PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SIXTY-EIGHTH MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York, on Saturday, October 18, 1913.

Vice-president Merritt presided at the meeting.

At the morning session the following papers were presented:

The Vapor Pressure of Metallic Tungsten. IRVING LANGMUIR.

The Form of the Ionization by Impact Function $a/p = f(x/p)$. BERGEN DAVIS.

Change of State Solid-Liquid at High Pressure. P. W. BRIDGMAN.

Notes on Some Integrating Methods in Alternating Current Testing. FREDERICK BEDELL.

Silvered Quartz Fibers of Low Resistance Obtained by Cathode Spray. HORATIO B. WILLIAMS.

The Critical Ranges $A2$ and $A3$ of Pure Iron. G. K. BURGESS and J. J. CROWE.

A Spectrophotometric Study of the Absorption, Fluorescence and Surface Color of Magnesium-Platinum Cyanide. FRANCES G. WICK.

Examination of the Omnicolore Screen Plate by Means of Microscope and Spectroscope. JOHN B. TAYLOR.

Relativity Theory; General Dynamical Principles. (By title.) RICHARD C. TOLMAN.

The Hall Effect in Liquid and Solid Mercury. W. N. FENNINGER.

Failure of Color Photography by Commercial Screen-Plate Methods for Spectroscopic Records. JOHN B. TAYLOR.

Some Experiments on the Magnetic Field of Two Electromagnets in Rotation. S. J. BARNETT.

(Adjourned at 1:00 P. M. for lunch.)—Afternoon Session.

An Electrolytic Determination of the Ratio of Silver to Iodine and the Value of the Faraday. G. W. VINAL and S. J. BATES.

Effect of Amalgamation on the Contact E.M.F. of Metals. F. J. ROGERS.

Relativity Theory; The Equipartition Law in a System of Particles. (By title.) RICHARD C. TOLMAN.

Condition Involving a Decrease of Primary Current with Increasing Secondary Current. F. J. ROGERS.

The Effect of Space Charge and Residual Gases on the Thermionic Current in a High Vacuum. IRVING LANGMUIR.

It was voted to approve the recommendation of the Council that in the case of the annual meeting, the Washington meeting and the Chicago meeting a local committee be given charge of the program for one half-day session, the appointment of this committee to be made by the president of the Society.

Adjourned at 4:30.

ALFRED D. COLE,
Secretary.

CHANGE OF STATE SOLID-LIQUID AT HIGH PRESSURES.[1]

BY P. W. BRIDGMAN.

THE melting temperature and the difference of volume between liquid and solid has been measured as a function of pressure for the following eleven substances: potassium, sodium, carbon dioxide, chloroform, anilin, nitrobenzol, diphenylamine, benzol, carbon tetra-chloride, orthokresol, and phosphorus. The range of the experiments is from 0° to 200°, and up to 12,000 kgm/cm^2. The melting curves (melting temperature against pressure) all are concave toward the pressure axis, the curvature becoming less at the higher pressures. The change of volume curves are also all similar to each other, but are different from the melting curves in that they are all convex toward the pressure axis. These two facts, together with Clapeyron's equation, indicate that at still higher pressures we are to expect neither a maximum nor a critical point, but that in all probability the melting curve continues to rise indefinitely.

In addition to the experiments on the transition liquid-solid, new allotropic modifications of the solid were found for four of the substances. Benzol and orthokresol have one new form stable at high pressures, carbon tetra-chloride has two new forms, and there are two new forms of phosphorus, one of which changes reversibly into the ordinary yellow phosphorus under the proper conditions, but the other is obtained from the yellow variety by an irreversible reaction at high pressures and temperatures, and is stable under atmospheric conditions. This new form is in appearance like graphite, and has the density 2.60.

THE JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

SILVERED QUARTZ FIBERS OF LOW RESISTANCE OBTAINED BY CATHODE SPRAY.[1]

BY HORATIO B. WILLIAMS.

LOW resistance quartz fibers suitable for use in the Einthoven galvanometer and similar instruments, are usually prepared by chemical silvering. Such deposits are rough and the amount of silver is high in proportion to the conductivity. Cannegieter has shown that smooth fibers can be produced by deposition of a cathode film, followed by electroplating. By the method here outlined, fibers of low resistance can be obtained by the cathode spray alone, thus diminishing the number of manipulations and avoiding all contact with chemical solutions. The cathode is of pure sheet silver bent to a half cylinder. The fibers are held in the discharge tube on a glass frame to which they are cemented with hot shellac. The tube is several times exhausted to .01 mm. and rinsed with dry electrolytic hydrogen. Discharge is maintained at .01 ampere with voltage from 1,200 to 1,500. Direct current is supplied by two small generators with armatures connected in series and fields separately excited. Much gas seems to be occluded during the discharge and a small stream of hydrogen is allowed to leak in steadily, maintaining the current constant. The time of discharge varies with the thickness of film desired. A fiber 140 mm. long, .002 mm. finished diameter with a resistance of 2,700 ohms was obtained by exposure for three hours. The fibers are microscopically smooth and the coating is very compact, uniform and strongly adherent. A liquid air block between the discharge tube and the other parts of the apparatus insures uniform success, but good results can sometimes be secured without it.

DEPARTMENT OF PHYSIOLOGY,
COLUMBIA UNIVERSITY, NEW YORK.

THE EFFECT OF SPACE CHARGE AND RESIDUAL GASES ON THE THERMIONIC CURRENT IN HIGH VACUUM.[1]

BY IRVING LANGMUIR.

THE mutual repulsion of electrons (space charge) in a space devoid of positive ions limits the current that flows from a hot cathode to a cold anode. For parallel plane electrodes of infinite extent, separated by the distance x, and with a potential difference v between them, the maximum current (per unit area) that can flow if no positive ions are present is

$$i = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{v^{\frac{3}{2}}}{x^2}.$$

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

For the analogous case of an infinitely long hot wire placed concentrically within a cylindrical anode of radius r, the maximum current per unit length is

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{v^{\frac{3}{2}}}{r\beta^2},$$

when β varies from 0 to 1, according to the diameter of the wire, but for all wires less than one tenth of the diameter of the anode, β is extremely close to unity.

Experiments show that in a very high vacuum (pressure less than .0001 mm.) and with electrodes which do not give off gas the space charge limitation often prevents the thermionic currents from exceeding a few milliamperes. Pressures of gas as high as .001 mm. with voltages above 40 volts usually lead to the formation of sufficient positive ions to neutralize the effect of space charge.

The presence of low pressures of most gases (.001 mm. or less) greatly decreases the electron emission from tungsten. This effect is especially marked at lower temperatures and tends to disappear at very high temperatures. This results in an increase in the value of b of Richardson's equation produced by practically all gases except the group of inert gases.

The proper conditions for obtaining the normal thermionic current from heated metals are discussed. This electron emission is found to be a true property of the pure metal and is not due to secondary chemical effects. For tungsten the thermionic current varies with the temperature in full accordance with Richardson's equation with the following constants:

$$a = 34 \times 10^6 \text{ amps. per sq. cm.},$$

$$b = 55{,}500.$$

Pure electron currents, of even several tenths of an ampere without any perceptible positive ionization, are thus readily obtained. No disintegration of the cathode occurs under these conditions.

The effect of nitrogen in decreasing the thermionic current depends on the voltage of the anode. In many cases much less current is obtained at high than at lower voltages.

The following theory is in full accord with the observed phenomena: The effect of gases in changing the saturation current is due to the formation of a film of an unstable compound on the surface of the metal. The extent to which the surface is covered depends on the relative rates of formation and of destruction of the film. The film may be formed by direct reaction of the metal with the gas or be produced by the bombardment of the metal by positive ions. The film is destroyed by decomposition, volatilization, or cathodic sputtering (bombardment by positive ions).

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

NOTES ON SOME INTEGRATING METHODS IN ALTERNATING CURRENT TESTING.[1]

BY FREDERICK BEDELL.

AN alternating current or voltage can be measured by a direct current instrument or galvanometer of the D'Arsonval type if a synchronous commutator is interposed between the circuit and the instrument. The reading of the instrument is the integral of the alternating current for half a period, the limits of the integral being determined by the setting of the brushes on the commutator. The brushes may be shifted so as to shift the half period over which the integral is taken. In this way successive instantaneous values may be found of one quantity the value of which depends upon the integral of the quantity directly measured. For example, if the quantity measured by means of the commutator and galvanometer is the current flowing in a condenser, the successive readings of the galvanometer are proportional to the instantaneous values of the charge q of the condenser, since $q = \int idt$. The integral readings of condenser current for any setting of the brushes gives the instantaneous value of q at the moment of commutation. Since potential v is proportional to q, this gives a method for determining the wave-form of potential. If the potential is taken across the terminals of a non-inductive resistance, the wave-form of current is determined.

This condenser current method for determining wave-form is much more sensitive and has a much wider range than various time-honored point-by-point methods. In this and in other integrating methods[2] variation in commutator resistance may be a source of error which may be reduced by perfecting the apparatus or may be made ineffective by choice of method.

CORNELL UNIVERSITY,
ITHACA, N. Y.

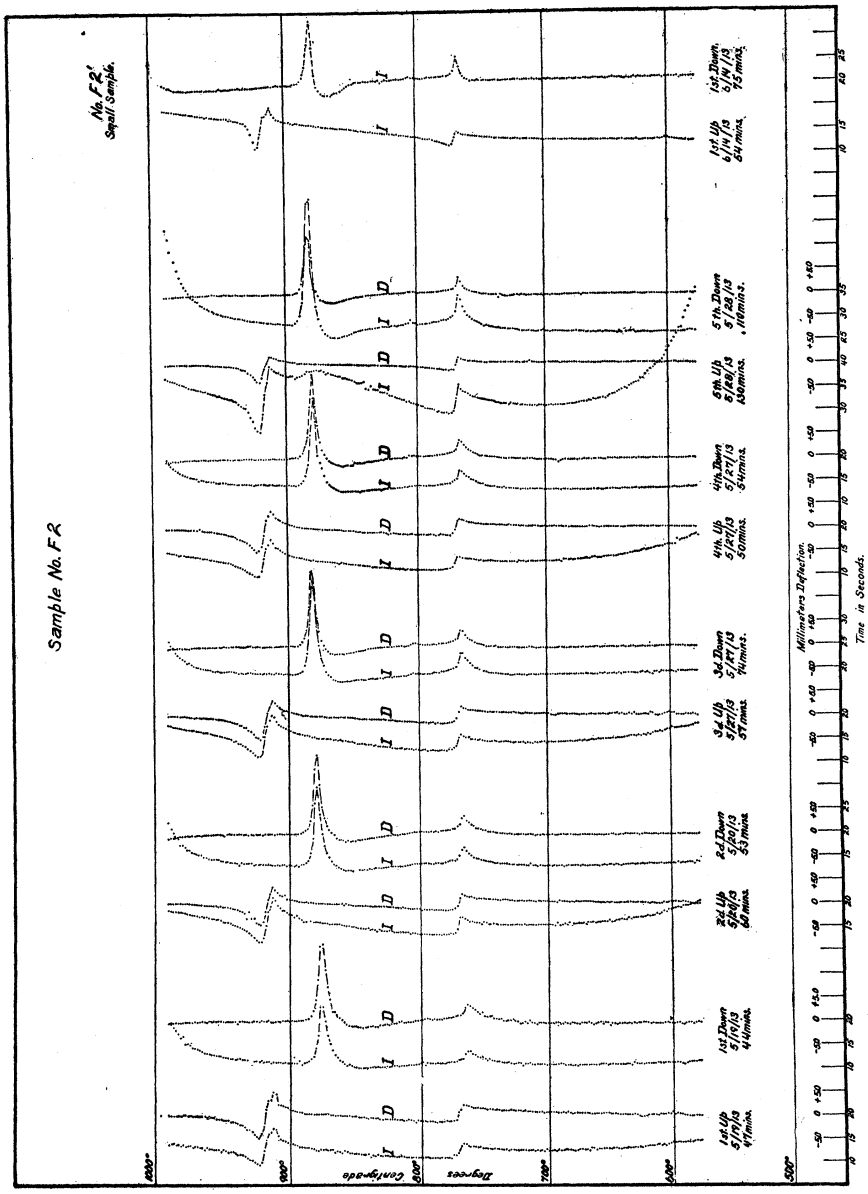
THE CRITICAL RANGES $A2$ AND $A3$ OF PURE IRON.[1]

BY G. K. BURGESS AND J. J. CROWE.

IN spite of a great amount of experimental work and even more theorizing, the question of the allotropy of iron is not yet satisfactorily settled. The separate existence of the lower critical range $A2$ has been seriously questioned by several recent writers; nevertheless all the physical properties of iron which have been studied, with the single notable exception of crystallo-

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

[2] For a detailed description of these methods, see the following papers by F. Bedell: "Condenser Current Method for the Determination of Alternating Wave Form," The Electrical World, August 23, 1913; "The Use of the Synchronous Commutator in Alternating Current Measurements," Journal of the Franklin Institute, October, 1913


Sample No. F R
No. F R
Small Sample.
Centigrade
Degrees
Millimeters Deflection.
Time in Seconds.

graphic structure, have shown, in the hands of one or more skillful experimenters, a distinct discontinuity for the lower critical range $A2$ as well as for the upper $A3$ range. For several of the phenomena, such as electrical resistance, thermo-electricity, specific heat, and magnetism, it would appear that the discontinuity is at least as great for $A2$ as for $A3$, while the thermal effect has of course been long recognized as being much the more pronounced at $A3$.

This investigation consisted in taking in vacuo some 130 heating and cooling curves by two methods simultaneously, the inverse rate and differential for 15 samples of pure iron prepared by various methods and analyzed by several chemists. Unusual precautions were taken to secure uniformity of heating of the samples, and it was also possible to take observations for samples of widely different mass and over a wide range of rates each maintained strictly constant. Two furnaces were used and temperatures were taken with six separately calibrated thermocouples. The observations show that in order to get consistent and reliable results in the thermal analysis of a substance such as iron, the properties of which are so readily susceptible to many minor influences, it is necessary to get rid of all the disturbing influences.

We find essential the following precautions:

1. The iron should be pure; our purest samples were 99.983 and contained 0.003 per cent. carbon or less; and it should be kept pure by heating it only in vacuo; a pressure of 0.01 mm. Hg suffices.

2. Either the occluded gases should be removed by premelting the iron, preferably in vacuo, or it will in general be found necessary to take a series of heating and cooling curves at widely different rates, in order to determine correctly the location of the critical ranges $A3$ and $A2$.

3. The iron should be in a single piece entirely surrounding and in contact with the thermocouple junction, otherwise the thermocouple will integrate the irregular progress of the heat through the sample and the curves will lose their sharpness; small samples (1.0 gram or so) give sharper results than large samples.

4. The interval of recording temperatures should be wide enough that sufficient sensibility is attained and narrow enough that the contour of the curves is not distorted; we have found a 2° interval satisfactory.

5. The sensibility of the apparatus indicating temperature and differences of temperature should be of the order of 0.01 degree and time should be measured to better than 0.2 second.

Among the results of this investigation may be mentioned the demonstration that the inverse rate and differential methods, the latter plotted as the derived differential curve, give identical results of the same sensibility for the critical ranges, and the two sets of curves are strictly similar, save for minor particulars.

The plotted curves give what seems to us conclusive evidence of the independent existence of $A3$ and $A2$, all of the 130 curves without exception showing both these critical ranges sharply defined and unquestionably distinct.

It was found impossible to eliminate or attenuate $A2$ by thermal treatment. The $A2$ transformation has not a double cusp, nor do there appear to be other transformations above $A3$ and below $A2$ between 300° and 1050°. With electrolytic iron, unless the sample has been premelted into a compact mass, erratic results will be obtained for both $A3$ and $A2$, the location of the critical points apparently depending in the main upon the rate of heating or cooling. The critical points may even be displaced by over 50°. It is possible, however, to reduce the observations on untreated electrolytic iron to exactly the same temperature basis as the gas-free, compact material by taking curves at several rates and reducing to zero rate. This would appear to indicate that the gases occluded, mainly hydrogen, play no essential chemical rôle in modifying the iron equilibrium.

Even with gas-free iron the $A3$ point is not entirely independent of the rate of heating or cooling, so that it is necessary to reduce the observations to zero rate in order to obtain correct results for $Ac3$ and $Ar3$. The range in the location of $Ar3$, for example, with premelted samples was found to be 876° C. at 0.155 deg./secs. to 897° C. at zero rate.

All preparations of pure iron, even those containing gases, when reduced to the common basis of zero rate of heating or cooling, have the same maximum for the $A2$ critical range, namely, $A2 = Ac2 = Ar2 = 768° \pm 0.5$. All but one of the 15 samples gave this result to within 2°, the other to 3°.

Similarly for zero rate, the value of the maxima of $A3$ are found to be $Ac3 = 909° \pm 1$ and $Ar3 = 898° \pm 2$.

It was not possible to infer a single equilibrium temperature $Ae3$ from these experiments, the $Ac3$ transformation on heating always being at a higher temperature than $Ar3$, the transformation on cooling.

It was found, however, that the beginning of $Ac3$ coincides in temperature with the beginning of $Ar3$ as closely as could be judged. It is as if the crystallographic change at $A3$ required, so to speak, a temperature inertia to complete itself both on heating and on cooling, although the effect of rate on the equilibrium appears to be slightly the greater on cooling.

It is possible that the $A3$ transformation is somewhat more complex than this as there are indications from some of the heating curves of a doubling of $Ac3$ although not of $Ar3$. This effect may be fortuitous.

The relative amounts of heat accompanying the two transformations, $A3$ and $A2$, is approximately $\frac{3}{4}$ to $\frac{1}{4}$ respectively.

An examination of some of the heating curves will perhaps give the erroneous impression that $Ac2$ is an evolution rather than an absorption of heat. The swing back at the maximum is very abrupt following what appears to be a gradual building up of this maximum from an indeterminate low temperature. This behavior would be in accordance with the gradual change in certain physical properties, such as magnetism and electrical resistance, as $A2$ is approached. On the other hand, the operations carried out on sample $F2$ failed to diminish sensibly the intensity of $Ac2$, which would imply that this

thermal transformation is limited to a narrow temperature interval; also some of the curves of $Ac3$ show that this long back swing appears to be in part at least a property of the heating conditions. The shading off on cooling through $Ar2$, if this effect is a real one, might be marked by a similar swing back from this peak, and therefore be indistinguishable.

We hesitate to express an opinion on the nature of the allotropy of iron. The fact that $A2$ appears to be accompanied by no crystallographic change, such as accompanies $A3$ requiring a violent rearranging of relatively large crystal masses and involving a considerable quantity of heat, may account for the sharpness with which $Ac2$ equals $Ar2$, and the $A2$ transformation may be merely molecular not involving the crystallographic structure as such. Whether we have any β iron or not to inhabit the region between $A2$ and $A3$ will depend on our definition of allotropy, but we hope that we have proved beyond a reasonable doubt that under standard conditions there is a definite transformation at 768° and a less well defined although more intense one at 898° to 909° in terms of their maxima on cooling and heating, respectively.

BUREAU OF STANDARDS,
WASHINGTON,
September 2 , 1913.