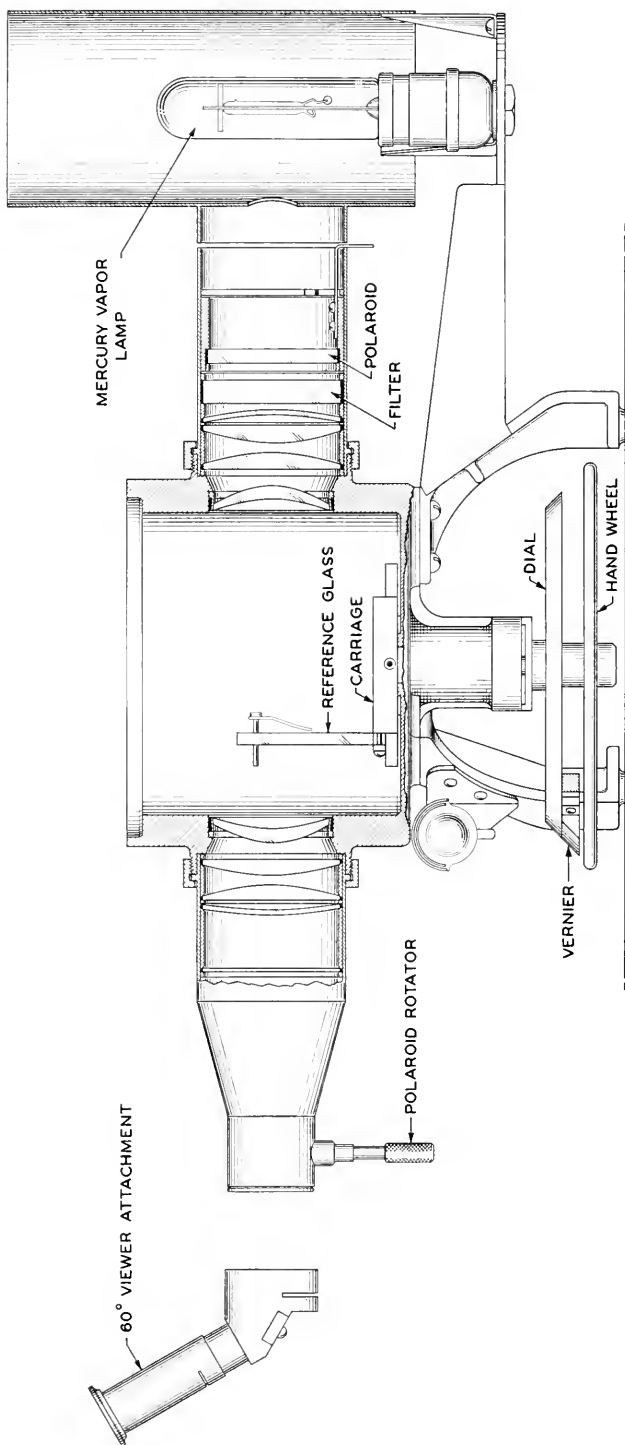


Fig. 2.32—The Western Electric conoscope

instead of the 1.546 of quartz. The dial is graduated into degrees and a vernier allows readings to tenths of degrees.

If a crystal plate is held against the glass reference surface one may read the angle between the optic axis and the surface normal. One should occasionally check the instrument (against slippage of the dial) by reversing the crystal and recentering the pattern. If the readings are not identical, the dial should be adjusted till they are. Even if the readings are not identical the mean value should be correct. If one is using the method of ring

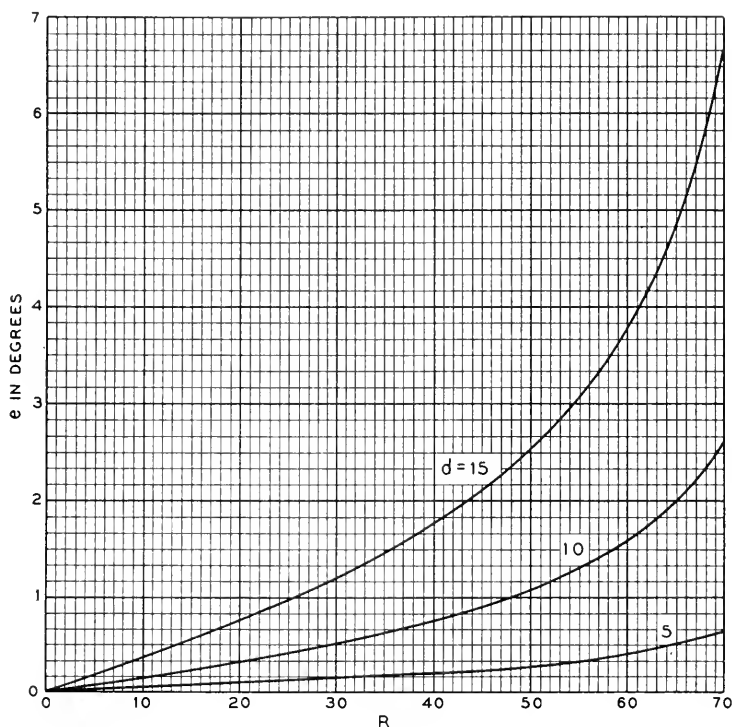


Fig. 2.33—The ring eccentricity correction chart

centering, the correction for eccentricity from Fig. 2.33 should be applied to this mean value.

The carriage may be slid back and forth and for very small crystals the carriage should be placed so that the crystal is near the center of the tank so that very little of the light cone by-passes the crystal. By the use of a block a thin crystal can be examined by viewing through its edge or length.

The carriage can be removed and "raw" crystals examined. The optic axis is plainly visible and quite accurate orientations can be made if there is not too much opaque material on the crystal. Excessive optical twinning

makes a confused pattern but good orientations can be made anyway. A "raw" crystal can be mounted adjustably in a jig that is lowered into the conoscope, the optic axis lined up, the jig transferred to a saw, and sections sawed directly.

Let us turn now to the quantitative analysis of the ring pattern seen in the eye piece when examining a uniaxial crystal. We wish to know the size of the smallest ring in the field, or rather the corresponding angle in the crystal. This first dark ring (analyzer and polarizer crossed) is the result of the slow wave falling *one* wave length behind the fast one. If the plate thickness (Fig. 2.34) is t' the path length in the crystal is

$$t = \frac{t'}{\cos \theta} \quad (2.8)$$

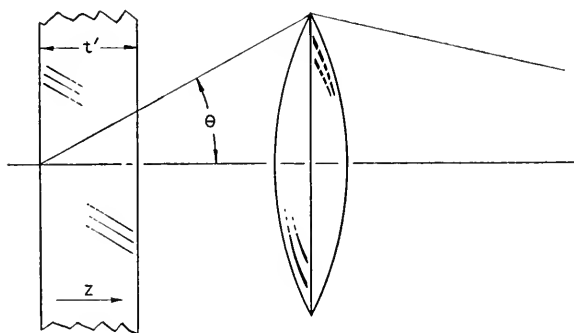


Fig. 2.34—The angle of the smallest ring

This is to be substituted in Eq. 2.7, namely:

$$N = \frac{t}{\lambda} (n_f - n_s) \quad (2.7)$$

Now it can be shown that, quite accurately, at the angle θ from the optic axis:

$$n_s - n_f = .00917 \sin^2 \theta \quad (2.9)$$

where .00917 is the difference in the refractive indices for the ordinary ray and the extraordinary ray for green mercury light traveling at right angles to the optic axis. (These are generally given the symbols n_o and n_e or n_ω and n_ϵ respectively.)

$$N_1 = \frac{t'}{\lambda \cos \theta} \times .00917 \sin^2 \theta = 1$$

and since $\lambda = .000546$ mm. for green mercury light this may be written

$$t' \sin \theta \tan \theta = 0.0595 \text{ mm.} \quad (2.10)$$

whence we solve for the values in this table

convergence	$\theta = 5^\circ$	10°	20°	30°
thickness	$t' = 7.8$	1.94	0.48	0.21

This shows that if we wish to examine thin plates in a conoscope the lenses must be strongly convergent. The conoscope used in the Western Electric has a convergence corresponding to about the 20° entry of the table so it

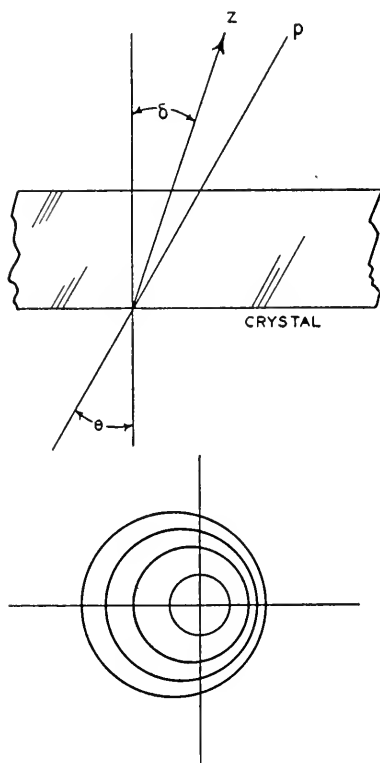


Fig. 2.35—Ring eccentricity

can be used on crystals down to a half millimeter thick—that is for *orientation* studies. In determining *handedness* we remember that this is a question of the rotatory power of quartz causing the rings to expand or contract on rotating the analyzer. Also we said that this rotatory power effectively disappears at 15° from the axis. If no ring is found within 15° of the axis there is no ring capable of expanding or contracting and we cannot test the handedness of such a thin crystal no matter how strong a lens we employ. We can then fall back on the succession of colors shown when we rotate the

analyzer using white light. Red, yellow, blue are observed for clockwise rotation with IRE right-hand quartz.

If the z section is not a true one, Eq. 2.9 will be replaced by one allowing for this error δ :

$$n_s - n_f = .00917 \sin^2 (\theta - \delta)$$

This will make the rings non-concentric and although the "cross" intersection is still the true optic axis the ring centers are not.

Hence if we are tempted to find the optic axis by centering a large sharp ring in preference to a small fuzzy one we find this eccentricity error must be allowed for.

2.8 ROTATION OF THE PLANE OF POLARIZATION

If we have a polarizer and an analyzer set for extinction (Fig. 2.36), then place a thin z section of quartz between them, the field brightens up but can be extinguished again by rotating the analyzer, Fig. 2.37. For the mineralogist's right-hand quartz the analyzer must be rotated 21.7° (yellow light assumed) clockwise to re-establish extinction, counter-clockwise 21.7° for left-hand quartz. The rotation is more for blue light, less for red. If the section is not a perfect z section the rotation is less than this, effectively disappearing at about 15° from the optic axis.

A thick slab can be examined in this way and, due to the color difference in rotation, "rainbows" will be seen in the quartz when held at just the right orientation. These rainbows will follow the contours of the specimen unless both right and left quartz are present in one piece. When this is the case the one kind generally occurs as spike- or blade-like intrusions in the other. It will then cause the rainbows to have sharp, jagged outlines bearing no relation to the specimen contour.

Also, since red, yellow, blue, are here in the order of increasing rotation, if we rotate the analyzer clockwise for right-hand quartz (I.R.E. RHQ) we will pass through best transmission for red, best for yellow and best for blue in that order so that the field will assume these colors in this order.

With uncut stones this examination is best made under an immersion fluid. The *inspectoscope* is made for this work. We spoke of the rotation of the plane of polarization and its complicating of the issue for the conoscope. Due to this the field at the center is not dark when the analyzer and polarizer are crossed. Also if we rotate the analyzer clockwise the rings of the pattern either expand or contract according to whether the crystal is right-hand quartz or left-hand quartz (IRE definition).

A different kind of pattern is visible in the conoscope when viewed perpendicular to z , a double set of hyperbolae as shown in Fig. 2.38. This pat-

tern has been used to check the orientation but much grief has ensued due to not recognizing one of its properties. This property is that, if z does not lie parallel to the crystal boundary the center of the pattern is not perpendicular to the optic axis and a rather involved correction must be used. This correction reduces the actual angle to about half the observed value.

This conoscope is an immersion instrument. The fluid is chosen to have an index of refraction to match the "ordinary" one for quartz. When this is done light is not bent in passing between fluid and quartz. When the fluid does *not* match there is a bending and all readings are subject to a

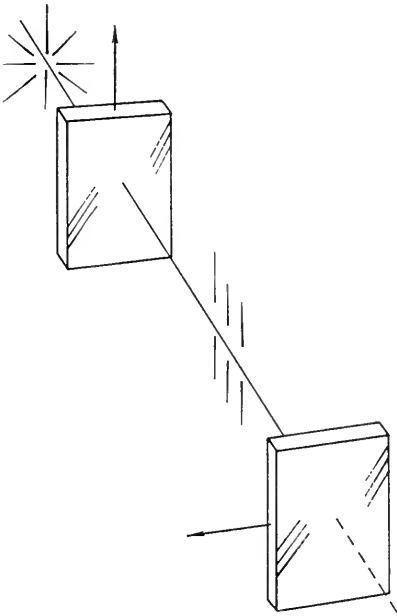


Fig. 2.36—Crossed polarizers

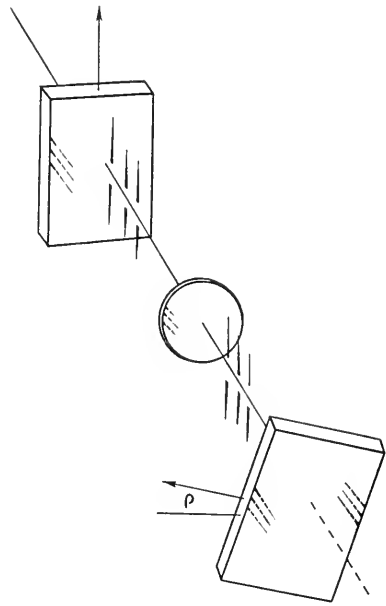


Fig. 2.37—Rotation of the plane of polarizer

correction. For example if we measure the angle of an AT plate in a fluid that is too low by .0048 (since n_o for quartz in green mercury light is 1.5462 this fluid has $n = 1.5414$), we will get a reading that is too high by a quarter degree (the 35° angle will then appear low). A temperature rise of 12°C will lower the relative refractive indices by this amount.

Also the more perfectly the fluid matches, the more nearly will the rough quartz surface disappear and seem smooth and clear. This greatly enhances the sharpness of the rings.

The *refractoscope* (Fig. 2.39) was designed by G. W. Willard to tell when the

match is good. It uses the elimination of the bending as a test for refractive match. It also demonstrates the existence of two velocities in quartz, for two images are seen where a glass prism would cause but one. Also by viewing through an analyzer we see that the two images are caused by plane polarized light, the polarization planes being mutually perpendicular.

If the fluid has an index lower than that of the prism the rays will bend towards the base of the prism. For this reason, light that reaches the eye e from s must travel by the path $s q_0 p_0 e$ for the ordinary ray, $s q_e p_e e$ for the

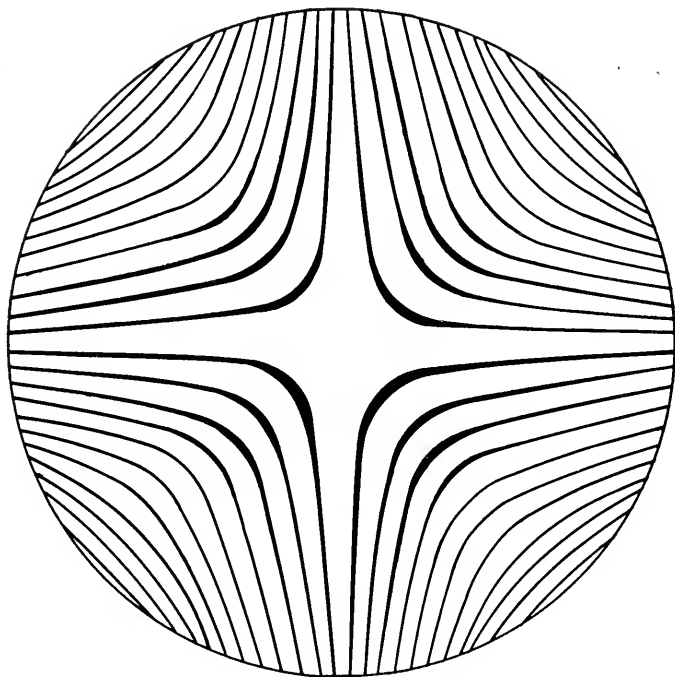


Fig. 2.38—Conoscope view normal to the optic axis

extraordinary ray. Hence the slit as seen through the prism will appear at s'_0 for the ordinary ray, at s'_e for the extraordinary while the slit as seen directly alongside the prism will appear at s . If the fluid index matches the quartz prism for the ordinary ray this ray will be unbent at p_0 and q_0 so that s'_0 will appear as a continuation of s .

If the fluid index is too high the image s'_0 will appear to the left of s with s'_e still to the right of s'_0 .

As the refractive indices of quartz for the ordinary and the extraordinary ray differ by .009 the apparent separation of s_0 and s'_e represents .009 and

can be used to judge the difference between the liquid index and the quartz ordinary index.

The liquid can be adjusted by placing a cap face of a crystal on the reference glass and setting the dial to read 51.8° the liquid being then blended to center the pattern.

If the refractive index of the fluid is low by an amount L the observed reading R must be corrected by adding to it an amount ϵ .

Since

$$(N_q - L) \sin R = N \sin (R - \epsilon)$$

we can compute ϵ . The accompanying refraction correction nomograph was computed from the above equation. If we know that the fluid in the conoscope is high, by an amount H , and we wish to know the correction to be applied to a conoscope reading R we locate H on the diagonal line HL and locate R on the horizontal line R . We join these two points with a straight line and read the scale $\epsilon - \epsilon$ where this straight line crosses the curved line $\epsilon - \epsilon$. This value tells the size of the correction and whether to add it to R or subtract it from R . Conversely, if we wish to find how closely the index of the fluid must be held in order to have the correction less than say $\frac{1}{4}^\circ$ at a reading of say $R = 50^\circ$ we join the points $R = 50^\circ$ and $\epsilon = \pm \frac{1}{4}^\circ$ and find $H = \pm 0.005$. A ten-inch-long lucite strip with a straight line ruled on it is a convenient tool with which to read this nomograph.

We now inquire as to whether the refraction correction can be made to annul the ring eccentricity correction. In the appendix it is shown that this is done if $H = -.530 \tan^2 d$ where $2d$ is the distance between the vertical reticule lines.

Experimentally it is easy to achieve this balance by using a cap face parallel slice. With the cap face against the reference glass and the dial reading 51.8° the fluid is blended to make a single ring tangent to both reticule lines. When this is done for $d = 10^\circ$ the fluid should have a refractive index of 1.5228 and the residual errors should be less than 2 minutes for R not over 60° .

2.9 IMMERSION FLUIDS

In order to match the refractive index of quartz we blend a substance which has an index that is too large with one that has an index that is too small. Such blended substances should be liquid at room temperature and hence should be perfectly mutually soluble. They should have low vapor pressure so that they do not evaporate quickly and should be harmless to the operator. Also they should be nearly colorless and clear. They should be fluent enough to be easily drained from the crystal and should have a

sufficiently high flash point that they would not present a fire hazard. The odor should not cause distress and finally the cost must be reasonable.

Dr. G. T. Kohman of the Bell Telephone Laboratories has prepared a list of such substances that can be mixed, any high one with any low one to

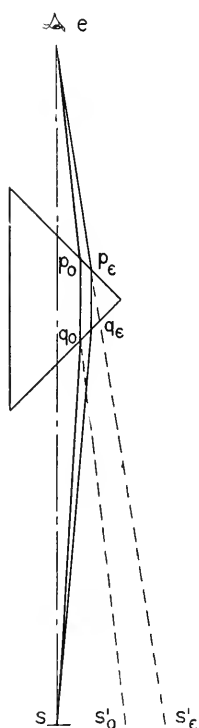


Fig. 2.39—The refractoscope

obtain a fluid satisfactory in all these respects. The following mixtures of substances are taken from his data.

Substance	Refractive Index	Mixture Parts by wt.	Density	Flash Point	Supplier
Dimethyl phthalate	1.51	73.9	1.193	255°F	Monsanto Chem. Co. Bakelite Co.
α monochlor naphthalene	1.63	26.1	1.194		
Dimethyl phthalate	1.51	73.9	1.193	285°F	Monsanto Chem. Co. Hooker Chem. Co.
Dichlor naphthalene (solid at room temp.)	1.63+	26.1	1.30		
Decalin	1.467	35.3	0.895	170°F	Dupont Co. Dow Chem. Co.
Dowtherm	1.586	64.7	1.1		
Kerosene				170°F	

An immersion fluid for Rochelle salt can be made by mixing decalin with any of the other substances. For example *b* mixture of 34 parts of dimethyl phthalate and 66 parts of decalin should give the necessary index 1.495.

2.10 APPENDIX

THE RING ECCENTRICITY CORRECTION

Referring to Fig. 2.41, we see that, at an angle α , from the optic axis towards the plate thickness direction the phase relation is, by Equations (2.7) and (2.9):

$$N_1 = \frac{.00917 t' \sin^2 \alpha_1}{\lambda \cos(\delta - \alpha_1)}$$

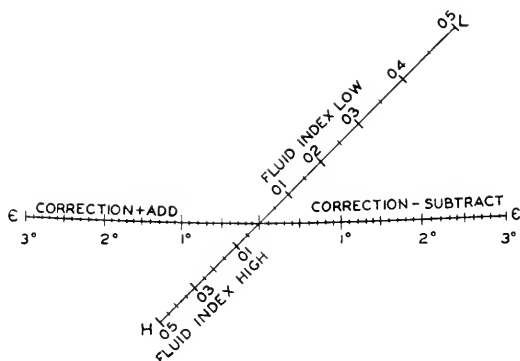


Fig. 2.40—Refraction correction nomograph

while at an angle α_2 away, it is:

$$N_2 = \frac{.00917 t' \sin^2 \alpha_2}{\lambda \cos(\delta + \alpha_2)}$$

Whence, if these are equal, we have:

$$\frac{\sin^2 \alpha_1}{\cos(\delta - \alpha_1)} = \frac{\sin^2 \alpha_2}{\cos(\delta + \alpha_2)} \quad (2.11)$$

These points, in the conoscope field, being of equal phase are parts of the same ring, and if matched to a pair of reticule lines, the optic axis is off their center line by an angle e , where

$$e = \frac{\alpha_1 - \alpha_2}{2}$$

If the separation of the reticule lines corresponds to an angle $2d$, we see that

$$d = \frac{\alpha_1 + \alpha_2}{2}$$

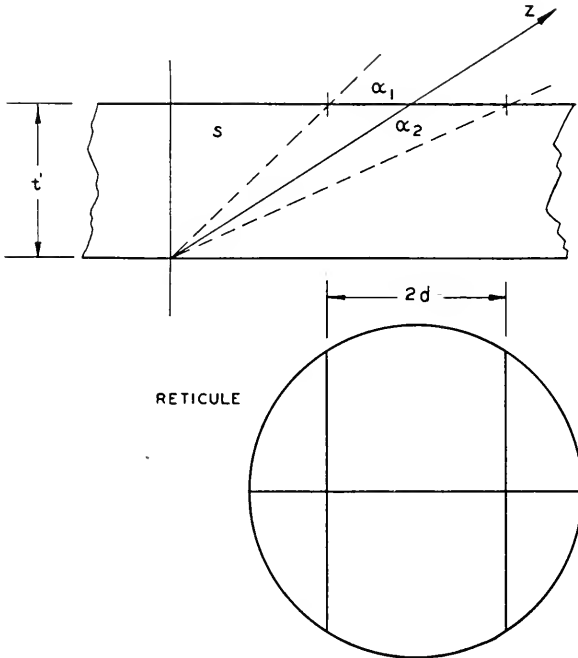


Fig. 2.41—Off center cross hairs

so that

$$\alpha_1 = d + e \quad \text{and} \quad \alpha_2 = d - e$$

The reading of the dial will be, at this match

$$R = \frac{1}{2}(\delta + \alpha_2 + \delta - \alpha_2) = \delta - \frac{\alpha_1 - \alpha_2}{2}$$

Hence we have

$$\frac{\sin(d + e)}{\sin(d - e)} = \sqrt{\frac{\cos(R - d)}{\cos(R + d)}} \quad (2.12)$$

For a given value of d , we can plot the values of e as a function of δ as given by (2.12). This plot is a chart of corrections to be added to the readings R to find the true angle δ .

Examination of Equation (2.12) shows us that the correction e is independent of the thickness t' and even of the birefringence; hence, the chart could serve for all uniaxial crystals. Equation (2.12) can be given an approximate solution:

$$\begin{aligned} e &= 1820 \tan^2 d \tan R \text{ minutes} \\ e &= 30.3 \tan^2 d \tan R \text{ degrees} \end{aligned} \quad (2.13)$$

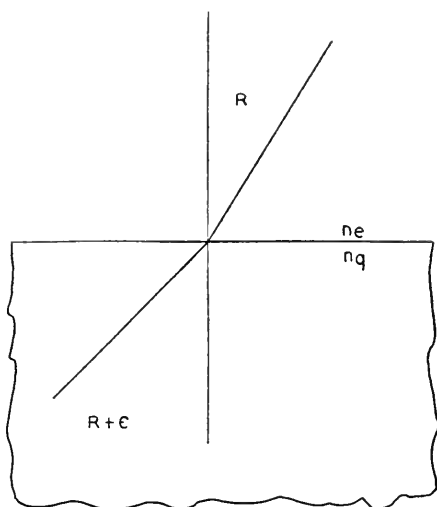


Fig. 2.42—Refraction at a surface

For R not more than 60 degrees and d not more than 15 degrees the error in e is not more than 5 minutes. Figure 2.33 is a chart of these corrections computed from the more exact equation (2.12).

ANNULING THE RING ECCENTRICITY CORRECTION BY MEANS OF THE REFRACTION CORRECTION

The difference in quartz index and liquid index is

$$H = N_q - N_l$$

and by the law of refraction:

$$N_l \sin R = N_q \sin (R + \epsilon)$$

whence

$$-H = N_q \frac{\sin \epsilon}{\tan R} - (1 - \cos \epsilon)$$

and if ϵ is small

$$H = -\frac{N_q \sin \epsilon}{\tan R}$$

From Eq. 2.13, $e = 0.530 \tan^2 d \tan R$ radians, and putting this in the equation for H we find that the correction for ring eccentricity approximately annuls the correction for refraction if

$$H = - .530 \tan^2 d$$

For $d = 10^\circ$ this gives $H = -.0255$, that is, a fluid index of 1.5207.

A Note on the Transmission Line Equation in Terms of Impedance

By J. R. PIERCE

INCREASED familiarity derived in handling Maxwell's equations, especially in connection with problems arising at very high frequencies, has resulted in a variety of forms for expressing certain laws and behavior. Especially, work by Schelkunoff in extending the impedance concept¹ shows that impedance can be quite as general and exact a means for expressing electromagnetic relations as are current, voltage, electric and magnetic fields, and vector and scalar potentials.

In reformulating certain problems in terms of impedance the content and ultimate solution must of course be equivalent. There may, however, be a considerable change of procedure and sometimes a simplification. For instance, in many cases a single impedance condition can replace the usual two boundary conditions for voltage and current.

One very simple case in which it is perhaps easiest to deal directly with impedance is in the derivation of the transmission line equation on a distributed constant basis. In the usual derivation, two linear second order differential equations are obtained, one for voltage and one for current. The impedance, in terms of which the engineer expresses many of his results, is obtained as a ratio from solutions for voltage and current. In treating the transmission line from the impedance point of view, without dealing with currents and voltages, a first order non-linear differential equation in terms of impedance and distance is obtained. This impedance equation is a Ricatti equation and could be obtained from the usual line equations. It is simpler, however, to derive it directly.

As the principal interest of such a treatment lies in the method and in the fact that the line may be tapered, rather than in losses, the derivations will be carried out for lossless lines. Losses can be taken into account by allowing the inductance per unit length, L , and the capacitance per unit length, C , to become complex quantities.

Consider the section of line dx long, shown in the figure, having an inductance $L dx$ and a capacitance $C dx$. We can write immediately

$$\begin{aligned} Z_x + dZ &= Z_{x+dx} \\ &= j\omega L dx + \frac{1}{j\omega C dx + 1/Z_x} \\ &= Z_x + j\omega[L - CZ_x^2] dx. \end{aligned} \quad (1)$$

¹"The Impedance Concept and Its Application to Problems of Reflection, Refraction, Shielding, and Power Absorption," *B.S.T.J.* Vol. 17, pp. 17-48, January, 1938.

Dropping the subscript x , the differential equation for the line in terms of the impedance Z may be written²

$$R \frac{dZ}{dx} = j \frac{\omega}{v} (R^2 - Z^2) \quad (2)$$

$$R = (L/C)^{1/2} \quad (3)$$

$$v = (LC)^{-1/2} \quad (4)$$

R is the nominal characteristic impedance, and v is the nominal phase velocity, which is constant for many tapered lines with the same dielectric material separating the conductors throughout their length. In such lines, if the dielectric is air or vacuum, v is c , the velocity of light.

It should not be surprising that (2) is of the first order. Although there are two boundary conditions, the impedances terminating the right and left ends of the line, there are two impedances, that looking toward the right and that looking toward the left. The impedance looking toward the right

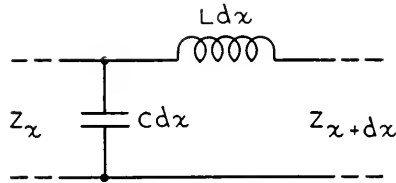


Fig. 1

is unaffected by the left end termination, and that looking toward the left is unaffected by the right end termination.

As R is real, it may be seen from (2) that the only case in which the impedance can equal the nominal characteristic impedance R at all points is for R constant. This tells us that the characteristic impedance of any lossless tapered line is complex. For very gradually tapering lines the characteristic impedance differs from the nominal characteristic impedance principally by a small imaginary component.

The simplest solution of (2) is of course that for a uniform line, with R a constant which will be called R_0 . In this case (2) can be integrated directly, giving the familiar result

$$\frac{Z}{R_0} = \tanh (j\omega x/v + K) \quad (5)$$

² It is interesting to note that the equation for admittance Y can be obtained by replacing Z by Y and R by $(1/R) = G$ in (2).

Dr. L. A. MacColl has pointed out to the writer that (2) is the same as the electrostatic electron optical equation for paraxial rays. To reduce (2) to the standard form:

$$-\frac{j\omega}{Rv} dx = dz \quad (6)$$

$$-R^2 = H(z) \quad (7)$$

$$\frac{dZ}{dz} = H(z) + Z^2 \quad (8)$$

The electron optical equation for paraxial rays is

$$\frac{d\Gamma}{dz} = \frac{3}{16} \left[\frac{V'(z)}{V(z)} \right]^2 + \Gamma^2 \quad (9)$$

$$\Gamma = C - \frac{V'(z)}{4V(z)} \quad (10)$$

Here z is distance along the axis, $V(z)$ is potential on the axis, and C is convergence, or the inverse of the focal distance.

It would seem, then, that from each solution of an electron optical problem, a solution of a tapered line problem could be found, and vice versa.

While it cannot be claimed that anything new has entered the transmission line equation in expressing it in terms of impedance, it does seem that the approach may be stimulating in uncovering hitherto neglected material and analogies.

Abstracts of Technical Articles by Bell System Authors

*Electronics in Telephony.*¹ FRANK A. COWAN. The historical development of the use of electronic devices by the telephone system is reviewed, showing how long distance telephony has grown with the increased use of, and improvements in, electronics. The number of telephone repeaters has grown from 16 in 1908 to 123,000 in 1942 and carrier circuit mileage has grown from 2,000 in 1920 to 2,300,000 in 1942, while copper usage per circuit mile has decreased from 400 pounds in 1910 to less than 70 in 1942.

A transcontinental telephone connection has grown from an open-wire circuit with a total loss, less repeaters, of less than 75 db (1915) to a present day cable circuit operating at carrier frequencies, which may have a total loss of over 10,000 db. The problem of matching enormous amplifications to compensate for huge losses with a precision of one or two db was a difficult one, which was solved by electronic techniques. The amplification necessary to compensate for the high losses on the cable layout may entail some 200 repeaters utilizing a total of more than 600 vacuum tubes in tandem. The automatic regulation and control of the amplification is accomplished by electronic devices, giving to the present day circuits a stability unequalled in the days before the vacuum tube.

There is available, except for the War, radiotelephone service to 83 foreign countries and overseas areas, and ocean liners at sea, and to boats in coastal and inland waters.

Such widespread dependence on vacuum tubes has stimulated research and design to achieve long life and a high degree of uniformity, stability and reliability. Among interesting future possibilities are transoceanic cables, the use of higher frequencies providing broader bands and larger numbers of circuits over a given path, and further application of remote and unattended stations.

*Deionization Considerations in a Harmonic Generator Employing a Gas-Tube Switch.*² WILLIAM G. SHEPHERD. A description is given of an experimental investigation of the properties of a thyatron operating as a high-frequency switch in a circuit which permitted the generation of a wide band of harmonics. The experiments indicate that there is an operating frequency below which no difficulties in deionization occur and above

¹ *Electronics*, March 1943.

² *Proc. I.R.E.*, February 1943.

which stable operation requires that the grid potential fulfill certain conditions dependent upon the frequency, wave form of the grid voltage, and circuit constants. It has been found possible to operate certain standard thyratrons at switching frequencies as high as several hundred kilocycles per second. For these higher frequencies the deionization of the tubes is incomplete but normal switching behavior is obtained.

Contributors to this Issue

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No. 3

Effect of Feedback on Impedance

By R. B. BLACKMAN

THE impedance of a network is defined as the complex ratio of the alternating potential difference maintained across its terminals by an external source of electromotive force, to the resulting current flowing into these terminals. If the network contains active elements such as vacuum tubes, the resulting current (or potential difference if the input current is taken as the independent variable) may be due in part to the excitation of the active elements. The definition of impedance does not discriminate between the part of the current (or potential difference) due directly to the external source of electromotive force and the part due to the excitation of the active elements by the external source. Hence the impedance will in general depend upon the degree of activity of the active elements.

These observations were made early in the development of feedback amplifiers by H. S. Black¹ who made two important uses of the effect of feedback on impedance. In the first place it afforded a method of measuring feedback which has some advantages over the method which involves opening the feedback loop, providing proper terminations for it and measuring the transmission around it. In the second place the effect of feedback on impedance was used to control the impedances presented by a feedback amplifier to the external circuits connected to it.

Relations between impedance and feedback were derived by Black and others for a number of specific feedback amplifier configurations. In some cases these relations turned out to be very simple. For the most part, however, these relations were so complicated that they defied reduction to a common form.² The difficulty seems to have been due, in part at least, to the attempt to formulate the relationship, in each case, in terms of the normal feedback of the amplifier. In some cases the difficulty seems to have been due partly also to the valid, but, as it turns out, irrelevant observation that the feedback is affected by the impedance of the measuring circuit as

¹ H. S. Black, "Stabilized Feedback Amplifiers", *B.S.T.J.*, January, 1934.

² Shortly after the general relationship between feedback and impedance was derived, it was independently established by H. W. Bode and J. M. West by examination of a variety of feedback amplifier designs. The generality of the relationship was also independently proved for amplifiers with a single feedback path by J. G. Kreer and by C. H. Elmendorf.

well as by the removal of any impedance elements or circuits which are normally connected to the amplifier.

These difficulties are avoided by the method of derivation adopted in this paper. Illustrative examples are then given of some of the uses to which the general relationship between feedback and impedance may be put.

DERIVATION

The derivation of the general relationship between feedback and impedance will be made here with reference to the diagram shown in Fig. 1.

One of the vacuum tubes in the network, namely that one to which the feedback is to be referred, is shown explicitly at the top of the box in the diagram. The grid lead to this tube is broken at terminals 2, 2'. In practice, the break in the grid lead would leave the grid still coupled to some

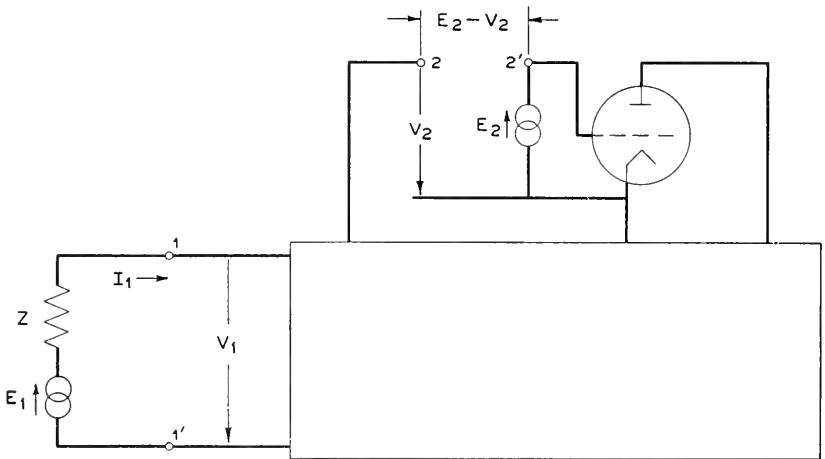


FIG. 1—Relation between feedback and impedance.

degree to the other electrodes of the tube through parasitic interelectrode admittance. For analytical purposes, however, it may be assumed that the parasitic admittances between the grid and the other electrodes of the tubes are connected not directly to the grid within the tube but to some point farther out along the grid lead. Under this assumption the break in the grid lead not only removes the feedback to the tube completely, but also leaves the parasitic admittances connected in the network in such a way that their contribution to the feedback is implicitly taken into account. Furthermore, the impedance looking into the grid of the tube is now infinite so that if a voltage is applied to the grid no current will be drawn from the source of the voltage.

At the left-hand side of the box in the diagram, terminals 1, 1' are brought out. These are the terminals to which the impedance is to be referred. In

the normal condition of the network these terminals may be connected through an external impedance branch. This is the case, for example, when terminals 1, 1' are the input terminals of a feedback amplifier whose input impedance is under investigation. However, this external impedance may also be zero or infinite according as terminals 1, 1' are "mesh-terminals" obtained by breaking open a mesh of the network, or "junction-terminals" obtained by bringing out two junctions of the network.

It is assumed that the network, including all of the vacuum tubes, is a linear system in which, therefore, the Superposition Principle holds. Hence, if an e.m.f. E_1 is applied in series with terminals 1, 1' and a second e.m.f. E_2 is applied between the grid and the cathode of the tube, the potential difference V_1 developed across the input terminals 1, 1' and the potential difference V_2 developed between the terminal 2 and the cathode of the tube will be linearly related to E_1 and E_2 . If the source of E_1 has internal impedance the coefficients in these relations will depend upon this impedance. However, if the input current I_1 is used as an independent variable in place of the e.m.f. E_1 the coefficients will not depend upon the impedance of the source of the current I_1 . It is also convenient to consider the potential difference $E_2 - V_2$ developed across the terminals 2, 2' as one of the dependent variables in place of V_2 . Therefore,

$$\left. \begin{aligned} V_1 &= AI_1 + BE_2 \\ E_2 - V_2 &= CI_1 + DE_2 \end{aligned} \right\} \quad (1)$$

where the coefficients are independent of Z .

From these equations we obtain

$$\begin{aligned} \left(\frac{V_1}{I_1} \right)_{E_2=V_2} &= \frac{AD - BC}{D} \\ \left(\frac{V_1}{I_1} \right)_{E_2=0} &= A \\ \left(\frac{E_2 - V_2}{E_2} \right)_{V_1=0} &= \frac{AD - BC}{A} \\ \left(\frac{E_2 - V_2}{E_2} \right)_{I_1=0} &= D \end{aligned}$$

Hence

$$\frac{\left(\frac{V_1}{I_1} \right)_{E_2=V_2}}{\left(\frac{V_1}{I_1} \right)_{E_2=0}} = \frac{1 - \left(\frac{V_2}{E_2} \right)_{V_1=0}}{1 - \left(\frac{V_2}{E_2} \right)_{I_1=0}} \quad (2)$$

This equation expresses the relationship between feedback and impedance. To make this more apparent the physical significance of each of the factors in this equation will be examined and suitable symbols will be substituted for them.

In equations (1) E_2 and I_1 were regarded as independent variables. However, the ratio $\left(\frac{V_1}{I_1}\right)_{E_2=V_2}$ implies that E_2 is adjusted to be equal to V_2 . This means that E_2 is dependent upon I_1 . The reason for the imposition of this dependence is that with E_2 equal to V_2 the terminals 2, 2' may be connected together and the source of E_2 may be removed without affecting, in particular, the potential difference V_1 across terminals 1, 1' and the current I_1 into these terminals.

Obviously, therefore, the ratio $\left(\frac{V_1}{I_1}\right)_{E_2=V_2}$ is the impedance which will be seen at the terminals 1, 1' when terminals 2, 2' are connected together and the only source of e.m.f. acting on the network is the external circuit connected to the terminals 1, 1'. This ratio will be symbolized by Z_A .

The ratio $\left(\frac{V_1}{I_1}\right)_{E_2=0}$ implies that no voltage is applied between the grid and the cathode of the tube. However, it is immaterial whether or not a voltage is applied to the grid of the tube if the amplification of the tube is nullified. Obviously, therefore, this ratio is the impedance which will be seen at the terminals 1, 1' when terminals 2, 2' are connected together and the amplification of the tube is nullified. This ratio will be symbolized by Z_P .

Finally, the ratios $\left(\frac{V_2}{E_2}\right)_{V_1=0}$ and $\left(\frac{V_2}{E_2}\right)_{I_1=0}$ are readily recognized from the definition of feedback to be the feedback to the vacuum tube with the terminals 1, 1' connected together in the first case, and left open in the second. These ratios will be symbolized by F_{sh} and F_{op} respectively.

Hence, equation (2) may be written in the more significant form

$$\frac{Z_A}{Z_P} = \frac{1 - F_{sh}}{1 - F_{op}} \quad (3)$$

DETERMINATION OF FEEDBACK

One of the uses to which the relationship (3) may be put is in the determination of feedback by impedance measurement. However, since this relationship involves two feedbacks, only one of which may be identified with the feedback to be determined, one of these feedbacks must be known.

In the most common types of feedback amplifiers it is possible to choose

terminals 1, 1' so that either F_{sh} or F_{Op} is zero. If $F_{Op} = 0$ and $F_{sh} = F_N$ where F_N is the normal feedback, then

$$F_N = 1 - \frac{Z_A}{Z_P} \quad (4)$$

On the other hand, if $F_{sh} = 0$ and $F_{Op} = F_N$ then

$$F_N = 1 - \frac{Z_P}{Z_A} \quad (5)$$

Fig. 2 shows a feedback amplifier in which the μ -circuit and the β -network are connected in series at one end and in parallel at the other end. At terminals 1, 1' in this figure the conditions for formula (4) are obviously fulfilled. Hence, if the impedance measurements are made at these ter-

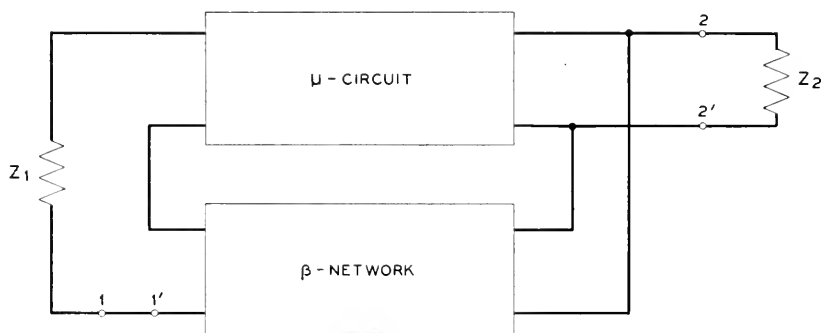


FIG. 2—Feedback amplifier with series feedback at one end and shunt feedback at the other end.

minals, the feedback is given by formula (4). On the other hand, at terminals 2, 2' in Fig. 2 the conditions for formula (5) are obviously fulfilled. Hence, if the impedance measurements are made at these terminals, the feedback is given by formula (5).

If the grid-plate parasitic admittance of a tube in a feedback amplifier is not negligible it is not possible to open any physical mesh in the amplifier so that $F_{Op} = 0$ for that tube. In such a case, therefore, (4) is not applicable. However, if the impedance measurements are made between the grid and the cathode of that tube the conditions for formula (5) are obviously fulfilled, and the feedback is given by formula (5). Hence, of the two particular forms (4) and (5) of the general relationship (3), only (5) enjoys complete generality in the determination of feedback by impedance measurements.

FEEDBACK DURING IMPEDANCE MEASUREMENTS

While the feedback computed from impedance measurements by formula (4) or (5) is the normal feedback, the feedback during the impedance measurements may be quite different, due to the impedance of the impedance measuring circuit. Referring to Fig. 1 we see that the feedback during measurement is by definition

$$F_z = \left(\frac{V_2}{E_2} \right)_{v_1 = -ZI_1}$$

where Z is the impedance of the impedance measuring circuit. By equations (1) this is easily reduced to

$$F_z = \frac{Z_P F_{sh} + Z F_{Op}}{Z_P + Z} \quad (6)$$

Under the conditions to which formula (4) applies

$$F_z = \frac{F_N}{1 + \frac{Z}{Z_P}} \quad (7)$$

It is clear therefore that even if F_N satisfies Nyquist's Stability Criterion, Z may be of such a character that F_z violates that criterion. In that case it will be impossible to make the impedance measurements.

Contrariwise, if F_N violates Nyquist's Stability Criterion, it is possible to choose Z so that F_z satisfies that criterion and make it possible to measure the impedance. Substituting (4) into (7) we find that a sufficient but not necessary condition in order that $|F_z| < 1$ is that

$$|Z| > |Z_A| + 2|Z_P|$$

Under the conditions to which formula (5) applies

$$F_z = \frac{F_N}{1 + \frac{Z_P}{Z}} \quad (8)$$

Similar observations may be made with respect to (8) as were made with respect to (7). Substituting (5) into (8) we find that a sufficient but not necessary condition in order that $|F_z| < 1$ is that

$$\frac{1}{|Z|} > \frac{1}{|Z_A|} + \frac{2}{|Z_P|}$$

FEEDBACK CONTROL OF IMPEDANCE

The application of the relationship (3) to the feedback control of impedance may be illustrated by a few concrete examples.

Let us assume that we are interested in the impedance faced by the line impedance Z_1 in Fig. 2. If the terminals 1, 1' in Fig. 3 are left open the feedback is obviously zero. Let the feedback when the terminals are shorted together be denoted by F_{sh} . If the impedances of the μ -circuit and the β -network are denoted by Z_μ and Z_β , respectively, then

$$Z_A = Z_P(1 - F_{sh}) \quad (9)$$

where

$$Z_P = Z_\mu + Z_\beta$$

This shows the now well-known fact that series feedback may be used to magnify impedance.

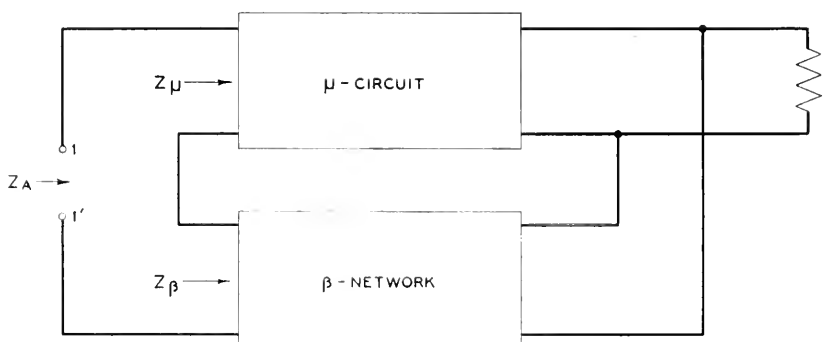


FIG. 3—Impedance faced by the line at the series feedback end of a feedback amplifier.

However, it should be noted that the feedback F_{sh} involved in (9) is not now equal to the normal feedback F_N as it was when the terminals 1, 1' were taken as in Fig. 2. The relation between F_N and F_{sh} may be obtained from (6) by identifying F_N with F_{Z_2} and Z_1 with Z . Hence

$$F_N = \frac{F_{sh}}{1 + \frac{Z_1}{Z_P}} \quad (10)$$

From (9) and (10) it follows that even with a very modest amount of normal feedback the magnification of the impedance may be very large. For example, if $Z_P = 1000$ ohms, $Z_1 = 1$ megohm and $F_{sh} = -1000$, then Z_A is better than 1000 times as large as Z_P although F_N is not quite unity in magnitude.

Similarly, the impedance faced by the line impedance Z_2 in Fig. 2, as shown in Fig. 4, is

$$Z_A = \frac{Z_P}{1 - F_{Op}} \quad (11)$$

where

$$Z_P = \frac{Z_\mu Z_\beta}{Z_\mu + Z_\beta}$$

This shows the now well-known fact that shunt feedback may be used to reduce impedance.

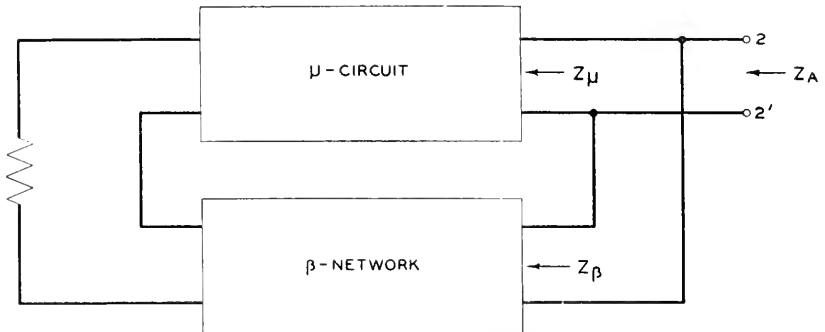


FIG. 4—Impedance faced by the line at the shunt feedback end of a feedback amplifier.

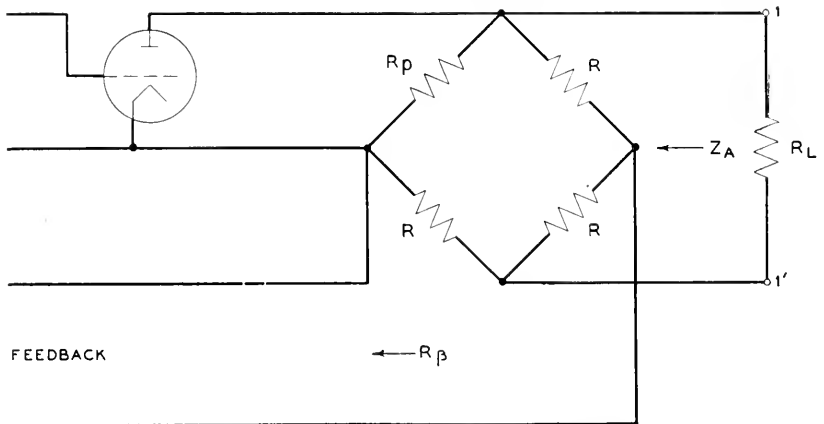


FIG. 5—Impedance faced by the line connected to a bridge feedback amplifier.

The relation between the normal feedback F_N and the feedback F_{Op} involved in (11) is, by (6)

$$F_N = \frac{F_{Op}}{1 + \frac{Z_P}{Z_2}} \quad (12)$$

From (11) and (12) it follows that even with a very modest amount of normal feedback the reduction in impedance may be very large. For example,

if $Z_p = 100,000$ ohms, $Z_2 = 100$ ohms and $F_{op} = -1000$, then Z_A is less than 100 ohms although F_N is not quite unity in magnitude.

The two examples given above illustrate the use of feedback to magnify or to reduce the impedance of a network. This impedance, however, will be correspondingly sensitive to changes in the characteristics of the vacuum tubes. A third example of the use of the relationship (3) will show that feedback may also be used to make the impedance of a network less sensitive to changes in the characteristics of the vacuum tubes.

In the case of the bridge-type feedback network shown in Fig. 5 we have, with respect to the terminals 1, 1'

$$Z_p = R(1 + Q)$$

$$F_{sh} = A \frac{1 + \frac{2R + 3R_\beta}{R + R_\beta} Q}{1 + Q}$$

$$F_{op} = A \left(1 + \frac{2R + 3R_\beta}{R + R_\beta} Q \right) = (1 + Q)F_{sh}$$

where A is the feedback designed for the condition $R_p = R$, and

$$Q = \frac{(R_p - R)(R + R_\beta)}{(R + R_p)(2R + R_\beta) + 2RR_\beta}$$

Then, by (3)

$$Z_A = R \left(1 + \frac{Q}{1 - F_{op}} \right)$$

Hence, if the feedback F_{op} is very large the effect of bridge unbalance on the impedance presented to the line will be very small. If, for example, the design feedback is 40 db the output impedance cannot change more than 1 per cent however severely the bridge might be unbalanced by R_p being larger than R .

The feedback when the line impedance R_L is connected may be obtained by identifying R_L with Z in formula (6). It is

$$F = A \frac{1 + \frac{2R + 3R_\beta}{R + R_\beta} Q}{1 + \frac{R}{R + R_L} Q}$$

whence

$$\frac{\partial \log F}{\partial \log R_L} = \frac{RR_L}{R + R_L} \frac{Q}{R_L + Z_p}$$

The effect of bridge unbalance is to make the feedback sensitive to changes in the line impedance R_L .

Design of Two-Terminal Balancing Networks

By K. G. VanWYNEN

This paper describes a simple graphical method for designing a two-terminal network, which will simulate a given line impedance to such a degree that return losses of the order of 25 db or better will be readily obtained. The method is particularly useful in those problems in which a reasonably accurate balancing network is adequate, but a high degree of precision is not required.

GENERAL

IT IS the purpose of this paper to describe a graphical method which has been found useful in the design of simple two-terminal networks to simulate the impedance of transmission lines or equipment. The discussion which follows is intended to emphasize the simplicity of the method and the rapidity with which it may be employed to arrive at a solution; it will also indicate the analytical background without attempting to develop or establish the rigor of the procedure involved. A solution can frequently be obtained in a fraction of an hour and it is thought that the graphical analysis will appeal to the pragmatist and the engineer who has a job to do, but very little time in which to accomplish his aim, rather than the person interested in the rigor of the solution.

The problem which is considered may be stated as follows: Design a two-terminal network with the minimum number of elements which will give a desired degree of approximation to a given impedance function $Z(\lambda)$, where $Z(\lambda)$ is a fraction whose numerator and denominator are polynomials in frequency in accordance with the customary usage in such problems.

ORIGIN OF PROBLEM

This problem has arisen most generally in providing balancing networks which will give satisfactory return losses against various types of telephone facilities. It is obvious that for a given impedance, $(r + jx)$, at a given frequency there are an infinite number of networks which will satisfy the given impedance. It has also been pointed out that the network which simulates a given impedance function is not unique. Hence there are also a large number of networks which will satisfy a given impedance function.

In designing networks for repeater circuits, it is generally satisfactory

if the return loss is equal to or greater than some specified number of db. This somewhat simplifies our problem and permits a double infinity of solutions. A method has been given by Brune¹ for designing such networks, in which it is pointed out that there is no unique solution to the problem of designing a finite two-terminal network and also states that any network which satisfies the impedance function may be considered a satisfactory solution to the problem. It is thought that the method which is given below will provide a solution which makes maximum use of the number of elements employed. That is, it will provide a given return loss with the minimum number of parts.

The required degree of approximation and the frequency range to be covered determine the number of elements required in this solution. In one simple case which will be discussed below in the first example, the approximation between the impedance of a transmission line and a network designed to simulate it is the approximation between the curvature of the impedance function and the arc of a circle.

GENERATING FUNCTION

The method discussed here differs from that outlined by Brune in that use is made of known generating functions which are added together in series to approximate the total function, similar to the manner in which sine functions may be added to approximate other functions. This series type network can readily be converted to the ladder type by well known network equivalence theorems and the solution will then have the Stieltjes fraction form pointed out by Fry² and Cauer.³

The generating function used here is an impedance consisting of a resistance in parallel with a pure reactance or a special case of this. This function plus a real corresponds to a bilinear transformation, the properties of which have frequently been discussed elsewhere. This particular configuration, for instance, has been pointed out both by Brune and by Guillemin³ at M.I.T. and a discussion of the bilinear transformation has been given by C. W. Carter⁴ of the Bell Telephone Laboratories. The series addition of such generating functions is similar to the form given in Foster's reactance theorem except that there only pure reactances are dealt with. The solution can also be worked out with admittances, but will not be discussed here since the average engineer is more accustomed to dealing with impedances.

In many problems, particularly those involving dissipative transmission

¹ *Jour. Math. & Physics*, Vol X, 1930-1931.

² *Bull. Am. Math. Soc.*, 35, 1929.

³ Guillemin—Vol. II.

⁴ *B.S.T.J.*, July 1925.

lines, the entire impedance function is found in the fourth quadrant of the complex plane. When this is so, the generating function is reduced to a resistance in parallel with a condenser.

GRAPHICAL REPRESENTATION OF FUNCTIONS

As a first step in utilizing the graphical procedure, it will be advisable to acquire some familiarity with the generating function in its general form

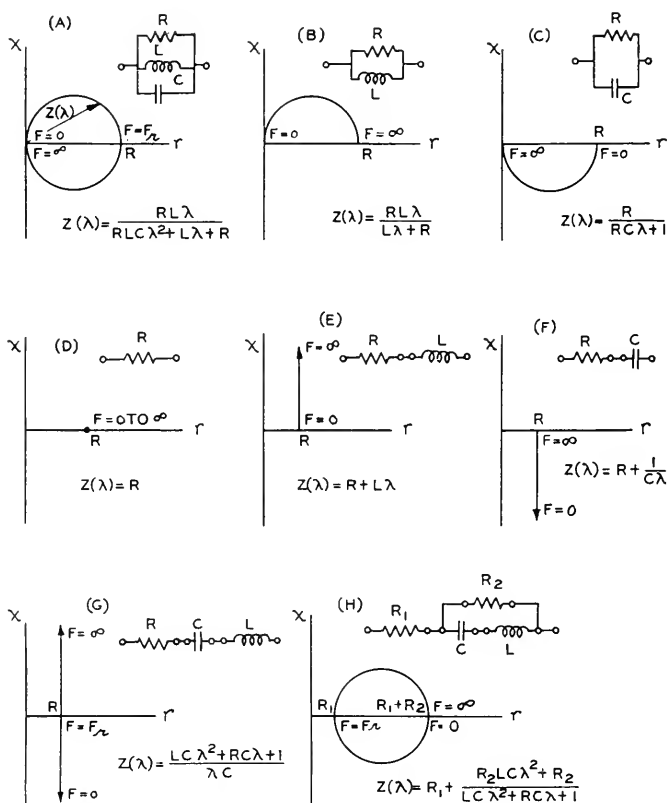


Fig. 1.—The impedance loci, $Z(\lambda)$, for several networks.

and some of its special cases. Plots of various cases are given in Figs. 1(a) through 1(h) together with the network configuration and the impedance function thereof. Obviously the summation of the properly selected generating functions corresponds to the addition of the partial fractions derived by Brune's method. For an accurate solution these partial fractions when combined should approximate the given $Z(\lambda)$.

Figure 1(A) shows the impedance locus of the parallel R, L, C generating

function as frequency varies from 0 to ∞ . At 0 frequency $Z(\lambda) = 0 + j0$ and at ∞ $Z(\lambda) = 0 - j0$. The locus is a circle and crosses the real axis at R and the frequency at which L and C are anti-resonant. The special cases will be readily apparent and without further discussion attention will be shifted to Fig. 1-c which is the generating function applied to obtain solution of the examples listed below, all of which are located in the fourth quadrant.

The impedance of this function (Fig. 1-c) at zero cycles is a real and has the value R , and at infinite frequency its impedance is $0 - j0$. The locus traced by this function in the fourth quadrant of the complex plane as f varies from zero to infinity is a semicircle of radius $R/2$ whose center is at $R/2$ on the axis of reals. Obviously, the impedance for any given frequency depends only on C when R has been fixed.

One of the most useful networks for voice frequency work is that in which two such functions are added together but the second function is the special case in which $C = 0$. We then have a network which consists of a resistance R_1 in series with the parallel combination R_2 and C_2 , and is represented by the semicircle just described but displaced to the right of the origin by the distance R_1 . This form corresponds to a special case of the bilinear transformation previously mentioned.

As stated earlier a given impedance function can be obtained from a large number of networks but when the impedance is to be simulated for a limited frequency range, such as the voice band, the selection of the best network is reduced to sorting through a relatively small range of networks to select that one which is the best compromise for the given conditions. This then is a restatement of the problem: *To find the network having the minimum number of circuit elements which will give the desired approximation to a specified impedance function.*

The other sections of Fig. 1 will be evident upon analysis.

METHOD OF SOLUTION

The first step to be followed in finding the solution to a given problem is to plot in the complex plane the locus traced by the given impedance function as the frequency varies over the range which is to be considered and to mark the frequency at those impedances which are essential to the problem. Having done this, the next step is to draw a semicircle with the center on the real axis such that an arc of the semicircle approximates part or all of the locus of the impedance function. In many cases this semicircle is a sufficiently good approximation but where it is not, it will be necessary to add other functions. The examples given below are illustrative of cases requiring three-, four- and five-element networks,

EXAMPLE 1—104 MIL OPEN WIRE

To demonstrate the method we will now consider the design of a network which simulates a 104-mil copper open-wire line with 12 in. spacing and CS insulators. The impedance function for this particular facility is plotted on Fig. 2. It is perhaps rather obvious that this locus can readily be approximated by a semicircle whose center is on the real axis and whose intercept on the real axis is not at the origin. Such a semicircle has been drawn, but it is recognized that the one shown is not unique, for it would be possible to draw several others which might do equally well. However, they

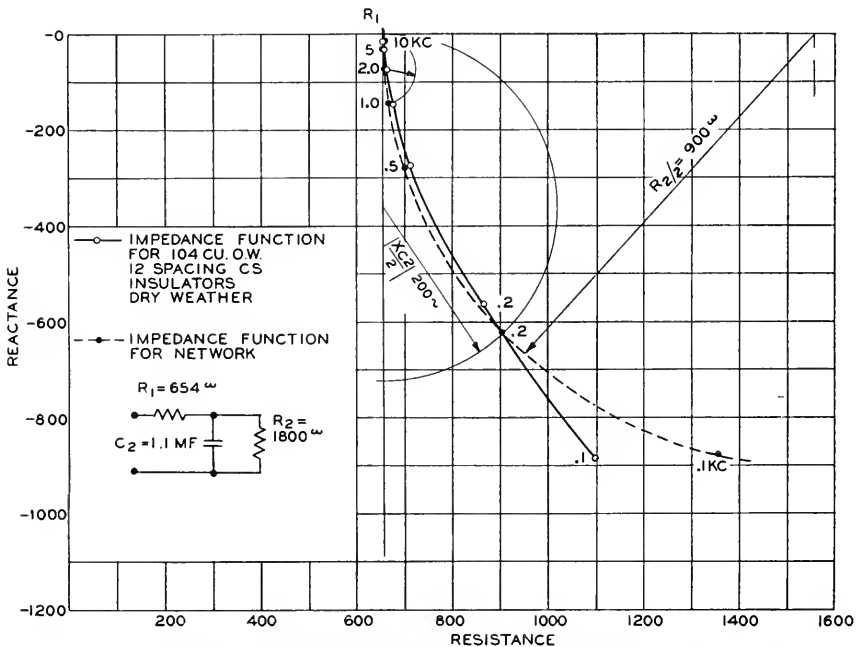


Fig. 2.—Graphical design of two-terminal balancing network for 104-mil. copper open wire.

would in general be fairly close to that shown. Having selected this semicircle, which approximates the impedance function, it is evident that a network consisting of a resistance, R_1 , in series with a parallel R_2C_2 combination will provide a reasonable approximation above 200 cycles. The series resistance R_1 , is, of course, the left-hand intercept of the semicircle and the R axis and the parallel resistance, R_2 , is the diameter of the semicircle. There remains, then, the problem of determining C_2 which obviously governs the distribution of frequencies along the semicircular locus. If C_2 is very small, the 1000 cycle impedance will be near the right-hand end of the locus since

R_2 is controlling and vice versa. The answer as to what value of C should be selected depends on what frequency range we are most interested in approximating closely. Suppose in this case that we say 1000 cycles is the frequency at which we wish to have the best degree of approximation. C_2 will then be determined by drawing a vertical axis passing through R_1 and inscribing a semicircle passing through R_1 and the 1000-cycle impedance of the open-wire line function and having its diameter on the vertical axis. The diameter of this semicircle represents X_c and therefore determines the capacity, C_2 , of the parallel combination.

Carrying out the procedure just described it will be seen by reference to Fig. 2, that $X_{c_2} = 145$ ohms at 1000 cycles and therefore $C_2 = 1.1$ mf. The 3-element network thus determined is a resistance of 654 ohms in series with the parallel combination of 1800 ohms and 1.1 mf. By arbitrary choice the 1000-cycle impedance of the line and network are in good agreement. It is now necessary to determine the network impedance at other frequencies in order to compare them against the open-wire line impedance.

As is well known the parallel impedance at any other frequency is the intersection of the corresponding X_c and R_2 semicircles. At 200 cycles $X_c = 725$ ohms. Drawing a semicircle of diameter 725 ohms on the vertical axis through 654 ohms the network impedance is located at the intersection of this semicircle and the R_2 semicircle, i.e., at $900 - j620$.

Thus the network impedance locus as a function of frequency may be completely determined over the desired frequency range and compared with the given impedance locus of the open wire.

This may be done visually. If corresponding points on the two loci are close together, the simulation will be a good one and vice versa. If it is found that the simulation is too good at one frequency and not good enough at other frequencies, it will be possible to alter the distribution of frequencies along the locus by changing C_2 or the locus may be shifted by changing R_2 or both C_2 and R_2 may be changed. No specific rule can be stated for this but with a little experience considerable dexterity may be acquired in this sort of juggling and a locus found which will give an approximately constant approximation over a reasonably wide frequency range. As may be seen by referring to Fig. 2, it was found that a network consisting of a 654-ohm resistance in series with the parallel combination of 1800 ohms and 1.10 mf. gives a very good simulation of a 104 mil copper open wire line over the voice range. As is obvious from the graphical method, the simulation rapidly deteriorates below 200 cycles due to departure of the network locus from the impedance locus of the open wire line. If it were necessary to improve this low-frequency simulation, it would be necessary to add further generating functions to the design or compromise at the higher frequencies.

Since this network was intended for use as a balancing network, it was

then tested in the laboratory against the open-wire impedances and found to give fairly high return losses as listed in Table I. The corresponding return losses were also computed and tabulated. The impedances are given for both the network and the theoretical line at typical frequencies over the range from 100 cycles to 20,000 cycles.

The impedance function for an open-wire line is given by the equation

$$Z(\lambda) = \left(\frac{R + L\lambda}{G + C\lambda} \right)^{\frac{1}{2}} \quad (1)$$

Expanding this function by the binomial theorem and taking the first approximation and further letting $G = 0$, the impedance function becomes

TABLE I
104 Mil Cu Open Wire, Dry Weather, 12" Spacing, CS Insulators

Freq. Cycles	Impedance				Return Loss of Net- work vs Line-db	
	Network		Line		Measured	Computed
	Rect.	Polar	Rect.	Polar		
100	1360—j878	1620/ $\sqrt{32.9}$	1101—j883	1410/ $\sqrt{38.8}$	20.9	21.3
200	904—j623	1097/ $\sqrt{34.7}$	865—j562	1032/ $\sqrt{33.0}$	27.4	29.4
300					34.4	
500	699—j281	754/ $\sqrt{21.9}$	712—j273	764/ $\sqrt{21.0}$	37.8	39.6
1000	665—j143	681/ $\sqrt{12.2}$	674—j144	689/ $\sqrt{12.0}$	42.3	43.6
2000	656—j72	660/ $\sqrt{6.3}$	662—j74	666/ $\sqrt{6.4}$	45.2	47.8
5000	654—j28	654/ $\sqrt{2.4}$	658—j32	659/ $\sqrt{2.8}$	43.1	48.4
10000	654—j14.5	654/ $\sqrt{1.0}$	653—j12	653/ $\sqrt{1.1}$	39.5	55.5
20000	654—j7.2	654/ $\sqrt{0.5}$	652—j10	652/ $\sqrt{0.9}$		51.2

$$Z(\lambda) = \left(\frac{L}{C} \right)^{\frac{1}{2}} + \frac{1}{(LC)^{\frac{1}{2}}(2/R)} \cdot \frac{1}{\lambda} \quad (2)$$

Applying the method of Brune, this equation yields a network consisting of 646.4 ohms in series with a condenser of 1.09 mf. It will also be apparent that eq. (2) has the same form as that of Fig. 1(f), i.e.,

$$Z(\lambda) = R_1 + \frac{1}{C_1} \cdot \frac{1}{\lambda}$$

and by a 1 to 1 comparison of terms it is evident that

$$R_1 = \left(\frac{L}{C} \right)^{\frac{1}{2}} \quad (3-a)$$

and

$$C_1 = (LC)^{\frac{1}{2}} \left(\frac{2}{R} \right) \quad (3-b)$$

Including G , the expression for the first approximation of the impedance function may be written in the form

$$Z(\lambda) = \left(\frac{L}{C}\right)^{\frac{1}{2}} \left[1 + \frac{\left(\frac{R}{2L} - \frac{G}{2C}\right)}{\lambda + \frac{G}{2C}} \right] \quad (4)$$

Following Brune's method or noting the correspondence with the impedance function given in Fig. 1(c), it is apparent that the network is a resistance, R_1 , of 646.4 ohms in series with a parallel R_2C_2 combination. C_2 is 1.09 mf as before but R_2 computes as 312,000 ohms which is so large compared to 1.09 mf. that the additional resistance provides negligible improvement over the previous network for the voice frequency range.

Obviously then, the analytical method requires at least a second order approximation entailing considerable additional analytical work and computation which will not be carried out here. This points out the advantages of the graphical method; namely, it is rapid, requires no special skill, and gives a reasonably accurate answer.

EXAMPLE 2—SIRAL FOUR CABLE—1320 FOOT SPACING—6 MILHENRY LOADING (SP4-1320-6)

In order to indicate the procedure when two complete RC regenerating functions are required, another example is given which covers an impedance simulation of a SP4-1320-6 line. A plot of this impedance function is shown on Fig. 3, and it is at once obvious that two semicircular generating functions should give a reasonably good approximation to the given impedance function.

The method of selecting these functions may be somewhat as follows: Consider first the simulation in the low-frequency range, i.e., 200 cycles to 500 cycles. For this region a semicircle may be selected much as in the first example and the one chosen yields a network consisting of $R_1 = 480$ ohms in series with the R_2C_2 parallel combination in which $R_2 = 1460$ ohms. C_2 was found by choosing an X_{C_2} at 500 cycles close to that of the line and from which C_2 was found to be 1.38 mf.

It is evident that to provide high-frequency simulation a condenser must be placed in parallel with $R_1 = 480$ ohms. Its value is determined by the intersection of the R_1 and X_{C_1} semicircles at 10,000 cycles and C_1 is found to be .0161 mf. The construction lines involved in these determinations are shown as light weight solid lines.

Since there are now two impedance functions to be added in series the locus will depart somewhat from the two semicircles. However, the departure will not be great since the effect of C_1 is small at low frequencies,

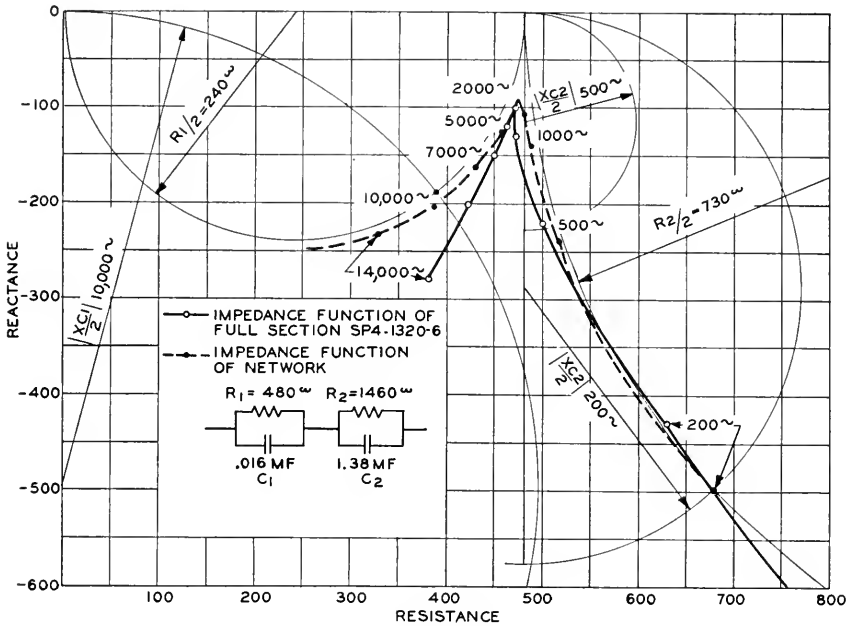


Fig. 3—Graphical design of two-terminal balancing network for spiral four cable.

TABLE II

Spiral Four Cable—1320 Foot Spacing—6 Milhenry Loading—Full Section Termination

Freq. Cycles	Impedance				Return Loss vs Theoretical Line-db		Measured Return Loss vs Artificial* Line-db
	Network		Line		Measured	Computed	
	Rect.	Polar	Rect.	Polar			
100	1046-j713	1266/ $\sqrt{34.3}$	810-j670	1051/ $\sqrt{39.6}$	14.8	19.8	21.8
200	701-j528	878/ $\sqrt{37.0}$	630-j430	763/ $\sqrt{34.3}$	22.8	22.6	22.9
500	516-j239	569/ $\sqrt{24.9}$	500-j220	546/ $\sqrt{23.8}$	33.2	33.0	25.2
1000	488-j139	507/ $\sqrt{15.9}$	470-j130	488/ $\sqrt{15.5}$	37.1	33.9	26.2
2000	479-j108	491/ $\sqrt{12.7}$	470-j100	481/ $\sqrt{12.0}$	41.2	38.1	26.6
3000							26.2
5000	456-j125	473/ $\sqrt{15.3}$	460-j120	475/ $\sqrt{14.6}$	39.9	43.4	26.3
7000	430-j163	460/ $\sqrt{20.8}$	450-j150	475/ $\sqrt{18.4}$	36.7	31.8	25.1
10000	389-j201	438/ $\sqrt{27.3}$	420-j200	465/ $\sqrt{25.5}$	32.4	29.3	23.5
12000							23.6
15000	328-j231	401/ $\sqrt{35.1}$	380-j280	472/ $\sqrt{36.4}$		21.8	

* 120 sections terminated in 450 ohms.

and that of R_2 is small at high frequencies. In this case the two functions may be thought of as virtually independent.

Table II gives the theoretical impedance of this facility and the computed

impedance of the network at frequencies from 100 cycles to 15,000 cycles and, as may be seen by the comparison, a fairly good simulation exists throughout the range. This fact has been verified by making return loss measurements in the laboratory against the theoretical line with the results indicated in the table. Return loss measurements have also been made between the network and an artificial line consisting of 120 sections of this facility terminated in 450 ohms. These results show a fairly constant return loss of about 25 db throughout the frequency range. This seems to indicate that the simulating network is a fairly close approximation to the artificial line so far as frequency is concerned and differs from it by a constant multiplying factor which is of the order of 1.12. It is therefore apparent that whenever it is necessary only to simulate the impedance of this particular facility, this four-element network will provide a fairly adequate simulation. The analytical derivation of this network will be omitted.

EXAMPLE 3A—NON-LOADED EXCHANGE AREA CABLE

Another case will be cited to show the application of the graphical method. This is the simulation of non-loaded cable of which the local plant is largely composed in urban areas. A first approximation of the analytical method does not yield a useful network but the graphical method provides a three-element network of the type discussed above which gives a return of about 20 db in the 300 cycles to 3000 cycles range. The graphical derivation of the three-element network is shown on Fig. 4 which also gives the impedance function for 22 ga. BSA non-loaded cable. This latter function is virtually a straight line in the voice range whereas the network is the arc of a circle. Hence it would be impossible to obtain an appreciably closer approximation throughout the range with a three-element network. However, the addition of elements will improve the match as will be shown in example 3B.

The network just derived can be expressed in terms of the 1000-cycle impedance and applied for any gauge of non-loaded cable as follows:

$$R_1 = .42 K \quad (5-a)$$

$$R_2 = 2.8 K \quad (5-b)$$

$$X_{C_2} = .9 K \quad (5-c)$$

where K is the magnitude of the 1000-cycle impedance and

$$X_{C_2} = \frac{1}{2\pi f C_2} \quad (5-d)$$

Table IIIa gives a comparison of the network and line impedances and the computed return loss for frequencies through the 200 to 3000 cycle range.

EXAMPLE 3B—19-GAUGE QUADDED NON-LOADED TOLL CABLE

Two complete RC functions plus a resistance are required to give a good simulation for non-loaded toll cable when the simulation is carried through the voice and carrier frequency ranges. The impedance function for 19 ga.

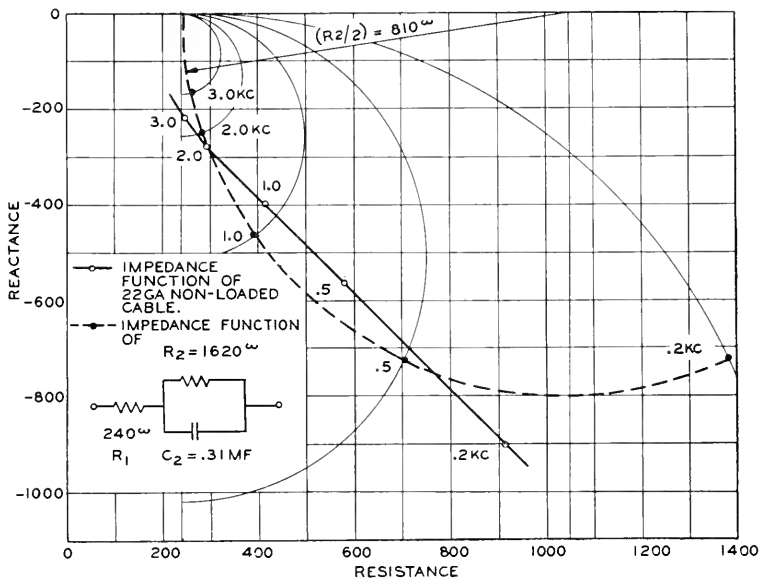


Fig. 4—Graphical design of two-terminal balancing network for 22-ga. non-loaded exchange area cable.

TABLE III-a

22 Gauge Non-Quadded Non-Loaded BSA Exchange Area Cable

Freq. kc	Line Impedance		Network Impedance		Computed Return Loss— db
	Rect.	Polar	Rect.	Polar	
0.2	915—j905	1287/ $\overline{44.7}$	1380—j725	1555/ $\overline{27.8}$	15.0
0.5	580—j565	808/ $\overline{44.2}$	705—j725	1010/ $\overline{45.8}$	19.1
1.0	415—j400	576/ $\overline{44.0}$	390—j460	603/ $\overline{49.7}$	25.2
2.0	295—j280	407/ $\overline{43.5}$	285—j245	376/ $\overline{40.7}$	26.6
3.0	250—j220	333/ $\overline{41.3}$	260—j165	308/ $\overline{32.4}$	21.2

toll cable is plotted on Fig. 5. The method followed in determining the elements is somewhat as follows: R_1 will be given by the intercept of the function on the R axis and is 130 ohms. Next look at the low-frequency range determined by R_3C_3 and draw a semicircle which approximates the given function in the range of 200–500 cycles. The diameter of this semicircle

determines R_3 as 2100 ohms and R_2 is then automatically determined as the difference between the R -intercept of the R_3 semicircle and R_1 , hence $R_2 = 420 - 130 = 290$ ohms. To determine C_3 , choose the X_{C_3} semicircle at 500 cycles to intersect the R_3 semicircle at a point near the 500-cycle impedance of the cable impedance function, but make some allowance for the added negative reactance of the R_2C_2 generating function. The determination of C_2 can be made in either of two ways. First an X_{C_2} semicircle can be drawn at 5000 cycles which intersects the R_2 semicircle at an impedance near the 5000-cycle impedance of the cable. The impedance at 1000 cycles can then be found graphically for R_2C_2 and R_3C_3 and added together to R_1 . This

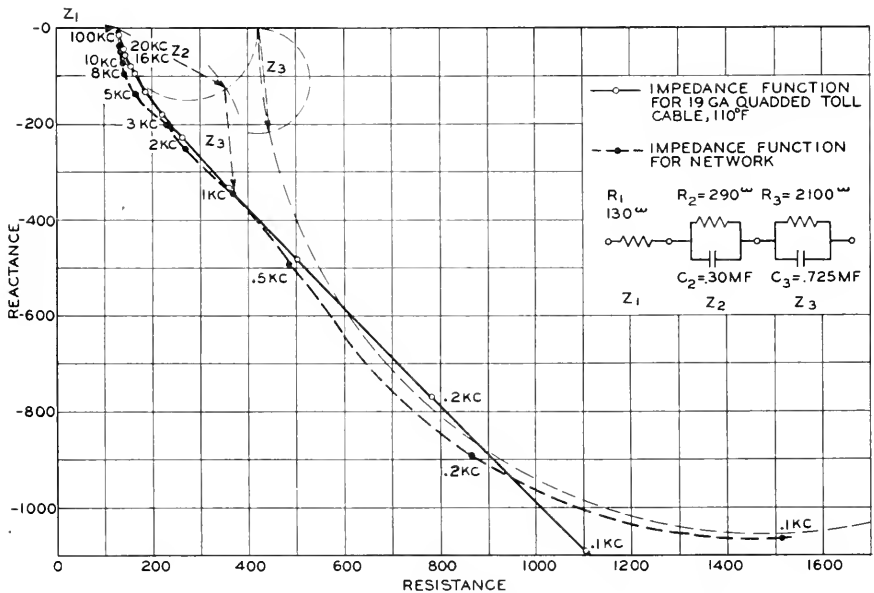


Fig. 5—Graphical design of two-terminal balancing network for 19-ga. quadded non-loaded toll cable.

total impedance at 1000 cycles should provide a good simulation of the 1000-cycle impedance of the cable. A second procedure for finding C_2 would be to follow a somewhat reverse process: Determine the 1000 cycle Z for the R_3C_3 function and subtract it from the 1000 cycle Z of the cable. Choose C_2 such that the intersection of the R_2C_2 semicircles is near the point determined by the subtraction of R_3C_3 from the cable.

To avoid confusion of lines the construction circles have been omitted from this last drawing except to show the addition of the 1000-cycle impedances. As may be seen this network shown in Fig. 5 provides a rather good simulation throughout the frequency range above 200 cycles.

As pointed out earlier, if the first guess is not a sufficiently good approximation a second try can be made based on the evident shortcomings of the first try. In this case if a closer approximation is required up to 20 kc the next step might be to change C_3 to .8 mf which would make the Z_3 contributions above .1 kc somewhat less negative and would therefore raise the network locus. Then changing R_1 to 140 ohms would shift the locus 10 ohms to the right. The resulting locus would be somewhat closer at the upper frequencies but the change would not be necessary unless a rather high degree of balance is required.

TABLE III-b
19 Ga. Quadded Non-Loaded Toll Cable

Freq. kc.	Network Impedance		Line Impedance		Computed Return Loss vs Theoretical Line-db
	Rect.	Polar	Rect.	Polar	
.1	1515 —j1064	1852 / $\sqrt{35.9}$	1103—j1093	1554 / $\sqrt{44.7}$	18.3
.2	867 — j893	1244 / $\sqrt{45.8}$	783— j770	1097 / $\sqrt{44.5}$	24.8
.5	488 — j493	693 / $\sqrt{45.3}$	501— j482	696 / $\sqrt{43.9}$	38.2
1.0	376 — j340	507 / $\sqrt{42.1}$	361— j335	492 / $\sqrt{42.8}$	36.0
2.0	271 — j254	371.6 / $\sqrt{43.2}$	265— j229	350 / $\sqrt{40.8}$	29.0
3.0	217 — j203	297.2 / $\sqrt{43.2}$	223— j180	287 / $\sqrt{38.9}$	27.8
5.0	166.5— j139	211.3 / $\sqrt{38.0}$	187— j131	228 / $\sqrt{35.1}$	26.1
8.0	145.5— j96.8	172.0 / $\sqrt{32.2}$	164— j94	189 / $\sqrt{29.8}$	25.8
10.0	140.0— j74.4	158.0 / $\sqrt{28.0}$	155— j79.2	174 / $\sqrt{27.1}$	26.5
16.0	134 — j47.2	142.1 / $\sqrt{19.5}$	145— j55.0	155 / $\sqrt{20.8}$	27.9
20.0	132 — j37.9	137.9 / $\sqrt{16.0}$	141— j45.1	148 / $\sqrt{17.7}$	27.9
100	131 — j7.3	131.0 / $\sqrt{3.2}$	130— j14.0	131 / $\sqrt{6.2}$	31.7

In general the success of a trial of the graphical construction may be determined immediately by comparing about three frequencies of the line and network.

Table IIIb gives the computed network impedance and the line impedance. The computed return loss is also given and equals or exceeds 25 db at all frequencies above 200 cycles.

It is apparent that the resistance and condenser elements of the generating functions are in descending order of magnitude with increasing frequency for the non-loaded cable the impedance locus of which is essentially a straight 45° line. As pointed out earlier, the series addition of such generating functions may be converted to a ladder structure⁵, whose sections will have a tapered characteristic rather than repetitive.

⁵ Appendix D of Transmission Circuits by K. S. Johnson.

RETURN LOSS

When designing such networks for balancing purposes, it has been found convenient to plot the function on a sheet such as Fig. 6 which divides the right half of the complex plane into circular regions such that all points on or within the boundary of a given region have a return loss against the network $1 + j0$ equal to or greater than that corresponding to the boundary. These circles are determined by the return loss voltage ratio k and the ratio

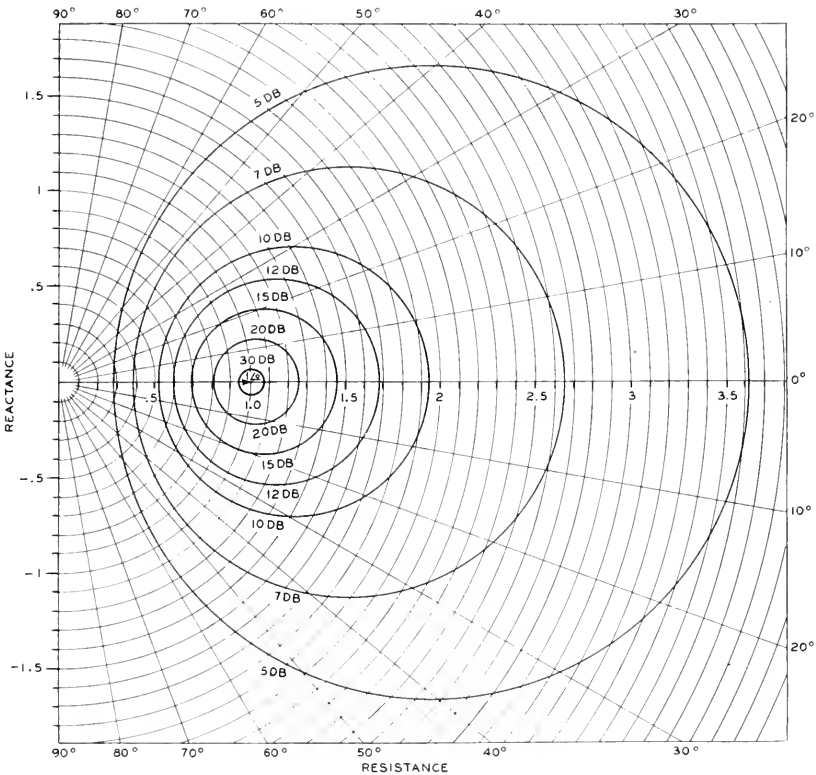


Fig. 6—Curves of constant return loss for the network $1 \angle 0 \equiv 1 + j0$.

of the line and network impedances. They may be computed from the equation

$$(1 + L/N)/(1 - L/N) = k \quad (6)$$

By plotting the line and simulating network loci on such a sheet it is generally possible to observe visually whether or not a given network meets the specified return loss requirement. If visual accuracy is not adequate,

it is always possible to measure off N and L and the angle between them, spot the complex ratio L/N on the complex plane and read immediately the approximate return loss.

CONCLUSION

The examples of the foregoing discussion have been confined to the fourth quadrant. It was shown that by graphical means a number of parallel resistance-condenser functions could be determined which when added together would yield a close approximation to the given function. In the most general case these functions would involve the generating function of R , L and C in parallel, the locus of which is a circle having impedance $+j0$ at zero frequency and $-j0$ at infinite frequency, and crossing the axis of reals at R and the frequency at which L and C are anti-resonant. A case which has been found useful in simulating such things as telephone sets and other inductive elements is the parallel combination of R and L which, of course, is the special case for $C = 0$ and occurs in the first quadrant.

The foregoing has been discussed with the thought that it may be useful where there is limited time and where the required degree of simulation is consistent with a graphical method. At some future time it may be possible to pursue the problem further and devise the analytic counterpart to the somewhat heuristic graphical method.

CHAPTER III

The Use of X-Rays for Determining the Orientation of Quartz Crystals

By W. L. BOND And E. J. ARMSTRONG

THIS paper is one of a series by the Crystal Research Group on the manufacture of quartz oscillator plates. Certain sections of it which are not original, but rather adaptations of text book material to the present problem, are included for purposes of completeness and for the convenience of those readers whose knowledge of the crystallographic literature may be limited.

3.1 PRODUCTION OF X-RAYS FOR QUARTZ CRYSTAL X-RAY WORK

X-rays are produced when electrons strike a metal target at high velocity. The wave-length of X-rays given off from an X-ray tube varies from the longest which can pass through the X-ray tube window to the shortest that can be produced from the given target by the applied peak voltage. By analogy to the visible spectrum this is referred to as "white" radiation. For each different metal, however, there are characteristic radiations of certain wave-lengths whose intensity markedly exceeds those of other wave-lengths (Fig. 3.1). The strongest of these characteristic radiations is known as the $K\alpha_1$, the next strongest (generally half as strong and of slightly longer wave-length) as $K\alpha_2$ and the third strongest (shorter in wave-length than $K\alpha_1$) is $K\beta$. The higher the atomic number of the target, the shorter will be the wave-length of the characteristic radiation. Therefore higher voltages will be required to excite the characteristic radiation from the heavier metals. (The minimum wave-length of X-rays that can be excited by any given voltage is given by the equation $\lambda_{\min.} = \frac{1.234 \times 10^{-4}}{V}$ where V is expressed in volts and $\lambda_{\min.}$ in Angstrom units).

Higher voltages also raise the intensity of the white radiation and, at any given voltage, the white radiation produced from a heavy metal target is more intense than that produced from a lighter metal target (see Figure 3.1). When "white" radiation is desired, as in Laue photography, heavy metal targets, such as tungsten, are used: when "monochromatic" radiation is desired, as in crystal goniometry, the lighter metal targets, such as copper, are used because, with a lighter metal target (wave-length of characteristic radiation long) the voltage, and therefore the intensity of the

white radiation, cannot be raised very high before exciting the characteristic radiation whereas, with a heavy metal target (wave-length of characteristic radiation short) considerable intensity of white radiation can be produced without exciting the characteristic radiation. This is illustrated in Fig. 3.1 which shows that a potential of 35,000 volts is high enough to excite the K group radiation from molybdenum, but not high enough to excite the shorter wave-length K radiation from tungsten which, further, gives more intense white radiation at this voltage. Even higher voltages, resulting in

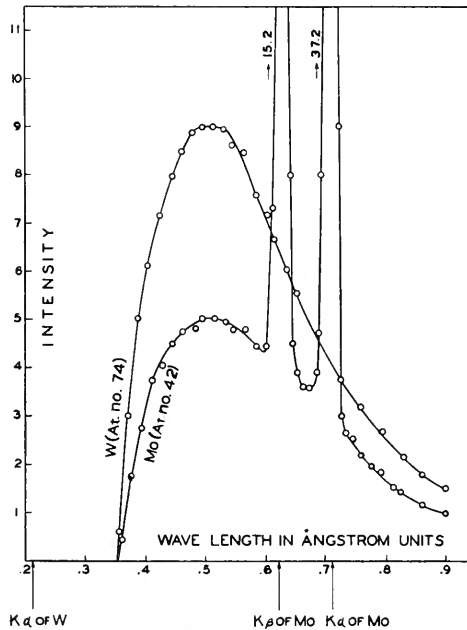


Fig. 3.1—Variation of intensity with wave-length of X-rays from tungsten and molybdenum targets at 35,000 volts

more intense white radiation, could be used with tungsten without exciting the characteristic radiation ($\lambda = .209$).

Figure 3.2 shows the I - λ curve (estimated) for copper, the target metal commonly used in quartz X-ray work, which has a small atomic number and can therefore be used as a source of "monochromatic" X-rays with moderate voltages. (A further advantage of copper for quartz work is pointed out at the end of this section).

The $K\alpha_1$ and $K\alpha_2$ wave-lengths are so close together that for most uses of "monochromatic" radiation no attempt is made to eliminate the $K\alpha_2$ radiation. The $K\beta$ radiation, however, gives a distinct intensity peak of shorter wave-length which must be reduced as much as possible by use of a metal filter having a high absorption coefficient for the $K\beta$ radiation of

the target used. In most cases the best filter-metal for the $K\beta$ radiation is the second element below the target metal in the periodic table. For example, a nickel filter 0.0005 inches thick is used with the copper target which is used for X-ray goniometry of quartz.

The minimum voltage that will excite the $K\alpha_1$ radiation of copper (wavelength $\lambda = 1.5374\text{\AA}$) is 8.86 kv., but a voltage of 30 or 40 kv. is usually used to obtain adequate intensity.

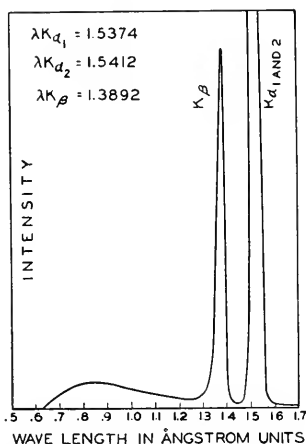


Fig. 3.2—Variation of intensity with wave-length of X-rays from a copper target at 20,000 volts (estimated)

3.2 DETECTION OF X-RAYS

X-rays may be detected by means of heat effects, fluorescence of appropriate screens, photographic effects and by ionization of gases.

Heat measuring devices are not suited to routine intensity measurements. The other three means of X-ray detection are all being used for various types of quartz work but the ionization of gases is used most widely.

The ionization method involves a chamber which consists essentially of a gas-filled metallic cylinder containing an electrode. A potential is maintained between the electrode and the cylinder so that when the gas is ionized by the X-rays the positive and negative ions produced are drawn to the oppositely charged electrodes, thus constituting an electric current, which current is proportional to the intensity of the X-rays entering the chamber. This current is commonly indicated by a current meter preceded by a special vacuum tube amplifier.

The gas used in the chamber is often air but methyl bromide is about 30 times more readily ionized, xenon 155 times. The only advantage of air is that the chamber need not be gas-tight. The entrance to a sealed ionization chamber must be closed by a substance which does not result in undesirable absorption of the X-rays. Since a nickel filter is needed

somewhere in the path of the X-rays to absorb the $K\beta$ radiation from the copper target, it may be used here to seal the entrance of the chamber.

The Geiger-Müller counter is similar to the ionization chamber, but is operated at such high voltage that the gas is always near breakdown, the passing of X-rays supplying the impetus to complete the breakdown. Because of the high voltage the ionization continues to be strong as the intensity of the radiation declines. Such a lag is likely to cause erroneous maximum readings in crystal measurement.

3.3 PHYSIOLOGICAL EFFECTS OF X-RAYS

Even a few minutes direct exposure to X-rays from such a source as the G. E. CA6 tube will result in a burn that will become apparent in a day or so. In most cases such a burn, if not repeated, will heal without ill effects, but because the physiological effect of X-rays is cumulative, repeated exposure to direct radiation could result in a burn that would not heal and might become cancerous.

Pinhole leaks which permit direct radiation to escape are thus exceedingly dangerous. They may be detected by use of a fluorescent screen in a darkened room. A sheet of lead-glass $\frac{1}{4}$ to $\frac{1}{2}$ inch thick should be held between the fluorescent screen and the observer.

X-rays are scattered from all substances which they strike and repeated exposure to this scattered radiation may result in a harmful decrease in the white blood corpuscles, in sterility, and perhaps in serious burns.

To test for scattered radiation dental X-ray films should be arranged as close to the instrument on all sides as any part of the operator's body can get and left for a period of two weeks of normal operation. If there is no position in which the film becomes fogged during the two weeks, the operator is safe. A narrow lead strip across the film will provide an unexposed portion for comparison with the exposed portion. It should be emphasized that a dental film carried in the pocket is an inadequate safety test, since the hands are frequently the most dangerously exposed part of the body.

The absorptive power of shielding materials is proportional to the density of the material. Minimum adequate shielding is provided by 1.5 mm. or about $\frac{1}{16}$ inch of lead or its equivalent for protection against X-rays generated at 70 kv.¹ Equivalent thicknesses of shielding materials are as follows:

Lead.....	$\frac{1}{16}$ inch
Lead rubber.....	$\frac{1}{8}$ - $\frac{1}{4}$ inch
Lead glass.....	$\frac{3}{8}$ - $\frac{1}{2}$ inch
Steel.....	$\frac{1}{2}$ inch
Bricks and concrete.....	6 inches
Woods.....	60 inches

¹ Davey, W. P., "Study of Crystal Structure and its Applications," McGraw-Hill, 1934.

The United States Bureau of Standards has issued a 28-page booklet entitled "X-Ray Protection" which may be obtained from the Superintendent of Documents, Washington, D. C. for 10 cents.

3.4 DIFFRACTION OF X-RAYS BY CRYSTALS

Following the work of the French crystallographer Haüy at the end of the eighteenth century the theory that crystals were made up of small identical units in orderly arrangement was widely held by crystallographers. In the late nineteenth century these units were thought of as intersecting planes of atoms. Then, in 1912, the German physicist von Laue conceived the idea that such a lattice of atoms should act as a three-dimensional diffraction grating for electromagnetic waves of wave-length approximating the interplanar spacing of the lattice. If X-rays were, as was suspected, electromagnetic vibrations of short wave-length, they might be of the right order of magnitude to obtain diffraction from crystals. When the experiment was tried it was found that a beam of X-rays (not monochromatic) passing through a crystal produced an orderly arrangement of spots on a photographic film, the type of photograph now known as a Laue photograph.

The term *reflection* may be used in place of *diffraction* since X-ray diffraction is like light reflection in that the entering and leaving beams make equal angles with the reflecting or diffracting atomic planes.² Since this concept is simpler, X-ray diffraction is commonly referred to as reflection.

Unlike light reflection, X-ray reflection can take place only under the conditions given by the following equation which is known as the Bragg law

$$n\lambda = 2d \sin \theta \quad (3.1)$$

where n = a small whole number,

λ = wave-length of X-rays used (generally stated in Ångstrom units)

d = distance between the atomic planes (generally stated in Ångstrom units).

θ = angle between the X-rays and the atomic planes ("The Bragg Angle").

That is, the angle of incidence must be such that the path-length of two rays reflected from different atomic planes differs by a whole number of wave-lengths so that the emerging rays will be in phase. If the difference in path-length of the two rays is one wave-length the reflection is called the first-order reflection ($n = 1$). At some larger θ angle the path difference will be exactly 2λ and reflection will occur again. This is the second order reflection ($n = 2$). Monochromatic X-rays are used so that only

² Compton, A. H. and Allison, S. K., "X-Rays in Theory and Experiment," D. Van Nostrand, New York, 1935, Pages 340-346.

one value of θ will satisfy the equation for each order reflection. Thus, with a monochromatic X-ray beam one may not obtain reflection from the planes at all angles as with visible light, but only at such specific angles as satisfy the Bragg law. Further, even with optimum conditions for reflection the ratio of the intensity of the reflected X-ray beam to that of the incident beam is of the order of 1:10,000. The Bragg angle θ is highly critical and the reflection of X-rays from atomic planes therefore serves as a precise method of crystal orientation.

Figure 3.3 is a diagrammatic representation of the relation $n\lambda = 2d \sin \theta$. On such a diagram the following laws of X-ray reflection become obvious:

(1) λ must be smaller than $2d$, that is, the wave-length of X-rays used must be less than twice the inter-planar spacing of the atomic planes to be X-rayed.

(2) The number of different orders of reflection n obtainable from atomic planes with interplanar spacing d is fixed by the expression $n\lambda < 2d$. In

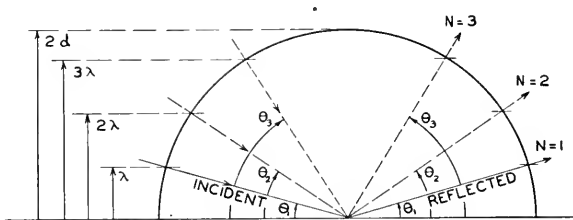


Fig. 3.3—A diagrammatic representation of Bragg's law, $n\lambda = 2d \sin \theta$

other words, since $\sin \theta$ cannot be greater than 1 the value of λ must be less than $\frac{2d}{n}$. The distance between the atomic planes parallel to the hexagonal prism of quartz is 4.2466 \AA^3 and the wave-length of the $K\alpha_1$ radiation from a copper target is 1.5374 \AA . Hence no reflection higher than the 5th order could be obtained from this set of planes using a copper target.

On the other hand, a target metal whose characteristic wave-length is very much shorter than $2d$ is undesirable since it gives so many orders of reflection from each set of atomic planes that the multitude of closely spaced reflections leads to confusion.

(3) Higher orders of reflection occur at larger θ angles.

(4) The relation of θ to λ is not linear but sinusoidal.

The reflected beam can only lie in a plane containing the normal to the atomic plane and the incident beam. Conditions are unchanged by rotating the crystal about the normal to the atomic plane being used.

³ R. B. Sosman, "The Properties of Silica," Chemical Catalogue Co., New York 1927.

3.5 THE NAMING OF ATOMIC PLANES IN CRYSTALS

It is convenient to be able to refer to any atomic plane in a crystal by some symbol that uniquely defines its orientation. The symbols commonly used for this purpose are known as Miller indices (or Bravais-Miller indices for the hexagonal system) and are the reciprocals of the intercepts of the atomic plane on a set of crystallographic axes chosen in accordance with the symmetry of the crystal. In quartz this set of axes is as shown in Fig. 3.4: a vertical axis c and three horizontal axes at 120° a_1 , a_2 , a_3 .

Measurement of the interfacial angles of thousands of quartz crystals has shown that the natural faces have intercepts on the crystallographic

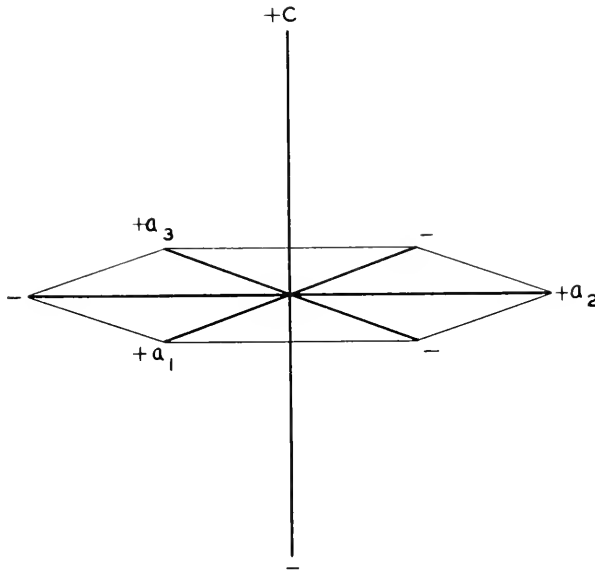


Fig. 3.4—Hexagonal crystallographic axes

axes that are integral multiples of a fixed distance, which is the same in the case of all three a axes and different in the case of the c axis. This fixed distance along the c axis is found to be 1.09997 times the fixed distance along the a axes. Therefore, the “unit length” of each of the a axes is said to be 1; that of the c axis 1.09997 and a face that cuts the c axis at 1.09997 a from the origin is said to have the c intercept of 1. (This unit axial length is different for different substances but the same for all crystals of the same substance.) For example, the front cap face in figure 3.5 has the axial intercepts 1, ∞ , -1 , 1, naming the axes in the order a_1 , a_2 , a_3 , c . The indices for this face are written $(10\bar{1}1)$ (general form $hkil$). The front vertical face has the intercepts 1, ∞ , -1 , ∞ and the

indices $(10\bar{1}0)$. The first two digits of the indices of any vertical prism plane are the same as those of the adjacent cap faces: the final digit is always zero because they are parallel to the Z (or c) axis. Since the intercepts on a_1 and a_2 uniquely determine the intercept on a_3 , the third digit of the symbol may be omitted. The omission is sometimes indicated by a dot, as $(10\cdot1)$ (general form $hk\cdot l$).

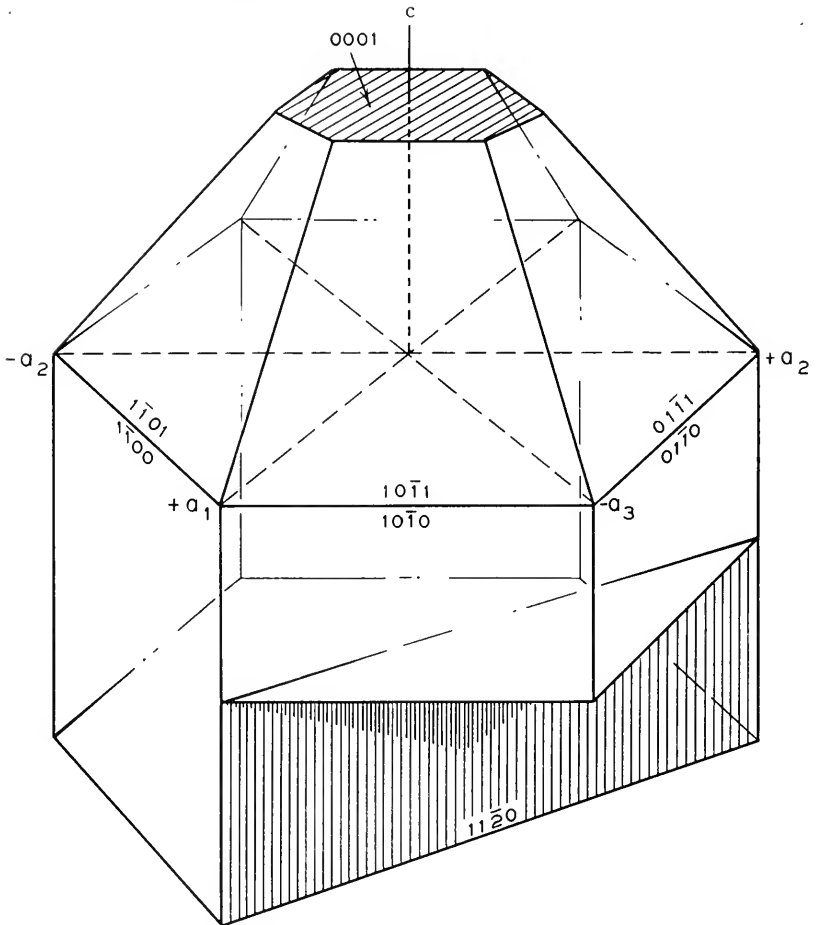


Fig. 3.5—Miller-Bravais indices of certain crystallographic planes in quartz

The use of indices instead of the actual intercepts simplifies the mathematics of crystallography in many ways. For example, the sum of the indices of two planes forms the indices of an intermediate plane that is parallel to the line of intersection of the first two. Thus the sum of $(00\cdot1)$, the atomic plane which is normal to c , and $(10\cdot0)$, prism face, is $(10\cdot1)$, the indices of the cap face directly above the $(10\cdot0)$ prism face.

Further, in the equation $n\lambda = 2d \sin \theta$, the interplanar spacing d of the atomic planes ($hk \cdot \ell$) is

$$d_{hk \cdot \ell} = \frac{a_0}{\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \frac{\ell^2}{(c/a)^2}}} \quad (3.2)$$

Where the axial ratio c/a is 1.09997 in quartz and a_0 , the distance between atoms along the a axis, is 4.903\AA .⁴

The n order reflection from the $hk \cdot \ell$ plane is sometimes spoken of as the reflection from the $n(hk \cdot \ell)$ plane as in Table I and Fig. 3.8 where, for example, the second order reflection from the 01·1 plane is listed as the reflection from the 02·2 plane. The justification for this notation is that the 02·2 planes would have a d value half that of the 01·1 planes (since the indices are reciprocals of the axial intercepts) and the first order reflection from such planes would have the same θ value as the second order reflections from the 01·1 planes i.e., if

$$2\lambda = 2d \sin \theta$$

then

$$\lambda = 2 \frac{d}{2} \sin \theta$$

Among manufacturers of piezoelectric units a rectangular coordinate system is used in place of the hexagonal one described above, but the indices as derived from the hexagonal axes are retained. One of the a axes is chosen as the X axis. The three a axes are identical (the vertical axis of quartz is an axis of 3-fold symmetry) and therefore any one of the a axes may be chosen as X . The c axis is called the Z axis and a Y axis, normal to X and Z is so chosen as to form a right-handed coordinate system for right-handed quartz or a left-handed coordinate system for left-handed quartz as described in Chapter II.

The indices of the cap faces of right and left-handed quartz crystals (as viewed from above) are given in Fig. 3.6 which should be compared with Fig. 2.4 and 2.6 of Chapter II. (Note that Z in Fig. 3.6 refers to the Z axis whereas z in Fig. 2.6 refers to the z faces or minor cap faces). The cap faces directly beneath those illustrated (i.e., on the other end of a doubly terminated crystal) would have the same indices except that the final digit would be negative since they cut the negative end of the Z (or c) axis. Thus $(0\bar{1} \cdot \bar{1})$ is beneath $(0\bar{1} \cdot 1)$ and parallel to $(01 \cdot 1)$.

Parallel crystal faces lie along the same set of atomic planes. Thus $(01 \cdot 1)$ and $(0\bar{1} \cdot \bar{1})$ represent the same atomic plane. Further, since the

⁴Wyckoff, W. G., "The Structure of Crystals," The Chemical Catalogue Co. (1931).

vertical axis is an axis of 3-fold symmetry, the major cap-face planes $(01 \cdot 1)$, $(\bar{1}0 \cdot 1)$ and $(1\bar{1} \cdot 1)$ have the same properties and this applies also of course to the parallel crystal faces (same atomic planes) which are, respectively, $(0\bar{1} \cdot \bar{1})$, $(10 \cdot \bar{1})$, and $(\bar{1}1 \cdot \bar{1})$. Thus we can choose any one of these symbols to represent this type of plane when speaking of such properties as distance between atomic planes, θ angle, or angle between atomic planes and the Z axis. The symbol that will be used in this paper for this type of plane is $(01 \cdot 1)$.

Similar considerations apply to the set of minor cap faces for which the symbol used here is $(01 \cdot \bar{1})$ which is chosen instead of $(0\bar{1} \cdot 1)$ because it simplifies tabulation, as in Table I and Fig. 3.8.

The indices $(hk \cdot l)$ of all faces or atomic planes with the same X-ray properties as those for any given plane may be derived as follows: First replace the omitted digit i in the indices of the given plane, which may be

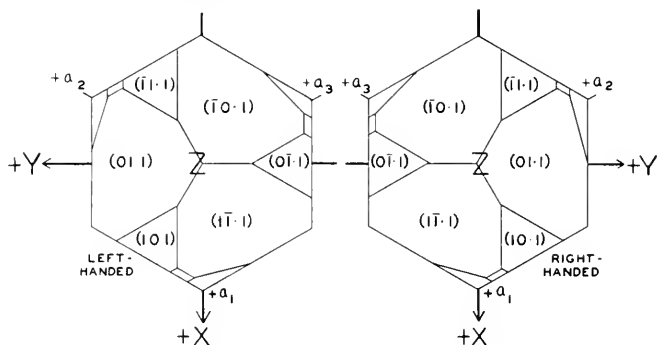


Fig. 3.6—Indices of cap-faces of right- and left-handed quartz crystals

determined from the equation $i = -(h + k)$. Rotary permutation of the first three indices is then permitted, as $abc\bar{l}$, $\bar{c}ab\bar{l}$, $b\bar{c}a\bar{l}$.

The other three of the six equivalent faces are found by interchanging any adjacent two of the first three indices and also changing the sign of l , as $abc\bar{l}$ becomes $a\bar{c}b\bar{l}$ or $b\bar{a}\bar{c}\bar{l}$. For example:

$$\begin{array}{ccc} 1\ 2\ \bar{3}\ 4 & \bar{3}\ 1\ 2\ 4 & 2\ \bar{3}\ 1\ 4 \\ 1\ \bar{3}\ 2\ \bar{4} & 2\ 1\ \bar{3}\ \bar{4} & \bar{3}\ 2\ 1\ \bar{4} \end{array}$$

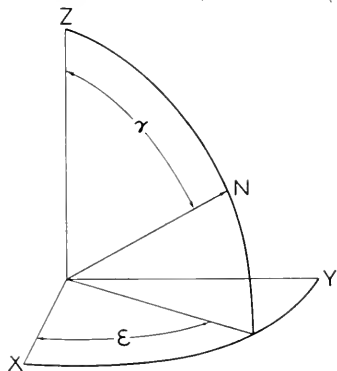
We could consider the $2\ 1\ \bar{3}\ \bar{4}$ as derived from cyclic permutation of $1\ \bar{3}\ 2\ \bar{4}$, and $\bar{3}\ 2\ 1\ \bar{4}$ as similarly derived from $2\ 1\ \bar{3}\ \bar{4}$ instead of by interchange of the sets above them.

The six symbols derived from the above by changing the sign of only the final digit refer to faces whose θ X-ray angle is the same as that of the above planes but whose intensity of reflection may be different.

TABLE I
QUARTZ X-RAY REFLECTION ANGLES

The Planes of Quartz from which the $Cu K_{\alpha}$ will reflect
 θ = Bragg angle of X-ray reflection for $Cu K_{\alpha}$ radiation
 γ = Angle that the plane normal N makes with the Z axis
 ϵ = The angle between X and the plane containing the normal and Z , measured in the XY plane
 I = Relative intensity of reflection

$hk \cdot \ell$	θ	γ	ϵ	I for $\ell+$	I for $\ell-$	$hk \cdot \ell$	θ	γ	ϵ
00·3	25°20'	0°	90°	.50	.50	11·0	18°17'	90°	60°
00·6	58°49'	0°	"	.38	.38	11·1	20° 9'	65°33'	60°
01·0	10°26'	90°	"	24.	24.	11·2	25° 5'	47°44'	60°
01·1	13°20'	51°47'	"	100.	75.	11·3	32° 3'	36°15'	60°
01·2	19°45'	32°25'	"	28.	85.	11·4	40°37'	28°49'	60°
01·3	27°41'	22°57'	"	45.	2.7	11·5	51°10'	23°45'	60°
01·4	36°45'	17°37'	"			11·6	65°41'	20° 8'	60°
01·5	47°21'	14°15'	"			12·0	28°38'	90°	70°54'
01·6	60°59'	11°57'	"			12·1	29°59'	73°26'	70°54'
02·0	21°14'	90°	"	28.	28.	12·2	33°53'	59°14'	70°54'
02·1	22°55'	68°31'	"			12·3	39°58'	48°15'	70°54'
02·2	27°27'	51°47'	"	26.	26.	12·4	46°44'	40° 2'	70°54'
02·3	34° 5'	40°16'	"	32.	63.	12·5	58°59'	33°54'	70°54'
02·4	42°30'	32°25'	"			12·6	78°41'	29°15'	70°54'
02·5	53° 6'	26°56'	"			13·0	40°46'	90°	76° 6'
02·6	68°17'	22°57'	"			13·1	41°56'	77°41'	76° 6'
03·0	32°54'	90°	"			13·2	45°35'	66°25'	76° 6'
03·1	34°10'	75°18'	"	40.	1.4	13·3	51°20'	56°46'	76° 6'
03·2	37°51'	62°18'	"	19.	27.	13·4	60° 7'	48°52'	76° 6'
03·3	43°45'	51°47'	"			13·5	75°11'	42°29'	76° 6'
03·4	51°58'	43°37'	"	6.3	3.2	14·0	56° 6'	90°	79° 6'
03·5	63°41'	37°19'	"			14·1	57°22'	80°15'	79° 6'
04·0	46°25'	90°	"			14·2	61°21'	71° 2'	79° 6'
04·1	47°35'	78°52'	"			14·3	69° 1'	62°44'	79° 6'
04·2	51° 8'	68°31'	"			22·0	38°51'	90°	60°
04·3	57°17'	59°26'	"			22·1	40° 3'	77°12'	60°
04·4	67°13'	51°47'	"	12.	0.7	22·2	43°34'	65°34'	60°
05·0	64°54'	90°	"			22·3	47°54'	55°43'	60°
05·1	66°27'	81° 3'	"			22·4	57°59'	47°44'	60°
05·2	71°42'	72°31'	"	.25	23.	22·5	71°45'	41°21'	60°
						23·0	52° 8'	90°	66°35'
						23·1	53°20'	76°40'	66°35'
						23·2	57° 4'	70° 8'	66°35'
						23·3	63°53'	61°33'	66°35'
						23·4	76°52'	54° 9'	66°35'
						24·0	73°24'	90°	70°54'
						24·1	75°40'	81°32'	70°54'
						24·2	88°54'	73°26'	70°54'
						33·0	70°15'	90°	60°
						33·1	72° 8'	81°23'	60°
						33·2	79°32'	73° 9'	60°



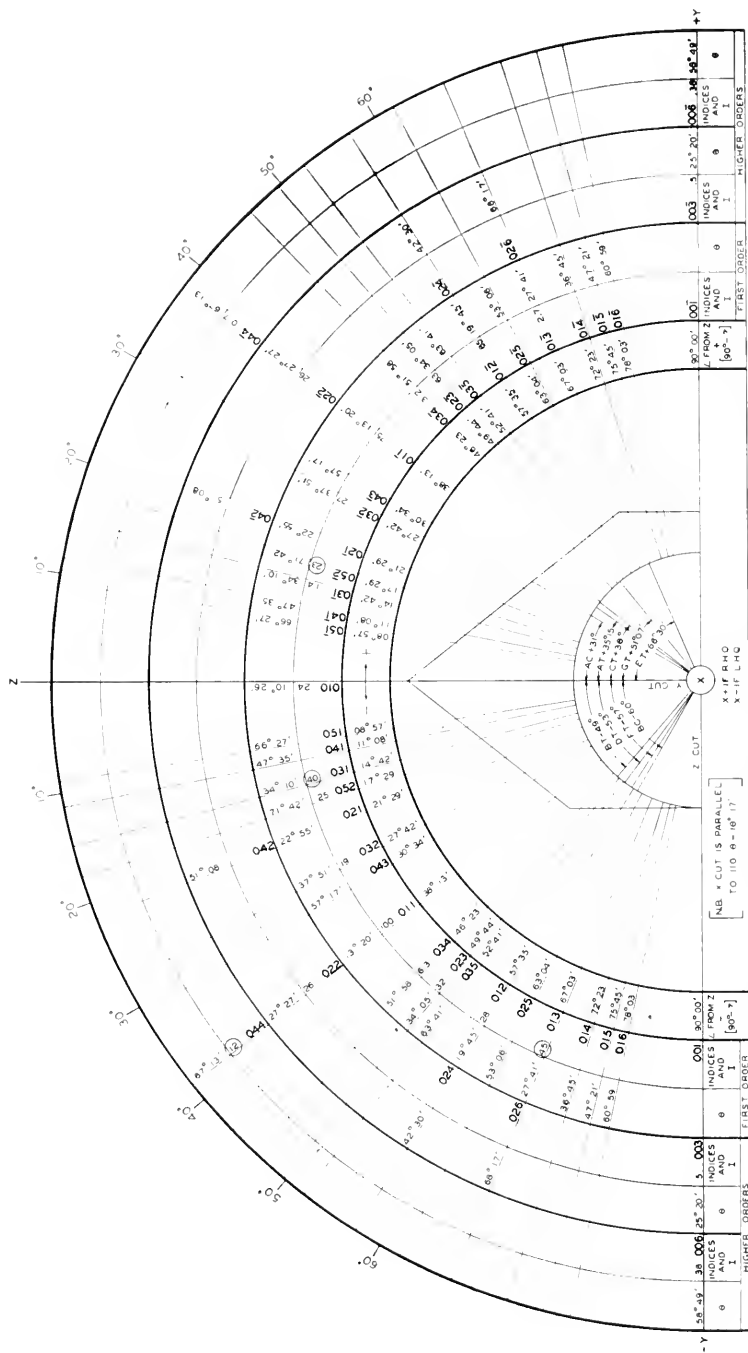


Fig. 3.8—Atomic-planes and common plate-cuts parallel to the X axis

the more important atomic planes of quartz, identified by their indices. Its usefulness in quartz work will be pointed out in Section 3.7B.

In many cases the reflecting power of an atomic plane differs from that of the symmetrical plane on the other side of the Z axis. (See, for example $01 \cdot 1$ and $01 \cdot \bar{1}$). When this difference is very great as with $04 \cdot 4$ and $04 \cdot \bar{4}$ the planes are useful in determining whether a plate is cut at a positive or negative angle from the Z axis. The intensities of planes that have been found useful for this purpose are circled in Fig. 3.8.

3.6 X-RAY GONIOMETRY

Since the angles θ and the intensities I are different for different planes we can use them to identify these planes, that is, to orient the crystal by measuring angles between recognized atomic planes and plate surfaces.

Figure 3.9 is a diagrammatic representation of an X-ray goniometer where

T is the tube target shown with its intensity pattern,

SS are slits that pass only a narrow beam,

C is the crystal,

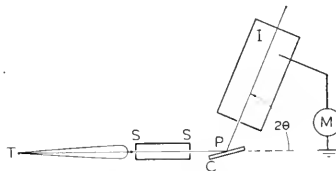


Fig. 3.9—Simplified diagram of X-ray goniometry

I is the ionization chamber

M is the meter that measures the ionization current.

The ionization chamber is placed at an angle 2θ to the incident beam, where θ is the Bragg angle for the atomic plane being used, and is not moved while reflections are being taken from that atomic plane. If C is then rocked about the vertical axis P (normal to the plane of the paper) the ionization chamber registers an electric current when an atomic plane is at the proper angle for reflection.

(a) Atomic plane parallel to plate-face.

Let us examine a simple case, that for which the existing face is parallel to an atomic plane (Fig. 3.10). The crystal is held against the reference points by a coil spring. The crystal holder is free to rotate about the vertical axis P (with respect to the X-rays) and the angle of rotation is read on the graduated scale. If the entering angle (the angle between the entering beam and the plate-face) is one that satisfies the equation $n\lambda = 2d \sin \theta$, we will have a reflected ray which is at a leaving angle of θ . Also the reflected ray is always deviated from the line of the original

ray by the angle 2θ . If, when the crystal gives a reflected ray, it is rotated in its own plane on the reference points the reflection is unchanged.

(b) Atomic plane intersecting plate-face in a line normal to the plane of the instrument.⁵

If in the above case the rotation of the crystal in its own plane does cause a change of ionization current the surface is not parallel to the atomic plane. Figure 3.11 illustrates a case in which the surface is at an angle δ to an atomic plane, this intersection lying normal to the plane of the paper in Fig. 3.11. In order that the angle between the X-ray beam and the atomic plane shall be θ , the angle between the beam and the plate-face must now be $\theta - \delta$ on one side and $\theta + \delta$ on the other. The deviation angle 2θ is the sum of these two. Therefore for atomic planes intersecting

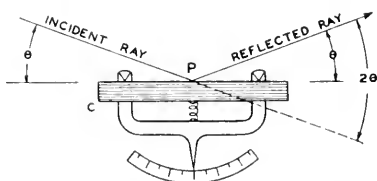


Fig. 3.10—Goniometry case (a): Atomic plane parallel to plate-face

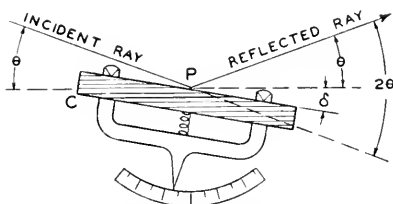


Fig. 3.11—Goniometry case (b): Atomic plane intersecting plate-face in a line normal to "the plane of the instrument"

the plate-face in a line normal to the plane of the instrument the ionization chamber is set at 2θ regardless of the angle between the atomic plane and the surface of the plate.

In Fig. 3.11 the entering angle is shown as $\theta - \delta$, the leaving angle as $\theta + \delta$. If the crystal is now rotated through an angle of 180° in its own plane the entering angle will have to be set at $\theta + \delta$ and the leaving angle will become $\theta - \delta$. The crystal holder will have been moved through an angle 2δ . Thus δ can be found by observing the angle through which the crystal holder must be rotated in order to achieve X-ray reflection from the same atomic plane when the crystal is rotated 180° in its own plane.

⁵ The *plane of the instrument* is a plane normal to the axis of rotation of the instrument and containing the incident ray.

It should be noted that δ should not exceed θ . If δ exceeds θ , it is necessary for the X-ray beam to pass through a great thickness of quartz which would so weaken the beam that the reflected rays could not be detected. Further, even when δ does not exceed θ there is still a variation of the reflected ray intensity with the angle between the entering ray and the plate-face, which may be expressed as follows:⁶

$$I_r = I_R \frac{\sin g_\ell}{\sin g_\ell + \sin g_e}$$

where

I_r = The intensity of the reflected ray

g_e = The "entering angle" = The angle between the entering ray and the plate face

g_ℓ = The "leaving angle" (In Fig. 3.11 $g_e = \theta - \delta$; $g_\ell = \theta + \delta = 2\theta - g_e$)

I_R = The maximum obtainable reflected intensity (i.e., when $g_e = 0$ and $g_\ell = 2\theta$).

or

$$I_r = I_R \frac{\sin (2\theta - g_e)}{\sin (2\theta - g_e) + \sin g_e}$$

The curves in Fig. 3.12 show the variation of I_r/I_R with $g_e/2\theta$ for various values of 2θ . It is seen that for plates as described above and figured in 3.11 a stronger reflection is obtained when $g_e = \theta - \delta$ than when $g_e = \theta + \delta$ (i.e., after 180° rotation in the plane of the plate-face). In other words the smaller g_e angle gives the larger intensity of reflection. It might be added, however, that in practice it may not be possible to obtain the maximum values of reflection intensity due to the fact that, as g_e approaches zero, the width of the reflected beam may exceed the width of the ionization chamber. (See inset, Fig. 3.12.)

Quartz plates containing an X axis are checked as described above (case *b*) for rotation around the X axis. For this check they are oriented as shown in Fig. 3.13, case *b* with the X axis parallel to the axis of the instrument. The stippled face in Fig. 3.13 represents the so-called "reference bevel", the remnant of the surface of the Z section, and is therefore normal to the Z axis.

(c) Atomic plane intersecting plate-face in a line parallel to the plane of the instrument.

The case described above and illustrated in Fig. 3.11 was the case of single rotation plates (AT, BT and others shown in Fig. 3.8) being corrected about the X axis by the use of atomic planes parallel to the X axis. When

⁶ Debye, P. and Menke, H., "Untersuchung der Molekularen Ordnung in Flüssigkeiten mit Röntgenstrahlung," *Ergeb. d. Techn. Röntgenkunde*, B.2, P. 16; Leipzig (1931).

such a plate is being rotated about the X axis as in Fig. 3.11 the normal to the atomic plane lies in the plane of the instrument. We can also use

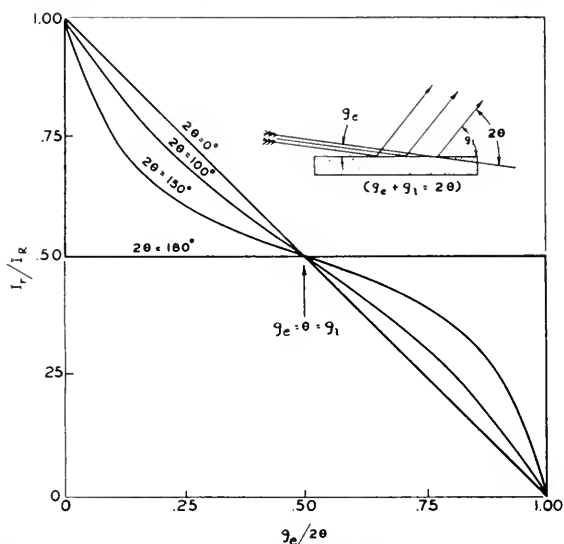


Fig. 3.12—Variation of intensity of reflected ray with entering angle g_e and the Bragg angle, θ

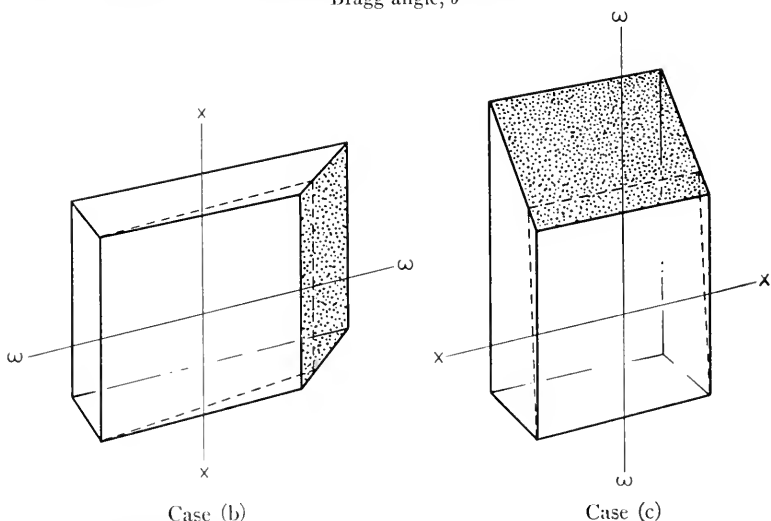


Fig. 3.13—Position of quartz plate relative to vertical axis of instrument in case (b) and case (c). (Stippled face is reference level, normal to Z axis.) In the absence of a reference level the X direction can be determined with polarized light. (See Chapter II, p. 246.)

the same atomic plane to correct the orientation of this plate about the axis $\omega\omega$ normal to the X axis (Fig. 3.13 and Fig. 3.14). Here, since the

atomic planes are at an angle δ to the axis of the instrument, the reflected ray will not lie in the plane of the instrument. If, however, the vertical angle β , between the reflected ray and the plane of the instrument is small, the reflected ray may still enter the ionization chamber. The maximum angle β which is permissible, is not the same for all instruments, but depends on the vertical length of the slit. In most cases it is about 5° .

The proper angular settings of the instrument are no longer θ for the slab and 2θ for the ionization chamber but are the orthogonal projection of these angles onto the plane of the instrument; g and $g + g'$, respectively.

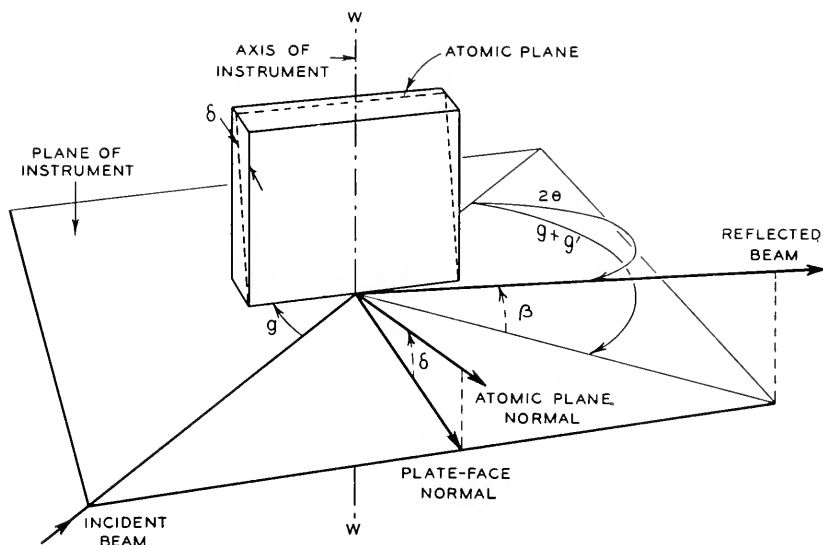


Fig. 3.14—Goniometry case (c): Atomic plane intersecting plate-face in a line parallel to "the plane of the instrument"

Formulae are given below for β , g , and $g + g'$ in terms of the Bragg angle θ and the angle between the atomic planes and the surface of the quartz plate, δ .

$$\sin \beta = 2 \sin \theta \sin \delta \quad (3.3)$$

$$\cos (g + g') = \frac{\cos 2\theta}{\cos \beta} \quad (3.4)$$

$$\sin g = \frac{\sin \theta}{\cos \delta} \quad (3.5)$$

The relations between β , $g + g'$, g , θ , and δ are shown by the curves in Fig. 3.15.

As an example, suppose that a BT plate is to be corrected about the

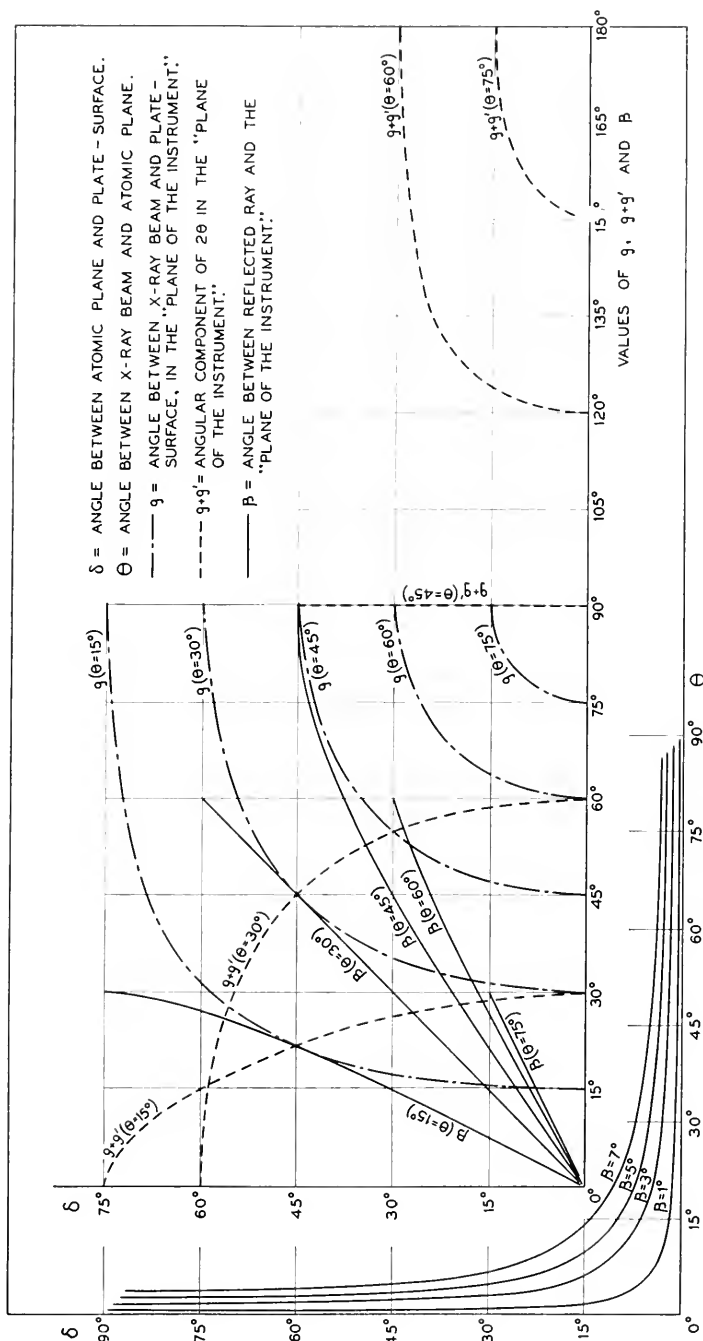


Fig. 3.15—Variation of β , g and $g + g'$ with δ and θ

ww axis using the atomic plane (01·1). (In actual practice the closer plane (02·3) is used.) Here:

$$\delta = 49^\circ - 38^\circ 13' = 10^\circ 47', \quad \theta = 13^\circ 20', \quad 2\theta = 26^\circ 40'$$

From which $\beta = 4^\circ 57', \quad g = 13^\circ 35', \quad g + g' = 26^\circ 34'$

Thus if the plate is correctly cut the reflected ray will enter an ionization chamber whose slit is long enough to receive rays which make an angle of 5° with the plane of the instrument. However, if the plate were in error by more than $6'$ around the XX axis (Fig. 3.13) β would exceed 5° and the center of the reflected beam would not enter the ionization chamber. In actual practice, therefore, the length of the ionization chamber slit should be enough greater than that required for the calculated β to admit reflections from erroneously cut plates.

Since the difference between $g + g'$ and 2θ is only $6'$ and since the width of the ionization chamber slit is usually great enough to accept reflected beams over a range of several times $6'$, no correction of the ionization chamber position may be necessary in this case.

On the other hand, the orientation of the plate with respect to the incident beam is highly critical and since g differs from θ by $15'$ this correction in the orientation of the quartz plate must be made.

Discussion of the general case (d), in which the intersection of the atomic plane and the plate face is neither normal nor parallel to the plane of the instrument, will be found in Section 3.9.

3.7 CHOICE OF AN ATOMIC PLANE FOR CHECKING THE ORIENTATION OF ANY GIVEN FACE

If the plate-face to be checked does not lie parallel to an atomic plane, the nearest usable atomic plane must be found and the orientation of this atomic plane in the plate must be determined. The procedure for these two steps is outlined in this and the following sections.

The problem of the choice of an atomic plane for checking the orientation of one of the faces of a given plate has two parts:

(A) Determination of the orientation of that face with respect to the X , Y and Z axes of the mother crystal and (B) discovery of the atomic plane whose orientation and X-ray properties are most suitable for use with that face.

(A) Determination of the orientation of the face with respect to the X , Y and Z axes of the mother crystal.

The orientation of the plate is commonly given in terms of the A_1 , A_2 and A_3 angular rotations as described and illustrated in Section 2.4 of Chapter II. Briefly, a basal section of crystal is placed initially with its Z axis vertical and its $+X$ axis toward the operator of a horizontal axis saw,

the saw blade being parallel to X and Z . The crystal is then turned through angle A_1 clockwise as seen from above about a vertical axis, then through angle A_2 counterclockwise about the original direction of the X axis. A slab is cut of thickness t and this slab layed down by rotating it 90° clockwise about the original X axis direction. It is then rotated through angle A_3 clockwise about a vertical axis and two cuts are made, separated by a width w (length l being cut last). The rotation through the A_3 angle begins with the linear edge of the reference level of the slab lying parallel to the saw.

The components of the plate edges P_1, P_2, P_3 (length, thickness, and width, respectively) on the $X, Y,$ and Z coordinates after rotation through the angle A_1 are given by the following matrix (See Section 5 of "The Mathematics of the Physical Properties of Crystals" by W. L. Bond, *Bell System Technical Journal*, Volume XXII, No. 1):

$$r' = \begin{matrix} X \text{ component} & Y \text{ component} & Z \text{ component} \\ \begin{pmatrix} \cos A_1 & \sin A_1 & 0 \\ -\sin A_1 & \cos A_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{matrix} \text{of } P_1 \\ \text{of } P_2 \dots \dots \\ \text{of } P_3 \end{matrix} \end{matrix} \quad (3.6)$$

The components of the plate edges on the X, Y, Z coordinates after rotation through angles A_1 and A_2 are:

$$r'' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos A_2 & -\sin A_2 \\ 0 & \sin A_2 & \cos A_2 \end{pmatrix} \begin{pmatrix} \cos A_1 & \sin A_1 & 0 \\ -\sin A_1 & \cos A_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{matrix} X \text{ component} & Y \text{ component} & Z \text{ component} \\ \begin{pmatrix} \cos A_1 & \sin A_1 & 0 \\ -\sin A_1 \cos A_2 & \cos A_1 \cos A_2 & -\sin A_2 \\ -\sin A_1 \sin A_2 & \cos A_1 \sin A_2 & \cos A_2 \end{pmatrix} & \begin{matrix} \text{of } P_1 \\ \text{of } P_2 \dots \\ \text{of } P_3 \end{matrix} \end{matrix} \quad (3.7)$$

The components of the plate edges on the X, Y, Z coordinates after rotation through angles A_1, A_2 and A_3 are:

$$r''' = \begin{pmatrix} \cos A_3 & 0 & \sin A_3 \\ 0 & 1 & 0 \\ -\sin A_3 & 0 & \cos A_3 \end{pmatrix} \begin{pmatrix} \cos A_1 & \sin A_1 & 0 \\ -\sin A_1 \cos A_2 & \cos A_1 \cos A_2 & -\sin A_2 \\ -\sin A_1 \sin A_2 & \cos A_1 \sin A_2 & \cos A_2 \end{pmatrix}$$

$$= \begin{matrix} X \text{ component} & Y \text{ component} & Z \text{ component} \\ \begin{pmatrix} \cos A_1 \cos A_3 & \sin A_1 \cos A_3 & \cos A_2 \sin A_3 \\ -\sin A_1 \sin A_2 \sin A_3 + \cos A_1 \sin A_2 \sin A_3 \\ -\sin A_1 \cos A_2 & \cos A_1 \cos A_2 & -\sin A_2 \\ -\cos A_1 \sin A_3 & -\sin A_1 \sin A_3 & \cos A_2 \cos A_3 \\ -\sin A_1 \sin A_2 \cos A_3 + \cos A_1 \sin A_2 \cos A_3 \end{pmatrix} & \begin{matrix} \text{of } P_1 \\ \text{of } P_2 \\ \text{of } P_3 \end{matrix} \end{matrix} \quad (3.8)$$

Since the edge P_2 (thickness direction) is the normal to the major face of the plate, its X , Y , Z components (second horizontal row) give the orientation of the major face of the plate in terms of X , Y , Z axes of the mother crystal.

For example, suppose the orientation of the major face of an NT plate is desired in terms of the X , Y , Z axes. The shop rotation angles for an NT plate are

$$\begin{aligned} A_1 &= 99^\circ 25' \\ A_2 &= 49^\circ 25' \\ A_3 &= -12^\circ 20' \end{aligned}$$

Substituting these values in the above matrix gives

$$r''' = \begin{pmatrix} 0 & .99027 & -.13917 \\ -.64279 & -.10662 & -.75852 \\ -.76604 & .08946 & .63653 \end{pmatrix} \dots \dots \dots (3.9)$$

the second row of which gives the components (direction cosines) of the unit normal to the plate surface on the X , Y , Z axes:

$$\begin{aligned} X &= .64279 \\ Y &= .10662 \\ Z &= .75852 \end{aligned}$$

(B) Discovery of the plane whose orientation and X-ray properties are most suitable for use with the face to be checked.

The first requisite for the atomic plane to be used is that it shall make as small an angle δ as possible with the face to be checked. This is desirable because (1) δ must be smaller than θ ; (2) if δ is small the same plane can be used for correction around P_1 as around P_3 since the β angle will be small. If δ is very small the difference between g and θ may be within the required limits of error so that the θ value may be used without correction; (3) if δ is large, the difference between g_e and g_ℓ will be large and if the plate is placed in the goniometer in such a way that g_e is the larger angle the reflected ray may be too weak to register on the ionization chamber meter.

By plotting the stereographic projection of the normal to the plate face on Fig. 3.7 the most promising planes may be found quickly. On this chart each concentric circle connects all points with the same Z direction-cosine; each arc that crosses the X axis connects all points with the same X direction-cosine; each arc that crosses the Y axis connects all points with the same Y direction-cosine.

For example, the normal to the major face of the NT cut is plotted as follows:

.64 units are marked off in a positive direction (down) on the X axis (to

a point between $(2\bar{1}\cdot3)$ and $(2\bar{1}\cdot2)$. Then, in the direction of the east-west arcs, .1 unit is marked off to the right of the X axis. The point so located is found to be about half way between the .7 and .8 concentric circles, that is, to have a Z component of about .75, as calculated above. It lies about half way between atomic plane normals $(2\bar{1}\cdot3)$ and $(3\bar{1}\cdot3)$.

The degree scale given in Fig. 3.7 may be used to determine roughly the angle between any two points on the diagram. The scale is non-uniform and for any particular region of the diagram that portion of the scale should be used that falls on that region when the zero mark on the scale is placed at the center of the diagram.

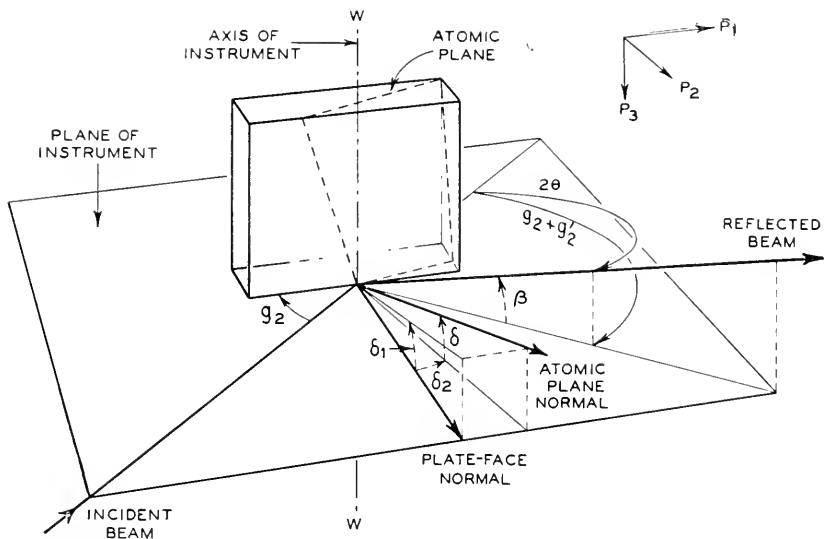


Fig. 3.16—Goniometry case (d): Atomic plane intersecting plate-face in a line which is neither normal nor parallel to "the plane of the instrument" (general case).

In the present example the part of the scale to be used is around the 40° mark and the plate face is found to make angles of less than 10° with both $(2\bar{1}\cdot3)$ and $(3\bar{1}\cdot3)$.

In general the atomic planes with the smaller indices are likely to give the stronger reflections. Therefore the better plane to try first is $(2\bar{1}\cdot3)$. The indices of this plane are not shown in this form in Table I, but by the method described in Section 3.5 it may be seen that a plane with indices $11\cdot3$ would have the same θ value for X-ray reflection. From Table I we see that θ for atomic plane $11\cdot3$ is $32^\circ 03'$.

In order to determine the angles g and $g + g'$ (Fig. 3.16) the orientation of the atomic plane with respect to the plate edges must be found.

3.8 DETERMINATION OF THE ORIENTATION OF AN ATOMIC PLANE WITH RESPECT TO THE PLATE-EDGES, GIVEN ITS MILLER-BRAVAIS INDICES

Since the indices ($hk \cdot \ell$) are the reciprocals of the intercepts of the atomic plane on the quartz crystallographic axes (See Section 3.5) of which the vertical axial unit is 1.09997 times that of the others, the intercepts on axes which were all divided into the same length unit would be

$$\frac{1}{h}, \quad \frac{1}{k}, \quad \text{and} \quad \frac{1.1}{\ell}$$

(If 1.1 is substituted for 1.09997 the error introduced is never greater than one minute.)

The intercepts on the orthogonal axes may be derived as indicated in Fig. 3.17. They are:

$$\frac{1}{h}, \quad \frac{\sqrt{3}}{h + 2k}, \quad \frac{1.1}{\ell}$$

These intercepts may be taken as the lengths of 3 vectors whose components on the X , Y and Z axes are as follows:

$$i_1(X \text{ axis vector}) = \begin{pmatrix} 1/h \\ 0 \\ 0 \end{pmatrix} \dots \dots \dots (3.10)$$

$$i_2(Y \text{ axis vector}) = \begin{pmatrix} 0 \\ \sqrt{3} \\ h + 2k \\ 0 \end{pmatrix} \dots \dots \dots (3.11)$$

$$i_3(Z \text{ axis vector}) = \begin{pmatrix} 0 \\ 0 \\ 1.1/\ell \end{pmatrix} \dots \dots \dots (3.12)$$

Now the two vectors ($i_3 - i_1$) and ($i_3 - i_2$) lie in the plane ($hk \cdot \ell$) (See Fig. 3.18), and therefore their vector product is the vector normal to the plane $hk \cdot \ell$

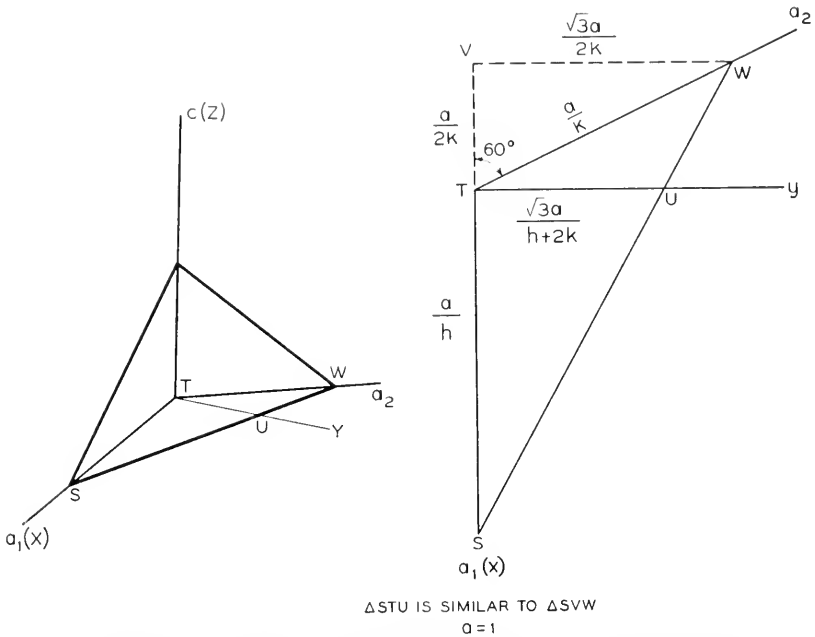


Fig. 3.17—Derivation of intercepts on orthogonal axes from intercepts on hexagonal axes

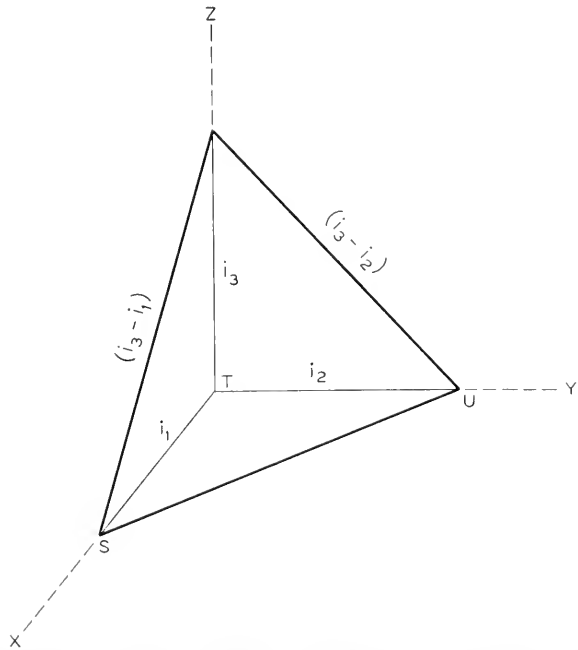


Fig. 3.18—Orientation of vectors $(i_3 - i_1)$ and $(i_3 - i_2)$ with respect to orthogonal axes

That is,

\bar{N} (the vector normal to the atomic plane $hk \cdot \ell$)

$$\begin{aligned}
 &= \left[\begin{pmatrix} 0 \\ 0 \\ 1.1/\ell \end{pmatrix} - \begin{pmatrix} 1/h \\ 0 \\ 0 \end{pmatrix} \right] \times \left[\begin{pmatrix} 0 \\ 0 \\ 1.1/\ell \end{pmatrix} - \begin{pmatrix} 0 \\ \sqrt{3} \\ h + 2k \\ 0 \end{pmatrix} \right] \\
 &= \begin{pmatrix} -1/h \\ 0 \\ 1.1/\ell \end{pmatrix} \times \begin{pmatrix} 0 \\ -\sqrt{3} \\ h + 2k \\ 1.1/\ell \end{pmatrix} \\
 &= \begin{pmatrix} 0 & -1.1/\ell & 0 \\ 1.1/\ell & 0 & 1/h \\ 0 & -1/h & 0 \end{pmatrix} \begin{pmatrix} 0 \\ -\sqrt{3} \\ h + 2k \\ 1.1/\ell \end{pmatrix} \\
 &= \begin{bmatrix} 1.1\sqrt{3} \\ \ell(h + 2k) \\ 1.1/h\ell \\ \sqrt{3} \\ h(h + 2k) \end{bmatrix} = \begin{pmatrix} h \\ h + 2k \\ \sqrt{3} \\ \ell/1.1 \end{pmatrix} \dots \dots \dots (3.13)
 \end{aligned}$$

The unit vector $N = \frac{1}{\sqrt{S}} \bar{N} \dots \dots \dots (3.14)$

where S is the sum of the squares of the three terms of \bar{N} . For example, for the (01·1) plane ($h = 0, k = 1, \ell = 1$), we find from equation (3.13) that

$$\bar{N} = \begin{pmatrix} 0 \\ 2/\sqrt{3} \\ 1/1.1 \end{pmatrix} \dots \dots \dots (3.15)$$

whence $S = 4/3 + \frac{1}{1.21} = 2.159 \dots \dots \dots (3.16)$

and the unit vector normal $N = \begin{pmatrix} 0 \\ .7857 \\ .6186 \end{pmatrix} \dots \dots \dots (3.17)$

which means that N is perpendicular to the X axis, makes an angle with Y whose cosine is .7857 ($=38^\circ 13'$) and an angle with Z whose cosine is .6186 ($=51^\circ 47'$).

For the atomic plane $(2\bar{1}\cdot3)$ we find from equation (3.13) that

$$\bar{N} = \begin{pmatrix} 2 \\ 0 \\ 3/1.1 \end{pmatrix} \dots\dots\dots (3.18)$$

Whence $S = 4 + 9/1.21 = 11.438 \dots\dots\dots (3.19)$

and, from equation (3.14) the unit vector normal to $(2\bar{1}\cdot3)$

$$N = \begin{pmatrix} .5914 \\ 0 \\ .8064 \end{pmatrix} \dots\dots\dots (3.20)$$

We have now determined the orientation of the atomic plane with respect to the orthogonal axes X , Y and Z . To determine its orientation with respect to the plate edges necessitates the construction of a matrix which expresses the components of the plate edges $P_1P_2P_3$ (length, thickness, and width respectively) in terms of the X , Y , Z axes. When the components of the unit normal to the atomic plane in terms of the orthogonal axes X , Y , Z are acted upon by this matrix they are converted to the components of the unit normal to the atomic plane in terms of the plate edges P_1 , P_2 , P_3 . (For fuller discussion see Section 5 of "The Mathematics of the Physical Properties of Crystals" by Walter L. Bond, *Bell System Technical Journal*, Volume XXII, No. 1, pp. 1-72.) Equation (3.8) gives such a matrix.

To continue with the NT cut as an example, the product of the matrix given in equation (3.9) for the NT cut and the components of the unit vector for the atomic plane $(2\bar{1}\cdot3)$ given in equation (3.20) gives us the components of the unit normal to the atomic plane $(2\bar{1}\cdot3)$ in terms of the plate edges P_1 , P_2 , P_3 as axes. Thus,

$$N_{P_1P_2P_3} = \begin{pmatrix} 0 & .99027 & -.13917 \\ -.64279 & -.10662 & -.75852 \\ -.76604 & .08946 & .63653 \end{pmatrix} \begin{pmatrix} .5914 \\ 0 \\ .8064 \end{pmatrix} = \begin{pmatrix} -.11223 \\ -.99180 \\ +.060293 \end{pmatrix} \dots (3.21)$$

That is, the components of the unit normal to the atomic plane in terms of the plate edges P_1 , P_2 , P_3 are:

$$\begin{aligned} N_1 &= -.11223 \\ N_2 &= -.99180 \\ N_3 &= +.060293 \end{aligned}$$

When the orientation of the atomic plane with respect to the plate edge has thus been determined the next and final step is the determination of the angles between the incident X-rays and the plate-face.

3.9 DETERMINATION OF ANGLES BETWEEN X-RAYS AND THE FACES OF A FINISHED PLATE

Procedures for determining the angles g and $g + g'$ for certain particular positions of the atomic plane with respect to the plate edges were described in section 3.6 under (a), (b), and (c). For the general case (d) in which the intersection between the atomic plane and the plate-face is neither normal nor parallel to the plane of the instrument, the problem is best solved vectorially, as follows:

(d) Atomic plane intersecting plate-face in a line which is neither normal nor parallel to the plane of the instrument (general case). (Fig. 3.16)

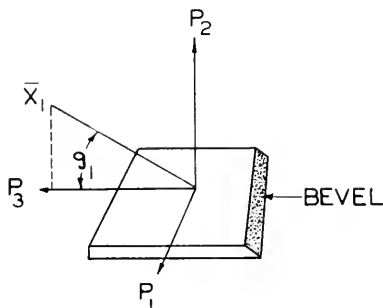


Fig. 3.19—Position 1 for a plate of general orientation (one in which no plate-edge is parallel to a crystallographic axis).

Let N_1, N_2, N_3 be the components of the unit normal \bar{N} to the atomic plane in terms of the plate edges P_1, P_2, P_3 , and X_1, X_2, X_3 the components of the unit vector \bar{X} along the incident beam. Then

$$\sin \theta_{hk\cdot\ell} = X_1 N_1 + X_2 N_2 + X_3 N_3 \quad (3.22)$$

(the inner product of these two vectors, which is thus equal to the cosine of the angle between the incident ray and the normal to the atomic plane or $\cos(90 - \theta)$).

In matrix form this may also be written:

$$\bar{X}_c \cdot N_{hk\cdot\ell} = \sin \theta_{hk\cdot\ell} \quad (3.23)$$

Where \bar{X}_c is the matrix X_1, X_2, X_3 ⁷

⁷ See Bond, W. L. "The Mathematics of the Physical Properties of Crystals," *Bell Sys. Tech. Jour.*, Vol. XXII, No. 1.

From Fig. 3.19 we see that, for the beam entering as shown, the components of the unit vector \bar{X}_1 along the beam are

$$\begin{array}{c} 0 \\ \sin g_1 \\ \cos g_1 \end{array}$$

so that equation (3.22) becomes

$$\sin \theta_{hk\cdot\ell} = N_2 \sin g_1 + N_3 \cos g_1 \tag{3.24}$$

which has the solution

$$g_1 = \theta' - \delta'_1 \tag{3.25}$$

where

$$\tan \delta'_1 = \frac{N_3}{N_2} \tag{3.26}$$

and

$$\sin \theta' = \frac{\sin \theta}{\cos \sin^{-1} N_1} \tag{3.26'}$$

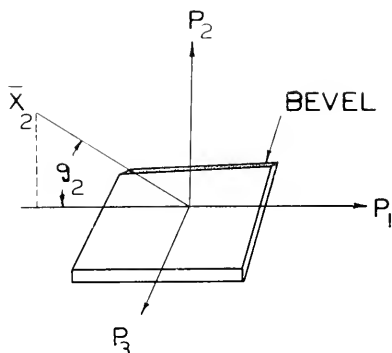


Fig. 3.20—Position 2 for a plate of general orientation

Again, with the plate rotated 90° around its normal (to position 2) so that the entering beam is in the position shown by the unit vector \bar{X}_2 in Fig. 3.20, the components of \bar{X}_2 are

$$\begin{array}{c} -\cos g_2 \\ \sin g_2 \\ 0 \end{array}$$

so that

$$\sin \theta = N_2 \sin g_2 - N_1 \cos g_2 \tag{3.27}$$

or

$$g_2 = \theta'' + \delta'_2 \tag{3.28}$$

where
$$\tan \delta'_2 = \frac{N_1}{N_2} \quad (3.29)$$

and
$$\sin \theta'' = \frac{\sin \theta}{\cos \sin^{-1} N_3} \quad (3.29')$$

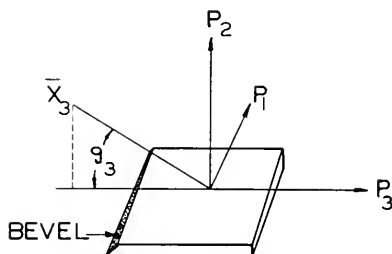


Fig. 3.21—Position 3 for a plate of general orientation

With the plate rotated 90° again (180° from position 1), so that the entering beam is in the position shown in Fig. 3.21, the components of the unit vector \bar{X}_3 along the incident beam are

$$\begin{array}{c} 0 \\ \sin g_3 \\ -\cos g_3 \end{array}$$

so that
$$\sin \theta = N_2 \sin g_3 - N_3 \cos g_3 \quad (3.30)$$

or

$$g_3 = \theta' + \delta'_3 \quad (3.31)$$

where

$$\tan \delta'_3 = \frac{N_3}{N_2} \quad (3.32)$$

and

$$\sin \theta' = \frac{\sin \theta}{\cos \sin^{-1} N_1} \quad (3.26')$$

$$\delta'_3 = \delta'_1 \quad (3.33)$$

Finally, with the X-ray beam entering as shown by the unit vector \bar{X}_4 in Fig. 3.22 (270° from position 1) the components of \bar{X}_4 are

$$\begin{array}{c} \cos g_4 \\ \sin g_4 \\ 0 \end{array}$$

so that
$$\sin \theta = N_2 \sin g_4 + N_1 \cos g_4 \quad (3.34)$$

or

$$g_4 = \theta'' - \delta'_4 \quad (3.35)$$

where
$$\tan \delta'_4 = \frac{N_1}{N_2} \quad (3.36)$$

and
$$\sin \theta'' = \frac{\sin \theta}{\cos \sin^{-1} N_3} \quad (3.29')$$

$$\delta'_4 = \delta'_2 \quad (3.37)$$

For example, suppose an NT finished crystal is to be checked by the $(2\bar{1}\cdot3)$ atomic plane as suggested in section 3.7B. The components of the unit normal to the atomic plane $(2\bar{1}\cdot3)$ in terms of the plate edges P_1 , P_2 , P_3 of an NT plate were found (at the end of section 3.8) to be

$$N_1 = -.11223$$

$$N_2 = -.99180$$

$$N_3 = .060293$$

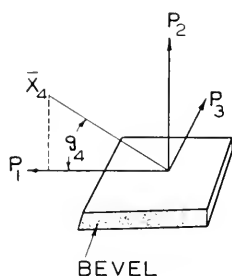


Fig. 3.22—Position 4 for a plate of general orientation

Substituting in equation (3.26):

$$\tan \delta'_1 = \frac{.060293}{-.99180}$$

$$\delta'_1 = -3^\circ 28.7'$$

and in equation (3.26')

$$\sin \theta' = \frac{\sin 32^\circ 3'}{\cos \sin^{-1} .11223}, \quad \theta' = 32^\circ 16'$$

and in equation (3.29)

$$\delta'_2 = \tan^{-1} \frac{-.11223}{-.99180} = 6^\circ 30'$$

and in equation (3.29')

$$\sin \theta'' = \frac{\sin 32^\circ 3'}{\cos \sin^{-1} .060293}, \quad \theta'' = 32^\circ 7'$$

so that in equation (3.25)

$$g_1 = 32^\circ 16' + 3^\circ 28.7' = 35^\circ 44.7'$$

Similarly

$$g_2 = 32^\circ 7' + 6^\circ 30' = 38^\circ 37'$$

$$g_3 = 32^\circ 16' - 3^\circ 28.7' = 28^\circ 47.3'$$

$$g_4 = 32^\circ 7' - 6^\circ 30' = 25^\circ 37'$$

In the case (d) of an atomic plane which intersects the plate face in a line which is neither parallel nor normal to the plane of the instrument, the angle δ that the atomic normal makes with the plane of the instrument will be different for different positions of the plate.

If N_V is the direction cosine of the normal to the atomic plane with reference to that plate edge (P axis) that is placed in the vertical position,

$$\delta = \cos^{-1} N_V - 90^\circ = -\sin^{-1} N_V$$

This value of δ may be used in determining β according to formula (3.3). For example, when the P_3 axis (width) of an NT plate is placed parallel to the axis of the instrument,

$$\delta = -\sin^{-1} N_3 = -\sin^{-1} .060293 = -3^\circ 27.4'$$

(The negative sign indicates deflection of the normal toward the negative end of the P_3 axis and may be disregarded in determination of β).

Whence

$$\sin \beta = 2 \sin 32^\circ 03' \sin 3^\circ 27.4'$$

$$\beta = 3^\circ 40'$$

This means that the beam reflected from the ($2\bar{1}\cdot 3$) atomic plane when the NT plate is placed with its P_3 (width) axis parallel to the axis of the instrument would be received by an ionization chamber which would accept a beam making an angle of $3^\circ 40'$ with the plane of the instrument.

When the P_1 axis (length) of an NT plate is placed parallel to the axis of the instrument

$$\delta = \cos^{-1} N_1 - 90^\circ = \sin^{-1} .11223 = -6^\circ 26.7'$$

Since this is a larger β value than most ionization chambers will accept, the ($2\bar{1}\cdot 3$) plane cannot be used in most cases to check an NT plate with its P_1 axis parallel to the axis of the instrument unless the ionization chamber is moved vertically.

(b) and (c) Atomic plane intersecting plate-face in a line which is either normal or parallel to the plane of the instrument.

For plates rotated about X only (as AT , BT , CT and DT) the problem

is so simple (See section 3.6, b) that the above procedure need not be followed.

For such plates the complete transformation is an A_2 rotation around N :

$$r''' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos A_2 & -\sin A_2 \\ 0 & \sin A_2 & \cos A_2 \end{pmatrix} \quad (3.38)$$

The planes used for checking these plates are of the type $(0k\cdot\ell)$ so that, from equations (3.13) and (3.14)

$$N = \begin{pmatrix} 0 \\ 2k/\sqrt{3} \\ \ell/1.1 \end{pmatrix} \frac{1}{\sqrt{S}} \quad (3.39)$$

whence

$$r'''N = \begin{pmatrix} 0 \\ \frac{2}{\sqrt{3}} k \cos A_2 \frac{\ell}{1.1} \sin A_2 \\ \frac{2}{\sqrt{3}} k \sin A_2 + \frac{\ell}{1.1} \cos A_2 \end{pmatrix} \frac{1}{\sqrt{S}} \quad (3.40)$$

$$\text{but } \frac{2K}{\sqrt{3}\sqrt{S}} = \sin \gamma_{0k\cdot\ell} \quad \text{and} \quad \frac{\ell}{1.1\sqrt{S}} = \cos \gamma_{0k\cdot\ell}$$

where γ = the angle between the normal to the atomic plane and the Z axis (note that for γ angles on the negative side of the Z axis the value given in Table I should be subtracted from 180° , as in the case of the AT cut given below).

Thus (3.40) may be written

$$N = \begin{pmatrix} 0 \\ \sin(\gamma - A_2) \\ \cos(\gamma - A_2) \end{pmatrix} \quad (3.41)$$

and (3.25) becomes

$$g_1 = \theta - \delta'_1 \quad \text{where} \quad \delta'_1 = 90^\circ + A_2 - \gamma \quad (3.42)$$

(Note that where A_2 is positive γ will be on the negative side of the Z axis)

$$\text{whence} \quad g_1 = \theta + \gamma - 90^\circ - A_2 \quad (3.43)$$

$$g_3 = 90^\circ + \theta + A_2 - \gamma \quad (3.44)$$

For position 2, equation (3.40) applied to equation 3.27 gives

$$\sin \theta = \sin(\gamma - A_2) \sin g_2$$

so that we may write

$$\sin g_2 = \sin g_4 = \frac{\sin \theta}{\sin (\gamma - A_2)} \quad (3.45)$$

As an example consider a *BT* plate for which $A_2 = -49^\circ$, corrected around the *WW* axis (Fig. 3.12) from the (02·3) plane. Table I gives us $\theta_{023} = 34^\circ 05'$, $\gamma_{023} = 40^\circ 16'$ whence

$$g_1 = 34^\circ 05' + 40^\circ 16' - 90^\circ + 49^\circ = 33^\circ 21'$$

$$g_3 = 90^\circ + 34^\circ 05' - 49^\circ - 40^\circ 16' = 34^\circ 49'$$

$$g_2 = g_4 = \sin^{-1} \frac{\sin 34^\circ 05'}{\sin 89^\circ 16'} = 34^\circ 05'$$

For an *AT* plate of $A_2 = +35^\circ 15'$ corrected around the *WW* axis from (01· $\bar{1}$) we find, under (01·1), that $\theta = 13^\circ 20'$, $\gamma = 180 - 51^\circ 47'$ whence

$$g_1 = 13^\circ 21' + 180^\circ - 51^\circ 47' - 90^\circ - 35^\circ 15' = 16^\circ 18'$$

$$g_3 = 2\theta - g_1 = 10^\circ 22'$$

$$g_2 = g_4 = \sin^{-1} \frac{\sin 13^\circ 20'}{\sin 92^\circ 58'} = 13^\circ 21'$$

A complete determination of the errors in a quartz plate includes the measurement of angle errors about *three* mutually perpendicular axes such as, for example, the plate edges. Therefore, in correcting a plate we must use three different X-ray "shots"; usually two on the major surface with the plate rotated 90° between the two "shots" and a third on a surface normal to the major surface, commonly called an "edge". If the plate is thin, the intensity of reflection from the "edge" is low and this measurement becomes difficult.

The goniometric procedure described above is best adapted to the routine measurement of errors in large numbers of plates which are known to be close to the correct orientation. If the error in a plate is large, however, or if the cut is a rare one or the orientation of the plate completely unknown, analysis by the goniometric method may be extremely difficult.

A simple, direct method of determining the orientation of such plates is that of the Laue camera.

3.10 USE OF LAUE PHOTOGRAPHS IN DETERMINING THE ORIENTATION OF A QUARTZ PLATE

In the original Laue photograph the X-ray beam passed through the crystal and was diffracted so as to give a spot pattern on a photographic

plate beyond the crystal. This necessitated either the use of a very thin crystal or a long exposure.

To avoid the variation due to crystal thickness we adopted the "Back Reflection Laue camera." As shown in Fig. 3.23 the X-ray beam passes through a hole in the photographic film before striking the crystal. It is collimated by two pinholes, one on each side of the film. Spot reflections from many planes fall on the film and in a few minutes exposure leave a record of their points of impingement. Most of these reflections are not due to the peaks of the radiation curve (Fig. 3.2) but each spot is due to a

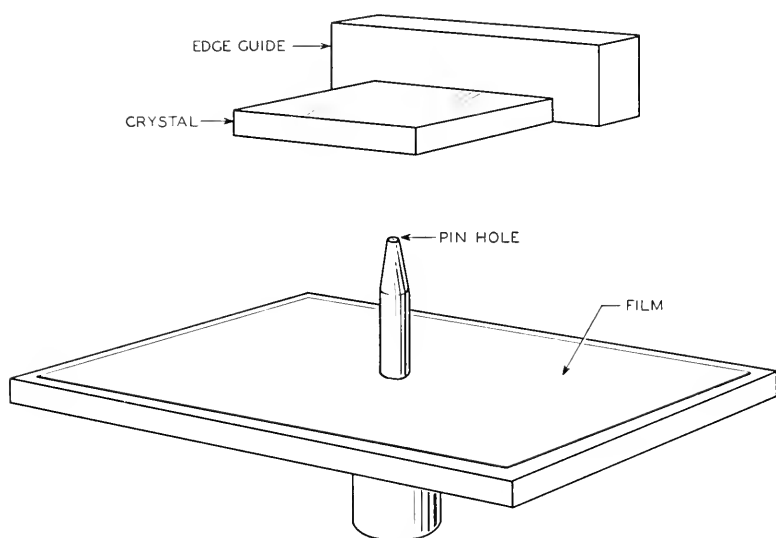


Fig. 3.23—Arrangement of collimator, film and crystal plate for a back reflection Laue photograph

different λ from the continuous background of Fig. 3.2. However, each satisfies the equation $n\lambda = 2d \sin \theta$.

Figure 3.24 is such a record with many of its spots marked. The spot (01·1) is recognized as the point of intersection of the greatest number of rows of spots. The spot (01·2) is the second most obvious intersection point.

On examining such a film we recognize such spot configurations and then mark the indices of the corresponding atomic plane for a few chosen spots. From these we can measure three angle-errors. For example, if the crystal, Fig. 3.25, is rotated about the vector t by amount e_t the spot pattern on the film will be rotated by the same amount $e_{t'}$. If the crystal is in error by amount e_w being rotated about w clockwise the spot pattern of the film

will be shifted to the left and the value of e_w' can be measured by means of a specially graduated scale. See Fig. 3.24. (Scale used is of Lucite and

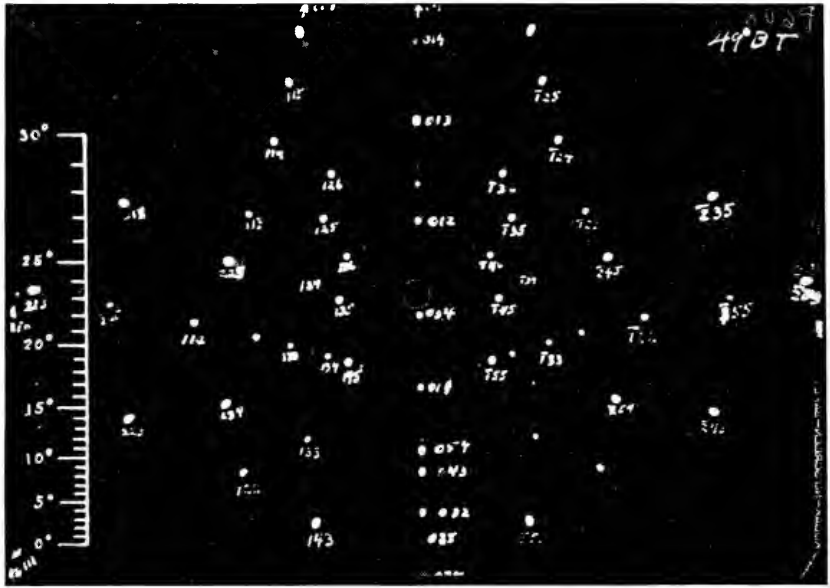


Fig. 3.24—Back reflection Laue photograph of a BT plate

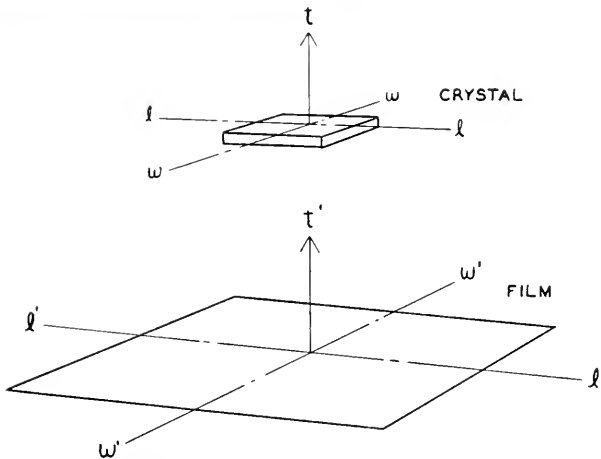


Fig. 3.25—Relation of displacement directions on the film to the $l-l$ and $w-w$ axes

calibrated to 10 minutes.) Similarly, if the crystal is misoriented about ll by amount e_l the spot pattern will shift along $w'w'$ and e_l' can be measured by the same scale used on e_w' . To compensate for film expansion due to

changes in temperature and humidity, measurements are made from two spots about equally removed from the center but on opposite sides.

If all three errors exist simultaneously they may still be measured in this way provided they are small.

Given e_ℓ , e_w and e_t for plates containing the X axis the errors in A_1 , A_2 and A_3 can be computed by the formulae

$$\text{Error in } A_1 = e_w / \cos A_2$$

$$\text{Error in } A_2 = e_\ell$$

$$\text{Error in } A_3 = e_t - e_w \tan A_2$$

Consider, for example, the negative (Fig. 3.24) for a BT plate. The row of spots $(01 \cdot 4)$, $(01 \cdot 3)$, $(01 \cdot 2)$, $(03 \cdot 4)$, $(01 \cdot 1)$, etc., results from reflections from the group of planes parallel to the X axis (see Fig. 3.8). (Such a group of planes all parallel to a given line is called a zone.) In the BT cut the A_2 angle results from rotation around the X axis. The effect of such a rotation on the photograph (Fig. 3.24) is a shift of the spots of the $(0k \cdot \ell)$ atomic planes along the line on which they lie. Therefore, to measure the A_2 angle from Fig. 3.24, we choose two spots along this line about equidistant from the center of the film such as $(01 \cdot 1)$ and $(01 \cdot 2)$ and measure the angular distance α between the incident X-ray beam and the reflected ray causing each spot by measuring the distance between the center of the film and each spot using the specially calibrated scale.

By "center of the film" is meant the point through which the center of the X-ray beam passed. This point is located as follows. When the film is in place in the camera, two reference points are pricked in it by pins built into the camera. These points may be seen in Fig. 3.24 as small white circles near the center of the right and left edges of the picture. The center of the X-ray beam is at the center of a line between these two points.

When the negative is to be measured it is placed on a glass plate engraved as shown in Fig. 3.26 with the reference points at P , P . The intersection X then marks the center of the film.

If A_2 is the plate angle around the X axis from the Z axis and γ is the angle between the atomic plane normal and the Z axis and α is the angle measured between the center of the film and the spot, then

$$A_2 = 90^\circ - \gamma_{hk \cdot \ell} + \alpha_{hk \cdot \ell} \quad (3.46)$$

For the two spots chosen for measurement of the BT plate of Fig. 3.24, $A_2 = 90^\circ - \gamma_{01 \cdot 2} - \alpha_{01 \cdot 2}$ (Rotation from the BT cut to the $01 \cdot 2$ plane is a negative rotation)

$$A_2 = 90^\circ - \gamma_{01 \cdot 1} + \alpha_{01 \cdot 1}$$

$$A_2 = 90^\circ - \frac{\gamma_{01 \cdot 2} + \gamma_{01 \cdot 1}}{2} + \frac{\alpha_{01 \cdot 1} - \alpha_{01 \cdot 2}}{2}$$

and substituting the values of $\gamma_{01.2}$ and $\gamma_{01.1}$ from Table I,

$$\begin{aligned}
 A_2 &= 90^\circ - \frac{32^\circ 25' + 51^\circ 47'}{2} + \frac{\alpha_{01.1} - \alpha_{01.2}}{2} \\
 &= 47^\circ 54' + \frac{\alpha_{01.1} - \alpha_{01.2}}{2}
 \end{aligned}
 \tag{3.47}$$

For more complicated cuts, such as the NT cut, four spots are chosen, two close to the line $\ell'\ell'$ and two close to the line $w'w'$. (See Fig. 3.25). The positions these spots should occupy on the film for a correct NT cut

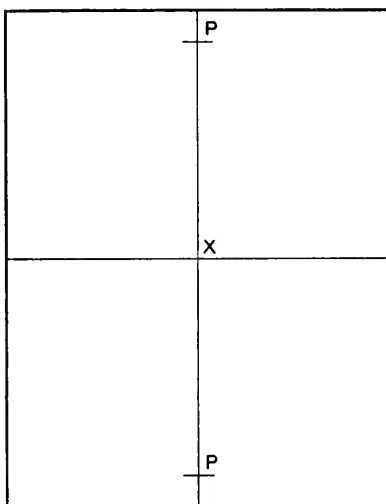


Fig. 3.26—Engraved glass plate for measuring Laue photographs

are computed and compared to the spot-positions on the measured film. From this comparison the following errors are determined:

- e_w error in rotation around the $w w$ axis of the plate from the average displacement along $\ell'\ell'$.
- e_ℓ error in rotation around the $\ell\ell$ axis of the plate from the average displacement along $w'w'$.
- e_t error in rotation around the t axis by the average angular displacement of the four spots about the center of the film.

The first step in determining the position of a spot for any given atomic plane in a correctly cut plate is the determination of the direction cosines of the normal to that atomic plane with respect to the plate edges. This procedure has been described in Section 3.8.

Figure 3.27 is a Laue photograph of an NT plate. Taking this as an example, we may choose the four spots $(31 \cdot 4)$, $(\bar{3}\bar{1} \cdot 5)$, $(2\bar{2} \cdot 3)$ and $(5\bar{2} \cdot 5)$

from which to make the measurements. From equations (3.13) and (3.9) we find that the direction cosines of the normals to these atomic planes in terms of the NT plate edges are

$$(31 \cdot 4) = \begin{pmatrix} .42561 \\ -.90357 \\ .04972 \end{pmatrix}_P, \quad (3\bar{1} \cdot 5) = \begin{pmatrix} -.01112 \\ -.99294 \\ -.11812 \end{pmatrix}_P,$$

$$(2\bar{2} \cdot 3) = \begin{pmatrix} -.42618 \\ -.90421 \\ .02816 \end{pmatrix}_P, \quad \text{and} \quad (5\bar{2} \cdot 5) = \begin{pmatrix} -.00898 \\ -.99140 \\ -.13062 \end{pmatrix}_P$$

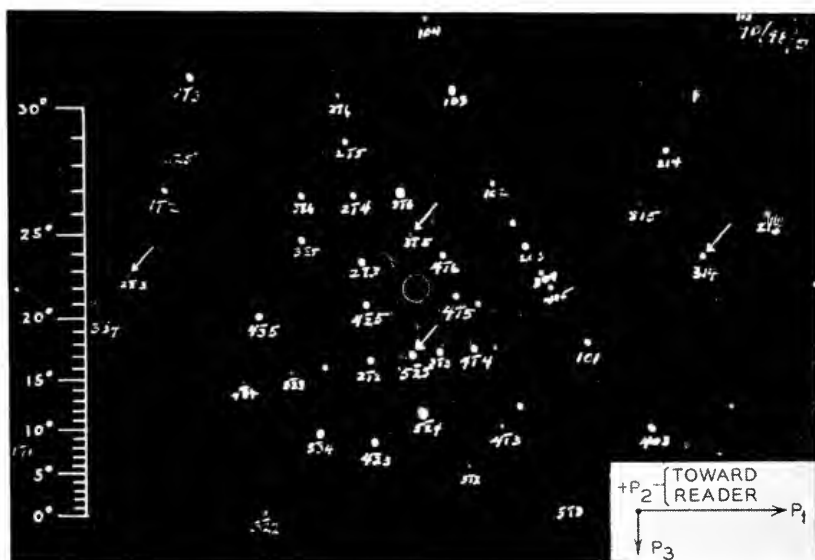


Fig. 3.27—Back reflection Laue photograph of an NT plate

The orientation of the unit normal to the atomic plane $(31 \cdot 4)$ with respect to the plate edges is shown in Fig. 3.28. Since $.90357 = \cos 25^\circ 22'$, the angle between the unit normal N and the P_2 axis is $25^\circ 22'$. Since $\frac{.04972}{.42561} = \tan 6^\circ 40'$ the angular component of the unit normal N in the P_1P_3 plane is $6^\circ 40'$ that is, the $(31 \cdot 4)$ spot should lie in a direction $6^\circ 40'$ from the long axis of the film and should be at a distance from the center corresponding to $25^\circ 22'$ as read from the special scale.

The correct locations of the other three spots are similarly calculated. These values are given below, with the values actually measured from the Laue photograph of the NT plate and the errors determined from a comparison of the calculated and measured values.

(n.b. clockwise and counter-clockwise directions are as seen when looking toward the — end of the axis of rotation)

<i>Distance from the Center</i>				
	<i>Calculated</i>	<i>Measured</i>	<i>Difference</i>	<i>Error</i>
(31·4)	25°22'	25°22'	0'	0'
(22̄·3)	25°17'	25°18'	+1'	
(31̄·5)	6°49'	6°18'	-31'	30' counter-clock-
(52̄·5)	7°31'	8°00'	+29'	wise about P ₁

<i>Azimuth</i> (counter-clockwise from +P ₁)				
	<i>Calculated</i>	<i>Measured</i>	<i>Difference</i>	<i>Error</i>
(31·4)	6°40'	5°48'	-52'	7' counter-clock-
(22̄·3)	176°12'	177°18'	+66'	wise about -P ₂
(31̄·5)	95°25'	95°36'	+11'	or clockwise about
(52̄·5)	266°03'	267°06'	+63'	+P ₂ ⁸

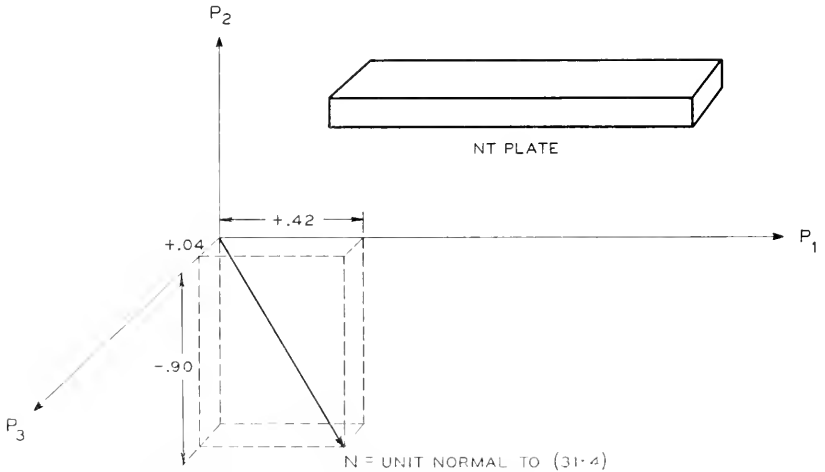


Fig 3.28 - Orientation of the (31.4) atomic plane in the NT plate

Now, a small rotation of amount E_1 counter-clockwise about P_1 followed by one of amount E_2 counter-clockwise about P_2 and a similar one E_3 about P_3 is given to the first order approximation by the matrix:

$$e = \begin{pmatrix} 1 & -e_3 & e_2 \\ e_3 & 1 & -e_1 \\ -e_2 & e_1 & 1 \end{pmatrix} \tag{3.48}$$

Where e_1 , e_2 and e_3 are the sines of the rotation angles E_1 , E_2 , E_3 .

⁸ This error is determined by averaging the "difference" values for the two planes.

From (3.48) we see that the order of application of e_1, e_2, e_3 is immaterial.

If the desired transformation is r° (i.e., with zero errors) ($=r'''$, equation 3.9 for the NT plate), and the actual one is r , we can consider that r° is made up from the desired rotations $.A_1^\circ, .A_2^\circ, .A_3^\circ$ and the r is made up of the rotations $.A_1 = .A_1^\circ + \Delta_1, .A_2 = .A_2^\circ + \Delta_2, .A_3 = .A_3^\circ + \Delta_3$; or alternatively r is made from the transformation r° followed by the transformation e so that

$$r = er^\circ \quad (3.49)$$

whence

$$\begin{aligned} -\tan A_1 &= \frac{(er^\circ)_{21}}{(er^\circ)_{22}} = \frac{r_{21}^\circ - e_1 r_{31}^\circ + e_3 r_{11}^\circ}{r_{22}^\circ - e_1 r_{32}^\circ + e_3 r_{21}^\circ} \\ -\sin A_2 &= (er^\circ)_{23} = r_{23}^\circ - e_1 r_{33}^\circ + e_3 r_{13}^\circ \\ -\tan A_3 &= \frac{(er^\circ)_{13}}{(er^\circ)_{33}} = \frac{r_{13}^\circ - e_3 r_{23}^\circ + e_2 r_{33}^\circ}{r_{33}^\circ - e_2 r_{13}^\circ + e_1 r_{23}^\circ} \end{aligned} \quad (3.50)$$

where $(er^\circ)_{21}$ is the term in row 2, column 1 of the matrix er° ; r_{23}° is the term in row 2, column 3 of the matrix r° (equation 3.9), etc.

From our unfinished example of the NT plate we have $e_1 = .0087, e_2 = -.0018, e_3 = 0$ whence

$$-\tan A_1 = \frac{-.64279 + .0087 \times .766 + 0}{-.10662 - .0087 \times .08946 + 0} = \frac{-.6361}{.1074}$$

$$\text{whence } A_1 = 99^\circ 36'$$

$$-\sin A_2 = -.75852 - .0087 \times .6365 + 0 = -.7649$$

$$\text{whence } A_2 = 49^\circ 49'$$

$$\tan A_3 = \frac{-.13917 - 0 - .0018 \times .6365}{.63653 + .0018 \times .1392 - .0087 \times .7585} = \frac{-.1403}{.6302}$$

$$\text{whence } A_3 = -12^\circ 33'$$

In starting work on a new cut of crystal one may have difficulty in finding the indices of the Laue spots. The easiest method is to photograph a crystal that has been carefully cut at measured angles from known planes (for instance natural faces). For example, from the angles laid off in the shop an NT plate such as that described should be sufficiently accurate that when P_2 is located on the atomic plane chart, Fig. 3.7, and several nearby planes of small indices are computed on the P axes, there should be no doubt as to which spots correspond to these locations.

From a few of these spots one can find many others by "zonal" relations. A zone is a family of atomic planes all of which are parallel to one line called the zonal axis. Just as there are indices of a plane there are zonal indices.

Two planes determine a zone. The zonal indices are computed by "cross multiplication" of the indices of the planes. The two planes $(h_1k_1 \cdot \ell_1)$ and $(h_2k_2 \cdot \ell_2)$ determine the zone $(k_1\ell_2 - \ell_1k_2, \ell_1h_2 - h_1\ell_2, h_1k_2 - k_1h_2)$. In practice this is developed by writing the indices of each plane twice; those of one under those of the other, then striking out the two end members of each and taking the difference of the cross products. Whereas plane indices are always enclosed in parentheses (), zonal indices are always enclosed in brackets []. For example $(0\ 0 \cdot 1)$ and $(0\ 1 \cdot 0)$ are in the zone:

$$\begin{array}{r|cccc|l} 0 & 1 & 0 & 0 & 1 & 0 \\ & \times & \times & \times & & \\ 0 & 0 & 1 & 0 & 0 & 1 \\ \hline & & & & & [1\ 0 \cdot 0] \end{array}$$

while $(2\bar{1} \cdot 0)$ and $(21 \cdot 2)$ are in the zone $[24 \cdot \bar{4}]$, or reducing, in the $[12 \cdot \bar{2}]$ zone.

This zonal relation is reciprocal in the sense that the plane common to two zones is derived in the same way as were the zonal indices. For example, the plane common to the zones $[10 \cdot 0]$ and $[12 \cdot \bar{2}]$ is

$$\begin{array}{r|cccc|l} 1 & 2 & \bar{2} & 1 & 2 & \bar{2} \\ & \times & \times & \times & & \\ 1 & 0 & 0 & 1 & 0 & 0 \\ \hline & & & & & (0\ \bar{2} \cdot \bar{2}) \end{array} \quad \text{or, } (0\ \bar{1} \cdot \bar{1})$$

If a given face with indices xyz lies in a zone with the symbol uvw , the following equation, known as "the zonal equation" will be true:

$$ux + vy + wz = 0$$

In the Laue photograph of the *BT* plate, Fig. 3.24, the row of spots $(12 \cdot 2)$ $(13 \cdot 3)$ $(01 \cdot 1)$ $(\bar{1}5 \cdot 5)$ $(\bar{1}3 \cdot 3)$ etc. is due to reflections from planes which belong in one zone. Other rows such as $(\bar{1}2 \cdot 5)$ $(\bar{1}2 \cdot 4)$ $(\bar{1}2 \cdot 3)$ etc. cross this row at some spot whose indices can be computed if two spots in each row are known. If the row passes through the center of the film all the spots lie on a straight line. If the row is off center it is curved, convex towards the center. Experience soon shows us how much curvature goes with how great a distance from the center for a series of spots to form a zone.

3.11 X-RAY CHECKS OF SLABS IN THE COURSE OF MANUFACTURING QUARTZ PLATE

In the course of manufacturing a quartz plate it is common practice to X-ray check the first sawn slab and correct the orientation of the quartz with respect to the saw before cutting the remaining slabs. Each of these slabs is then cemented to the head of a barrel jig so built that the orientation

of the head can be adjusted through small angles and clamped in the adjusted position. The jig is then placed in an X-ray goniometer set for reflection from the plane to be used and the slab adjusted until maximum reflection is obtained. The jig itself is not moved. If the slab were perfectly cut the maximum reflection would be obtained when the head of the jig was normal to the jig axis. A miscut will give maximum reflection at some other angle and, when clamped at this angle of maximum reflection,

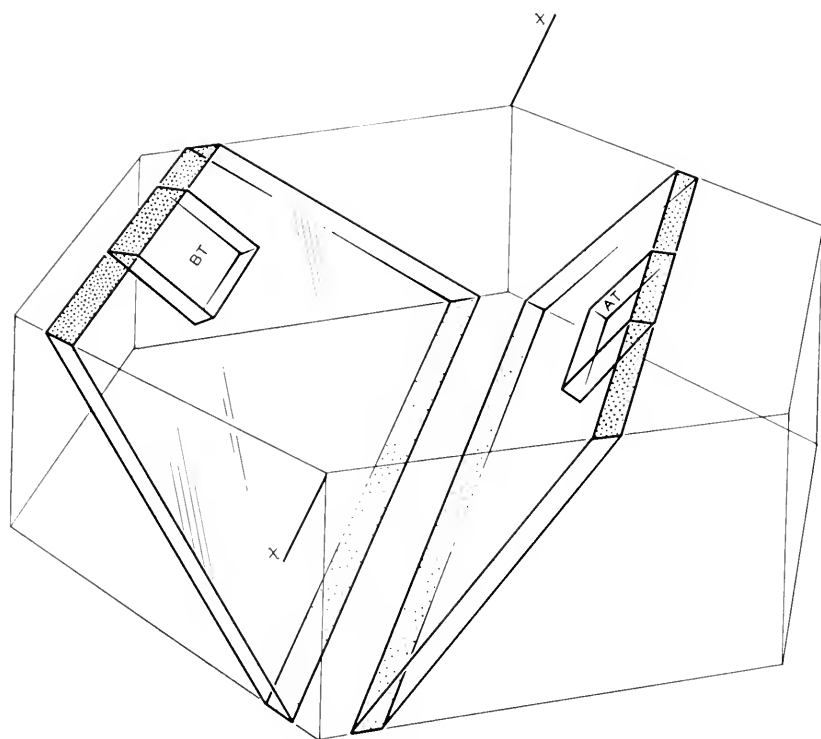


Fig. 3.29—Orientation of *AT* and *BT* plates and slabs with respect to *Z* section (+*X* toward reader for right-handed quartz)

will have a surface ground on it normal to the axis of the jig. This surface will have the desired orientation of the plate.

As in the case of the finished plate the slab must be checked for angle-error around two mutually perpendicular axes in the plate surface. The intersection of the slab surface with the *Z*-cut surface is commonly taken as one axis and the normal to this as the other.

For the *AT* and *BT* cuts these two axes are the same ones used in correcting the finished plate and the same settings for jig holder and ionization chamber may be used (See Fig. 3.29). For any cut with an A_3 angle that

is not 0° , such as the *NT* cut, these two axes will not be the same as those used in checking the finished plate and different settings of the jig-holder and ionization chamber will have to be calculated. The procedure is similar to that for the determination of the g angles for the finished plate except that the components of the unit vector of the atomic plane used are multiplied by the matrix which expresses the transformation after two rotations (A_1 and A_2) (equation 3.7) instead of the matrix for three rotations.

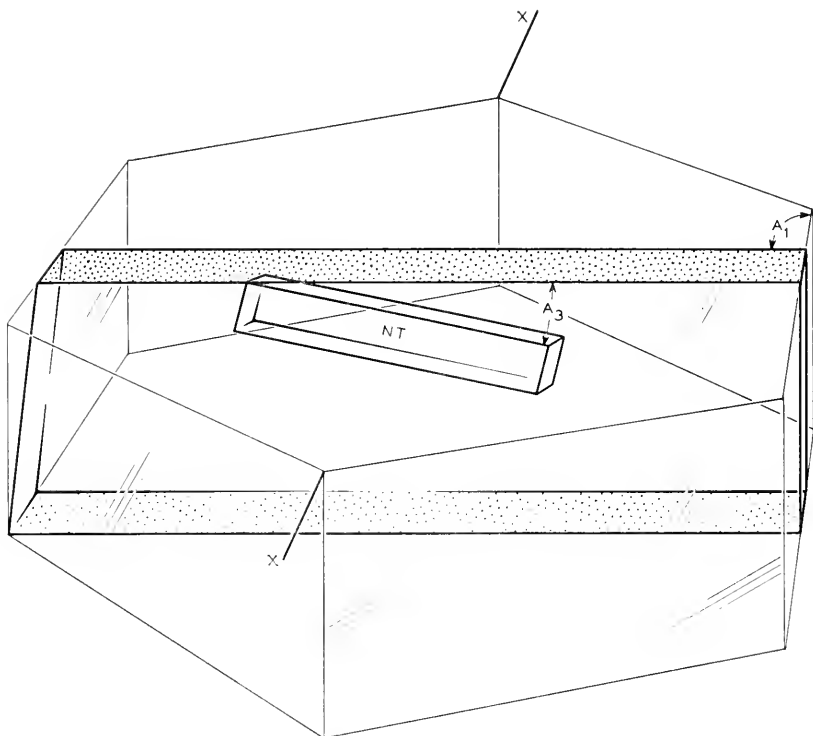


Fig. 3.30—Orientation of *NT* plate and slab with respect to Z section ($+X$ toward reader for right-handed quartz)

For example, in the case of the *NT* cut, $A_1 = 99^\circ 25'$ and $A_2 = 49^\circ 20'$ so that the A_1, A_2 matrix (equation 3.7) becomes

$$r'' = \begin{pmatrix} -.1636 & .9865 & 0 \\ -.6429 & -.1066 & -.7595 \\ -.7483 & -.1241 & .6517 \end{pmatrix}$$

which, multiplied by the components of the unit normal to the atomic plane ($2\bar{1}\cdot 3$) in terms of the X, Y, Z axes $\begin{pmatrix} .5914 \\ 0 \\ .8064 \end{pmatrix}$ gives the components of the unit

normal to the atomic plane ($2\bar{1}\cdot3$) in terms of the reference edges of the slab after rotations A_1 and A_2 (See Fig. 3.30). These are

$$N = \begin{pmatrix} -.0966 \\ -.9919 \\ -.0830 \end{pmatrix}$$

Substituting in equation (3.26)

$$\begin{aligned} \tan \delta'_1 &= \frac{-.0830}{.9919} \\ \delta'_1 &= -4^\circ 48' \end{aligned}$$

and in equation (3.29)

$$\begin{aligned} \tan \delta'_2 &= \frac{-.0966}{-.9919} \\ \delta'_2 &= 5^\circ 35' \end{aligned}$$

and from equations (3.25), (3.28), (3.31), and (3.35):

$$\begin{aligned} g_1 &= 27^\circ 25' \\ g_2 &= 37^\circ 45' \\ g_3 &= 37^\circ 1' \\ g_4 &= 26^\circ 35' \end{aligned}$$

which are the g angles for X-raying the NT slab where the reference edge is the intersection between the slab-surface and the Z -section surface.

CHAPTER IV

Raw Quartz, Its Imperfections and Inspection

By G. W. WILLARD

4.1 INTRODUCTION

QUARTZ is one of the commonest of crystalline minerals and occurs in many variations of size, color, purity, and structural perfection. It is used for such varied purposes as jewelry, fusing into heat and chemical resistant dishes, and for optical and piezoelectric units. However, the following discussion will be concerned mainly with such raw quartz as is commercially used in the manufacture of piezoelectric circuit elements. It might be added that the terminology used may be more in keeping with the language of the piezoelectric manufacturers than of the geologist. Further, description of many unusual types of defects, and variations of common types has been omitted. An attempt is here made to describe such defects as are of most interest in the piezoelectric art and in such a manner as to be most widely useful. Following is a description of raw quartz and its defects, the means of observing these defects, their appearance as recorded photographically, and a discussion of their effects on finished plates.

The words *defects* and *imperfections* as used in this article mean a deviation from a perfect specimen of raw quartz; they do not necessarily mean that the material is not entirely satisfactory for the purposes intended.

4.2 SOURCE, SIZE, SHAPE

Quartz crystals of usable quality and size come mainly from the interior of Brazil. From other sources the supply is negligible, or the size too small, or the imperfections too predominant. Even from Brazil only one in a hundred of the mined stones is usable. The size of stones most commonly used run from one-half to five pounds (about one-half cup to one quart size). The shape of the stones varies from well faced material, with all of the original natural faces intact, to stones in which the faces are broken or eroded away. When the faces are entirely broken away by mining operations the stones resemble chunks of broken glass. When the faces are eroded away by having been washed along river beds the stones are called RIVER QUARTZ, and the appearance is that common to river stones. River quartz usually exhibits a network of shallow surface cracks resulting from the continual bumping along a river bed, and hence is more subject to thermal and mechanical shock than uncracked stones.

With defaced quartz (river and broken) the orientation of the crystal structure cannot be determined from the surface shape. Since the stones must be cut at specific orientations relative to this structure, special means must be employed to determine the structure orientation. For this reason many users of quartz prefer faced stones. However, defaced stones are usually more free from defects than faced stones, since optical twinning is commonly concentrated near the natural faces of the original stone and other defects near the base. Thus by making use of special means (in-spectroscope, conoscope, oriascope) defaced quartz may be cut to good advantage.



Fig. 4.1—Quartz may show smoky or citrine coloring throughout or only in restricted regions, irregularly as at the left, or in PHANTOM planes as at the right.

4.3 COLOR

Usable quartz is transparent internally (though the exterior surface may be opaquely coated), never translucent (milky). The color of the quartz varies from perfectly clear through slightly smoky to fairly dark. The obviously dark stones are called **SMOKY QUARTZ**. Smokiness may be uniform throughout a piece, or varying from clear to dark, or confined to plane sheets within a single piece, see Figure 4.1. Dark smoky stones are not used because they cannot be inspected for defects and optic axis. With stones that are used this coloration is seldom so dense that it may be detected in the small finished plates with ground surfaces.

Because the smokiness is due to so slight a deviation from the pure quartz its analysis is extremely difficult. The coloration is variously explained, as due to minute traces of impurities (organic or inorganic), as due to the dissociation of a few SiO_2 molecules into free silicon and oxygen, and otherwise.

An important fact about smoky quartz is that it may be cleared of color-

tion merely by heating to 350°C. to 450°C. for a short time¹ (see Fig. 4.2). The clarity of cleared stones, even though originally very dark, rivals that of normally clear quartz, thus leading to the belief that most commercial quartz is colored to a slight degree.² Further, it is claimed that irradiation of either cleared or normally clear stones with radium rays causes them to become

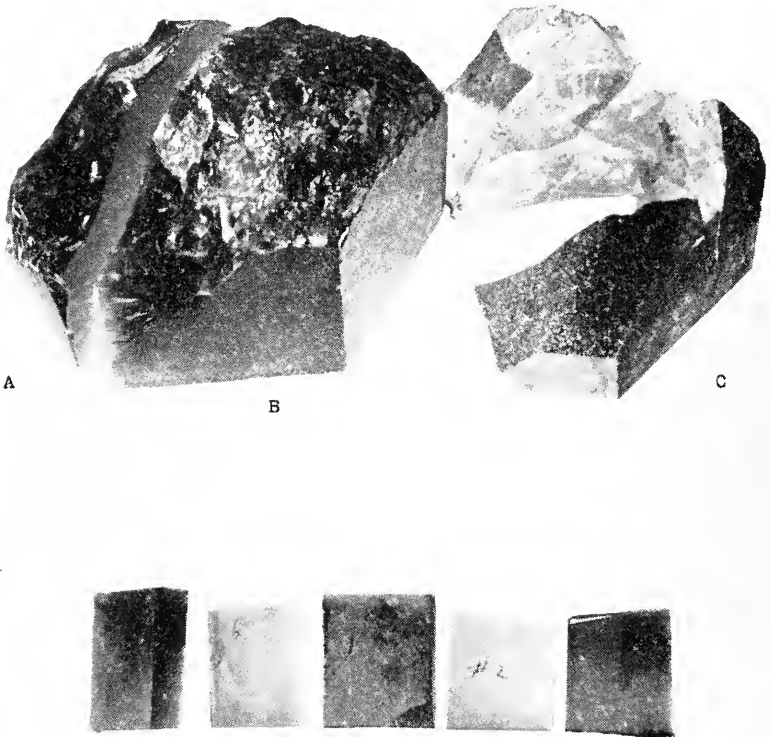


Fig. 4.2—Coloration in quartz may be cleared by heating to temperatures below 500°C. A, B and C are adjacent portions of one dark, smoky stone, only C having been cleared. The five, small blocks were likewise cut from a single stone, the second and fourth having been partially cleared at 350°C and fully cleared at 500°C.

smoky. It is then questionable whether there is a material difference in clear and smoky quartz, or only a difference in condition of the material. By the limited studies that have been made light smokiness has not been found to have any definite effect on finished plates. It might be added that such quartz plates as are normally heated to 400°C. to 500°C. in the process of manufacture, would of course be cleared of any smokiness originally present.

¹ Stones so cleared 8 years ago are still clear.

² Arkansas quartz (not used commercially) is noted for its unusual clarity.

What has been said of smoky quartz applies equally well to CITRINE QUARTZ except that here the coloration is straw colored (yellow to brown). Citrine quartz is even more uncommon, commercially, than smoky quartz.

4.4 TWINNING

Electrical and optical twinning are among the most common defects of crystal quartz. There are few stones without one or both present. Either type is usually difficult or impossible to detect from the exterior form of the crystal. Presence of either type in a finished piezoelectric element interferes with its perfect operation. Twinning is an abnormality of growth, in which an apparently homogeneous crystal is not actually of the same handedness, electrical sense, or orientation throughout. In the case of both electrical and optical twinning (the only common twinning types in quartz), the electric and optic axes in all parts remain parallel each to each.

In a crystal which is only ELECTRICALLY TWINNED, the stone is entirely of one handedness (either right or left), but one portion is of OPPOSITE ELECTRICAL SENSE to another portion. This change in sense of structure is NOT detectable by ordinary optical means. However, at the surface it is detectable by, (1) the piezoelectric effect (determination of electric charge on squeezing); (2) x-ray reflection intensities (using certain sense determining planes, see Chapter III); and (3) most readily and extensively, by etch-pits and etch-pit figure techniques.³ Commonly electrical twins are sufficiently large that they may be separated near a twinning boundary and both parts used.

In a crystal which is only OPTICALLY TWINNED, one portion of the crystal is of OPPOSITE HANDEDNESS and electrical sense to another portion. This change in handedness of structure is detectable by optical means (i.e. by examining between crossed polarizing filters). Optical twinning may also be detected, at the surface, by the etch technique in the same manner as electrical twinning. Usually a stone will be mainly of one handedness with only small, thin, interlayered growths of opposite handedness, thus making it impossible to use both handed portions separately.

Further discussion of both electrical and optical twinning will be found in Chapter V, where means for simultaneously detecting both are described.

4.5 CRACKS

Many quartz stones contain cracks which are not readily seen by a casual surface examination. As mentioned above river quartz commonly exhibits a network of shallow cracks extending inward from the surface, caused by bumping. All types of stones commonly contain one or more cracks, es-

³ In finished plates, of course, the effects of twinning are also determined by measuring the resulting piezoelectric and elastic constants of the plate (i.e., their effect on frequency and activity).

pecially when badly twinned or full of inclusions. Some of these cracks may be due to rough handling, but others are due to growth conditions, or result from temperature changes after growth.

Though large cracks are readily detected by means to be described, it might be noted that when cracks are sufficiently fine (small separation compared to light wave-lengths) they will no longer be seen. Thus every visible crack may be considered to extend beyond its visible range, and some actual cracks will not be visible at all. Because of such cracks and other defects in quartz, special care should be taken in handling uncut and partially cut stones to prevent their subjection to mechanical or thermal shocks. On the other hand, small, flawless, finished plates will stand considerable shock. It is even common practice to solder to finished plates (after metallizing).

4.6 INCLUSIONS (BUBBLES, NEEDLES, PHANTOMS, VEILS, ETC.)

The remaining abnormalities of raw quartz (used for piezoelectric elements) may be classed as inclusions. Among these are inclusions of solid, liquid, and gaseous material. The size of individual inclusions may vary from submicroscopic, to those easily visible with the naked eye. The inclusions may be isolated, or arranged in lines, or planes, or curved surfaces. In many cases the arrangement forms of inclusions (bubbles, needles, phantoms, veils) have been used to describe inclusions, with little regard to the nature or size of the individual inclusions. This is because inclusions which are too small to analyze individually, are still visible when grouped by hundreds in lines or surfaces.

When inclusions are sufficiently small and closely grouped they give a BLUISH cast (Tyndall effect) to the group. Thus the bluish cast is recognized as indicating fineness of grouped inclusions. When the individual inclusions are larger, the group appears white. With still larger inclusions one may actually see separate, individual inclusions, looking like minute bubbles. Thus, describing the group as blue, white or bubble textured is of considerable importance, when analyzing or estimating the usability of quartz with grouped inclusions.

BUBBLE INCLUSIONS look like small bubbles (i.e., small spheroidal cavities) in the quartz. When bubbles appear individually, or randomly scattered, they are referred to as just bubbles. When bubbles occur in organized groups the group is referred to as a bubble phantom, bubble veil, etc. Smaller bubbles appear only as light reflection points and their shape is not seen.

In general such bubbles may be filled with gas, liquid, solid, or any combination of phases. They may be of the same nature as rare, large cavities in which one can easily see a liquid moving about. Analysis of the contents of such cavities has indicated the presence of CO₂, water, salt solutions, and

other substances that might have been present during growth conditions. That these cavities are seldom in the form of negative crystals, i.e. having the plane natural faces characteristic of quartz, is not easily explained.

NEEDLE INCLUSIONS appear as long, thin lines or needles. They may be straight or curved, blue, white or otherwise. Whether they are continuous or composed of rows of individual inclusions is usually not discernable. Needles, visible without concentrated illumination (and fluid immersion), are likely to be inclusions of crystalline material, such as rutile (brown), tourmaline (black). Usually such needles are called rutile needles, because of the commonness of rutile and the difficulty of determining whether they are rutile or some other material. They might better be called DARK needles. BLUE NEEDLES are fine textured, and may appear singly or in parallel groups, which may be at angles to other parallel groups. In other cases they spread from a bubble point, like a comet. Blue needles may also be feathered (having short feathery rays along the sides), may be hard (very fine and sharply distinguishable), or soft (diffuse). Probably the most important characterization of all blue needles is their blueness, which indicates fine texture. WHITE NEEDLES are similarly hard or soft. CHUVA is a special type of white needle which would be extremely elusive except for the fact that along its length are small bubbles, giving chuva the appearance of dew drops along a thin fiber. For piezoelectric usage an important distinction between needles is whether they are blue, white, chuva, or dark.

PHANTOMS are an arrangement form of inclusions (or coloration), in plane sheets which are parallel to possible natural crystal faces (usually the prism or pyramid faces). Often several, differently oriented, phantom planes are formed together so as to give the appearance of a crystal within a crystal, thus the name phantom (or ghost). Phantoms may also appear as groups of parallel sheets. Phantoms may be of smoky, blue, white, or bubble texture and should be so noted when describing their effects on piezoelectric elements. That phantoms are closely related to disturbed growth conditions is apparent from their close relationship to crystal faces.

VEILS are an arrangement form of inclusions in curved sheets. They are most commonly of a tenuous bubble texture, but may also be white or bluish. Again this distinction is of importance in estimating their deleterious effects. The cause of inclusions appearing in veil form is not clear.

CLOUDS (a term not widely used) refer to inclusions irregularly distributed in restricted regions of the crystal.

4.7 INSPECTION MEANS

The raw quartz inspectoscope is the name of an instrument used for the inspection of raw quartz. This inspectoscope may, of course, be also used

for the inspection of quartz in various stages of processing, and for other transparent materials than quartz.

By means of a polarized light optical system the stones are examined for optical (but not electrical) twinning. By this same means the direction of the optic axis through the stone is also determined. By means of concentrated high-power illumination the stones are inspected for cracks, color and inclusions. By both means the stones are illuminated and inspected while immersed in an immersion fluid of matching index of refraction.

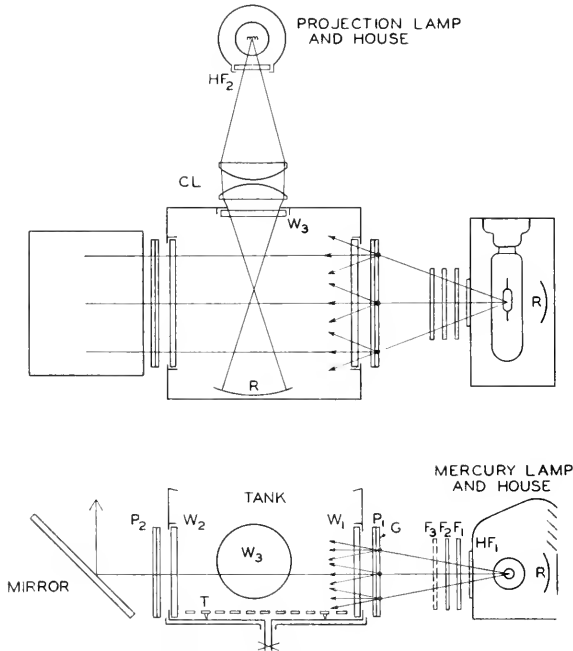


Fig. 4.3—The raw quartz INSPECTOSCOPE, top and front views. The stones are held in the immersion tank and viewed from above. Polarized light from the mercury lamp is used for locating the direction of the optic axis and for detecting optical twinning. Concentrated light from the projection lamp is used for detecting other interior defects. See also Fig. 4.5.

Without such immersion it is difficult or impossible to illuminate the interior properly, or to see into the interior, of oddly shaped or rough surfaced stones. Such immersion eliminates refraction (bending of light rays) at the surface. The interior of stones with ground, fractured, or other surfaces, are as easily examined as a piece of plate glass.

The important design features, maintenance and operation procedures are given below. Figure 4.3 is a diagram of the instrument, and Fig. 4.5 shows an early model utilizing many of the features described below. Three plate glass windows W are cemented into apertures in the open-top, steel

immersion tank, Fig. 4.3. A raised perforated table T rests on the bottom of the tank. For polarized light inspection of twinning and of optic axis direction, the right to left optical system is used. This comprises an AH-4, 100 watt, mercury-vapor lamp (requiring special transformer) isolated in a well ventilated housing with window HF_1 , a set of color filters F_1 , F_2 , (and possibly F_3), a polarizing filter P_1 with ground surface G (for light diffusion), the immersion tank, the polarizing filter P_2 (crossed to P_1), and the mirror (mounted at 45° to the vertical) to reflect light vertically up through a window in the drain pan (not shown in Fig. 4.3), to the eye. For inspection of defects other than twinning, a high powered projection system is used. This comprises a projection lamp (isolated in a housing by window HF_2 , and with forced draft), condenser lenses CL , and the immersion tank. Here one looks down directly into the tank at the stone. Reflectors R may be added to both systems to increase the illumination.

This instrument resulted from a restudy of long-used "inspection tanks" and methods, and includes some features not originated by the author. Since this inspectoscope is believed to be superior to many inspection-tank equipments now in use, the more important design features will be described.

The tank should be large enough to allow easy handling of the stones in the fluid, with allowance for positioning any portion of the stone in the projection beam, and allowance for rise in level of the fluid as the stone is immersed. However, the size should not be made larger than necessary, for it has been found in practice that the fluid very rapidly collects lint and dirt, which (being kept in suspension by agitation) scatters or diffuses the light. This, besides scattering the light from its proper paths, interferes with the polarized light inspection by depolarizing the beam. In large tanks with dirty oil the light becomes almost completely depolarized and no patterns can be seen. If, however, the crystal is large enough to nearly fill the length of the tank (along the polarized light beam), this depolarization is small.⁴ Thus, a tank as small as is consistent with the size of the stones to be examined should be used. The smallest convenient size and shape of tank would be about 8 inches in the polarized light direction, 8 inches in the projection light direction, and $5\frac{1}{2}$ inches high (all elements of Fig. 4.3 are drawn in proportion to these tank dimensions). This permits easy examination of two to three pound stones (pintsized), and six-inch long stones may be used without great difficulty.

Isolation of lamp heat is an important consideration in both optical systems. In the projection system the high wattage lamp would dangerously heat up the whole instrument if the heat were not properly dissipated. In

⁴ In an emergency small stones can be examined in a large tank with polluted fluid by placing the stone at the mirror end of the tank and introducing a polarizing filter directly in the fluid, close to the stone, on the lamp side (Polaroid J-Film is only slowly attacked by many of the immersion fluids).

the polarized light system the heat must be isolated from the color filters and especially from the polarizing filter P_1 , for it is extremely important that polarizing screens should not be overheated. They deteriorate (lose their polarizing property) rapidly above 60°C., and should not reach a temperature uncomfortable to the touch. Their deterioration by heat or otherwise is not usually discernible except by examining their extinction quality with the aid of a good piece of polarizing material (turned for extinction, they should pass practically no light). Since the polarizing filters and the color filters all absorb some light themselves it is important to ventilate these units, as well as to isolate the mercury lamp heat with a separate housing. The window HF_1 in the mercury lamp housing may be of one-eighth inch pyrex glass, or better the heat filter HF (specified later), and may be a moulded filter (since there is no focusing required here). However, the window for the projection lamp housing should be polished, either pyrex or heat filter as above (since here the light is used in a focused beam).

The polarizing filter P_1 and P_2 may be glass filters (polarizing film cemented between glass plates by the manufacturer) or film filters held between sheets of one-eighth inch plate-glass, with taped edges. The latter arrangement is less expensive, and the film is usually obtainable without delay. Extra filters should be kept on hand. The two filters must be mounted, relative to each other, in a crossed position (for extinction). Since light entering the tank from P_1 must be diffuse it is necessary to introduce a ground glass surface. This is accomplished without adding an extra glass plate by grinding one surface of the polarizing filter, the outer surface if a cemented glass filter, an inner surface if using loose film between glass plates (the inner surface may be used here to provide for protection from dirt). In either case the ground surface must be on the lamp side of the filter or it will depolarize the light.

In the past a carbon arc has been used as the projection light source. Such arcs are not handily turned on and off, nor adjusted, and are now difficult to obtain. An incandescent projection lamp overcomes these difficulties. A 500 to 1000-watt lamp with double-plane filament structure (filament in two planes, and staggered relative to each other, giving a solid square of illumination) is ideal for this purpose. Such lamps operate at high efficiency, are a concentrated source, have a short life, and generally require forced ventilation. A recommended lamp is the Mazda, Clear Projection, 750W-120V, T-12, C-13D Fil., Med. P.F. base. This lamp requires a small blower for ventilation and when operated with a foot switch, only during that part of the inspection that it is needed, gives a satisfactory replacement schedule.

It is important in the projection system to use large, short-focus condenser lenses, and to focus the lamp image near the center of the tank. This allows

the great concentration of light which is necessary for detecting fine-textured defects, and makes it easier to determine just where in the crystal (in depth) the defect lies. Further, with the large angle of illumination available, those defects which require a specific angle of illumination may be found with less hunting. It should be noted that in figuring the object and image distances, the refractive index n of the immersion fluid must be taken into account (the window to image distance with fluid present is about n times that with fluid absent).

The color quality of the light used in the polarized light system has a considerable effect on the ease of observing the light patterns obtained when inspecting for twinning and optic axis. A typical light pattern of a piece of raw quartz viewed along the optic axis is shown in Fig. 4.8. The broad dark and light contours, "thickness-contours," are the ones used in locating the optic axis. The finely "toothed-patterns" at A , B , and C show twinning. The conditions that make the former most pronounced are not necessarily the same as those that make the latter most pronounced. The broad thickness-contours are most pronounced in monochromatic light, but barely visible in white light. This is due to the large variation of rotatory power with color, which, in all but the smallest stones, causes such overlapping of the white-light color contours as to result in practically no appearance of contours at all. This effect does not apply to the twinning regions, since in most cases the thickness of oppositely handed material is too small to develop overlapping. The result with white light is that the stone appears mainly white, except for regions of twinning where the toothed pattern is seen in color. For twinning detection, then, the advantage of white light is largely due to removal of the extraneous thickness contours. This possible advantage for the novice is not obtained without some loss of factors necessary for complete identification.

On the other hand, in determining the direction of the optic axis, the thickness contours are essential, and hence monochromatic (or a restricted spectrum) light is necessary. This illumination is most easily achieved with a mercury arc and color filters. The mercury arc emits a restricted spectrum (mainly $.578\mu$ yellow, $.546\mu$ green, $.436\mu$ far-blue lines and weak red and blue-green bands), and is very efficient. Even without filtering it gives far better thickness-contours for axis determination than does white light. The insensitivity of the eye to blue leaves mainly yellow and green. The yellow may be largely removed without appreciable loss of green by using filter F_2 and the blue and blue-green may be removed with filter F_1 . However, the red can be removed only with considerable loss of green by filter F_3 . The use of F_1 and F_2 alone are recommended as giving sufficient restriction of spectrum and yet high illumination. (All three filters, as used in the conoscope, give a fairly monochromatic green.) The filters need not

be polished, only moulded, since here there is no focusing of light. The filters described above are the Corning glass filters:

F_1 , Code 3484, H.R. Traffic Shade Yellow,

F_2 , Code 5120, Didymium,

F_3 , Code 4303, Dark Shade Blue Green,

HF , Code 3966, Extra Light Shade Aklo (a heat filter).

A corresponding set of filters passing more light, but giving a less monochromatic light are:

F_1 , Code 3486, H.R. Yellow Shade Yellow,

F_2 , Code 5920, H.R. Illusion Pink,

F_3 , Code 4308, Light Shade Blue Green.

It might be added that the pronounced effects of filters are easily observed with any instrument by holding small polished filters over the eye. These same filters give some improvement even with white light, for optic axis detection. Further, if the filter were not so heavy, polished filters might be better applied at the eye than at the light source, since here they would also cut down extraneous illumination from the room. Or the same result might be obtained with large polished filters (expensive) and an eye chute at the viewing end of the system.

Several factors are of importance with regard to the immersion fluid used in the inspectoscope. The fluid should have a refractive index matching that of quartz, and be clear and colorless (to eliminate loss of light). It should be of low viscosity, so that dirt and dust may settle and air bubbles rise, rapidly (to prevent depolarization of the polarized light beam). Low viscosity also aids in the draining of oil from the stones after inspection. Water solubility of the fluid would be an aid to cleaning. Necessarily the fluid must be non-toxic and non-flammable, and preferably odorless, inexpensive and commercial. Various fluids satisfying these requirements to varying degrees have been used. Since there is no majority agreement as to which of the fluids now in commercial use is most satisfactory, no particular fluid can be recommended. (Three are listed in Chapter II, page 258.)

However, a word may be added about the required degree of refractive index match. Mineral oils of index 1.47 to 1.48 are, definitely, very poor immersion fluids for quartz. With them it is difficult to see into the interior of stones without plane polished surfaces. Ground and unpolished surfaces still cause considerable diffusion. For good inspection viewing the fluid should have an index between 1.53 and 1.56 (preferably between 1.54 and 1.55).

The refractoscope is a simple instrument especially designed for the purpose of easily and exactly checking the index match of fluid to quartz. The principle having been already noted (p. 255, Chapter II), it suffices here to describe the use of the instrument. A test tube, Fig. 4.4, filled with the

fluid to be examined, is mounted in an adjustable-height stand, the optical system lowered into the test tube until the flat bottom surface of the lens contacts the fluid, and the stand is placed in an inspectoscope, conoscope, or in front of a lamp (the stand being adjusted to proper height for good illumination). The optical system comprises a lens L (for magnification and elimination of ripples on the liquid surface), a thin Z-cut quartz prism Q ,⁵ and a narrow slit diaphragm S . When the slit is viewed simultaneously through, and at the sides of the prism, a view similar to one of those shown

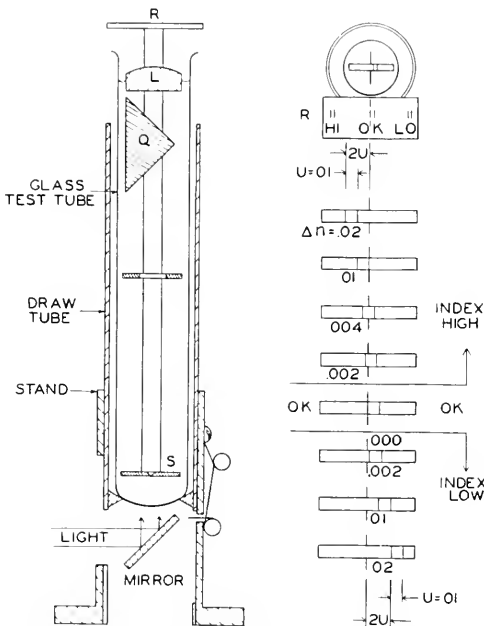


Fig. 4.4—The immersion REFRACTOSCOPE may be used in conjunction with an inspectoscope or conoscope for determining the degree of refractive index match (or mismatch) of the immersion fluid relative to quartz. At the right is shown the manner of reading the instrument.

in the figure may be seen. The two short lines are always the same distance apart and are used as a unit of index mismatch, the unit being $u = .009 \approx .01$. The left-hand short line is the one to be aligned with the long line for perfect match, and the actual mismatch Δn , is measured by the separation of these two lines. The remainder tab is added to remind the operator which indications represent perfect match, too high and too low fluid index. Since the indices of both quartz and fluid vary with temperature and with color of light used, the refractoscope was especially designed for immersion directly

⁵ The larger the prism angle the greater will be the sensitivity of reading, and the smaller will be the readable range of mismatch.

in the instrument using the immersion fluid. When, in such instruments, a polarizing filter is so oriented as to cut off one or both short prism-lines, these lines may be restored to view by rotating the test tube in the holder (upon continuous rotation one line and then the other will disappear). With vertical conosopes the mirror may be removed for bottom illumination. When monochromatic light is used all three lines are the same color as the illuminant. When using non-monochromatic or white light, the long, slit line is the color of the source, while the short lines develop into two, separate spectra. In this case, that portion of the spectrum is used for alignment which is most predominantly used in the immersion instrument. The sensitivity of the refractoscope, when approaching perfect match, is about $\Delta n = .001$. This sensitivity is of course attained when one adjusts the fluid to match the quartz, by addition of the proper high or low-index component. When the fluid does not match there is a less accurate measure of mismatch, but this measure is still good for determining the degrees of fluid adjustment to be made.

The principle of the refractoscope may be even more simply applied to measuring the fluid to quartz mismatch, by making use of the inspectoscope and a basal section of quartz, using the 120° prism formed between two good, clear, adjacent natural faces. The section is placed base down in the tank at the far side from the mercury lamp, and so positioned that a vertical slit diaphragm, placed on the other side of the tank, may be viewed through the two prism faces. With the polarizing filters removed, the two images of the slit as seen through the prism do not (in general) align with the slit as seen above the prism. The image farthest from the prism vertex is the one that should be aligned with the slit, for perfect match of refractive indices. The necessity of removing the polarizing filters can be obviated by tilting the prism and slit about the line of sight, preferably at 45° from the vertical (or this might have been obviated, if the polarizing screens had been out with their plane of polarization at 45° to the vertical).

Finally, experience indicates that the importance of keeping the immersion fluid clear and clean is not generally realized. As noted above, contamination not only gives bad scattering of the projection beam, but also depolarizes the polarized light. A perforated plate raised from the bottom of the tank is an aid in keeping the settled dirt from being recirculated again. More effective is the provision of simple, easy means for draining, filtering and refilling the tank. One or more thicknesses of chamois makes a good filter, provided the chamois is occasionally washed out with a solvent.

4.8 PHOTOGRAPHIC STUDY OF INTERIOR DEFECTS

The original inspectoscope of Fig. 4.5 was used at the Hawthorne plant of Western Electric Company, in obtaining the accompanying photographs.

For inspecting twinning and direction of optic axis, the stones were viewed horizontally through the polarizing filter *E* and window, with mirror *F* removed (using mercury lamp *I*). Normally the operator looks directly down into the mirror to see the same view. For observing other interior defects, the view is from directly above the tank, through the fluid surface (with projection lamp in housing *H* being used). This is the normal manner of observation. *B* mounts heat and color filters; *C* is a polarizing filter with diffusing surface; *E*, a polarizing filter crossed to polarizer *C*; *G*, a glass window; and *I* is a rudimentary lamp house normally fitting over *A* to edge of *B*. The tank *D* has two rectangular windows parallel to *C* and *E*, and a circular window in rear wall for entrance of projection illumination.

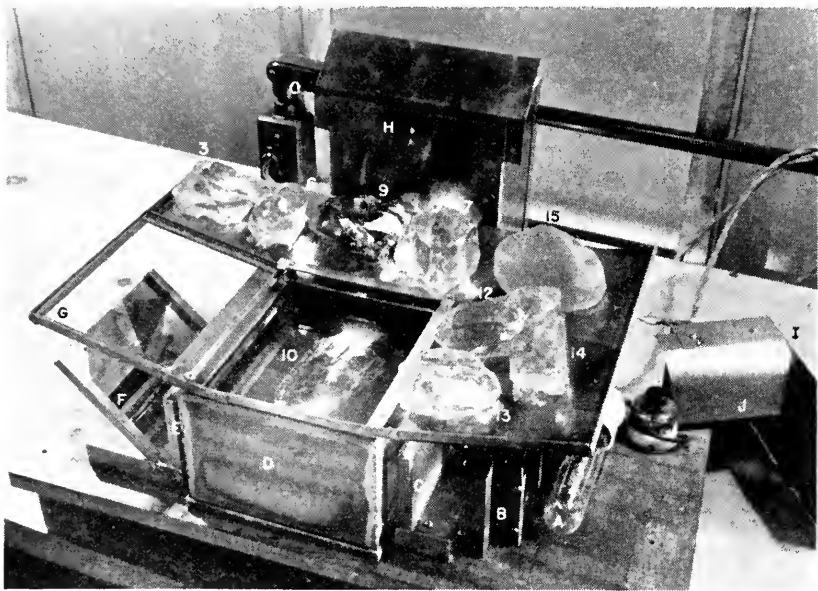


Fig. 4.5—The inspectoscope and stones used for the following figures. See also Fig. 4.3

Most of the following photographs are of stones shown, Fig. 4.5, on the drain pan and in the tank. Note that stones 3, 6, 9, 12, 14 are well faced stones; 9, 7, 13 have fractured surfaces; and 15 is typical river quartz (nearly perfect internally). The special manner of orienting the stones in the tank to obtain the desired views will appear from the following descriptions. The views are one-half to full size.

Figure 4.6 is a polarized light view of a wedge shaped basal section (one-fourth inch thick at the left, to three-fourths inch thick at the right). The wedge is viewed along the optic axis with the plane faces approximately perpendicular to the line of sight (i.e., parallel to the polarizer *C* of Fig. 4.5).

The back face is larger than the front face so that outside the borders of the front face the thickness tapers off very rapidly. Since the dark contours here show thickness of the section (as the lines of a contour map show height above sea level) one may easily determine the shape of the wedge. The inner contour *AA* is near the greatest thickness, contour *BB* intermediate thickness, and outer contour *AA* near the thinnest portions at the edges. It might be added that the thickness-contours do not exactly indicate a region of equal thickness unless the eye is distant from the stone, and unless the stone is viewed exactly along its optic axis.

Figure 4.7 is a polarized light view of an inch-thick basal section (i.e., *Z*-cut) with the parallel ground surfaces perpendicular to the line of sight

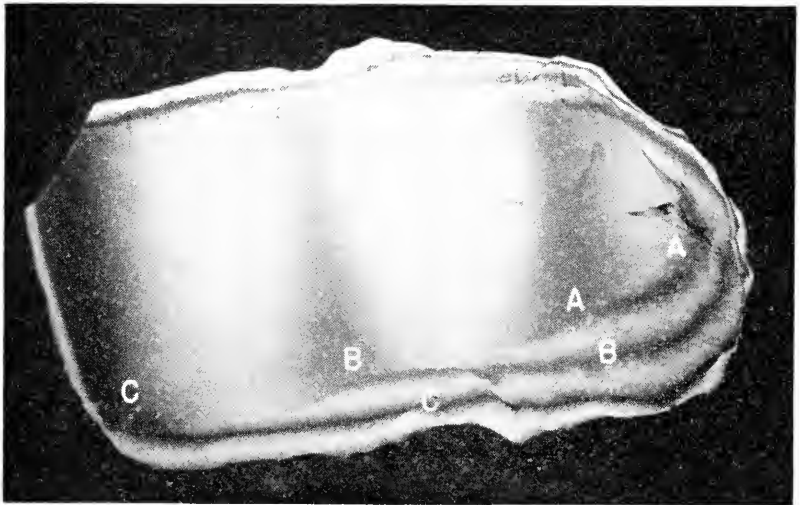


Fig. 4.6—A wedge-shaped basal section of quartz viewed along the optic axis in polarized light. The THICKNESS-CONTOURS locate regions of equal thickness, A-A thickest to C-C thinnest.

(i.e., the stone is viewed along its optic axis). Neglecting for the moment the ring pattern *C*, one observes a wide, diffuse vertical thickness-contour at *B*. With parallel surfaced stones a thickness-contour should cover the whole stone, since the thickness of the stone is uniform. Here the stone is not viewed *exactly* along the optic axis. If the eye be placed close these contours become circular.

Further, this view shows the effect of placing a lens between the tank window and polarizer at *E*, Fig. 4.5. The result is a ring pattern, the real image of which is at the focal distance of the lens on the eye side. The image may also be obtained on a ground glass at this point and its location is independent of the distance between quartz and lens (no rings will appear

if too far separated). This ring pattern is due to conical illumination (or more correctly to conical viewing; here the illumination of the stone is diffuse). This simply illustrates the basic principle of the conoscope. The principle is further illustrated by tilting the section out of its present position, which causes the ring system to move in the direction of tilting. The theory of these effects is given in Chapter II.

Figure 4.8 is a polarized light view of a pyramidal cap of quartz with a fractured back surface (stone 3, Fig. 4.5). Here the stone is viewed along the optic axis (the six natural cap faces making equal angles with the line of sight). The continuous dark bands are thickness-contours, and again

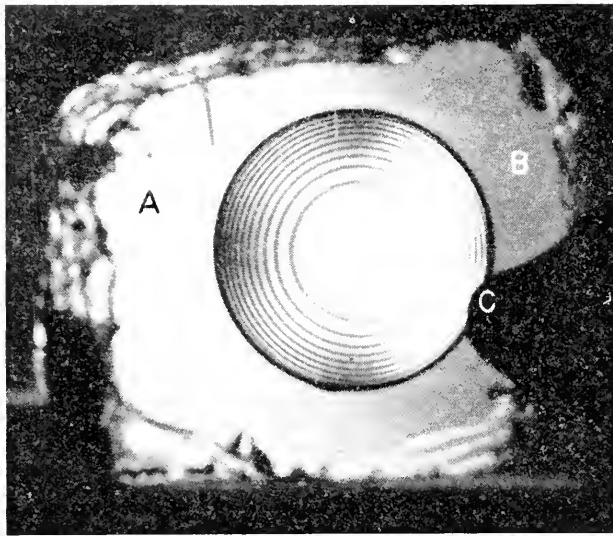


Fig. 4.7—A parallel faced, basal section of quartz viewed along the optic axis in polarized light. Note the vertical thickness-contour at B. The conoscope ring-pattern C may be obtained by introducing a lens.

represent regions of equal thickness in the optic axis direction. Had the fractured surface been flat instead of broken these contours would have been hexagonal and parallel to the hexagonal edges of the cap. The toothed-patterns at A to G are due to optical twinning (thin layers of the quartz whose handedness is opposite to that of the main stone). Although the exact shape and location are not determinable, the approximate location and extent are observed by tilting the crystal while viewing. The contour and pattern changes resulting from angularly moving the crystal (away from the position of viewing directly along the optic axis) are shown by Fig. 4.9, which should be compared with this figure.

Figure 4.9 is a polarized light view of the same stone as shown in Fig. 8,



Fig. 4.8—A broken cap of quartz is viewed along the optic axis in polarized light. Few, broad thickness-contours show good alignment with the optic axis. The fine TOOTHED-PATTERNS are due to optical twinning.



Fig. 4.9—The same cap as in Figure 4.8, but viewed slightly off the optic axis. Note the increased number of thickness-contours, and their fineness, also that some twinning regions are enhanced.

the only difference being that here the crystal is viewed slightly off the optic axis. Comparing the two views it is noted that here there are many more, and narrower, thickness-contours.⁶ As the crystal is further rotated away from optic-axis-viewing, the contours multiply until they are no longer visible. Thus, it is by so positioning the stone as to obtain the fewest and widest thickness contours that the optic axis direction is determined, the axis then being parallel to the line of sight from eye to stone. It might be parenthetically noted that the handedness of raw stones may be determined in the inspectoscope, if the polarizing filter on the viewing side be rotatably mounted, by observing the contour contraction or expansion as the filter is rotated (for stones progressively thicker from outer boundary inward, the handedness rule is opposite to that for the conoscope).

A further effect of tilting the stone away from optic-axis-viewing is to enhance the toothed, twinning-patterns. Certain of these patterns are enhanced by tilting one way, others by tilting differently (note that regions *A*, *C* and *G* are much clearer here than in Fig. 4.8). Also, since the thickness-contours move about and the toothed patterns remain fixed, motion of the stone is an aid to location of twinning (except in the rare cases of large sized twins, where this does not hold). Note that optical twins usually extend inward from the original natural faces. The twin *G* which appears to be internal, actually extends inward from a cap face.

Figures 4.10 and 4.11 show projection illumination views of typical, parallel BUBBLE-PHANTOMS (in stone 7, Fig. 4.5). The light from the left converges into the stone, focuses about centrally, diverges and passes out of the stone at *B*. Due to an internal fracture in the right end the light is also reflected upward at *C*. The light beam is visible in the fluid but not in the stone, because a slightly contaminated fluid scatters far more light than does quartz.

In Fig. 4.10 the stone is held so that the phantom planes *A-A* are viewed edge on (the only way finer textured planes are visible), while in Fig. 4.11 the planes are viewed at a slight angle, to show area of the planes. These planes have a texture of distinguishable bubbles. The planes are long, about an inch wide (with rectangular boundaries at their left end) and are parallel to a possible natural face (no actual faces present on this broken stone). Such bubble phantoms are probably not permissible in any finished piezoelectric plate.

Figure 4.12 shows bubbles, cracks, veils, and phantoms (in stone 9, Fig. 4.5) and pairs of angularly joined phantom planes, *B-B*, parallel to the natural faces *A-A*; each pair forms two faces of interior phantom crystals. The texture of the phantom planes near *A-A* changes along their length from bubbly at the left to bluish at the right. A dense curved blue veil is seen at *C-C*,

⁶ Actually the thickness contours are not now as closely related to the thickness as before (due to the birefringence effects being added to the rotatory effects; see Chapter II).

while a disperse, curved, bubble veil is shown at *E*. Above and to the right of *D* are two small fractures.

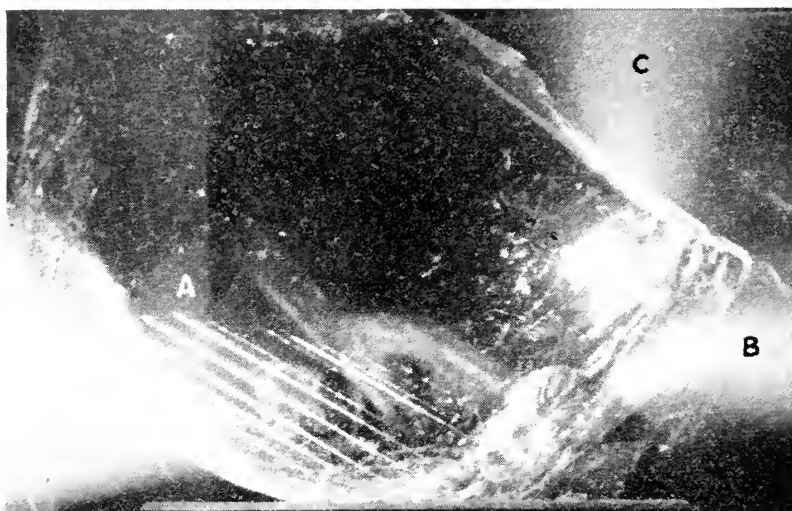


Fig. 4.10—An edge view of BUBBLE-PHANTOMS using the concentrated projection light. See also Fig. 4.11

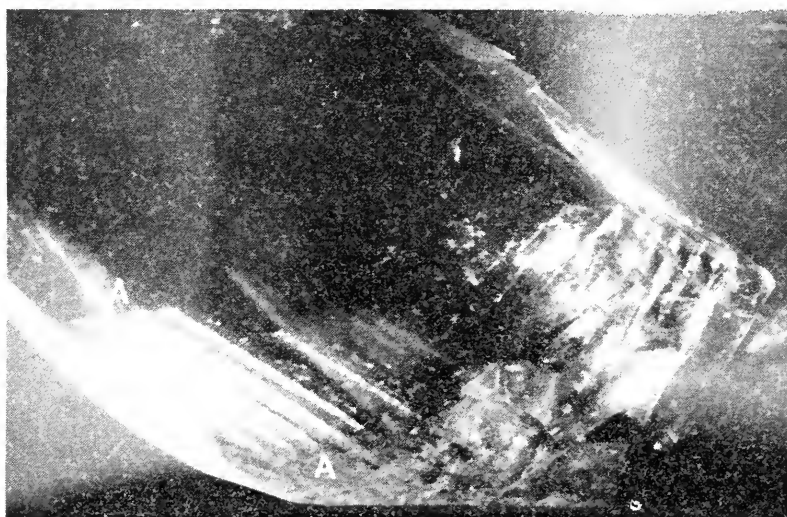


Fig. 4.11—The same stone as in Fig. 4.10, viewed at a slightly different angle. Note the bubble-texture, and the width of the planes.

Figures 4.13 and 4.14 show blue needles in two parts of a single stone which contains needles throughout (stone 10, Fig. 4.5). Only those needles

which are near the concentrated focal point of the projection illumination are visible in each view. The length direction of the needles must be nearly parallel to the direction of illumination to be seen well (thus wide angle of illumination is an aid in finding the needles). Needles elsewhere in the stone may be observed by moving the stone about. The flares at the ends of the stone are due to exterior surface conditions. The needles of Fig. 13 are of the comet type (radiating from a point), while those of Fig. 14 lie in parallel groups. In each case a few of the needles are slightly feathered, and all are soft needles.

Figure 4.15 shows a stone (14, in Fig. 4.5) in which the defects are concentrated in the base, a common occurrence. Were this stone to be proc-

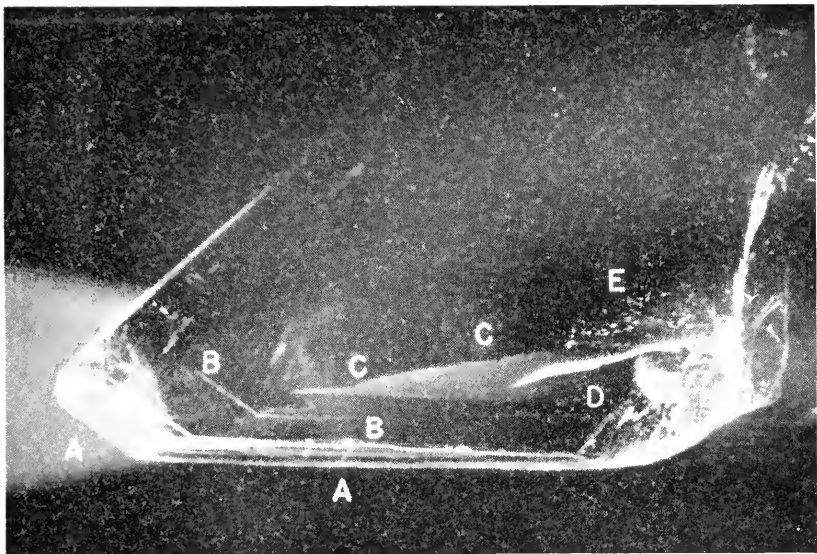


Fig. 4.12—This stone, viewed in the projection light, shows phantoms A-A to B-B, blue-veil C-C, bubble-veil E, and two fractures near D.

essed by *Z*-sectioning, a saw cut near the line C-C would divide the stone into a large, nearly perfect portion, and a small unusable portion which need not be further processed. Otherwise sawn, bad portions will have to be processed, or good portions of a largely bad section would be too small to obtain plates from. This points out the importance of coordinating processing with inspection, even though the stones have been already inspected and judged to be worth processing.

Bubbles and cracks fill the end of the stone at B, scattered bubbles appear in a veil at A, and a few isolated bubbles are at D. Note the clarity of the stone relative to the fluid, as shown by the beam of light entering the stone from the left, not visible internally.

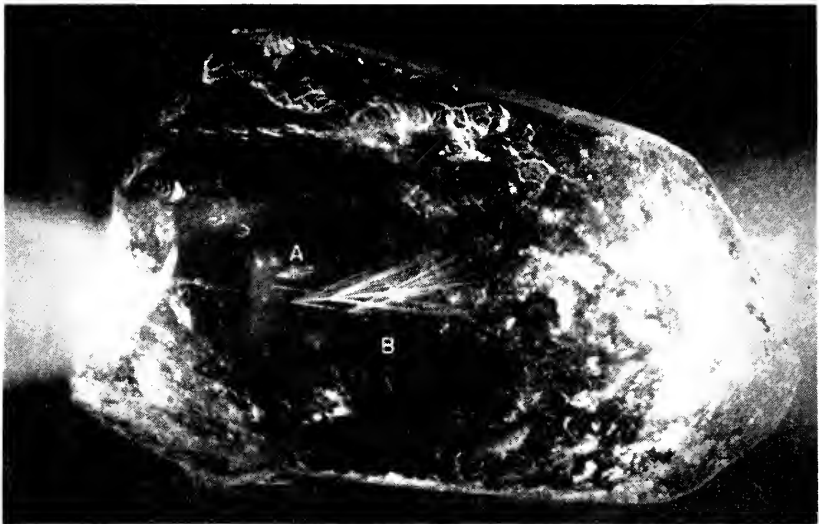


Fig. 4.13—This stone is full of blue needles, though only those located in the focus of the light beam are visible. See also Fig. 4.14.

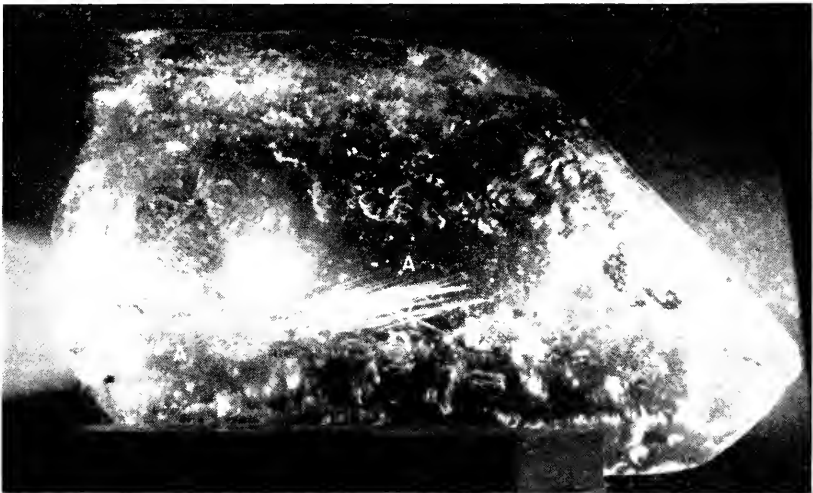


Fig. 4.14—The same stone as in Fig. 4.13 shows other blue needles in a different arrangement, by holding the stone differently with respect to the light.

4.9 EFFECT OF INTERIOR IMPERFECTIONS ON FINISHED PLATES

The practical effect on the finished piezoelectric plates, of the various types of interior defects, is one of the least understood factors directly related to economic use of the strategic material, raw quartz. This is because of the

wide variation of the types, sizes and concentrations of defects, and the further variation of the types, sizes, and requirements to be met in the finished plates. However, an analysis of the factors involved leads to some important conclusions. The various factors may be correlated as follows.

Fine textured inclusions are less objectionable than coarse textured inclusions (i.e., smokiness, and blue needles and phantoms, than white, or bubble needles and phantoms). Isolated defects are less objectionable than concentrated defects of the same texture size (i.e., isolated bubbles, than bubble phantoms). Cracks should never be permitted in finished plates. Twinning will be discussed in detail in Chapter V.

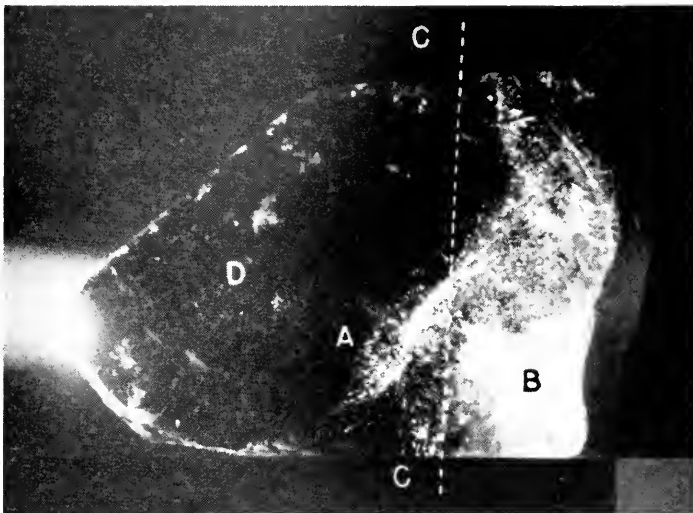


Fig. 4.15. This stone could be economically processed by cutting off the base rear line C-C. A few scattered bubbles appear at D, fractures and bubbles fill the base B, and A is a bubble veil.

Further, a given defect is more likely to be tolerated in: (1) large piezoids (finished piezoelectric elements) than in small ones; (2) in low-frequency-mode plates (*CT* and *DT* types) than in high-frequency-mode plates (*AT* and *BT* types); (3) in plates to be operated at low amplitudes of vibration (filter elements, and oscillator plates with low drive) than those driven to maximum amplitudes (oscillator plates with high drive); and (4) plates having low rather than high-quality requirements (on activity, temperature-coefficient, frequency adjustment).

Thus, blue needles have long been permitted in some types of large, low-frequency-mode filter elements. While breakage has resulted from the use of blue needles in high-frequency oscillators with very high drive, it is not

known that blue needles may not be used in many other types of oscillators. It is likely that smokiness is less objectionable than blue needles (very lightly-smoky material not recognized as such has been widely used).

A further important factor, often disregarded, is related to high-frequency-mode plates and their method of manufacture, and more specifically to the method of finally adjusting the dimensions to give the required activity, frequency, and temperature characteristic. When such plates are made by the PRE-DIMENSIONING technique, which requires very small tolerances on the machined dimensions and orientation, they are finally finished by hand adjustment of only one dimension, the thickness. On the other hand, when the plates are machined to only moderate accuracy of dimension and orientation, they must be finally hand adjusted on all three dimensions to obtain satisfactory characteristics. By this method of adjustment it is possible to correct, not only for misdimensioning and misorientation, but for small defects in the quartz itself. However, with pre-dimensioning and a single dimensional adjustment practically no correction may be made for errors, or quartz defects. Thus, higher quality quartz may be necessary for manufacture by the pre-dimensioning technique than otherwise.

The conclusions that may be drawn from these considerations are: (1) only by a quantitative statistical study can it be determined whether a given type of defect will be permissible in a given type of finished plate, (2) known usability of a given type of defect in a given type of plate does not prove its usability in a different type of plate (the type includes size, mode of vibration, and required electrical operating characteristics), and (3) the method of manufacture is also related to the usability of defective quartz (i.e., pre-dimensioning vs. non-predimensioning).

Since in the past very little defective quartz has been used in the manufacture of piezoelectric elements, especially oscillators, there is little manufacturing experience that may be used as a guide to its introduction now. The quickest means of obtaining this information, and of making use of the reservoir of defective quartz, would seem to result from trial manufacture first of the most likely to succeed types of plates, from quartz with the most likely tolerable types of defects. If and when this utilization is found to be practical the less likely cases may be examined, while at the same time defective material is being used and experience is being gained in grading the raw quartz into usably defective and non-usably defective. This special grading of quartz will be difficult to control exactly. It will be easier to grade into types of imperfections than into quantities of defects per-unit-volume. Further, it will be easier in manufacturing trials to determine whether a given type of defect is permissible if the defects appear in large quantities, than if in very small quantities (where they may actually be absent in some finished plates). For these two reasons it will be preferable

in trial manufacture, to select for processing stones which have the desired type of defect in large (to maximum) quantities per-unit-volume. Due to the many variables involved in both selection of material and in manufacture, a large quantity of stones must be processed for a fair trial. The criterion of usability of the defective material will then be related to number of usable finished plates (satisfying the required electrical and physical specifications on the finished plate) that can be obtained from a given quantity of raw quartz (and thus to the relative costs of producing satisfactory finished plates from defective and from non-defective quartz).

If and when a type of defect has been shown to be harmful by the above method, steps may then be taken to ascertain if some method of selection or measurement can be made on the defective raw quartz to separate the economically usable from the economically unusable material during inspection.

The New Statistical Mechanics

By

KARL K. DARROW

THIS is the second article upon statistical mechanics which I have published this year in this Journal. The first, which appeared in the January (1943) issue, was devoted to the oldest form of the theory, which is variously known as the old, the classical, or the Boltzmann statistics. The word "statistics," I repeat from the former article, is a synonym for statistical mechanics, objectionable but (because of the length of the alternative) hardly to be avoided. The "new statistics," frequently divided into "the Bose-Einstein statistics" and "the Fermi-Dirac statistics," emerged in the middle twenties and ever since it has been gradually pushing its ancestor aside. In this article I propose to expound the new statistics, laying especial emphasis on the theory of monatomic gases, to which the former article was strictly limited.

A definition of statistical mechanics may well be asked for at this point, especially since in the former article I failed to give one. Like many other things either subtle or familiar, statistical mechanics cannot fully be defined till it is fully understood, by which time a definition may seem nugatory. As an attempt at an advance definition, I suggest that *statistical mechanics is the theory which, starting from the assumption that matter (and, in due course, radiation) is an assemblage of particles, undertakes to explain (1) entropy, (2) temperature, (3) specific heats, and (4) the distribution-in-energy of the particles in thermal equilibrium.* The critical reader may justly say that these are four aspects of a single problem, but I think it well to separate them notwithstanding. The word "particle" often has to be construed as standing for an elaborate structure, but in dealing with monatomic gases (and with radiation) we may let it stand for a point endowed with energy and momentum.

How does the classical statistics succeed in handling these four problems? To take them in reverse order: it does very well with the fourth, for material gases (but not for radiation). It does very well with the third, for monatomic gases (but not for polyatomic gases nor for radiation). It produces an adequate theory of temperature for monatomic gases, identifying the temperature with the mean kinetic energy of the atoms multiplied by a certain factor. It has a very strange adventure with entropy, producing a theory which in part is remarkably successful and in part is disconcertingly

fallacious, and has to be altered in awkward and dubious ways to be made completely successful.

To consolidate these statements and introduce the new theory, I review the Boltzmann statistics.

The N atoms of a gas in a container are represented by N numbered balls, identical in every way except the numbering. In the earlier article a game was proposed in which a collection of numbered baskets was provided for these balls, and the balls were tossed into the baskets in a predetermined way: N_1 of them into the first of the baskets, N_2 into the second, and so on until each of the baskets contained its preassigned number of balls with N_M in the M th or last basket. The set of numbers $N_1, N_2, N_3, \dots, N_M$ was called a "distribution," and the question was asked: in how many different ways can this distribution be realized? It demands a previous answer to another question: how can a given distribution be realized in more than one way? It is the numbering of the balls which makes this possible. If for instance we exchange two balls in different baskets, the distribution is not changed, and yet there is a difference between the second situation and the first, for an inventory of all the balls in all the baskets shows that in those two particular baskets the assortment has been changed. We thus have realized the same distribution in two different ways. If we had exchanged two balls in one basket, this would not have been regarded as a change; we should still be realizing the same distribution in the same way, in the sense of the Boltzmann statistics. It was shown in the earlier article that the number W of ways of realizing a distribution—or in more technical language, the number of complexions in the distribution—is given by the formula:

$$W = N! / \Pi N_j! \quad (1)$$

I have said that in the Boltzmann statistics, the balls stand for the atoms of a gas. For what then shall the baskets stand? The baskets stand for compartments in space; but "space" may have several different meanings.

Giving "space" the ordinary meaning: imagine the gas contained in a box, and the box divided mentally (not physically!) into M compartments of equal volume. I called these by the name of "cells" in the previous article, but now, for a reason which will shortly appear, I rebaptize them "regions." These are the baskets. W has its smallest value, which is unity, when all of the atoms are in the same region. It has its greatest value, which is $N! / ([N/M]!)^M$, when in each of the regions there is the same number N/M of atoms. But this corresponds, as nearly as the picture is able to correspond, to the uniform spreading throughout the box which by vast experience we recognize as the natural permanent state of the gas "in equilibrium." The uniform distribution is outstanding because it has the

greatest value of W . If now we baptize W with the name of "probability," we may then say that the state which in Nature is the prevailing one is in the Boltzmann statistics the most probable one. In the theory it is described by the equation:

$$N_j = N/M \quad (2)$$

Now think of "momentum-space" in which there is a dot for every atom, and the Cartesian coordinates of the dot are the momentum-components p_x, p_y, p_z of the atom. The coordinates of the dot determine the energy E of the atom, by virtue (for material particles) of the relation:

$$E = (1/2m)(p_x^2 + p_y^2 + p_z^2) \quad (3)$$

This is a fact of the first importance, as will shortly appear. Let us divide the momentum-space into regions of equal volume. Each of the regions will correspond to a small range of energy-values, as a sample of which we may take any particular one among them. Therefore when we distribute the dots—or let me say simply, the atoms—in any manner among them, we have perforce a certain value of the total energy U of the gas, which we may consider as preassigned if we so wish. Now we are to compare this distribution only with such others as show the same value of U . Among these there is one which is outstanding because it has the greatest value of W . This was shown in the earlier article to be the canonical or Maxwell-Boltzmann distribution, described by the formula:

$$N_j = NA \exp(-BE_j) \quad (4)$$

in which N_j stands for the number of atoms in the region numbered j ; E_j for the value of E appropriate to that region, *i.e.* obtained by substituting into (3) the coordinates of some point in that cell; A and B for constants, whereof A depends on B while B depends upon U/N the average energy of the atoms of the gas. This distribution also is attested by experiment as being truly that of a gas in its normal natural abiding state of equilibrium.

Now I mention the concept of a six-dimensional space which comprehends both the ordinary space and the momentum-space, and is divided into six-dimensional regions of equal volume. By this device one is able to speak of (2) and (4) as two aspects of a single distribution in the " μ -space." This is the distribution outstanding among those with which it may legitimately be compared by reason of having the greatest W -value. It is the most probable distribution, in the sense given in the Boltzmann statistics to the word "probable."

This is the first triumph of the Boltzmann statistics, attained by numbering the atoms. Its other triumphs, and its ultimate confusion, come when

it copes with the task of interpreting entropy. But if I continue longer this review of the conclusions of the former article, the reader's tolerance may be exhausted. Let us make haste to find out how the newer statistics sets forth to find out the most probable distribution.

One of the most appealing features of the new statistics is, that it does not impose on atoms of a single kind that peculiar distinction which I described above as "numbering" them. We therefore now remove the numbers from the atoms, restoring thus to atoms of a single kind—it might for example be helium—that quality of absolute indistinguishability which the classical statistics took away from them in order to achieve its aims.

Having de-numbered the atoms, we start anew to play that very game with numbered balls and numbered baskets which we played in the classical statistics with such remarkable but incomplete success. But now that the atoms are de-numbered, they can no longer be the balls (nor, for that matter, the baskets). Something drastically new must now be done, and is.

In the new statistics, the balls stand for the compartments and the baskets for the populations.

I must define the word "population." It means the number of atoms in a compartment, or as I will say from this point onward, in a "cell." The balls which are tossed into the basket numbered 0 stand for the cells containing no atoms; the balls which go into the basket numbered 1 correspond to the cells containing one atom apiece, and so forth indefinitely. C_i shall be the symbol for the number of balls in the i th basket, which is to say, the number of cells containing i atoms apiece. C shall stand for the total number of cells.

Let the cells at first be compartments of equal volume in the ordinary space, obtained by dividing up (mentally) the box containing the gas. For the number of complexions or inventories corresponding to a given distribution, defined by given values of the quantities C_i , we have as before:

$$W = C! / \Pi C_i! \quad (5)$$

and taking the logarithm:

$$\ln W = C \ln C - \sum C_i \ln C_i \quad (6)$$

In using this expression I have again, as often in the previous article, assumed the validity of what I there called "the super-Stirling approximation"; but notice that this no longer means that I assume each of the cells to enclose an enormous number of atoms—it means instead that there is an enormous number of cells having each particular population.¹

¹ Clearly this cannot be so for all populations no matter how great! This is a difficulty which also pops up in the old statistics, though there it is not met until the ordinary space is replaced by the momentum-space.

We seek a set of values C_i such that when it is realized, the quantity W shall have a value stationary with respect to all variations δC_i conforming to *two* conditions: first, that the number of cells shall remain the same, which is to say, $\Sigma \delta C_i$ shall vanish; and second, that the number of atoms shall remain the same, which is to say, $\Sigma i \delta C_i$ shall vanish.

Such a set is the following:

$$C_i = C\alpha e^{-i\beta} \quad (7)$$

α and β standing for constants yet to be determined; for taking the first variation of $\ln W$ from (6), we find:

$$\begin{aligned} \delta(\ln W) &= -\Sigma \delta C_i (1 + \ln C_i) \\ &= -\Sigma \delta C_i (1 + \ln C\alpha) + \beta \Sigma i \delta C_i \end{aligned} \quad (8)$$

and the required condition is fulfilled. Assuming without proof that the *stationary* value of W is also a maximum value, and referring to W as the "probability" of the distribution of cells among populations, we have come to the startling conclusion that the most probable distribution is the one given by (7)!

I call this a startling conclusion, because it contravenes our inbred conviction that the natural distribution of a gas in ordinary space is the uniform distribution. Of course, in the last two sentences I have used the word "distribution" in two senses, and this must be rectified at once. What I have just called "the uniform distribution" is the uniform distribution in the *old* sense—the same number of particles in every cell. In the new sense of the word, this is a distribution in which all of the cells have the same population, and therefore in which one basket contains all of the balls. Definitely, this is not, in the new statistics, the most probable distribution! Indeed it is not even a conceivable distribution, for the number of cells is infinite.

To mitigate this clash of theory with experience we can do nothing else than assume our cells to be so tiny that in any region of the gas large enough to be surveyed by observation, there is a mighty number of the cells. Then at worst we can take it from experience that in the normal natural abiding state of the gas the number of atoms in each region will be the same if all the regions are of equal volume, while within each region we can distribute the atoms among the cells as the new statistics tells us to. However, it may yet be possible to come to this conclusion from the theory. In preparation for the effort, I sketch the procedure for evaluating the constants α and β in the distribution (7).

A similar task was set before us in the earlier article: that of evaluating the constants of the Maxwell-Boltzmann law in terms of the total number and the total energy of the atoms. Here for any region we are to evaluate the constants α and β in terms of the number of cells C and the number of

atoms N . The task is greatly eased by the opportunity of using two well-known formulae:

$$1 + x + x^2 + \dots = (1 - x)^{-1} \quad (9)$$

$$1 + 2x + 3x^2 + \dots = (1 - x)^{-2} \quad (10)$$

The start is made from the two self-evident equations:

$$C = \Sigma C_i = C \Sigma \alpha e^{-i\beta} \quad (11)$$

$$N = \Sigma i C_i = C \Sigma i \alpha e^{-i\beta} \quad (12)$$

By putting x for $e^{-\beta}$ and using (9) and (10), the student can easily win through to the results,

$$\alpha = (1 - e^{-\beta}), \quad C/N = e^{\beta} - 1 \quad (13)$$

and then to the final form of the distribution-law (7):

$$C_i = C \frac{C}{N + C} \left(\frac{N}{N + C} \right)^i \quad (14)$$

and finally, after consulting (5), to the expression for the number of ways W_{\max} in which this the most probable distribution—"most probable" in the eyes of the new statistics—can be realized. Its logarithm is:

$$\ln W_{\max} = C \ln \frac{N + C}{C} + N \ln \frac{N + C}{N} \quad (15)$$

This is the most important formula of the new statistics, as will presently be clear.

Divide now the space containing the gas into "regions" of equal size, each comprising the same number C of cells, which number shall be great. For the benefit of those to whom the memory of the previous article may still be vivid, I say now that insofar as there is any correspondence of the new to the old statistics, these "regions" correspond to the "cells" of the older theory. This is the reason why, in my recent brief synopsis of the old statistics, I used the word "region" to replace the word "cell" used in the prior article. Let the subscript j be the marker for these regions, so that N_j shall stand for the number of atoms in the j th region. Put N_j for N in (15). Now each member of (15) refers explicitly to the j th region, and on the left I should put $(\ln W_{(\max)_j})$, but for two purposes—one of which is brevity, while the other will appear in due time—I put $\ln W_j$ instead:

$$\ln W_j = C \ln \frac{N_j + C}{C} + N_j \ln \frac{N_j + C}{N_j} \quad (16)$$

The quantity W_j is an odd sort of "probability" relating only to the contents of the region j . It is, to repeat, the number of ways in which the

most probable distribution of the C cells among the possible populations can be realized, there being N_j atoms in the region. Nothing of the sort appeared in the old statistics.

Now form the product of all of the quantities W_j . This is a "probability" relating to the entirety of all the regions, therefore to the whole of the gas. It is the total number of ways in which the most probable distribution can simultaneously be achieved within each of the regions. It is taken to be the total number of ways in which the most probable distribution of the gas-as-a-whole can be realized; for in the new statistics we have no other way of defining the most probable distribution of the gas-as-a-whole, than this way of subdividing first into cells and then into regions comprising many cells. The symbol for this product shall be W , for although I have already used that symbol in this article, its former meaning is now taken over by $W_{j,i}$, and it is free again. We have:

$$\ln W = \sum \ln W_j \quad (17)$$

the quantities W_j being still those functions of N_j which were shown in (16).

We seek now a set of values of N_j such that when it is realized, $\ln W$, and therefore W also, shall have a value stationary with respect to all variations δN_j conforming to the sole condition that the total number of atoms shall remain the same, which is to say, $\sum \delta N_j$ shall vanish.

It may be recalled that a similar problem arose in the old statistics. I treat it here in a more general and hardly less simple way, by writing the self-evident equation:

$$\delta \ln W = \sum \frac{d(\ln W_j)}{dN_j} \delta N_j \quad (18)$$

For the fulfilment of our wish it is a sufficient condition that all of the derivatives on the right-hand side should have the same value; since than $\delta \ln W$ will be $\sum \delta N_j$ multiplied by a constant, and when one vanishes so will the other. For this it is in turn a sufficient condition that all of the independent variables N_j should have the same value.

Uniform spreading of the atoms among the regions, with equal numbers in all regions of equal size, is therefore the condition in which $\ln W$ has a "stationary" value, which as always is assumed to be a maximum value. With the new definition of probability, the state of uniform spreading becomes the most probable in the new statistics, as with the old definition of probability it was in the old.

We go into the momentum-space to see whether the Maxwell-Boltzmann law results from the new statistics.

The momentum-space is now to be divided into regions of equal size,

each large enough to comprise a great number C of cells and small enough so that the function E of equation (3) may be deemed sensibly constant throughout it; E_j shall stand for the value of E appropriate to the region. (It is convenient to imagine the regions as layers separated from one another by concentric spheres having the origin for their common centre). For each of the regions W_j , the number of ways in which the most probable distribution of the cells among the possible populations can be realized, is given again by (16); and W , the number of ways in which the most probable distribution can simultaneously be achieved within each of the regions, is given again by (17).

We now seek a set of values of N_j such that when it is realized, $\ln W$ shall have a value stationary with respect to all variations δN_j conforming to two conditions: first, that the total number of atoms shall remain the same, which is to say, $\Sigma \delta N_j$ shall vanish; and second, that the total energy of the gas shall remain the same, which is to say, $\Sigma E_j \delta N_j$ shall vanish.

Referring back to (18), we see that for the fulfilment of our wish the following is a sufficient condition:

$$\frac{d(\ln W_j)}{dN_j} = P + QE_j \quad (19)$$

P and Q standing for constants; for when these substitutions are made into every term of the summation on the right of (18), the expression to which $\delta \ln W$ is there equated may be regrouped into one term proportional to $\Sigma \delta N_j$ and one proportional to $\Sigma E_j \delta N_j$, and vanishes when it ought to vanish.

Gone is the comfortable ease with which we disposed of the corresponding problem in the ordinary space! There we did not even have to know what sort of function W_j is of N_j ; whatever it might be, we were able to conclude that N_j must be the same for every region. Here the outcome must depend upon the functional relation between W_j and N_j . There is, however, no ground for apprehension, for though the function in question looks rather involved in equation (16), its derivative is surprisingly simple, and we come with ease to the condition which we seek:

$$\ln(N_j + C) - \ln N_j = P + QE_j \quad (19)$$

which may be rewritten thus:

$$\frac{C}{N_j} = -1 + e^{P+QE_j} \quad (20)$$

This is *not* the Maxwell-Boltzmann law, but approaches that desired law in what I will call the "limit of extreme rarefaction," where the number of cells in the region exceeds manyfold the number of atoms. As C/N_j grows

greater and greater, the first term on the right recedes into relative insignificance; and with an ever-increasing degree of approximation, we have:

$$N_j = NAe^{-BE_j} \quad (21)$$

with NA put for Ce^{-P} and B for Q —which is the Maxwell-Boltzmann law and the law confirmed by experiment.

A helpful and troublesome coincidence between two different quantities

When in the earlier article I used the section-heading repeated just above, it referred to the near-equality between the logarithms of two different numbers: one number being that of all the complexions compatible with the *most probable distribution* (of numbered atoms sprinkled among numbered cells in ordinary space) and the other being that of all the complexions compatible with *all conceivable distributions altogether*. The most probable distribution had so great a share of all conceivable complexions, that no grave error was committed in pretending (so long as we were dealing with $\ln W$) that it actually had them all without exception!

A similar coincidence occurs in the new statistics, and will now be set forth.

Consider the j th region by itself. In (15) I have given the expression for $\ln W_{\max}$, the logarithm of the number of ways in which the *most probable distribution* of cells among populations can be realized. This is now to be compared with $\ln W_{\text{tot}}$, the logarithm of the total number of ways in which *all possible distributions* of cells among populations can be realized. Note that I say "all possible" and not "all conceivable" distributions! The only possible ones are those which are compatible with the fixed number N_j of atoms. This limitation prevents us from proceeding by the easy route of the earlier article. Indeed in order to solve the problem "in how many ways can all possible distributions of cells among populations be realized?" it is necessary, or at any rate customary, to restate it in a very different manner, which is the following:

In how many different ways can N_j un-numbered balls be distributed among C numbered baskets? Two ways are considered as different unless $n_i = n'_i$ for every value of i (n_i and n'_i standing for the populations of the i th basket in the two ways).

Notice that again the balls stand for the atoms and the baskets for compartments in space, as they did in the old statistics! We are playing a new game with the old baskets and the old balls, instead of playing the old game with new balls and new baskets as we have just finished doing. It has to be a new game, for the numbers have been removed from the old balls and the old game is therefore unplayable.

This is, to put it mildly, one of the less perspicuous problems of the

“theory of probability.” I cannot do better than repeat, with slight changes in wording, the process of solution given by the Mayers in their book.² “A distribution is characterized by the number of balls in each of the numbered baskets, since the balls are indistinguishable. Consider the arrangement in a line of the symbols $z_1, z_2, \dots, z_C, a_1, a_2, \dots, a_N$, as for instance,

$$z_1 a_2 a_4 z_8 a_9 z_5 z_4 z_9 a_6 \dots$$

Such an arrangement could be used to define an assignment of N numbered balls, the a 's, to C numbered baskets, the z 's, by adopting the convention that the balls to the right of each numbered z belong to the basket of that number. For instance, the above corresponds to balls 2 and 4 in basket 1, balls 8 and 9 in basket 8, no balls in baskets 5 or 4, and ball 6 in basket 9. One must observe the convention that the row starts with a z , and we shall consider only arrangements of the symbols which start with z_1 . However, $(C - 1)!$ such arrangements of the symbols correspond to one arrangement of numbered balls in the same baskets, since permutations of the $(C - 1)$ groups of each z_i with its following a 's correspond to the same arrangement of numbered balls in the baskets. In addition all $N!$ permutations of the a 's correspond to the same distribution of un-numbered and indistinguishable balls in the baskets. In all, each distribution of the indistinguishable balls among the numbered baskets corresponds to $N!(C - 1)!$ arrangements of the symbols, and the $(N + C - 1)$ symbols (after the first) may be arranged in $(N + C - 1)!$ different ways.”

Thus we come to the formula³ for W_{tot} , the total number of ways in which all possible distributions of the cells of a region among the populations can be realized; it is,

$$W_{\text{tot}} = \frac{(N_j + C - 1)!}{N_j!(C - 1)!} \quad (22)$$

Dropping the “ones” for the amply sufficient reason that they are insignificant by comparison with N_j and C , and taking the logarithm with use of the super-Stirling approximation, we find:

$$\ln W_{\text{tot}} = (N_j + C) \ln (N_j + C) - N_j \ln N_j - C \ln C \quad (23)$$

which with a little regrouping of terms is found to be the very same expression appearing in (15) for $\ln W_{\text{max}}$.

² J. E. and M. G. Mayer, “Statistical Mechanics” (John Wiley & Sons, 1940); p. 438. Reprinted by permission.

³ For the historian of science it is interesting to note that the formula (22) was used by Planck in his earliest derivation of the black-body radiation law. His un-numbered balls were quanta of energy, his baskets were linear oscillators, and his $k \ln W$ was the entropy of the system of C oscillators sharing N_j quanta among themselves. Cf. *Naturwissenschaften*, April 2, 1943.

I review the situation. We began by dividing space (ordinary space, or momentum-space, or μ -space) into what were called cells in the earlier article and are now designated "regions." We wanted to reach, as most-probable-distribution of the atoms among the regions, the uniform spread in ordinary space and the Maxwell-Boltzmann law in momentum-space. To do this by the method of the new statistics, we divided each region into many "cells." The first stage of the argument then consisted in taking a typical region, and ascertaining the most probable distribution of the cells among the populations. We then evaluated W_{\max} , the number of ways in which this distribution could be realized. Inserting $\ln W_{\max}$ into the argument we continued into the second stage, and attained the wanted result. But now it turns out that in the first stage we might have omitted to ascertain the most probable distribution of the cells among the populations in the typical region. Anybody might win through to the same desirable outcome without even suspecting that there is a most probable distribution of cells among populations. All he needs is to evaluate W_{tot} , the number of ways in which all possible distributions of cells among populations within the region can be realized. He may then replace $\ln W_{\max}$ by $\ln W_{\text{tot}}$, and proceed with the second stage as before. Since the two logarithms are practically equal, the outcome is the same.

There are accordingly two routes to the result, which do not merge until the argument is carried partway to the conclusion. Is one of them right and the other wrong? Or to ask a milder question: is either to be preferred to the other?

So far as I can see, neither can be proved wrong, and the question must be asked in the milder form. For myself I stand by the preference exhibited in this article, for the basic reason that along this route each of the stages of the argument consists in finding a most probable distribution: first for the cells among the populations of each region by itself, and then for the atoms among the regions. By the other route the two stages are differently handled, since in the first stage one considers all the distributions (of cells among populations in each region by itself) and then in the second stage the most probable distribution (of atoms among regions). There is also the minor advantage, that the value of W_{\max} is much easier to derive than the value of W_{tot} , or at least so it seems to me.⁴ However, many physicists of eminence have preferred the second route. Anyone may say of course that the question is foolish, since the number of complexions subsumed under the most probable distribution is so large a fraction of the total number of complexions altogether that no danger arises from confusing them. This is what the equations have been saying, and now I have said it again in words.

⁴ It was the other way about in the somewhat similar case which was treated in the earlier article.

Yet any policy which leaves this basic law unsaid, or even fails to emphasize it, is (I think) a bad one for all but the very few to whom it is already obvious.

Another question: may the old statistics be regarded as the limiting form of the new statistics, in the limiting case of "extreme rarefaction" where in every region the number of atoms is very much smaller than the number of cells?

It may seem that this question has already been answered with a *yes*, in view of the fact that in the limiting case the new statistics gives the same distribution-law—in momentum-space as in ordinary space—as the old one does. Nevertheless the answer is *no*. Mathematically this appears in the following way. In the old statistics the Maxwell-Boltzmann law springs from the denominator $\Pi N_j!$ in the right-hand member of equation (1), which turns up as $(-\Sigma N_j \ln N_j)$ in the expression for $\ln W$. Now we look at the equation (23) and see the term $-N_j \ln N_j$ appearing with several other terms in the right-hand member. In the limit of extreme rarefaction it outweighs all the others and survives by itself. We summed it over all the regions and so arrived again at $(-\Sigma N_j \ln N_j)$, from which again the Maxwell-Boltzmann law emerged. But in this method of the new statistics each term of the summation comes by itself from the corresponding region, whereas in the method of the old statistics the whole summation arrived upon the scene *en bloc* or all in a single piece. The former method does not pass into the latter method in the limiting case. The conclusions agree in the limit, but the methods do not.

I have mentioned this because not infrequently one finds in print the careless statement that the old statistics is the limiting case of the new statistics, or words to that effect. Actually one can find more potent ways of contradicting that statement, as for example by emphasizing that the old statistics numbers the atoms and the new one leaves them un-numbered, and in no way can the one policy be regarded as a limiting case of the other. More convincing yet would it be to show that the new statistics and the old lead to results which definitely differ even in the limiting case of extreme rarefaction. This is what I next undertake to show as an incident of the explanation of entropy which the new statistics affords.

THEORY OF ENTROPY

For a substance of a single kind in a single phase, the basis of thermodynamics is the single equation,

$$dU = TdS - PdV \quad (31)$$

in which there are five variables: pressure P , volume V , absolute temperature T , energy U and entropy S . Two may be varied independently, and

any two of the five may be taken as these two, the remainder becoming the dependent variables.

From (31) we deduce, to begin with,

$$T = (\partial U / \partial S)_V \quad (32)$$

an equation which shows that if ever someone sets up a theory in which entropy is expressed as a function of energy and *vice versa*, it is *per se* a theory of absolute temperature. This, however, will find its due place later. What is of instant importance is a second deduction,

$$(\partial S / \partial T)_V = T^{-1} (\partial U / \partial T)_V \quad (33)$$

for making use of which we take note of the fact (not explicitly stated till now) that when the volume does not change no mechanical work is done upon or by the substance, and therefore all of the change in energy is that brought about by the inflow or outflow of heat. This fact is expressed in another equation,

$$(\partial U / \partial T)_V = H_v \quad (34)$$

H_v standing for the amount of heat that must be fed into the substance to raise its temperature, at constant volume, by one degree—the “heat-capacity at constant volume,” as some would call it. Combining the two,

$$(\partial S / \partial T)_V = H_v / T \quad (35)$$

Envisage now the entropy S as a function of volume and temperature, and view the equation:

$$dS = (\partial S / \partial V)_T dV + (\partial S / \partial T)_V dT \quad (36)$$

An equivalent for the coefficient of dT has been provided, and now it is needful to find one for the coefficient of dV . To do this we use the function $(U - TS)$, to be denoted by A , which by aid of (31) is seen to have the following differential:

$$dA = -PdV - SdT \quad (37)$$

Out of this one draws the following two deductions,

$$(\partial A / \partial V)_T = -P, \quad (\partial A / \partial T)_V = -S \quad (38)$$

Differentiating both sides of each of these equations, the former with respect to T while holding V constant, the latter with respect to V while holding T constant, one gets two expressions for what is one and the same quantity, to wit, the second derivative $\partial^2 A / \partial T \partial V$. Equating these two expressions, and saying goodbye to A which has fulfilled its purpose, one has,

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V \quad (39)$$

which by the way is one of four equations collectively known as Maxwell's relations—a memorial of Maxwell's creative work in early thermodynamics, as the name of the distribution-in-energy law is of his work in early statistics.

Substituting from (35) and (39) into (36), we find:

$$dS = (\partial P/\partial T)_v dV + (H_v/T)dT \quad (40)$$

a usable and a useful expression for the entropy S —usable, that is to say, to anyone who knows the heat-capacity H_v and the derivative $(\partial P/\partial T)_v$, as functions of volume and temperature, for the substance in question.

Now take it on faith that there exists a gas having the following qualities: *first*, its pressure and volume and absolute temperature are linked together by the equation,

$$PV = LT \quad (41)$$

L being a constant; whence follows,

$$(\partial P/\partial T)_v = L/V \quad (42)$$

second, if the attempt is made to express its energy U as function of T and any one of the remaining variables (to wit, P or V or S), then the latter variable drops right out of the picture, leaving U as a function of T alone. I suppose this seems a needlessly longwinded way of saying that U does not depend on P or V , but it is necessary to provide for the fact that U may be expressed as (say) a function of S and V , whereupon it will be found that neither variable drops out of the picture. This is one of the features that make the science of thermodynamics very like a maze.

third, the heat-capacity H_v is independent of all the variables.

With these stipulations, (36) becomes:

$$dS = (L/V)dV + (H_v/T)dT \quad (43)$$

integrating which, we readily find that for the peculiar kind of gas presented just above as an article of faith, the entropy is given by the formula:

$$S = L \ln V + H_v \ln T + C \quad (44)$$

The symbol C stands for one of the most useless things in the world: an arbitrary additive constant of integration. The only purpose normally served by such a constant is, to prevent people from thinking that the equation is right if the constant is left off. Its presence means that the absolute value of S is undeterminable, is beyond the reach of experiment to determine. Nevertheless this constant is one of the principal themes of statistical theory; and we shall see that in defiance of what I have just said, and no part of which I retract, it *does* make sense to assign a particular value to this constant, and remarkably good sense at that.

I propose to begin very soon on the proof that the new statistics, applied to a flock of atoms which are merely mass-points, gives an excellent description of just such a gas. However, there is a detail, or rather an element of the structure, waiting to be inserted correctly—a trivial one in appearance, but in all of thermodynamics and all of statistics there is nothing further removed from the trivial. It is the dependence of the entropy on the quantity of the substance, the dependence of S upon N the number of atoms. To put a question seemingly so simple that it almost answers itself: given two samples of the same kind of gas under identical conditions, one comprising twice as many atoms as the other, what is the ratio of their entropies?

This is a remarkable question, because it seems so absurdly simple and is actually so very complex.

Before the advent of statistical theory, anyone versed in thermodynamics would probably have answered it by replying either that S is proportional to N , or that the question has no meaning. The first reply is suggested by the consequences of the fact that thermodynamics proposes no way of measuring the entropy of a gas (or other substance), but only ways of measuring the entropy-difference between two states. Let V_1, T_1 and V_2, T_2 stand for the values of V and T in two states of one gas. Equation (43) informs us that the entropy-difference is $L \ln (V_2/V_1) + H_v \ln (T_2/T_1)$. The constant C has vanished; the remaining terms are proportional to N because L and H_v are proportional to N . The entropy-difference is therefore proportional to N . It seems reasonable to conclude that S is proportional to N , but so long as there is no specific assertion about C the conclusion is not binding; and the proper reply is actually, that the question has no meaning.

But the statistical theories do make assertions about C , and the question is on the verge of acquiring a meaning; so it might be a good idea to ask in advance what sort of answer we should like to have. It seems natural to expect S to be proportional to N , so that the "double sample" shall have twice the entropy of the "single sample" under identical conditions. But what are "identical conditions?" Here is the catch. No more than two of the three variables P, V, T can be made the same for both the samples. I suppose that almost anyone would choose T for one of these two, so unpalatable would it seem to expect the double sample to have twice the entropy of the single sample if their temperatures differed. But after this is decided, shall we make V the same for both, and accordingly give doubled pressure to the double sample? or shall we make P the same for both, and accordingly give doubled volume to the double sample?

This is no mere quibble, for the choice will determine the dependence of C on N .

The first alternative requires that C be proportional to N . This is

obvious from inspection of (44) when one remembers that L and H_v are both proportional to N . I rewrite that equation accordingly, and put N_0 for the number of atoms in a gramme-molecule, R and C_v and RK_0 for the values of L and H_v and C appropriate to N_0 atoms:

$$S = (N/N_0)R \ln V + (N/N_0) C_v \ln T + (N/N_0)RK_0 \quad (45)$$

S is doubled if N is doubled while V and T stay the same, which is what was intended.

This equation will not suit the second alternative; for if V is doubled along with N , S will be more than doubled. Over and above the doubling, S acquires an extra term $2(N/N_0) R \ln 2$. Now if the constant C just happened to include a term $-2(N/N_0) R \ln 2$, the extra term would be obliterated, and S would just be doubled if N and V were to be doubled while P and T remained the same. Such a term is provided by replacing (45) with the equation:

$$S = (N/N_0)R \ln V + (N/N_0)C_v \ln T - (N/N_0)R \ln N + (N/N_0)RK_0 \quad (46)$$

where the last two terms on the right are to be regarded as forming the constant C . This then is the dependence of C on N which is demanded by the second alternative.

To guide the choice between the two alternatives there is, so far as I know, but the one argument; it is, however, a powerful one, and seems likely to hold the field unchallenged.

We have been thinking of two samples of identical gas at identical temperature. Think of them now as divided by a removable partition. When the partition is taken away, what happens? If the initial pressures are not the same, there is a swirling and a surging, dying away in time into a state in which the pressure is the same throughout the volume now common to the samples, but is not the same as it was before in either separate gas. This is just the sort of trend of events with which one likes to think that an entropy-change, and indeed an entropy-gain, is linked. Notice also that if the partition is replaced, the state of affairs on either side does not become the same as it was before! But now suppose the initial pressures to be the same. The partition can be removed and replaced without entailing any perceptible change in the gas such as one likes to associate with a change in entropy.

The second alternative is in harmony with these facts, the first is not. So to the question "is the entropy of a gas of $2N$ atoms double the entropy of a gas of N atoms?" the acceptable answer is: "yes, *if* the volume of the double gas is twice that of the single gas, their temperatures being the same." Now, this is also the answer given by the new statistics; for as we shall presently see, it leads to a formula like (46). It is not the answer given by the old statistics, which (as I said in the earlier article) leads to a formula

like (44). This is one of the dominant reasons for preferring the new statistics to the old.

Now I proceed to the theory of entropy and temperature derived from the new statistics.

NEW STATISTICAL THEORY OF ENTROPY

Entropy is identified with the quantity $\ln W$, multiplied by a constant k which as yet is disposable:

$$S = k \ln W \quad (47)$$

It is now to be shown that for the picture of a gas which is a flock of mass-points in the "most probable state" as defined by the new statistics, and in the limit of extreme rarefaction, this expression becomes the same as (46), with further consequences of much value.

As in the previous article, I separate the entropy into S_v the "contribution of volume to entropy" which springs from the sprinkling of the mass-points in ordinary space, and S_m the "contribution of temperature to entropy" which springs from the sprinkling of the mass-points in momentum-space. This is an artificial separation and worse than artificial, for it leads to a fault in a detail which is not trivial. Nevertheless I think that for ease of exposition the procedure is justified, and the detail will be made correct at the end of the argument.

We must now take (16) down to the "limit of extreme rarefaction." I repeat this equation:

$$\ln W_j = (N_j + C) \ln (N_j + C) - C \ln C - N_j \ln N_j \quad (16)$$

The journey toward the limit is menaced by some of the oddest pitfalls, and must be travelled with care. I recall that by Taylor's expansion, $\ln (N_j + C)$ is equal in first approximation to $(N_j/C + \ln C)$ when N_j is small by comparison with C . Making this substitution into (16), one finds that the right-hand member consists of six terms. The two largest of these, $C \ln C$ and $-C \ln C$, destroy one another. The smallest, N_j^2/C , is to be neglected (if we couldn't neglect it, the dependence of entropy upon N would be hopelessly misrepresented). All of the remaining three terms must be kept, for even the smallest—which is N_j —will play a perceptible part in the check of theory with experiment. We have:

$$\ln W_j = N_j \ln C - N_j \ln N_j + N_j \quad (48)$$

The quantity $\ln W$ is the summation of $\ln W_j$ over all the regions. Notice that we are interpreting entropy in such a way, that the entropy of the gas in the container is the sum of the entropies of the portions thereof in the individual regions. This is why we are destined to come to a result

in harmony with the "second alternative" aforesaid, wherein the total entropy of two gases of identical P and T is the sum of their separate entropies! It is otherwise in the old statistics, and that was the source of the troubles of that elder theory. But to proceed:

$$\ln W = \sum \ln W_j = N \ln C - \sum N_j \ln N_j + N \quad (49)$$

In the ordinary space and in the most probable state, N_j is the same for all the regions, as we have found already (page 363) and therefore is equal to N divided by V/V_0 , or to NV_0/V ; here V_0 is the volume of the *region* (not the cell!). The next step is to put this into (49), realizing now that each term becomes the same and the whole summation is V/V_0 times the typical term. One is agreeably surprised to find that V_0 tumbles out of the expression: this is a feature of the new statistics—the regions have but an intermediate and an auxiliary quality, the size assigned to them is gone from the final equations. In its place appears the volume of the *cell*, which is V_0/C , and which I denote by q_c . For S_c we have:

$$S_c = Nk \ln V - Nk \ln N - Nk \ln q_c + N \quad (50)$$

Note the last three terms, for future comparison with the two last of (46); but at this moment note especially the first, and compare it with the first of (46). Entire agreement is attained by assigning to k the value,

$$k = R/N_0 \quad (51)$$

as in the old statistics. The "Boltzmann constant" k is the "gas-constant" R divided by the "Avogadro number" N_0 .

Seeking now the "contribution of temperature to entropy," S_m , we turn to the momentum-space. Here the most probable distribution is given by (21), and is to be inserted into (50):

$$\begin{aligned} \ln W &= N \ln C - \sum N_j \ln N_j + N \\ &= N \ln C - N \ln A + N \sum ABE_j e^{-BE_j} + N \end{aligned} \quad (52)$$

It will be recalled from the earlier article, or failing this can easily be seen, that,

$$N \sum A^{-BE_j} = N, \quad N \sum ABE_j e^{-BE_j} = U \quad (53)$$

U standing as heretofore for the total energy of the gas. The expression (52) is simplified of aspect, and multiplying it by k , we find for S_m ,

$$S_m = k \ln W = kN \ln C - kN \ln A + kB U + kN \quad (54)$$

Though I have spoken of this as the contribution of temperature to entropy, the temperature is nowhere to be seen! It is waiting on the doorstep; but before allowing it in, I wish to operate on the quantity $\ln A$.

This quantity, by (53), is given thus:

$$-\ln A = \ln \Sigma e^{-BE_j} \quad (55)$$

The so-called "partition-function," which is the sum appearing on the right, is made of terms contributed one from each region, the term from the j th region being $\exp(-BE_j)$ —herein E_j stands (it is proper to say) for the average value in the j th region of the function,

$$E = (1/2m) (p_x^2 + p_y^2 + p_z^2) \quad (56)$$

If the regions were of unit volume, this summation would be (approximately) equal to the triple *integral* of $\exp(-BE_j)$ over the whole of momentum-space. But the volume of each region is $C_j q_m$, wherein q_m stands for the volume of the *cell*. This signifies that while the integral contains one term for each unit of volume, the summation comprises $1/C_j q_m$ terms for each unit of volume. The summation is accordingly $1/C_j q_m$ times as great as the integral. Denoting the integral by I , we have in place of (55),

$$-\ln A = \ln I - \ln q_m - \ln C_j \quad (57)$$

and in place of (54),

$$S_m = kN \ln I - kN \ln q_m + kBU - kN \ln N + kN \quad (58)$$

We note with satisfaction that the size of the *region* has disappeared, even as it did while we were operating in ordinary space!

The next step is to consult a table of definite integrals for the value of the integral I (or to work it out one's self, if one's memory of the mathematical technique is vivid). The tables give:

$$I = (2 \pi m/B)^{3/2} \quad (59)$$

Before returning the table of integrals to the library, the student should also look up the value of the definite integral $\int_0^\infty x^2 e^{-ax} dx$; for with its aid he will be able to find a very simple relation between B and U . I have already said that either determines the other, and now for this special case we shall find the relationship. The procedure consists in going back to the second of equations (53), realizing that

$$\Sigma E_j \exp(-BE_j) = (1/C_j q_m) \iiint E \exp^{-BE} dp_x dp_y dp_z \quad (60)$$

and performing the triple integration over the whole of momentum-space, a feat which is not so hard as it looks. Multiplication by A , as indicated in (53), removes the factor $(1/C_j q_m)$, and the simple conclusion is,

$$U = 3N/2B \quad (61)$$

a relation valuable in two ways.

In the first place, (61) enables us to eject either B or U from the expression for S_m . It seems more sensible to do away with B , leaving S_m expressed as a function of the energy of the gas; but I will let the reader do that for his own instruction. In view of the peculiar significance of B this is for our purposes the better one to keep.

Now it is high time indeed to show what is that peculiar significance. Differentiating S with respect to U , we find kB for the derivative. Turning back to (32) we are reminded that this derivative is $1/T$ by the definition of the absolute temperature T . Now the temperature has stepped across the threshold, and S_m assumes the form:

$$S_m = (3/2) Nk \ln T - Nk \ln N + Nk \ln [(2\pi mk)^{3/2} e^{5/2}/q_m] \quad (62)$$

Notice that the term $+ kN$ has been absorbed into the final term, so that $e^{3.2}$ has been replaced by $e^{5/2}$ in the argument of the logarithm: this is a usage with which the student must become familiar. (Some writers also incorporate $-Nk \ln N$ into this final term, which thereby acquires a factor N in the denominator of the argument; the term then ceases to be a constant, which is why I do not follow this policy.)

Comparing (62) with (46) we see that S_m embodies correctly the dependence of entropy on temperature, provided that C_v (the specific heat per gramme-molecule) is equal to $(3/2)kN_0$. Since a value for k —to wit, R/N_0 —has already been forced upon us as a necessary and a sufficient condition for making S depend correctly on the volume, this new requirement is that C_v should be equal to $(3/2)R$. Now this is a fact of experience for the gases called monatomic!

I said that the relation of U and B expressed in (61) is valuable in two ways. The second is only the first seen from a different viewpoint, for which I rewrite (61) in the form:

$$U/N = U = (3/2)kT \quad (63)$$

For the flock of mass-points distributed in momentum-space in the manner indicated as the most probable by the new statistics (as, for that matter, by the old) the average energy is $(3/2)k$ times the absolute temperature. This is the very result obtained from simple kinetic theory for the ideal-gas scale of temperature. The statistical theory therefore identifies the absolute scale of temperature with the ideal-gas scale, which is as it should be. It is therefore an adequate theory of temperature and (as we lately saw) of the specific heat of monatomic gases.

Now I have given an expression for S_e , the "contribution of volume to entropy," which is (50); and an expression for S_m , the "contribution of temperature to entropy," which is (62); and it seems natural to proceed by

adding the two and identifying their sum with the entropy of the gas. But each of the summands contains the so-ardently-wanted term $-Nk \ln N$, and therefore the sum must contain a term $-2Nk \ln N$, which is $-Nk \ln N^2$. This term is not at all of the wanted form, and its mere presence in $(S_m + S_c)$ spoils the chance of identifying that sum with entropy. We have in fact come to a result in contradiction with equation (46) and with the assumption on which that equation was founded, viz. that if two samples of a gas are at the same pressure and temperature their entropies are in proportion to their volumes. The reasoning has not been suited to its aim.

The origin of this final misadventure lies in the circumstance that in the hope of making easier the exposition, I made what now has proved to be an undue separation between the two "contributions" to the entropy. The gas was mentally divided into groups of atoms, each occupying a certain region of limited size and distribution among the cells of that region according to the law of the new statistics. In computing S_c I defined the j th region as a small piece of ordinary space, and then counted all the atoms in that region regardless of the fact that they have very diversified momenta. In computing S_m I defined the j th region as a small piece of momentum-space, and then counted all the atoms in that region regardless of the fact that they are sprinkled all through the total volume of the container. I may properly say that I used a six-dimensional region throughout, but in the first stage it was a region limited in ordinary space and comprising the whole infinity of momentum-space, while in the second stage it was a region limited in momentum-space and comprising the whole volume of the box in ordinary space. I should instead have carried through the operation in a single stage, using a six-dimensional region limited in both ordinary space and momentum-space. It may seem that this procedure must either lead to the same result as the other, or must be much more difficult, or both. Neither is the case.

Instead of writing down a number of new equations which would look precisely like the old ones, I invite the student to go back to page 368 and recommence the argument at the words "We go into the momentum-space. . . ." If he will replace "momentum-space" by " μ -space," he need make no other change as far along as equation (21); the argument is just the same. Now let him turn ahead to page 379, and equation (52): this is valid for the μ -space as it was for the momentum-space, and so are equations (53). The novelty, however, is latent in the first of equations (53), which reappears as (55), and which I now rewrite for one more time:

$$-\ln A = \ln \sum e^{-BE_j} \quad (64)$$

On page 380, the summation was shown to be equal to $(1/C_j q_m)$ times a certain integral denoted by I ; the integral was over the three dimensions of momentum-space; q_m was the size of the elementary cell in momentum-

space. In μ -space, however, the corresponding integral is over the six dimensions, and may be written thus:

$$\iiint dx dy dz \iiint e^{-BE} dp_x dp_y dp_z$$

This sixfold integral is nothing but the product of V the volume of the container (resulting from the first three integrations) by the integral heretofore denoted as I (resulting from the last three integrations). It is to be multiplied by $(1/C_j h^3)$, C_j now standing for the number of cells in the six-dimensional region and h^3 for the volume of the six-dimensional cell (I explain the curious symbol later). The product is the reciprocal of A , and therefore:

$$k \ln W = kN \ln V + \ln I + kBU - kN \ln N + kN - kN \ln h^3 \quad (65)$$

The term $(-kN \ln N)$ appears just once, and not twice as it did in the sum S_c and S_m : all is well in this regard. The presentation of I , of B and of U as functions of T follows just the same lines as above.

(Notice, for future reference, that we should have attained to the same result had we ignored the ordinary space, operated in the momentum-space exclusively, and assigned the value h^3/V to the volume of the elementary cell in momentum-space.)

So, identifying $k \ln W$ with S , we come to the consummation of the new statistical theory of entropy, the equation:

$$S = kN \ln V + (3/2)kN \ln T - kN \ln N + kN \ln [(2\pi mk)^{3/2} e^{5/2} / h^3] \quad (66)$$

The dependence on volume is right; it was qualitatively so to start with, was made exactly so by choice of the value of k as R/N_0 . The dependence on temperature is exactly right, since it is a fact of experience that for monatomic ideal gases the specific heat at constant volume is $(3/2)R$ per gramme-molecule. The dependence on number of atoms is exactly right, that is to say, it makes S proportional to N for given P and T . The additive constant is fixed in value absolutely, or will be when we assign a numerical value to h^3 ; for k is a universal constant, e the base of natural logarithms, and m the mass of an atom of the gas.

For the benefit of such as may still be interested in comparing the old statistics with the new, I recall that the old statistics in its theory of entropy furnished the first and the second terms of (66), and apparently furnished also the fourth term though with $e^{3/2}$ in place of $e^{5/2}$. The third term it omitted, thereby lending itself to the untenable doctrine that entropy should be proportional to N for given V and T (and not for given P and T). Since there was no term $kN \ln N$, I committed no error when in the previous article I deduced S_c and S_m separately and then added them together to get S .

This procedure is right in the old statistics, becomes wrong in the new. I suppose that this is what some expositors mean when they say that in the new statistics there is a correlation between positions and momenta, or words to that effect. I say that the old statistics *apparently* furnished a term equal to the fourth of (66) except for the power to which e is raised. Actually the old statistics gives an additive term $Nk \ln [(2\pi m k e)^{3/2}/Q]$ and the new statistics gives an additive term $Nk \ln [(2\pi m k)^{3/2} e^{5/2}/Q]$, but Q in the former case is the volume of the *region* and in the latter case is the volume of the *cell*. Giving the same value h^3 to Q in the two cases is positively *not* doing the same thing. However by doing this notwithstanding, and by "tampering" with the old statistics in a certain way which I described at the end of the previous article, it is possible to produce an expression exactly like (66).

SIZE OF THE ELEMENTARY CELL

We have reached the final step, which consists in assigning a value to the size of the elementary cell in μ -space. For this I have used the symbol h^3 , implying (as everyone has guessed already) that it is taken to be the cube of Planck's constant h so promiscuously found in Nature. What arguments can be advanced to justify this choice?

It may be remarked very simply, that since the volume of the elementary cell has the "dimensions" of the cube of the product of length by momentum, and since these are also the dimensions of h^3 , and since both h^3 and that volume are very fundamental things, what could be more natural than to identify them the one with the other? This was the argument used when formula (66) was first derived from the old statistics with the aid of judicious tampering.

An argument more precise of aspect may be adduced from wave-mechanics. Imagine the box containing the gas to be a cube, its edges—these being of length L so that $L_3 = V$ —being along the coordinate-axes x, y, z . The doctrine of wave-mechanics avers that the momentum-components p_x, p_y, p_z of any atom are perforce integer multiples of $h/2L$; for this is the condition that the waves which are associated with the atom shall form a stationary wave-pattern with nodes at the walls of the cube, and upon this condition wave-mechanics is insistent.⁵ Now let us reenter the momentum-space, and place a dot at every point for which p_x, p_y and p_z are integer multiples of $h/2L$. The dots form a cubic lattice, and it would seem very

⁵ The wave-length of the waves associated with a particle moving parallel to the x -axis is h/p_x , and there must be an integer number of half-wave-lengths between the walls of the cube which are perpendicular to the axis of x and face one another at a distance L . The same may be said, *mutatis mutandis*, of a particle moving parallel to the axis of y or z , with momentum p_y or p_z ; while if an atom is moving obliquely so that two or all three of its momentum-components differ from zero, each of these components is to be treated as if it alone existed.

nice if I could say at once that the elementary cube of this lattice has the volume h^3/L^3 which is h^3/V . However, this cannot be said, for there is an obstinate factor which makes the elementary cube have the volume $h^3/8L^3$. People get around this by remarking that since an atom reverberating to and fro between the walls of the cube changes the sign of one of its momentum-components whenever it strikes against one of the walls, therefore every dot is one of a group of eight dots all of which correspond to the same motion of the atom, and all eight should be counted as though they were one.⁶ Therefore in the region of momentum-space enclosed between any two spheres centred at the origin (such as we used in determining the distribution-in-momentum) we are to count one-eighth of the dots. The number so obtained is the same as the number of cells of volume h^3/V contained in the region. Thus it comes to the same thing whether one says that the atoms are distributed among one-eighth of the dots or among cells of volume h^3/V . Now I recall my remark (page 383) that equation (66) down to the last detail can be derived by playing the game of balls and baskets by the rules of the new statistics *in the momentum-space alone*, provided that to the elementary cell in this space we assign the volume h^3/V . For doing this last, wave-mechanics has now offered a kind of retroactive basis. There seem to be flaws in the basis, but they are of a kind which cannot be mended (if at all) without a thorough study of a very hard subject, to wit, the art of interpreting wave-mechanics in the ordinary language of space and time.⁷ I think it will be better to proceed at once to the test by experiment.

TEST BY EXPERIMENT OF THE NEW STATISTICAL FORMULA FOR ENTROPY

Enough has been said already to cover the first three terms of the formula (66), which correctly give the dependence of entropy S upon volume V , temperature T , and number of atoms N . The present question is: what does experiment say of the fourth term, the additive constant which involves the mass m of the atom and the universal constants k and h ?

Having treated this question at length in the June 1942 issue of this Journal, I will here give only the barest outline. For this purpose I rewrite (66), by the aid of the equation of state of the perfect gas,

$$PV = NkT \quad (67)$$

⁶ If (a, b, c) are the coordinates of one dot, those of the other seven of its group are: $(a, -b, c)$; $(a, b, -c)$; $(a, -b, -c)$; $(-a, b, c)$; $(-a, -b, c)$; $(-a, b, -c)$; $(-a, -b, -c)$.

⁷ In previous pages I said that the proper way of playing the game of balls and baskets is to play it in the six-dimensional space, with N_j representing a definite number of atoms located in a six-dimensional region which is composed of a narrowly-limited region in ordinary space and another narrowly-limited region in momentum-space. Wave-mechanics, in the current interpretation, will not allow this; it claims that, if the N_j atoms are located in a limited region of momentum-space, they are spread all over the box containing the gas.

so as to give entropy S as function of *pressure* and temperature:

$$S = -kN \ln P + (5/2)kN \ln T + kN \ln \left[\frac{(2\pi m)^{3/2} (ke)^{5/2}}{h^3} \right] \quad (68)$$

Notice that here every term is strictly proportional to N , in accordance with the "second alternative" of page 377.

Let P and T be so chosen that the gas is in equilibrium with its solid crystalline phase. To keep this choice in mind, I will replace T by T_s , signifying "temperature of sublimation" at pressure P . Let the N atoms of gas now be cooled to the absolute zero. First they will condense, still at temperature T_s , into the crystalline solid. In so doing they will disgorge the "heat of sublimation," L per gramme-molecule, amounting to NL/N_0 ; and their entropy will decline by NL/N_0T_s , since the process is reversible. Let the cooling continue. As the crystal declines in temperature from any T down to $(T - dT)$, it disgorges heat in the amount of $(N/N_0)C_p dT$ and entropy in the amount of $(N/N_0)(C_p/T)dT$; here C_p stands for the specific heat (per gramme-molecule) of the crystal. The pressure is supposed to remain the same throughout the entire process. When the crystal arrives at absolute zero, its entropy has the value:

$$S_0 = -kN \ln P + (5/2)kN \ln T_s + kN \ln \left[\frac{(2\pi m)^{3/2} (ke)^{5/2}}{h^3} \right] \\ - (N/N_0)(L/T_s) - (N/N_0) \int_0^{T_s} (C_p/T) dT \quad (69)$$

The right-hand member of this equation embodies the new statistical theory of entropy. If on the left I put the value *zero* for S_0 , I express what is known as "Nernst's Heat Theorem" or the "Third Law of Thermodynamics." If experiments say that the right-hand member of (69) is equal to zero, they ratify not indeed the statistical theory by itself or the Third Law by itself, but the assumption that both are true. Now, this is what the experiments *do* say. Better to describe the situation, they say that the first three terms on the right of (69) are equal to the last two terms with sign reversed. All of the noble gases have been tested with suitable accuracy, and eight or nine of the metals with accuracy not so high, yet better than "order-of-magnitude accuracy." For further details I must refer to my article already cited.⁸

⁸ I cannot refrain from mentioning a detail of the statistical theories, which is amusing if one sees it at once and confusing if one sees it belatedly (mine was the latter experience). It pertains to the power to which e is raised in the third term on the right in (69). If in the new statistical theory we leave out the term N in (49), thus stopping with a first approximation instead of going on to the second, we arrive ultimately at $e^{3/2}$ instead of $e^{5/2}$. If in the old statistical theory as modified by Tetrode we use the first-order Stirling approximation instead of the second-order one for $N!$, we arrive ultimately at $e^{3/2}$ instead

THEORY OF RADIATION

Black or total radiation, which is the electromagnetic radiation within a cavity enclosed by walls at a uniform temperature, may be regarded as a monatomic gas of which the atoms are called "photons." It has two peculiarities. First, the relation between energy and momentum is not the same for a photon as for a material atom. If by p I represent the magnitude $\sqrt{p_x^2 + p_y^2 + p_z^2}$ of the momentum, then the energy E is given no longer by the familiar equation (3), but rather by this one:

$$E = pc \quad (70)$$

c standing, of course, for the speed of light. This is no insignificant change, but recedes into secondary importance when compared with the other contrast. Not only the distribution-law for the photons, but the actual total number of photons itself, is fixed by Nature when the temperature of the walls of the cavity is fixed by the observer. To the quantity called N , the number of atoms in a container of volume V , no specific value has ever yet been assigned in these pages; for with a material gas it may be raised or lowered at will, by pumping gas into or out of the box. In this section, however, it will have to have a value, for Nature has given it one.

Can the theory achieve what Nature demands of it? It can, and this is the way.

The momentum-space is divided as heretofore into regions of equal volume, each containing C cells of volume q_m . A distribution is described by giving the number of photons in each region, N_j standing for the number in the j th region. The probability W of a distribution is given as always by the formula (16) and this is it:

$$\ln W = \sum \ln W_j = \sum [(N_j + C) \ln (N_j + C) - C \ln C - N_j \ln N_j] \quad (71)$$

We are not now proceeding to the limit of extreme rarefaction! Radiation presents itself to us under conditions remote from this limit, and must be treated without recourse to the approximation hitherto used in these pages.

When the quantities N_j are altered by the small amounts or "variations" δN_j , W undergoes the slight alteration or variation given thus to first approximation:

$$\delta W = \sum \left(\frac{\partial W}{\partial N_j} \right) \delta N_j = \sum [\ln (N_j + C) - \ln N_j] \delta N_j \quad (72)$$

of $e^{5/2}$ (see the text preceding equation (35) of the prior article on page 134 of the January issue of this Journal). Thus in both cases we arrive at $e^{3/2}$ or $e^{5/2}$, according as we pause at a first approximation or go on to a second; *but* I discern no mathematical or physical similarity whatever in the two situations in which these approximations are made.

In the quest for the "most probable distribution" this quantity is required to vanish for variations which are controlled by a certain condition.

On a previous page (368) where we were dealing with *material* atoms in *ordinary* space, the sole condition was that the total number of atoms should remain the same (and equal to N). This led to the uniform distribution, $N_j = \alpha$; here α stands for a constant, which turns out to be the product of N by the ratio of the volume V_0 of the region to the volume V of the box.

On another previous page (369), where we were dealing with *material* atoms in *momentum* space, the condition imposed was twofold: that the number of atoms N and the total energy U of the atoms should remain the same. This led to the distribution (20), which in the limit of extreme rarefaction became the Maxwell-Boltzmann or canonical distribution $N_j = NA \exp(-BE_j)$; here E_j stands for the energy-value appropriate to the j th region, and A and B for two constants which were shown to be determined by N and U .

In this case where we are dealing with *photons* in *momentum* space, the condition which leads to the right result is simple but surprising. We must admit only such variations as leave the total energy constant, but we must *not* require that the total number of photons should likewise remain the same. Applying this strange condition, we find it taking the form,

$$\ln(N_j + C) - \ln N_j = BE_j \quad (73)$$

with only one constant, which is going to be controlled by the total energy U . Rewriting this:

$$\frac{N_j}{C} = \frac{1}{e^{BE_j} - 1} \quad (74)$$

One sees immediately that N , which is the sum of all the quantities N_j , is no longer at liberty to take whatever value the experimenter pleases!

Hitherto I have assumed that all the regions are of equal volume, but I can free myself from this assumption by pointing out that N_j/C is the average number of photons per cell in the portion of momentum-space where E has the value E_j . Now let us carve up the momentum-space into regions separated by spherical shells all centred at the origin. The region extending from the sphere of radius p to the sphere of radius $p + dp$ will be of volume $4\pi p^2 dp$, and will accordingly contain $4\pi p^2 dp/q_m$ cells, if by q_m I denote the volume of a cell. The appropriate value of E will be pc . The number of photons in the region will accordingly be given thus:

$$dN = \frac{4\pi p^2}{q_m} \frac{1}{e^{Bpc} - 1} dp \quad (75)$$

Unrecognizable as it may seem, this is actually a statement about the spectrum of black radiation! This is because a photon of momentum p and energy pc is associated with light-waves of wave-length given by the "Rule of Correlation":

$$\lambda = \frac{h}{p} \quad (76)$$

If I therefore multiply both members of (75) by pc , I have an expression for the amount of energy associated with the waves ranging in wave-length from h/p to $h/(p + dp)$.

There are instruments able to sort out the waves of different wave-lengths with their associated photons; they are called spectroscopes. There are instruments able to indicate the total energy borne by the photons thus sorted out; they are called by such names as bolometer and thermopile. There are people able to use these instruments; and so (75) can be tested. It is customary to rewrite (75) so that either wave-length or frequency becomes the independent variable, in place of p ; but nothing would be gained for the purpose of this article by doing so. The fact of experience is, that (75) is a correct description of black radiation provided that three modifications be made:

a) For q_m we are to write h^3/V , presuming that this comes to the same as though we had operated in six-dimensional space and put h^3 as the volume of the elementary cell therein (page 383);

b) For B we are to put $1/kT$;

c) We must double the right-hand member of (75), the factor 2 being ascribed to the fact that light is polarizable.

Making these modifications, and putting $V = 1$ so that the forthcoming equation shall refer to the radiant energy contained in *unit* volume, we have

$$dN = \frac{8\pi p^2}{h^3} \frac{1}{e^{pc/kT} - 1} dp \quad (77)$$

for the number of photons in unit volume endowed with momenta between p and $p + dp$, energies between cp and $c(p + dp)$. This is the distribution-formula for black radiation of temperature T , commonly known as "Planck's law."

To have derived this law is the first, the great and the historic achievement of the new statistics. Other ways have indeed been found for deriving it, beginning with Planck's own; but the way of the new statistics is smoothest and quickest. Quite different is this story from that of the theory of material gases! There, the distribution law was correctly given by the old statistics long before it was tested. Here, the distribution-law was found

by experiment years before it was explained, and a great puzzle it was. There, the old statistics and the new (in the limit of extreme rarefaction) led to the same result. Here the old statistics was impotent, and the new had to be invented.

Reverting to the identification of B with $1/kT$: this may be proved in the following way⁹. Refer back to equations (74) and (71), and for ease of operation write x_j for $(e^{BE_j} - 1)^{-1}$. We then have:

$$N_j = Cx_j \quad (78)$$

$$S = k \ln W = k \sum \{C(1 + x_j) \ln [C(1 + x_j)] - Cx_j \ln [Cx_j] - C \ln C\} \quad (79)$$

$$U = \sum N_j E_j = C \sum E_j x_j \quad (80)$$

Differentiate S with respect to B and do the like with U , and divide the former derivative by the latter, so as to get the derivative dS/dU . It will be found that this is equal to kB ; and since by definition of absolute temperature it is also equal to T^{-1} , the identification is made.

THE BOSE-EINSTEIN AND THE FERMI-DIRAC STATISTICS

Hitherto in this article, except for one protective allusion, I have spoken as if the new statistics were one and indivisible. There are, however, two branches of it, known respectively as the Bose-Einstein statistics and the Fermi-Dirac statistics. It is the former of which I have treated throughout this essay. The point at which the latter branches off is to be found on page 365, where I introduced the game of balls and baskets, the balls standing for cells and the baskets for populations. On reaching this point the game is to be played with the supplemental assumption that there are only two baskets, those numbered 0 and 1. That is to say: a cell may either be empty or may contain a single atom, but never more than one.

I leave to the student the task of revising equations (7) to (16) accordingly, but I take it upon myself to point out how easily the problem can be solved by the second method—that of pages 370–71, the method involving the counting of *all* the different ways in which un-numbered atoms can be distributed among numbered cells. In the Bose-Einstein case the fundamental formula is (22), which is not very easy to derive. In the Fermi-Dirac case we proceed by playing anew the game of balls and baskets. There are but the two baskets, one being set out to receive the balls corresponding to the empty cells and the other for the cells containing one atom each—the “filled cells,” we may call them. There being in the j th region N_j atoms and C cells all together, the first basket is destined to contain $(C - N_j)$ balls and the second to contain N_j . The question is then: in how many

⁹I am indebted for this proof, as well as for much other assistance in the preparation of the article, to Dr. L. A. MacColl.

ways can C numbered balls be distributed among two baskets, these to contain $(C - N_j)$ and N_j of the balls respectively, two ways being considered as different unless the inventory of each basket is just the same for both ways? But this is the problem set up and solved in the earlier article, though there the balls stood for atoms and the baskets for regions. The answer is:

$$W_{\text{tot}} = C! / (C - N_j)! N_j! \quad (85)$$

instead of equation (22). Using the first or second order Stirling approximation—it doesn't matter which—one comes to the analogue of (23), which is:

$$\ln W_{\text{tot}} = C \ln C - (C - N_j) \ln (C - N_j) - N_j \ln N_j \quad (86)$$

Different as this looks from (23), the two become alike in the limit of extreme rarefaction, and in this limit equation (48) expresses the result both of the Bose-Einstein and of the Fermi-Dirac statistics. Since equation (48) is the parent of the Maxwell-Boltzmann distribution-law and of the expression (66) for the entropy of a monatomic gas, both of these flow from either type of statistics, and experiment does not decide for either over the other.

When we avoid the limit of extreme rarefaction, the two forms of statistics *do* depart from one another. If photons obeyed the Fermi-Dirac statistics, the distribution-law for black radiation would not be (75). We should be obliged, in the denominator on the right-hand side of that equation, to replace the negative sign of the second term by the positive sign. In so doing we should contradict the data of experiment in an unmistakable way; and for photons accordingly, the Fermi-Dirac statistics is to be rejected.

This form of the new statistics being no better than the other for material gases, and definitely wrong for radiation, where is it to be preferred and why?

To answer the first question, I point to the "electron-gas" which pervades the metals and is accountable for their quality of being excellent conductors. Experiment (as I recounted in these pages fourteen years ago¹⁰) confirms that these intra-metallic electrons form a gas which obeys the Fermi-Dirac statistics. It is not, however, the limit of extreme rarefaction which here we meet but the opposite one, the limit of extreme condensation. These electrons are as densely concentrated as the atoms of the solid itself, a degree of condensation never even approached by any ordinary gases. In this limit the distribution-law attains a form entirely different from both the Maxwell-Boltzmann law and the black-radiation law, and very remarkable. I dare not, however, expose this article to the risk of a doubling in length, which a treatment of this topic would probably entail; and I can avoid it with a fairly clear conscience, for the experimental evidence that electrons

¹⁰ This Journal, 8, 672 (1929); also *Physical Review Supplement* (Reviews of Modern Physics) 1, 90 (1929).

obey the Fermi-Dirac statistics has been enlarged but little since my article of 1929.

As for the second question, I can give only the shadow of an answer. The reason for adopting sometimes the Bose-Einstein and sometimes the Fermi-Dirac statistics springs from wave-mechanics, and that requires an article of its own. I can say, without proof, that the choice depends upon the number of elementary particles in the atom. The gas is supposed to conform to the Bose-Einstein or the Fermi-Dirac statistics, according as that number is even or odd. An electron is an elementary particle all by itself, wherefore the preceding paragraph.

For material gases, the crucial number is obtained by adding up the numbers of the protons and the neutrons in the nucleus, and the number of orbital electrons which surround the nucleus and complete the atom. In nature the atoms for which the crucial number is even vastly outnumber those for which it is odd, and the Bose-Einstein statistics is therefore the prevalent one. The principal isotope of nitrogen and the second isotope of hydrogen do indeed belong to the rarer category, but in the gaseous state their atoms always pair themselves into diatomic molecules, a circumstance which restores these gases to the realm of Bose and Einstein. A detail in the band spectrum of a diatomic molecule is available for telling which form of statistics the individual atom would obey if free; it confirms what I have just been saying—but this is an intricate story.

Electromagnetic Waves

A Textbook* (530 pages, \$7.50 net) by S. A. Schelkunoff, published by D. Van Nostrand, Inc., New York City, 1943.

THIS new addition to a well-known series has been awaited with much interest by all those acquainted with Dr. Schelkunoff's contributions to propagation theory, and it will be found that their expectations have been entirely fulfilled. This monumental piece of work is equally remarkable for the originality and consistency of its approach as for the wealth of information contained in its five hundred densely packed pages.

The author's systematic use of the harmonic oscillation, with complex variables and coefficients, is in line with the marvelous development which has occurred in the communication field during the last fifty years. Alternating current theory, then acoustics, then vibrational mechanics successively dropped the differential equations which physics offered as a basis and systematically restricted themselves to harmonic oscillations. This has resulted in the replacement of the differential operator by $i\omega$, leading to a tremendous simplification of steady-state analysis, which has been reduced to the calculation of amplitude ratios and phase differences. The genuinely difficult problems have not disappeared for all that but are now relegated to Fourier or Laplace transform theory, and it has become apparent that an enormous field of application can be covered by purely algebraic processes.

Not the least advantage of this method has been the unification brought into the three chapters of technical science mentioned above. Electrical impedances gave the model after which acoustical and mechanical impedances were fashioned; and mixed mutual impedances, thereafter, made it possible to write the equations of electro-mechanical or acoustico-mechanical transducers. There was an exciting era of intense development in this field during the twenties; and it was amusing to hear at that time, and even a good deal later, irate die-hards denouncing "impedances" with bitter irony or viewing with alarm the spread of "analogies."

Dr. Schelkunoff has set about to carry this point of view into Electromagnetic Theory, and it may well be that his will be the honor of having brought into the fold of harmonic oscillation theory the last chapter of Physics which still had to be incorporated. (One might think of Optics, but of course half of the book is really Optics.) Having given, in the first pages of his fourth

*This review by P. Le Corbeiller is reprinted from *Quarterly of Applied Mathematics*, Vol. 1, No. 2 by permission of the editors. Mr. Le Corbeiller, until coming to the United States where he has joined the faculty of Harvard University, was an engineer with the Administration Française des Postes, Télégraphes et Téléphones.

chapter, a short and quite personal derivation of Maxwell's equations (1-15, p. 69), Dr. Schelkunoff without taking breath adds immediately: "Since we are concerned primarily with fields varying harmonically with time, we replace the instantaneous field intensities and current densities by the corresponding complex variables and write Maxwell's equations as follows:

$$\begin{aligned} \int E_n ds &= - \iint i\omega\mu H_n dS - \iint M_n dS, \\ \int H_n ds &= \iint (g + i\omega\epsilon) E_n dS + \iint J_n dS." \end{aligned} \quad (1-16)$$

Thus the sacrosanct Maxwell equations are swept away with movie-like swiftness, and instead we have the steady-state equations of a medium characterized by a distributed series impedance $i\omega\mu$ and a distributed shunt admittance $g+i\omega\epsilon$ (p. 81).

The analogy with a transmission line whose series inductance is μ , shunt conductance g and shunt capacitance ϵ , all taken per unit length, is inescapable (p. 243). In particular the above primary constants simply beg to be transformed into the familiar secondary constants of transmission line theory; here the intrinsic propagation constant σ and the intrinsic impedance η are defined by

$$\sigma = \sqrt{i\omega\mu(g + i\omega\epsilon)}, \quad \eta = \sqrt{\frac{i\omega\mu}{g + i\omega\epsilon}} \quad (9-1)$$

(p. 81) (σ is in neper/meter, η in ohms; the book is written in MKS—p. 60). For free space we shall have $g = 0$, and the following numerical values of the fundamental constants (p. 82):

$$\begin{aligned} \text{impedance of free space } \eta_0 &\approx 120\pi \text{ ohms,} \\ \text{characteristic velocity } v_0 &\approx 3.10^8 \text{ meters/second.} \end{aligned} \quad (9-4)$$

* * *

Surprising as it may appear to transmission engineers and sound engineers, who daily handle their respective characteristic impedances Z_0 or ρc , there still are very competent physicists who balk at the idea of free space having a characteristic impedance of about 377 ohms. Yet, in the words of Professor Ronold W. P. King:¹ "The existence of such a characteristic resistance for electromagnetic effects is just as mysterious, but not more so, than the existence of the finite velocity v_0 ." Dr. Schelkunoff explains very well how this constant could have been overlooked by the builders of the classical theory: "The physicist concentrates his attention on one particular wave: a wave of force or a wave of velocity or a wave of displacement. His original differential equations may be of the first order and may involve both force and

¹ Mimeographed "Notes on Antennas" for the course of Electronics and Cathode Ray Tubes (Eng. 270), Harvard University.

velocity; but by tradition he eliminates one of these variables, obtains a second order differential equation in the other and calls it the 'wave equation.' Thus he loses sight of the interdependence of force and velocity waves . . ." (p. vii). Still, it is surprising to see that one has started with two constants ϵ_0 and μ_0 , and recognizing the fundamental importance of their product, yet has not enquired about their ratio.

Then, the reader will ask, how can the Theory of Relativity give a leading role to the velocity of light and not mention the impedance of free space. Has Einstein no use for η_0 ? Well, he has, and he has not. First, an essential point in Special Relativity is the merging of the magnetic and the electric fields into one skew-symmetrical tensor. When doing this in the MKS system, homogeneity requires the use of the components of E and of $\eta_0 H$; but the factor η_0 is not apparent, for instance, in the equations on p. 44 of "The Meaning of Relativity" (by A. Einstein, Princeton Univ. Press, 1923) which uses a system of units in which $\eta_0 = 1$. Secondly, if we try to connect the universal constant η_0 with other members of this interesting family, we find that η_0 times a (charge)² has the dimensions of "action," and more precisely that

$$\eta_0 e^2 = \frac{2h}{137}$$

(e = charge of the electron, h = Planck's constant). We see from this that there is more to η_0 than appears in Special Relativity, the first step in the successive Einsteinian extensions of Maxwell's theory.

* * *

We have dealt at length with this question of the "impedance of free space" because it exemplifies the spirit of the whole work. It occurs in the course of a short but apt presentation of the "Fundamental Electromagnetic Equations" (Chapter IV), immediately applied to harmonic oscillations. The book as a whole is devoted not to Electromagnetism in general but, as specified in the title, to *Electromagnetic Waves*.

Three preliminary chapters introduce the more advanced mathematical tools which will be used, but sparingly, in what follows: such topics as contour integration, Bessel and Legendre functions. Chapter V is a short and original presentation of Network Theory.

The central part of the book begins with Chapter VI, "About Waves in General," a sort of preview of the questions which will be treated in detail later, during which we are introduced to radiation from given currents, propagation along wave guides, and to such general tools as electric and magnetic current sheets, the method of images and conformal representation.

In the following four chapters, we meet the most thorough treatment

² See *Quarterly of Applied Mathematics*, 1, 78 (1943).

available of the propagation of waves, guided or bounded, in one, two and three dimensions. It is impossible to do justice here to the richness of the material, which must have cost tremendous labor and which is in great part taken from the author's own publications. We find in Chapter IX, however, classical problems of Fresnel optics, adroitly adapted to contemporary radio needs. Chapter XI is a relatively short treatment of antenna theory, principally of conical antennas, and in the last chapter we return to wave guides and solve various problems involving discontinuities, even to an iris or a transversal wire. This subject is still under development by the author, and the readers of the *Quarterly* have had the benefit of one of its recent extensions.²

The specialist in wave propagation has no need to be told of the value of this book; but the reviewer would like to explain to his fellow non-specialists why it is particularly important that they should not miss it. When the results of much present-day research will suddenly be made available, it will be a hard task to catch up, not only with the new knowledge, but still more with the new modes of attack. The borderland between radio and optics is one of the fields from which great things can confidently be expected. Dr. Schelkunoff's book is a great opportunity for those not at present engaged in research to get familiar with methods which they will want to use tomorrow.

P. LE CORBEILLER.

Abstracts of Technical Articles by Bell System Authors

*Paracon—A New Polyester Rubber.*¹ B. S. BIGGS and C. S. FULLER. Paracons are high molecular weight linear polyesters which are soft enough to be rubbery and are capable of undergoing a vulcanization reaction. They are prepared by the condensation of dibasic acids with glycols or by the self condensation of hydroxy acids, and the name is intended to signify "condensation rubber." Paracon looks and feels like rubber, and in comparison with other rubbers it has some distinct advantages and some definite limitations. Its outstanding properties are oil resistance, high heat and light resistance, lack of odor and fast curing cycle. Tensile strength ranges from 1500 to 3000 pounds per square inch with elongations of 400 to 600 per cent.

Rubber pigments and compounding techniques may be used with it but vulcanization is accomplished in most cases by the action of benzoyl peroxide rather than sulfur.

Aside from its practical aspects the development of paracon is of theoretical interest because of the light it throws on rubber structure and the mechanism of vulcanization processes.

*Unsaturation of Butadiene and Related Polymers as Determined by Iodine Chloride Addition.*² A. R. KEMP and HENRY PETERS. This paper describes procedures which have been developed to determine the unsaturation of various butadiene and related polymers and copolymers, as well as mixed vulcanizates of Buna S and rubber. These methods are based on the use of *p*-dichlorobenzene as a solvent and iodine chloride as the addition agent, following the general technique employed in the standard Kemp-Wijs method for the determination of the unsaturation of natural rubber.

The ratio of butadiene to styrene in copolymers has been calculated from the iodine value and from the carbon-hydrogen ratio; however, the accuracy of these procedures is subject to several variables which are discussed.

Unsaturation data are presented on highly purified emulsion-type polymers of butadiene-isoprene and butadiene-styrene which agree closely with the presence of one double bond for each diolefin molecule present. The reaction rate of Buna S with halogens is shown to agree closely to that of natural rubber hydrocarbon.

*Brittle Temperature of Rubber under Variable Stress.*³ A. R. KEMP, F. S. MALM and G. G. WINSPEAR. This paper supplies the need for a method to

¹ *Chem. and Engg. News*, June 25, 1943.

² *Indus. & Engg. Chemistry, Analytical Edition*, July 1943.

³ *Indus. & Engg. Chem.*, April 1943.

determine the temperature at which rubber and similar materials fracture under variable bending stress. Although the brittle temperature is sharply defined under high-speed bending through a sharp angle, it is lower as the speed of application or the magnitude of the stress is reduced. In some instances decreases of more than 28°C. in brittle temperature resulted from reductions in bending stress such as might be encountered in service.

Vulcanized pure gum natural rubber and plasticized polyvinyl chloride-acetate copolymer showed the largest changes, whereas the compounded and vulcanized natural and synthetic rubbers involved in this study exhibited a reduction in brittle temperature from 5° to 10° C. in going from the highest to the lowest stress employed.

*American Science Mobilizes for Victory.*⁴ ROBERT W. KING. There are no accomplishments of the Bell System in which its men and women take greater pride than those marking the continuous activities in developing and applying the art of communication.

The Bell Telephone Laboratories' accomplishments, reflected for decades in improved instrumentalities and systems for the transmission of electrical signals and speech, have been possible because vast resources of scientific knowledge have been devoted as part of the System's general responsibility to the public, to a broad and fundamental program of exploration, experiment and design.

Today the more than 6,000 members of these Laboratories are engaged on hundreds of development projects requiring research, invention and design, for the Army, the Navy, and the National Defense Research Committee.

That this should be both logical and inevitable will not surprise any one who considers the vital part played by communications in modern warfare. Rapid movement of troops and supplies over far-flung lines of action on land and sea and in the air are possible only when directed through effective communication systems. More and more the electrical transmission of intelligence is becoming the unifying influence pervading all branches of war organizations. It coordinates the movement of naval and aerial fleets; it enables infantry, tank columns and formations of aircraft to operate as a single unit. It shrinks a thousand-mile battle line to the compass of a single sector.

The article by Dr. King points out the place of independent military research, although its actual volume is less than that carried on directly by the Army and Navy. It also draws upon experience in industrial research to show that the sudden solution of war problems by appeal to science is scarcely to be expected.

⁴ *Bell Tel. Mag.*, June 1943.

*Filtered Thermal Noise—Fluctuation of Energy as a Function of Interval Length.*⁵ S. O. RICE. Let a source of thermal noise be connected to the input of a band-pass filter. Consider the energy which would be dissipated during the interval t_1 to $t_1 + T$ if the output current were to flow through a resistance of one ohm. When T is held fixed and t_1 regarded as a random variable, the resulting energies have a distribution whose average and standard deviation depend upon T . Here this dependence is studied. The standard deviation of the difference of the energies of two contiguous intervals, each of length T , is also obtained.

*Ultra-Short Electromagnetic Waves. IV—Guided Propagation.*⁶ S. A. SCHELKUNOFF. Doctor S. A. Schelkunoff presented the material contained in this article as a lecture before the basic science group of the New York Section. He treated the subject in a "non-mathematical" manner. Certainly the electrical engineer will welcome any concept which allows an easier approach to the solution of certain problems involved in wave guides than the more complete equivalent field-theory method. In this fourth article in a series of six on ultra-short electromagnetic waves, Doctor Schelkunoff combines transmission-line theory with optical analogy and derives useful relations for both wave guides and cavity resonators. The three preceding articles appeared in the March, April and May issues of *Electrical Engineering*.

*Variable-Frequency Bridge-Type Frequency-Stabilized Oscillators.*⁷ W. G. SHEPHERD and R. O. WISE. Results are given of a theoretical and experimental investigation into two types of bridge-stabilized oscillators incorporating a thermal device for amplitude control. One circuit employs only resistances and capacitances in the frequency-determining network and consequently is useful for low-frequency operation. The other circuit uses an inductance-capacitance network which is well adapted to the higher-frequency network. Conditions for optimum stability and the variation of the stability with frequency determined experimentally are found to be in general agreement with theoretical results.

*Beyond the Ultra-Short Waves.*⁸ G. C. SOUTHWORTH. This article reviews briefly the work done many years ago by the pioneering physicists with the so-called electric waves as well as the more recent efforts by engineers to put these waves to practical use. It also describes some of the expedients and changes of technic used to overcome difficulties as this work progressed to

⁵ *Jour. Acous. Soc. Amer.*, April 1943.

⁶ *Elec. Engg.*, June 1943.

⁷ *Proc. I. R. E.*, June 1943.

⁸ *Proc. I. R. E.*, July 1943.

higher and higher frequencies. One, of fairly recent origin, is the wave-guide or hollow-pipe technic. The latter not only provides a simple and efficient way of propagating microwave power from one point to another but there have also grown from it some very interesting counterparts of the tuned circuits, the matching transformers, and the filters that have been in common use for some time at the lower frequencies. The possible bearing of this new technic on the future of electrical communications, as, for example, television, is pointed out.

*The Impact of War on Long Distance Service.*⁹ MARK R. SULLIVAN. The article gives in narrative form much of Vice President Sullivan's testimony concerning toll board service before the Federal Communications Commission on December 16, 1942.

Increasing traffic and severe curtailment in additions to plant, make it progressively more difficult to maintain service performance at its usual level. In the last two years Long Lines toll traffic has nearly doubled, this increase being almost equivalent to the total level of business reached over a period of some 65 years. Plant materials available for telephone construction, on the other hand, have been sharply curtailed. Copper, for example, had been used in building telephone plant at the annual rate of more than 90,000 tons; now only about 8,000 tons are used.

The increased volume of long distance calls has been accompanied by increased complexities in the handling of calls; more attempts required per call, a greater proportion of person-to-person calls, and greater length of haul requiring more switching. Over all, the results still average well. However, not all calls fall on or near the average due to the uneven distribution of increased calling which has followed generally the path of war activity and varies tremendously in different localities. Just as growth in calling has not been uniform throughout the System, so has circuit congestion been most pronounced in cities most affected by war activities. A customer whose individual call is delayed well beyond the average may appraise the service by that call, even though he may realize that the average speed of all calls is much faster.

Despite the increased traffic volume, complexities and the shortage of facilities, there have been some truly notable achievements. Accuracy and speed of answer have suffered relatively little. Additions to the operating force of 150,000 were made in the past two years to handle the increased load and to replace losses. Operators, seasoned and new, have faced the challenge to the service and, true to the finest traditions of the service, are giving their best to a difficult job—willingly and cheerfully.

⁹ *Bell Tel. Mag.*, June 1943.

*Drying of Textiles.*¹⁰ A. C. WALKER. In 1937 a textile-drying research project was initiated by the United States Institute for Textile Research and supported by the textile industry, for the purpose of evaluating the effects of temperature and humidity on the physical and chemical properties of important textile fibers. The present paper gives a comprehensive report of the results obtained and points out the basis upon which the industry must proceed in problems relating to textile drying. In all cases, consideration should be given to the theories relating to the form in which the moisture is distributed within the fiber structure and to data of the type discussed by the author.

¹⁰ *Trans. A.S.M.E.*, May 1943.

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