SUPPLEMENTARY PROGRAMME

SP1. Integral Expressions for Nuclear Magnetic Moments. Enos E. Witmer, *University of Pennsylvania*.*—The magnetic moment of the proton is $[1876/(1836\times 671)](1-1/861)$ Bohr magnetons, yielding 1.521013×10^{-3} B.m. in remarkable agreement with experiment. Believing that M_p/m is exactly 1836, this is formula (1): $[k/671](1-1/861)\mu_N$ with $k=1876$. The known magnetic moments of other nuclei are apparently represented by formula (1) with k usually an integer, and in one case at least a simple rational number. For n^1, H^1, H^2, H^3, Be^9, and B^{11} the experimental values of k are very close to integers. For He^3 k is $35^2\times 7/6$. For C^{13} and F^{19} the k, though less accurately known, appear to be integral. Note that (1) has the factor $(1-1/861)$, whereas the magnetic moment of the electron is $(1+1/861)$ Bohr magnetons.

* To be given after Session L if the Chairman rules that time permits.

MEETING OF THE DIVISION OF ELECTRON PHYSICS AT WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY, JANUARY 31 AND FEBRUARY 1, 1950

(Joint Meeting with the Panel on Electron Tubes of the Research and Development Board)

Invited Papers

Thoria as a cathode emitter. W. E. Danforth, *Bartol Research Foundation.*

Government support and thermionics. E. R. Piore, *ONR.*

Experimental techniques involved in thermionic studies of clean metals. W. B. Nottingham, *M. I. T.*

Effect of impurities on thermionic emission from platinum. A. Ertel, *Westinghouse.*

Oxide-cathode research at the University of Missouri. A. Eisenstein, *University of Missouri.*

Photoelectric techniques in the study of ionic semiconductors. Leroy Apker, *G. E.*

Principal processes in thermionic emission and electrical conductivity of BaO. L. P. Smith, *Cornell University.*

Review of some facts on temperature variation of activation energies. Conyers Herring, *Bell Telephone Laboratories.*

Contributed Papers

EP1. Notes on Thoria and Other Refractory Materials. Leo J. Croning, *Ratheon Manufacturing Company.*—The occurrence and purification of thoria is discussed to provide a better understanding of experimental results obtained by various investigators. The chemistry of thorium compounds is complex and closely connected with that of the rare earths. "Thoria" may contain over three percent impurities; its specific surface may vary from lot to lot by an enormous amount; the supplier may be any one of a dozen commercial sources or private laboratories each of whom may have several grades. A simple experiment was devised to obtain comparative data on the reaction of thoria with metals. The design and construction of a special secondary emission tube is described. The ratio of secondary to primary emission of a directly heated thoria cathode was found to be 1.4 at room temperature and increased to 1.9 at 900°C. A study was conducted on evaporation of refractory materials including Al_2O_3, B, BN, B_4C, Cb, CeO_2, Cr, CrC, Cr_2O_3, Ir, Mo, MoC, Os, Pt, Rh, Ru, SiC, Ta, TaC, Th, ThO_2, Ti, TiC, TiN, VC, W, WC, ZrC, and ZrO_2. Equipment, procedure and results are described. The experiments illustrate the adverse effects of poor vacuum on tube deposits in addition to eliminating substances with unsuitable vapor pressure.

EP2. Rate of Disappearance of Thoria from Coated Filaments. E. Shapiro, *Bartol Research Foundation* (Introduced by W. E. Danforth).—Studies were made of the rates of disappearance of thoria from thoria-coated tungsten and molybdenum filaments as functions of temperature and emission. It was found that, in the temperature range 2050° to 2250°K, the drawing of current from the coated filament did not affect the rate of disappearance of thoria. In this temperature range, the rate of evaporation of thoria is given by the equation: $\log r$ (g cm^{-2} sec.$^{-1}$) $=-3.71\times(10^4/T)+9.84$, and the calculated vapor pressure of thoria is $\log P$ (mm Hg) $=-3.71\times(10^4/T)+11.53$. The heat of vaporization is 171,000 cal./mole.

EP3. Thermal Emissivity Changes of Thoria-Coated Tungsten Filaments. O. A. Weinreich, *Bartol Research Foundation.*—The total and spectral emissivities of thoria-coated W filaments are being investigated with particular reference to effects of thermal processing and other activation procedures. The filament temperature is measured by its resistance using potential leads. Reversible and irreversible changes of emissivity are observed. These occur as a result of heat treatment and passing current through the coating. In some cases the change of the emissivity can be correlated with changes of thermionic emission. Fresh coatings heated to 1300°C showed initial emissivity values as low as 0.2 for $\lambda=0.655$. After flashing to 2600°C the emissivity increased to 0.65 at 1300°C but prolonged heating at this temperature dropped the emissivity to 0.4. The increase is believed to be brought about by a reaction between thoria and tungsten. The total emissivity of the fresh cathode was about 0.2 at 1400°C and after flashing to 2600°C, it increased to about 0.4. Reverse electron bombardment causes increases in emissivity, comparable to those caused by flashing to 2600°C. At present, only the total and spectral emissivities at 0.655μ have been investigated. Measurements of the energy distribution between 0.6 and 12μ for different states of the thoria-coated W filaments are under way.

EP4. Experimental Use of Thoria Cathodes in High Voltage Rectifier Tubes. S. T. YANAGISAWA AND T. H. ROGERS, *Machlett Laboratories, Incorporated* (Introduced by H. D. Doolittle).—Thoria has been used as an emitting material in magnetron cathodes and in cathodes for medium voltage transmitting tubes. However, the use of thoria cathodes with extremely high inverse voltages has not been previously investigated, even though earlier experiments have indicated high emission efficiencies and ability to withstand the effects of ion-bombardment. The purpose of this investigation was to determine the feasibility and desirability of the use of thoria cathodes in high voltage rectifier tubes for x-ray service, as this application constitutes a most suitable medium for evaluating their performance under maximum voltage conditions. Cathode life, emission efficiency, and the effect of thoria evaporation upon high voltage performance were examined in particular. The existing methods of fabricating thoria cathodes were surveyed and tried. The emission and high voltage characteristics of the various types of thoria cathodes were empirically investigated by incorporating them into standard high voltage x-ray valve tube designs. Pure thoria ceramic cathodes were used with good stability up to 130 PKV inverse. Catephoretically coated tantalum wire had the best emission characteristics and was used successfully in tubes up to 110 PKV inverse. Tentative conclusions were that thoria cathodes are feasible for tubes rated up to 110 PKV.

EP5. Base-Metal Effects in Thoria-Coated Filaments. HERBERT NELSON, *Radio Corporation of America.*—Adherence of the thoria to the metal base, ease of thermionic activation, and level of thermionic emission reached have been studied as a function of base material. The base metals used in the investigation were tungsten, molybdenum, tantalum, and platinum. Thoria adherence was found best with platinum and tantalum, and poorest with tungsten. Thermionic activation was easily achieved in all cases except with platinum. The final level of thermionic emission reached at 1900° K.B.T. was the same, about 5 amp./cm^2, for molybdenum, tungsten, and tantalum. At lower temperatures, however, higher values were invariably obtained with molybdenum than with tantalum.

EP6. Electrical Conductivity of Sintered Thoria. W. E. DANFORTH AND F. H. MORGAN, *Bartol Research Foundation.*—The conductivity of sintered thorium oxide in good vacuum is being studied, the temperature range of the present experiment extending to 1800°C. Specimens are subjected to currents up to several amperes per square centimeter and the resistance determined between potential leads. Resistance is essentially ohmic over this range and contact phenomena with the molybdenum endpieces are not prominent. The state of activation is variable, dependent upon heat treatment and passage of current. In the highest activation yet reached, resistance values as low as 1 ohm-cm at 1200°C were obtained by prolonged passage of 10 Amp./cm^2. Exposure to atmospheric pressure produces deactivation. Relatively unactivated material showed two activation energies 3.4 and 0.8 ev, the former possibly corresponding to thermionic emission through interstices following Loosjes and Vink. Activation by drawing current gives a single component of about 1.8 ev effective. An attempt was made to account for activation by current as electrolytic generation of (thorium) impurity centers. Reasonable assumptions regarding mobility and percent ionic conduction fail to account for the rapidity of this activation.

EP7. Investigation of Contaminants in Vacuum Tubes. PAUL D. WILLIAMS, *Eitel-McCullough, Inc.*—In an ONR sponsored program, vacuum tube materials are being studied on the mass spectrometer as a means of identifying the volatile components released under temperature and in vacuum. Of four glasses so far studied, Nonex glass yields carbon monoxide and water at temperatures below previous bake-out temperatures. "705–2" glass contributed only oxygen after bake-out. Ceramic "Ai-200" is considerably freer of volatiles below 1000°C. Above this temperature carbon monoxide is evolved. Ceramic "Ai-200" and quartz heated to their softening points, have not contaminated carburized thoriated tungsten emission in zirconium-gettered tubes.

EP8. Certain Refractory Compounds as Thermionic Emitters. D. L. GOLDWATER, AND R. E. HADDAD, *Bartol Research Foundation* (Introduced by W. E. Danforth).—Several refractories of the nitride, boride and carbide families are investigated as sources of thermionic electrons. An activation pattern qualitatively common to several of the compounds is observed. Emission data for the final state of activation is presented. Data concurrently obtained for thoria are also given for comparison. True temperature used in the Richardson equation is obtained by correction from brightness temperature. Temperature correction curves have been obtained by two methods. These curves can be satisfactorily represented in the region of thermionic emission by one value of spectral emissivity, which values are listed, for the materials studied.

EP9. Refractory Thermocouples and Emissivity Determinations. F. H. MORGAN, *Bartol Research Foundation.* (Introduced by W. E. Danforth).—The thermoelectric power of several refractory thermocouples was investigated. W-Ta for temperature measurements up to 3000°C, W-Mo up to 2600°C, Ta-Mo up to 2600°C and W-W/Mo (alloy 50 percent Mo/50 percent W) up to 2900°C. The resulting curve for W-Ta was quite different from that found in existing literature. The validity of the curve was checked by taking the difference between the W-Mo and the Mo-Ta curves. Basic calibration was carried out using several melting points and the results interpolated by means of an optical pyrometer. Employing these thermocouples, the spectral emissivity of thoria and other cathode materials was easily obtained. For thoria $e=0.4$ up to 1800°C, further increase in temperature increases the spectral emissivity, e being 0.55 at 2000°.

EP10. Effect of Impurities on Thermionic Emission from Platinum. A. ERTEL, *Westinghouse Electric Corporation* (Introduced by J. W. McNall).—Previous investigators reported high values of the thermionic work function ϕ and emission constant A for platinum before rigorous heat treatment resulted in more dependable results. This paper describes emission measurements on # 1 grade and C.P. platinum (Baker) both of which had low values of ϕ and A before continued heat treatment at high temperatures. Experiments with # 1 platinum indicated the presence of an electropositive impurity. Emission-temperature curves show a "clean-up" temperature between 1850° and 1930°K and a gradual decrease in emission to that of pure platinum. Electron projection studies showed the "eruption" of the impurity from the wire surface. Richardson data taken at higher temperatures for the semi-clean wire yielded $\phi=5.27$ ev and $A=64$ amp./cm^2 deg.^{2} Although the C.P. material showed a similar impurity, another impurity was indicated by the violent bursts of emission occurring for decreasing temperatures in the range from 900° to 1100°K. Electron projection study showe eruptions in this temperature range. The thermionic constants for relatively clean wires were found to be $\phi=5.32$ to 5.47 ev and $A=100$ to 160 amp./cm^2 deg.^{2} Results of spectroscopic and x-ray diffraction analyses are presented.

EP11. Thermionic and Secondary Emission Properties of Magnetron Cathodes and Their Influence on Magnetron Operation.* ROBERT L. JEPSEN, *Columbia University.*—The use of various pure metals as cathodes, with and without an auxiliary "priming" cathode, has made it possible to separate, to a considerable extent, the roles of thermionic and secondary emission. It is found that an important operating characteristic of a magnetron employing a secondary emission cathode is the existence of a maximum current boundary on the V-I performance chart. This boundary is directly correlated with the secondary emission properties of the cathode. It is also found that in the low current region percentage back bombarding power increases rapidly as anode current is decreased. It is further indicated that back bombarding electrons strike the cathode within a preferred angle range, thus increasing the effective secondary emission ratio over what it would be for normal incidence. A simple picture has been proposed for understanding, qualitatively, the maximum current boundary. In this picture it is necessary to consider only stable thermionic and secondary emission properties of pure metals. The chief unsolved problem remaining seems to be an electron dynamical one. It relates to some type of interaction in which the electrons participate, and which results in the observed dependence of percentage back bombarding power on anode current.

* Work supported jointly by the Signal Corps and the ONR.

EP12. Noise Spectra from Vacuum Tubes at Ultra Low Frequencies.* R. W. BOGLE,† *University of Michigan.*—Spectral measurements of vacuum tube emission noise have been made for the frequency range from 10,000 c.p.s. to 1/100 c.p.s. This work was undertaken to test the Johnson "flicker effect" theory[1] which relates the frequency dependent characteristic encountered at low frequencies with cathode hot spots of finite lifetime. Attention was particularly directed toward the inverse proportionality dependence of r.m.s. noise voltage on frequency required by this theory, and also the point of frequency below which the noise spectrum should become flat. The experiments showed no sure evidence of flattening. Further, a marked deviation from simple inverse frequency proportionality was found. The frequency-determining elements used in the experimental equipment were Twin-T feed-back amplifiers. At the lowest frequencies, a Brown recording d.c. galvanometer was used as an output voltmeter. Spectral measurements were made on a variety of tubes, including commercial types as well as some specially constructed. Tubes with all of the common emitting materials were tested.

* Supported by Navy contract.

† Now at Applied Physics Laboratory, The Johns Hopkins University.

[1] J. B. Johnson, Phys. Rev. **26**, 71 (1925).

EP13. A Preliminary Study of the Work Function of Contaminated Metal Surfaces. P. H. MILLER, JR. AND B. J. ROTHLEIN,* *University of Pennsylvania.*—A beam of electrons is passed between a reference plate and a metal surface to be studied and these plates are electrically connected with each other. A change in work function causes a change in the field between the two plates, which in turn produces a deflection of the electron beam. The apparatus in its present form is capable of measuring a change in work function of 0.05 volt. Observations have been made on the changes of work function in partially outgassed tantalum, zirconium, and tungsten, as these surfaces are allowed to cool from temperatures between 1000° to 2000°C. There is evidence for two types of layers which can influence the contact potential difference by as much as several volts.

* Now with Sylvania Electric Products.

EP14. Thermionic Emission, Conductivity, and Contact Potential Difference Measurements.* WILLIAM J. PRICE,† *Battelle Memorial Institute.*—A special vacuum tube was built for the study of cathode materials. By means of this tube, measurements of the thermionic emission and conductivity were made on the same cathode; also, the contact potential difference between the cathode and a tungsten foil was obtained. The tube consisted of a stationary cathode and two movable anodes arranged so that they could be alternately moved into position. The cathode was a molybdenum cylinder with the emitting material coated on the closed end. Conductivity measurements were made by observing the voltage required to produce a given cathode current as the distance between one movable anode and the cathode was decreased to zero. Thermionic emission data were obtained by observing the saturation current drawn to the same electrode. The other movable anode, consisting of a tungsten foil, was used for measuring the contact potential difference between the cathode and tungsten; the Kelvin method was employed. Cathodes, with thoria coatings, were studied in this tube. The conductivity was found to be proportional to the thermionic emission over a considerable temperature range and for widely differing conditions of activation. The change in the work function following thermal activation of the cathodes was obtained by thermionic emission measurements and by contact potential difference measurements. This change was found to be essentially the same by the two methods.

* Supported by Wright-Patterson Air Force Base and Evans Signal Laboratory.

† Now at USAF Institute of Technology, Wright-Patterson Air Force Base.

EP15. The Use of Radioactive Sr in Some Thermionic Experiments on Thin Films. H. W. ALLISON AND GEORGE E. MOORE, *Bell Telephone Laboratories.*—Radioactive strontium isotopes are being used as tracers to measure the minute quantities of Sr and SrO involved in thermionic emission experiments on thin film (1–10 monomolecular layers) cathode systems. These thin film systems consist of an evaporated deposit of Sr or SrO on tungsten ribbons. Electron emission measurements at low temperatures on these definable systems indicate a thermionic activity comparable to that of the more complex commercial BaO – SrO cathode. The sensitivity of the tracer method permits measurement of the following properties of these films: 1. The amount of SrO (or Sr) required to produce any observed activation. 2. The rate of loss of Sr (or SrO) on heating the films at any practical operating temperature. 3. Whether the deposited Sr (or SrO) migrates to the reverse side of the receiver ribbon at specific test temperatures. Sr was chosen rather than Ba because of the more convenient properties of its radioactive isotopes. The technique will be described and quantitative results given.

EP16. Electrical Conductivity of Oxide Cathode Coatings. D. A. Wright, *G. E. C. Research Laboratories, Wembley, England* (Introduced by Geo. E. Moore).—Conductivity measurements on activated coatings give results in agreement with the Vink-Loosjes theory, which it is shown implies Ba concentration of the order 10^{20} atoms/cm^3. Hall effect measurements indicate 10^{14} electrons/cm,^{3} at 1100°K, and free path 2.10^{-5} cm. This result may not in fact be inconsistent with the Vink-Loosjes theory. P-type conductivity is not encountered in well activated coatings, and is a feature developing while drawing emission under non-activating conditions. It is due to oxidizable impurities in the coatings. Rapid poisoning or activating effects at low temperatures emphasize the importance of phenomena at surfaces, and it is suggested that these are associated with electron or hole movement rather than ion movement.

EP17. On the Interpretation of Conduction and Thermionic Emission of (Ba$-$Sr)O Cathodes. F. K. du Pré, R. A. Hutner, and E. S. Rittner, *Philips Laboratories, Inc.*—A semiconductor model for (Ba$-$Sr)O cathodes is proposed comprising a full band and a conduction band separated by a gap $\sim$1.7 ev, donor levels $\sim$0.3 ev and acceptor levels $\sim$1 ev below the conduction band, and an electron affinity $\sim$1 ev. It is assumed, for simplicity, that there is a fixed concentration of acceptors. ($\sim 1.5\times 10^{17}$/cm^3) in a given cathode, and the process of activation is interpreted as a gradual increase in the concentration of the donors (up to $\sim 3\times 10^{17}$/cm^3). The combination of this model with Vink's[1] concept of conduction by an electron gas in the pores of the oxide coating explains the following facts (exclusive of those already enumerated by Vink): the variation in conductivity slope and Richardson work function with increasing activation, the existence of p-type conductivity changing to n-type with increasing temperature, the magnitude of the emission current density (i), the difference between the Richardson work function (ϕ_{Rich}) and that determined from contact p.d. measurements, the linear relationships between log$o$ and log$i$ and also between logA_{Rich} and ϕ_{Rich} for different stages of activation.

EP18. An Investigation of Magnesium as an Additive to the Nickel Base of an Oxide Cathode. Ralph Forman and Glenn F. Rouse, *National Bureau of Standards.*—The degree to which small amounts of magnesium added to the nickel base of an oxide cathode may affect the thermionic properties of the cathode is being investigated. Techniques for adding magnesium to an electrolytic nickel base have been worked out and the rate of diffusion of magnesium through nickel at elevated temperatures is being studied. A double diode of planar type has been chosen as the means for comparing the thermionic properties of two cathodes. Direct current and pulsed emission tests are made, the pulse voltages being of 250 and 500 microseconds duration. The performance of a cathode on an electrolytic nickel base has been checked by making a tube in which all metal parts, other than the tungsten heater, were of electrolytic nickel. It has been found that under certain conditions an oxide cathode on an electrolytic nickel base activates more rapidly than does one on a Mg$-$Ni base. Current decay effects which are often observed in pulsed emission are believed to be due in part, or perhaps wholly, to processes occurring at the anode.

EP19. Diode Studies of Oxide-Coated Cathodes. H. E. Kern and R. T. Lynch, *Bell Telephone Laboratories* (Introduced by J. A. Burton).—A description of the Bell Laboratories planar-type test diode will be given, together with a brief summary of the diode standard processing procedure. This will include a description of a precision method for the application of cathode coatings. The method of determining cathode emission, the conditions of aging and lifeing of the diode, and the criteria for tube failure will be discussed. The quality control chart method for analyzing emission and life data will be described. This will be illustrated by a chart showing the reproducibility of the standard diode. Finally, some typical results obtained from the diode program will be reported.

EP20. Thermionic Properties of Dense Oxide Cathodes. J. A. Burton, H. E. Kern, and R. T. Lynch, *Bell Telephone Laboratories.*—The thermionic properties of the smooth, dense alkaline earth oxide coatings described by Kern and Lynch in the preceding paper have been investigated as a function of cathode temperature and pulse duration. The voltage-current characteristics of these diodes have been measured using pulses varying in duration from one microsecond up to one thousand seconds. The decay of cathode emission with time under these conditions will be discussed briefly. A comparison will be made between the observed current-voltage characteristics and those expected for an ideal diode of similar geometry in the retarding field region, the space charge limited region, and also for accelerating fields up to 50,000 volts per centimeter. At normal operating temperatures and for pulses sufficiently short so decay effects are negligible, the observed slopes of Schottky plots agree closely with those theoretically expected for a patch free surface.

EP21. A Study of Cathode Behavior in Fluorescent Lamps. E. F. Lowry, E. L. Mager, and H. H. Homer, *Sylvania Electric Products, Inc.*—In the mercury vapor atmosphere of fluorescent lamps, oxide-coated cathodes exhibit phenomena requiring consideration in any theory of emission from oxide-coated metal surfaces. Visible manifestations on the tube wall of these phenomena are: (1) *Spots*—occurring during electrode operation as anode (alternating half-cycles on a.c.), chiefly alkaline earth metal. (2) *Bands*—rings of discoloration, chiefly mercury oxides. The cathode coating, responsible for discolorations, is continuously disintegrating during operation. End of life occurs when the coating is completely stripped from the core metal. Addition of about five percent zirconium dioxide to such cathode coating nearly tripled the life of the fluorescent lamp, allowing life rating to be increased from 2500 to 7500 hours. Simultaneously, discolorations have been practically eliminated for the first 5000 hours. The formation of *spots* and *bands* is explainable in absence of zirconium dioxide by reactions occurring at the interface between the core metal and the alkaline earth oxides. The action of zirconium dioxide in suppressing discoloration and disintegration is less readily explainable, being complicated by the fact that when ZrO_2 is added in proper amounts both spots and bands are absent, but excess ZrO_2 will produce greater blackening than if none at all were used.

EP22. The Decay and Recovery of the Pulsed Emission of Oxide-Coated Cathodes. R. M. Matheson and L. S. Nergaard, *Radio Corporation of America.*—The decay and recovery of the pulsed emission of cathodes consisting of BaO on nickel is studied. The emission of the cathodes is measured in diodes of cylindrical geometry having water-cooled copper

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[1] H. J. Vink, thesis, Leiden (1948). See also R. Loosjes and H. J. Vink, J. App. Phys. **20**, 884 (1949), and Philips Research Reports **4**, 449 (1949).

anodes spaced 0.019 inch from the cathode. Most of the diodes show a decay of anode current when first put in pulse operation. Decays of 2–50 percent are observed during 150 μsec. pulses. The decay tends to disappear when the tubes are aged under pulse conditions. The peak current is a linearly decreasing function of the logarithm of the duty cycle, even when there is no perceptible decay during the pulses. The rate of decrease is independent of the pulse repetition rate and decreases with cathode temperature. Current-voltage characteristics during the pulse and recovery periods are obtained by short sampling pulses. A comparison of these characteristics with computed ideal characteristics does not discriminate unambiguously between a variation of emission and a variation of internal cathode impedance as a source of current decay. Studies to separate the contributions of these effects are in progress.

EP23. Life Tests of Oxide-Coated Cathodes—An Engineering Report. J. O. McNally, *Bell Telephone Laboratories.*—The continued use for many years of the oxide-coated cathode in thermionic vacuum tubes for communication purposes has led to the development of types of tubes having in general satisfactorily long thermionic lives. This paper describes a number of the factors involved in obtaining these lives. The mortality curve is shown and discussed for a number of tube types. It is shown that the cathode temperature at which the tube is operated is important in establishing the life. The effects of operating the cathodes at various current densities are discussed.

EP24. Convenient Methods for Thermionic Emission Calculations. H. F. Ivey and C. L. Shackelford, *Westinghouse Electric Corporation.*—Calculation of the temperature at which a given thermionic emission will be obtained from a certain material (assuming the thermionic constants are known) is complicated by the presence of the T^2 term in Richardson's equation. The desired temperature can, of course, be found by trial and error and interpolation. It is the purpose of this paper, however, to present four simple methods of calculating the temperature. These methods may, of course, be used to calculate any one of the quantities ϕ, A, T, and J if the other three are known. The first of these methods is algebraic and involves reducing Richardson's equation to a simple form involving the temperature only in the exponential term. Two graphical means of determination will also be described. The fourth method presents the results in the form of a nomograph. The accuracy to be expected from each method is discussed.

EP25. A "Figure of Merit" and a "Quality Ratio" for D.C. Emission from Oxide-Coated Cathodes. C. D. Richard, Jr., *Superior Tube Company* (Introduced by A. Lederman).—A graph of d.c. emission as a function of cathode temperature is often used in test work with oxide-coated cathodes, particularly with diode tubes where other characteristics are not feasible. Previously E_f-I_s curves were judged by visual comparison only. The portion of this emission curve of greatest value in rating performance of tubes is the "knee" of the curve. This knee, which varies widely in curvature, is a transition point between the "space-charge limited" and "temperature-limited" emission regions of the E_f-I_s curve. A "figure of merit" (the slope of a tangent to the knee from an arbitrary origin) makes it possible to specify this point with a number. When the figure of merit for a test material is divided by the figure of merit for the control lot, a "quality ratio" is obtained. Use of this method correlates well with visual judgments of the curves and also with actual radio tube performance of the cathode materials. It works with lots of close similarity as well as those of wide differences. Previously proposed methods lack this range of application.

EP26. Determination of Oxide Cathode Performance in Diode Tubes through Figures of Merit. Thomas H. Briggs, *Superior Tube Company* (Introduced by A. Lederman).—Richard's paper described a method for calulating a "figure of merit" and "quality ratio" for standard diode tubes. Particular use of them has been made in evaluation of certain cathode performance characteristics. *Rate of cathode activation* and *life performance* are clearly indicated by this method. Migrations of the knee of the E_f-I_s curve are concisely shown. This is the best measure of d.c. emission quality found so far. Through the figure of merit, changes in cathode activity with time can be traced. The quality ratio allows comparison at any period with the control standard. *Chemical composition* of cathode base metals is important to d.c. emission performance. Correlation of the effects of various alloy additives is made more simple and reliable through use of FM and QR figures. A linear relationship has been found between the arbitrarily determined figure of merit for d.c. emission and quality ratings of the log of low field and log of pulsed emission ratings proposed by Cardell and others. This is the first time such a correlation has been shown, and it should be of value in development of the theory of thermionic emission.

EP27. Ceramic Heaters and Cathodes for Electron Tubes. T. R. Palumbo, *Ceramic Heater Cathode Resistor Company* (Introduced by A. Bramley).—A specially prepared conductive ceramic rod has been applied as a tube heater and filamentary cathode. The conductive material is prepared by subjecting a preformed pure ceramic material, such as Al_2O_3, to a hydrocarbon atmosphere, e.g., methane, at a temperature ranging from 700°C–900°C. The coefficient of conductivity of the resultant product varies with the carbon content of the gas or gas mixtures, the furnace temperature and the time of exposure, i.e., the speed at which the rods are fed through the furnace. We have shown, however, that conductivity is not induced by a cracking of the hydrocarbon followed by a deposition of free carbon on the ceramic, but by the formation of a chemical compound involving the ceramic material and the carbon. X-ray studies have been made. The material so obtained has a negative coefficient of resistance and high current carrying characteristics. An unusual property of this ceramic is that when it is used as a base with a standard cathode coating such as (Ba, Sr, Ca) carbonates or azides, it will support the same thermionic emission as the customary coated nickel sleeve under the same conditions of operation.

EP28. Effects of Controlled Impurities in Nickel Core Metal on Thermionic Emission from Oxide-Coated Cathodes.[*] Harold Jacobs,[†] George Hees,[‡] and Walter Crossley,[||] *Sylvania Electric Products, Inc.*—Emission measurements were made over a 500-hour life period on oxide-coated cathodes having 18 different binary nickel-alloy core metals. The samples of nickel and of the additive (both of highest purity) were vacuum melted together in order to provide a rigid control on the composition of each alloy. All tubes were processed under the same controlled conditions. An empirical emission equation $I=A'\exp(-e\Psi/BT)$ was used. The parameters Ψ and A' were found to vary in such a manner that, over life, the following relationship existed: $\log A'=K\Psi+B$ where K and B are constants. Some alloys which appear to be especially suitable as base metals for oxide-coated cathodes are aluminum-nickel, chromium-nickel, molybdenum-nickel, and thorium-nickel. Alloys which resulted in poorest emission were boron-nickel, beryllium-nickel, and iron-nickel.

[*] This work was undertaken in cooperation with the United States Army Signal Corps Engineering Laboratories, Evans Signal Laboratory, Belmar, New Jersey.

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[‡] Sylvania Product Development Laboratories, Kew Gardens, New York.

[||] Now at Polytechnic Institute of Brooklyn, Brooklyn, New York.

MEETING OF THE DIVISION OF HIGH-POLYMER PHYSICS AT THE POLYTECHNIC INSTITUTE OF BROOKLYN, FEBRUARY 1 AND 3, 1950

HPP1. Incubation of Plastic Shocks in Certain Polymeric Films. JOHN KAUFFMAN AND WALLER GEORGE, *Naval Research Laboratory.*—The existance of a time delay between the rapid application of a load and the appearance of plastic flowing has been demonstrated in mild steel by Clark and Wood. Recently, the authors have discussed a similar time delay for the appearance of a form of localized plastic flowing in commercial polyamide films. The localization involves a through-the-thickness reduction of the specimen (a type of local necking) which can be made to propagate along the specimen. It has been tentatively interpreted in terms of von Kármán's plastic wave theory as a "plastic shock." Under suitable dead weight loading the "shock" is observed to propagate after the elapse of the delay time. Plastic flowing events occur within this delay time which lead to the abrupt formation of the shock. The collection of these events preceeding the final localization of flowing is termed its "incubation." This paper will describe the incubation processes with the aid of motion pictures and polarized light for selected polyamide and polyethylene films. The description will include the initiation and growth of "bands" of distortion in regions of maximum average shear stress and their collapse into the fully formed shock.

HPP2. Fracture Markings in Plastics. J. A. KIES AND A. M. SULLIVAN, *Naval Research Laboratory.*—Many of the gross features of fracturing in solids can be modeled and chosen features can be emphasized on fractures in selected polymeric solids. Discontinuous fracture and backward propagation of isolated elements simultaneous with the advance of crack head are demonstrated. The origins of chevrons and other geometrical markings, such as ellipses, hyperbolas and river systems on the fracture surface are explained in terms of multiple initiations and relative propagation speeds of fracturing. The sequence of events by which rod-shaped shards are thrown out during conchoidal fracturing is described. Shatter markings provide a mechanistic explanation of brittle behavior under high overloads. Variations of fracture appearance with over-all speed of propagation in cellulose acetate and Lucite plates are discussed. A few examples of the applicability of these studies to the interpretation of some large scale fractures in various materials are cited.

HPP3. Crystallization and Second-Order Transitions in Silicon Rubbers.* C. E. WEIR, W. H. LESER, AND L. A. WOOD.—In the course of an investigation to determine which rubbers might be suitable for use at low temperatures, interferometric measurements of the length-temperature relationships of silicone rubbers have been made. Crystallization was found between −60° and −67°C in Dow-Corning Silastic X-6160 and in General Electric 9979G silicone rubber, the latter of which contains no filler. Crystallization between −75° and −85°C was found in Silastic 250. Melting occurred over a range of temperature above the temperature of crystallization. The volume change on crystallization varied from 2.0 to 7.8 percent. No crystallization or melting phenomena were observed in Silastic X-6073 between −180° and +100°C. All types of silicone rubber exhibited a second-order transition at about −123°C, the lowest temperature at which such a transition has been observed in a polymer. The coefficient of linear thermal expansion of silicone rubbers containing no filler was found to be about $40\times10^{-5}/°\mathrm{C}$ between −35° and 0°C.

HPP4. Random Noise in Dielectric Materials. R. F. BOYER, *The Dow Chemical Company.*

HPP5. Equivalent Effects of Time and Temperature in the Shear Creep and Recovery of Elastomers. F. S. CONANT, G. L. HALL, AND W. JAMES LYONS, *Firestone Tire & Rubber Company.*—An explicit relationship is set forth for the time-temperature dependence of the *viscoelastic* phenomena in the superelastic polymers. An empirical equation that was found to represent adequately the above-mentioned relationship over the entire multiple-temperature curve is of the form: $\log t=[C_\alpha/(T-b)]+C_\beta$. Experimental verification is given for the equivalent influence of time and temperature on the creep and recovery of compounds based on Hevea, GR-S, Neoprene GN, butaprene and butyl rubber. A comparison of the empirical equation with that of a theoretical reaction-rate equation of Tobolsky and Eyring indicates a temperature dependence of the energy of activation.

HPP6. Elastoviscous Properties of Polyisobutylene III. Relaxation of Stress in Whole and Fractionated Polymers; Effect of Carbon Black. R. D. ANDREWS, F. H. HOLMES, AND A. V. TOBOLSKY, *Princeton University.*

HPP7. A Non-Destructive Mechanical Test for Wool Fibers and Some Preliminary Results. HARRIS M. BURTE, *Textile Research Institute.*—The slope of the force extension curve in the linear region before the yield point can, for wool fibers, be non-destructively measured at five- to ten-minute intervals. The change of this slope with time is used to follow the course of the heterogeneous reaction between wool and some reagent. Woods[1] determined the dependence of Young's modulus on relative humidity, but did not investigate any rate phenomena. Data are presented on the interaction between concentrated aqueous solutions of neutral salts and wool fibers. Two processes occur: (a) relatively rapid hydration or dehydration of the fiber until equilibrium with the partial pressure of water over the salt solution is attained; (b) relatively slow absorption of salt ions by the fiber. Very concentrated salt solutions dehydrate the fiber so completely that absorption of salt ions is not possible. Swelling experiments, and experiments involving other mechanical properties, confirm this view. The interaction between wool fibers and aqueous solutions of large organic molecules follows a similar pattern. The effect of fiber size and type on the rate of absorption has been studied. The absorption of ions is probably diffusion rate controlling.

HPP8. Some Theoretical Considerations of Dynamic-Property Data on Textile Specimens. W. JAMES LYONS, *The Firestone Tire & Rubber Company.*—Early stretch-vibrometer data, of quite extensive character, on the frequency dependence of the interval friction μ of a Nylon monofil, has been found to conform to the relation $\mu=[\mu_2/(1+\omega^2\tau_2^2)]+\mu_3$ which was deduced independently by Tobolsky and Eyring from considerations of molecular structure. Among other constants evaluated was the relaxation time for the secondary-bond network τ_2, which was found to have the value 9.3 sec. By more sensitive graphing methods than had been used heretofore, it was confirmed for the Nylon data that the hyperbolic relationship between resonant frequency ω_0 and internal friction μ holds equally as well as the foregoing

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[1] Woods, Proc. Leeds Phil. Lit. Soc. (Sci.) 3, 577 (1940).

equation. The two relationships are shown to be nearly equivalent in the experimental range. On evaluation of graphical parameters, the equation $\mu\omega_0 = 2.47\times10^9$ ergs/cm^3 was obtained. Using the same graphical method with a set of data on 11/4/2 cotton cord the relation $(\mu+0.9)\omega_0 = 7.05\times10^9$ ergs/cm^3 was established.

HPP9. Fundamental Studies of Plasticization of PVC. M. L. Dannis, *B. F. Goodrich Research Center.*—The softening of a hard resin, polyvinyl chloride, by a liquid, dioctyl phthalate occurs through a set of processes in sequence. Imbibition of the liquid is accompanied by volume reduction in the system. Dilatometer methods evaluate the amount and rate of volume decrease. The rate is temperature dependent, activation energy about 80 kcal. Solution of liquid into the resin follows with no further volume, but large dielectric change. Dielectric changes are measured on material in a cylindrical condenser, using a Schering bridge, and are rate dependent, activation energy about 110 kcal. Data are best described, assuming that segments of the polymer molecule "react" independently of one another. At fixed temperatures, "reaction" rates are directly proportional to vapor pressure of the liquid. The dielectric change may be treated similarly to a chemical reaction between a solid and a vapor, and free energy of activation, ΔF^{**}, evaluated. ΔF^{**} is constant for various liquids with one resin. $\Delta E^{**} = \Delta H^{**} + L$ in this system, where ΔE^{**} is Arrhenius activation energy, ΔH^{**} energy barrier, L latent heat of vaporization of the liquid.

HPP10. Load-Induced X-Ray Line Broadening in Nylon Filaments. Waller George and John Kauffman, *Naval Research Laboratory.*—The load-induced microscopic structural changes in highly oriented Nylon filaments were followed by changes in the x-ray fiber diffraction pattern as a function of the resulting strain. Observations made include (1) changes in the dimensions of the fiber spots, and (2) a decrease in ratio of the intensity of amorphous to crystalline x-ray scattering. These new results for Type 200 du Pont Nylon indicate a change in the microdeformation mechanism at a strain corresponding to the inflection of the load-strain diagram (14 percent elongation). The mechanism for smaller plastic strains appears to involve a rotation of the crystallized domains toward alignment with the fiber axis, accompanied by a small over-all additional crystallization. For strains larger than the inflectional strain, the mechanism seems to involve a progressive reduction in the domain size, and a reduction in alignment with the fiber axis. Both effects appear to saturate in the vicinity of the rupture strain. These results are discussed in terms of load-induced effects found in metal single and polycrystals. It is suggested that the qualitative features observed may be representative of a wide class of load or strain induced microdeformation reactions in the solid state.

HPP11. Emulsion Polymerization with Ultrasonic Vibration. A. S. Ostroski and R. B. Stambaugh, *The Goodyear Tire and Rubber Company.*—Emulsion-type polymerization reactions have been accelerated by irradiation with ultrasonic energy. A magnetostriction oscillator at 15 kc gave essentially the same results as a piezoelectric oscillator at 500 kc. The rate of formation of polystyrene was doubled and higher final yields obtained using about 0.03 watt of vibrational power per cc of latex. Experiments were made to separate local heating effects from the pure vibration energy. A thermostatted stainless steel cell was developed for irradiating butadiene emulsions under pressures up to 60 p.s.i. About ½ watt of vibrational power per cc of latex doubled the rate of reaction for GR-S, Redox and Redsol formulas. The ultrasonic intensity apparently must exceed a critical value before any appreciable accelerative effect is observed. The time to reach a given yield of polymer is approximately inversely proportional to the power used.

HPP12. A Rotating Specimen Mount for Use with X-Ray Spectrometer in Measuring Crystallite Orientation of Cellulosic and Other Textile Fibers. Leon Segal, Joseph J. Creely, and Carl M. Conrad, *Southern Regional Research Laboratory.*—The quantitative evaluation of crystallite orientation in textile fibers by x-ray methods is discussed. It is found that photographic recording and photometering of the resulting films can be replaced by automatic recording on a strip chart with the aid of an x-ray spectrometer with Geiger-Müller counter. The design and details are given for a specimen holder capable of properly positioning and rotating a bundle of fibers in the x-ray beam so that the 002 or other selected diffraction arc passes before the window of the counter. A tentative procedure is outlined for evaluating with the aid of this apparatus, the crystallite orientation of a bundle of cellulose fibers. Some typical recordings of the intensity curves of the 002 arcs from ramie, cotton and high tenacity rayon are presented.

HPP13. On Crazing of Linear High Polymers. C. C. Hsiao and J. A. Sauer, *The Pennsylvania State College.*—The effect of various variables, such as type of stress, stress magnitude, duration of stressing, and environment on the initiation and development of crazing in linear polymers is discussed. The basic nature of crazing is investigated in some detail for polystyrene specimens by means of the light microscope, the electron microscope and the x-ray spectrometer. The results of these observations and their bearing on the fundamental group structure of the polystyrene molecules is presented. The relationship between crazing and orientation is discussed, as well as the effect of both of these factors on the mechanical properties. The experimental results are compared, wherever possible, with the previously reported data of other investigators. A short discussion is then given of a theory of crazing from the point of view of the molecular structure of the material.

HPP14. Equation of State for High Polymers. R. S. Spencer and G. D. Gilmore, *The Dow Chemical Company.*—In a former paper,* the authors suggested the following equation of state, $(P+\pi)(V-\omega)=RT$, where π is the internal pressure (or cohesive energy density) and ω is the volume at absolute zero. It was found that this equation was in good agreement with data on the thermal expansivity and isothermal compressibility of polystyrene. The present paper reports isothermal compression measurements on polymethyl methacrylate, polyethylene, cellulose acetate, and ethyl cellulose, within the fabrication range of temperature. The above equation of state is shown to apply equally as well to these thermoplastics as to polystyrene and values are given for the constants π and ω. The usefulness of this relationship is illustrated in a brief discussion of some phases of the injection molding process.

HPP15. Behavior of Granulated Polymers under Pressure. R. S. Spencer, G. D. Gilmore, and R. M. Wiley, *The Dow Chemical Company.*—In such fabricating processes as extrusion and injection molding it is frequently necessary to force a granulated polymer through a channel. Frictional forces between polymer and channel walls lead to a drop in pressure through the granular material. Simultaneously, the applied pressure causes a compaction of the granules. Assuming that the granular mass has certain fluid-like properties, a simple theoretical expression for pressure transmission

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* R. S. Spencer and G. D. Gilmore, J. App. Phys. **20**, 502 (1949).

is derived. Comparison with data on Saran powders and granular polystyrenes shows good agreement between theory and experiment. The effect of lubrication is shown also. The compaction of granular polystyrene follows the same pattern as that observed in the earth's crust. The porosity decreases exponentially with increasing pressure. The "compressibility coefficient" for the porosity of granular polystyrene is comparable with that given for clays and shales.

HPP16. Mechanical Properties of Oriented Polystyrene Films. LAWRENCE E. NIELSEN AND ROLF BUCHDAHL.—Cast films of polystyrene were oriented by stretching at temperatures above the softening temperature of the material and then cooled. A factorially designed experiment was carried out in which the amount of stretching, temperature of stretching, time held in the stretched state before cooling, and effect of several cycles of stretching before cooling were investigated as they affect the birefringence, the stress-strain properties, dynamic modulus and damping, and the softening temperature of polystyrene. In general, the value of the stress-strain properties (modulus, elongation to break, and ultimate strength) in the direction of stretch, the dynamic modulus, and the birefringence all increase with an increase in the amount of stretching, a decrease in temperature, an increase in rate of cooling after stretching, and a decrease in the number of times the film was stretched before finally cooling. The values of many of the mechanical properties are more closely related to the birefringence than to the amount of hot stretching. The softening temperature is decreased in direct proportion to the birefringence. Annealed films give higher softening temperatures than films which have been stretched and then allowed to shrink before cooling.

HPP17. The Transition Phenomenon of Polymeric Substances. R. BUCHDAHL, L. E. NIELSEN, AND R. E. POLLARD, *Monsanto Chemical Company.*—The mechanical properties of high polymers are determined by the location of the transition range on the temperature scale; the transition region is defined as the temperature range where the mechanical loss factor goes through a maximum and where the dynamic elastic modulus changes by several decades. Below the transition temperature the polymer is a rigid brittle solid and above this temperature the polymer is a rubber-like material. The addition of low molecular weight plasticizer to the polymer lowers the transition temperature and changes the width of the transition. Quantitative changes of the transition temperature will be explained in terms of plasticizer concentration, compatibility of the plasticizer-polymer system and in terms of a transition in the plasticizer. For copolymers the transition range can be predicted from the volume of the two components and their respective transition temperatures. The behavior of polymer blends in terms of the transition phenomenon is discussed briefly and a possible interpretation of the general transition phenomenon will be given.

HPP18. Dispersion of Dynamic Rigidity and Viscosity in Concentrated Polyvinyl Acetate Solutions. JOHN D. FERRY, W. M. SAWYER, GEORGE V. BROWNING, AND ARTHUR H. GROTH, JR., *University of Wisconsin.*—Data for the dynamic mechanical properties of solutions of polyvinyl acetate in 1,2,3-trichloropropane, obtained from both transducer and wave propagation measurements, superposed for all concentrations from 5 to 40 percent and all temperatures from $-3°$ to 41°C when the reduced dynamic rigidity, $G'T_0/Tc$, and the reduced dynamic viscosity, η'/η, are plotted against the reduced frequency, $\omega\eta T_0/Tc$; G' = real part of complex dynamic rigidity, η' = real part of complex dynamic viscosity, η = steady flow viscosity, c = concentration in g/cc, T = absolute temperature, $T_0=298°\text{K}$. This behavior can be predicted by postulating that each elastic mechanism has a rigidity proportional to T and to c and that the relaxation times of all mechanisms have the same dependence on c and T. The two universal dispersion curves are characteristic of a given polymer sample, representing the mechanical properties in a hypothetical standard state of unit density and unit viscosity at 298°K. From either dispersion curve, the distribution of relaxation times may be obtained over about 5 cycles of logarithmic time. The distribution indicates a relatively sharp cut-off at the upper end which may be attributed to the finite molecular length of the linear polymer.

HPP19. The Effect of Excluded Volume on the Configurations of Long Chain Molecules. GILBERT W. KING, *Arthur D. Little, Inc., and M. I. T.*

HPP20. Concentration Dependence of Viscosity of Solutions of Macromolecules. JACOB RISEMAN AND ROBERT ULLMAN, *Polytechnic Institute of Brooklyn.*—The method of Kirkwood and Riseman, used to account for hydrodynamic interaction between elements of the same chain are extended to include interactions between elements of different chains, responsible for the hydrodynamic effects leading to the concentration dependence of viscosity. The dumbbell and rod-shaped molecule will be treated. Smoluchowski's result for pair interaction appears as a first-order approximation. The viscosity calculation is carried out by considering the average shearing stress across a plane and yields for the viscosity a generalized binomial form, $\eta=\eta_0/1-f(c)$. $f(c)$ depends on the distribution function of elements on the same and different chains. At low concentrations, a uniform distribution has been assumed, leading to a $k'[\eta]^2$ as the coefficient of the C^2 term. A method of iteration would give $f(c)$ as an infinite power series in the concentration, and the corresponding viscosity as a doubly infinite power series. The generalized binomial form thus obtained therefore bears some resemblance to empirically proposed equations for the viscosity.

HPP21. The Stress-Strain Behavior of Thermally Shortened Collagen Tendons. NORMAN M. WIEDERHORN AND GERALD V. REARDON, *United Shoe Machinery Company.*—In order to gain information concerning the structure of collagen, the stress-strain behavior of thermally contracted (denatured) kangaroo tail tendon was studied. It has been determined that when this material is highly swollen with appropriate swelling agents it obeys the kinetic theory of rubber elasticity for relatively large deformations. The material is apparently cross-linked by covalent linkages and the average molecular weight of the chain between points of crosslinking has been determined to be 54,000±7000. This corresponds to approximately 600 amino acid residues, so that the concentration of amino acids involved in cross-links is of the order of 0.2 percent.

HPP22. Molecular Weights from Flow Birefringence and Intrinsic Viscosities. M. D. SCHOENBERG AND F. R. EIRICH, *Polytechnic Institute of Brooklyn.*—An empirical relationship is proposed relating the quotient $(n_e-n_0)/q\eta_0C$ to the molecular weight and intrinsic viscosity. The constant obtained for a single fraction in a given solvent from experimental flow birefringence and intrinsic viscosity data, when applied to flow birefringence and intrinsic viscosity measurements on other fractions of the same polymer in the same solvent, gives molecular weights that are in agreement with those obtained by other measurements. The molecular parameters b and ζ are obtained by calculating the rotatory diffusion constant of Riseman-Kirkwood. At large gradients the above relationship no longer is applicable, which effect is attributed in part to a "stretching" phenomenon.