for the Rydberg constant, the value of the Rydberg constant being $cR_\infty =$ 3.2899 $\times$ 10^{15} cm.; and (c) Einstein's quantum equation. The experimental values of e and of h are not used in this calculation of m_0, nor are the results of any other experiments than ours on the reflection of x-rays by calcite, and the experimental determinations of the fundamental constants d and cR_∞. From our value of m_0 and from measurements by others of e/m_0 we can calculate first e and then h.

AN INSTRUMENT FOR THE PHOTOMETERING OF THE NEW X-RAY LINES

By William Duane

Physical Research Laboratory, Harvard University

In the Proceedings of the National Academy of Sciences for January, 1932, appears an article in which I describe experiments on the new K series x-ray lines, of which I spoke in a paper presented to the American Physical Society at its New York meeting in February, 1931. The end of the article contains several photometer curves of the β doublet, the γ line and a few of the new lines belonging to the molybdenum K series spectrum. The photometer now existing in the Jefferson Laboratory produced some of these curves, and for the other curves it gives me great pleasure to thank Dr. DuMond of the California Institute of Technology.

Recently I have designed and had set up in our new Physical Research Laboratory a photometer for drawing curves of x-ray spectra. The photometer contains some new features. Figure 1 represents the instrument. At the extreme right of the figure appears a box of considerable size, which contains a high powered electric lamp (a one-kilowatt lamp, for instance). The photographic negative of the x-ray line spectrum to be examined by the photometer lies just below "a." An accurately ground lens system made by Leits for producing microphotographs lies at "b" and projects the spectrum lines to the vertical front side of a small metal box at "c." In this particular case the two lines of the β doublet in the K series of molybdenum appear at "c." The photograph resembles one of those shown in the previous article (New Lines in the K Series of X-rays, The Proceedings of the National Academy of Sciences, Vol. 18, No. 1, pp. 63–68, January, 1932). The two β lines appear clearly separated from each other although the difference between their wave-lengths amounts to only 0.000563 Å.

I have used the well-known photo-electric cell to examine the lines. The lines are horizontal.   Just below them is a horizontal black line in the figure at the center of which lies a very narrow horizontal slit in the side of the small metal box.   The metal box contains the photo-electric cell just behind the slit.   The positive anode of the photo-electric cell is joined to earth through the metal box, all connections being soldered.   The inner negative surface of the cell, from which the electrons proceed, is connected to the negative pole of a battery contained in the larger metal box "*d.*"   To complete the electrical circuit of the photo-electric cell, the positive pole of the battery is joined through a heavily insulated,
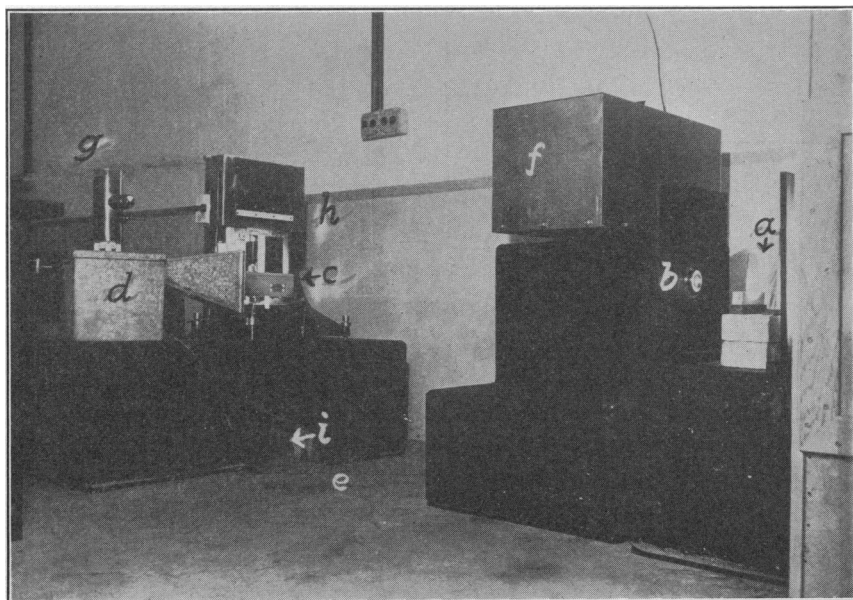

FIGURE 1

lead-covered wire "*e*" to a d'Arsonval galvanometer in the large iron box "*f.*"   The second terminal of the galvanometer is joined by separate wires to the box "*f*" and then to earth.   The lead covering of the circuit "*e*" is soldered to the box "*d*" and to the box "*f.*"   There is, therefore, a complete circuit running through the photo-electric cell, the battery and the galvanometer, and this entire circuit is completely protected from electrical disturbances by the metal boxes and the lead covering of the wire circuit.   The galvanometer deflection is observed by means of a beam of light coming from the lamp "*g*" (which has in front of it a narrow vertical slit).   This beam of light after passing through an opening in the far side of box "*f*," is reflected from the galvanometer mirror to a scale at "*h.*"

At this scale lies a long narrow horizontal slit held fixed in space. Behind this slit at "*h*" is an undeveloped photographic plate in a light-tight box, fixed in space and having the fixed slit "*h*" in its front surface. The plate lies in a vertical plane. It and the photo-electric cell with its slit lying just behind the projected spectrum lines are mechanically joined together. They lie on a vertical holder which can be moved slowly up and down by means of a worm gear and suitable screw mechanism lying on the floor at "*i*" between the concrete supporting blocks. As the photo-electric cell and its slit move up or down the slit crosses behind the image of the lines at "*c*," and, as the light entering the cell varies, the photo-electric current varies and the galvanometer deflection at "*h*" varies. During this variation the undeveloped photographic plate behind "*h*" changes its position and thus the deflection, corresponding in magnitude to the blackness of the spectrum negative, traces out a curve on it. Evidently there is an exact one to one relation between the points on this curve and the points in the image of the spectrum lines, and no elaborate system of cogwheels, etc., is necessary in order to get the proper relations between the coördinates of the curve—an important characteristic of the new photometer I am describing. The slit at "*c*" has a breadth of only 0.2 mm. and as the β doublet has a breadth of approximately 20 mm. the machine produces curves corresponding to very high resolution.

The photo-electric cell in the metal box is one that has a maximum of sensitivity in the neighborhood of the visible wave-length 5500 Å. It gives me great pleasure to thank Mr. Ives and Mr. Olpin of the Bell Telephone Research Laboratory in New York for this photo-electric cell. They very kindly spent some time in preparing a cell that would have its maximum sensitivity in the section of the spectrum that produces the greatest effect on the human eyes. Since this light belongs to a fairly narrow band, there is very little error due to the lens system, which is highly corrected for the most visible light. This facilitates properly focusing the spectral lines at (*c*) and reduces any error that may be due to lack of focus. This point has been investigated by taking curves with precisely the same negative of the β doublet, one curve with a beam of light the wave-lengths of which did not differ from each other very much, and a second curve with a beam containing a much larger number of different wave-lengths. In the former curves the portion between the β_1 and β_2 lines appears to be much less intense than in the latter.

In making detailed studies of the errors which may be produced in drawing the above-mentioned curves I have had taken a great many photographs. The errors may be classified somewhat as follows:

Figure 2 contains curves representing the two lines in the β doublet belonging to the K series of molybdenum shown in figure 1. I have had the curves of figure 2 produced in such a way as to illustrate the various

errors that may occur in making measurements; which errors must be guarded against and corrected.

The uppermost curve in this figure 2, aa', was photographed with a solid black body in front of the slit c (Fig. 1). During the drawing of this line the photo-electric cell, its slit and the photographic plate were lowered through a distance of about 4 cm. During this motion no light entered the photo-electric cell and aa' appears to be perfectly straight and to contain no jiggles. Early photograph records of this kind did contain jiggles which have been eliminated. The fact that the line is now straight means that there are no mechanical jars, no variations in the current passing through the photo-electric cell and no changes of zero of the d'Arsonval galvanometer capable of producing changes in the galvanometer's deflection of sufficient magnitude to be seen.

The two curves bb' and cc' represent the current through the photo-electric cell when light was allowed to enter and when its slit moved up and down, back of the projections of the β doublet. The curve bb' corresponds to motion downward and the curve cc' to motion upward. I have had these curves drawn purposely in such a way as to illustrate the effects due to the galvanometer's period and damping. The speed of taking one of the curves (four minutes from a to a') was purposely made fairly large and so also was the period of the galvanometer (sixteen seconds).

The dots lying between these two curves represent static deflections. To produce one of the dots, the light reflected from the

FIGURE 2

galvanometer's mirror was shut off and the photo-electric cell was raised 1 mm. After sixteen seconds the galvanometer needle had come to rest and the light reflected from its mirror was allowed to pass through the slit h long enough to register on the photographic plate. It was then cut off, and the slit raised another millimeter in order to take another point, etc., etc. A line drawn through these points would represent a static curve. The curves in the figure are shifted, one to the right and one to the left of the static curve, this shift being due to the fact that owing to the period of the galvanometer, its deflection lags slightly behind the motion of the slit and photo-electric cell. The curve is shifted to the right or to the left according to whether it is being produced in the right hand direction or in the left hand. By decreasing the speed at which the curves are drawn or by decreasing
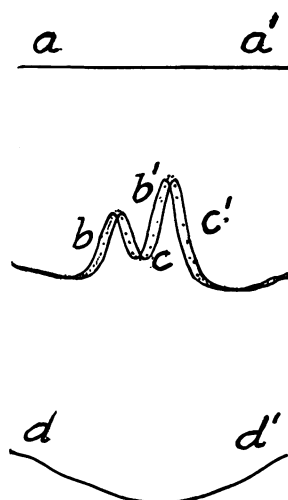
the period of the galvanometer the curves may be caused to approach each other and become superposed as illustrated in figure 3.

Although the two curves bb' and cc' appear superposed at points on the β peaks, they become separated at their right hand ends near c'. This separation occurs in the vertical direction and cannot be due to the period of the galvanometer. The separation comes from a slight decrease in the voltage of the storage battery that was delivering current through the projection lamp. The curve bb' was taken in the direction from b' to b, and then the curve in the opposite direction from c to c' was taken.
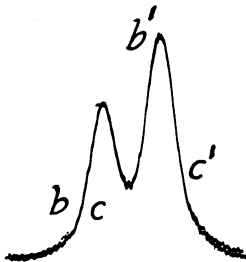
The velocity was so small that nearly ninety minutes of time elapsed between the instants corresponding to the two right hand ends of the curves. Toward the end of this period the battery ran down slightly and cc' at its end represents a slightly smaller deflection than bb'.

For many purposes I feel that it is best not to reduce the horizontal shift between the two curves so as to make them absolutely coincide in order to detect any variations in the curve which may be purely transient. If the curves are very nearly superimposed upon one another variations that appear up or down at corresponding points on both curves must be due to the variation of the light coming through the photographic negatives which are permanent and not transient.

Curve dd' represents the variation of the photo-electric current after the photographic negative had been removed. Its variations correspond to changes from point to point in the intensity of the beam of light striking and passing through the photo-electric slit. As illustrated in figure 3 the intensity of this light has been made much more uniform. A correction for the variation in intensity, however, may be obtained obviously by dividing the distances from aa' to bb' by the corresponding distances from aa' to dd'.

FIGURE 3

As stated above the reason for designing this photometer, and for having it constructed and set up, has been to examine in some detail the x-ray K series spectrum in which I have found a number of new lines. The new lines were presented to the Physical Society at the New York meeting in February, 1931. They appear also on the photographs reproduced in the previous article in the January number of the PROCEEDINGS of the

National Academy of Sciences.   The new features of the x-ray spectrum include (a) a band ·apparently containing a number of lines somewhat shorter than the delta line (O-K electrons), which may be due to conductivity electrons in the molybdenum target falling into the K position; (b) a line called "x" half way between β doublet and the γ line, (c) a line very close to the β_1 line and on the short wave-length side of it and (d) various very weak lines on the sides of the β lines and of the γ line, especially a long series of satellites on the short wave-length side of the β_1 line.   According to the photographs, however, these rows of satellites must extend on both sides of the main K series lines.   Apparently they prevent the curves from falling to zero between the β_1 and β_2 lines and between the γ and δ lines.

Professor Patterson of the Troy Polytechnic was at Harvard as a NATIONAL RESEARCH FELLOW some thirteen years ago and was working on the x-ray line spectra.   He made some observations which led him to suggest that there might be weak satellites of this kind near the strong lines themselves.   We therefore tried to get by the ionization methods which we were using at that time, definite and completely satisfactory evidence for the existence of such satellites.   We did not obtain evidence by the ionization method that was completely satisfactory.   The photographs of the K series of molybdenum, however, which I presented a year ago to the Physical Society at its New York meeting in February and which were discussed in the article in the January, 1932, PROCEEDINGS and in this article, seem to furnish evidence in favor of their existence.

Obviously the above-described photometer may be employed to examine spectra in a variety of ways.   For instance, a large photograph of the spectral lines may be taken by means of an ordinary projection lantern and then this large photographic negative may be placed before the photo-electric cell slit at c (Fig. 1).   Then, illuminating the part of the negative which one wishes to examine by means of a powerful lamp at some distance from the photometer, the photo-electric slit may be moved up or down and a photographic curve taken of the spectral lines.   This method has enabled us to study more thoroughly the faint lines in the molybdenum spectrum referred to above.   Some of the curves thus obtained will be published later, together with wave-length measurements of the lines.

Professor P. A. Ross of the University of Stanford has recently published two letters in the *Physical Review* (February 1, and February 15, 1932), in which he mentions some extraordinarily interesting ionization curves representing the K series spectrum of molybdenum.   He verifies by these ionization observations the above-mentioned new lines in the K series of molybdenum.   He also finds similar lines in the K series of other chemical elements (Tel—Pal—Ag—Cd—Sn— and Sb).   Obviously this discovery is of very great importance.   The suggestion by Professor Ross

that some of the new lines may correspond to so-called forbidden lines will greatly interest those who like to look in that way at lines that are not explained by the electron theory.

THE PRESSURE VARIATION OF THE HEAT FUNCTION AS A DIRECT MEASURE OF THE VAN DER WAALS FORCES

BY FREDERICK G. KEYES AND SAMUEL C. COLLINS

CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY. SERIAL NO. 291.

The heat function or thermodynamic potential, $\chi = \epsilon + pv$, where ϵ is the energy, p the pressure and v the volume, is a function of the greatest importance in the applications of thermodynamics to chemistry and engineering. In the present note a brief account will be given of a direct method whereby it has been found possible to determine the change of χ with pressure at constant temperature.

The differential coefficient $\left(\dfrac{\partial \chi}{\partial p}\right)_T$ possesses among other properties a most intimate relation to the departure of gases from the simple equation $pv = RT$. It will be shown that the coefficient is most closely related to and is, in fact, a measure of, the molecular van der Waals forces, attractive and repulsive, operative in giving to gases their known physical properties.

Starting with Gibbs' equation (90)[1] we find

$$\left(\frac{\partial \chi}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + v + \Sigma\mu_1\left(\frac{\partial m_1}{\partial p}\right)_T \tag{1}$$

where S, μ and m represent the entropy, the thermodynamic potential and the mass. The change of entropy with pressure under the conditions of constant temperatures is equivalent to $-\left(\dfrac{\partial v}{\partial T}\right)_T$ assuming the state of the system to be only a function of the variables P and T. In the special case of a single pure substance (1) becomes,

$$\left(\frac{\partial \chi}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial v\tau}{\partial \tau}\right)_p, \tag{2}$$

where τ is used to denote T^{-1}.

The Joule-Thomson coefficient, $\left(\dfrac{dT}{dp}\right) = \eta$, is given on the other hand