

REVIEWS OF MODERN PHYSICS

VOLUME 11

APRIL, 1939

NUMBER 2

The Atomic Constants A Revaluation and an Analysis of the Discrepancy

FRANK G. DUNNINGTON

Department of Physics, Rutgers University, New Brunswick, New Jersey

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INTRODUCTION

THE object of this review is twofold: (1) to offer a revaluation of significant experimental data with the results based on a consistent set of auxiliary constants; (2) to present what evidence can be found in these experimental data

as to the origin of the discrepancy; (3) to indicate what experimental work is needed to aid in resolving the difficulty.

The notable discrepancy between the three most accurately known constants, namely the electron charge e , the specific charge of the

electron e/m_0 and the ratio of Planck's constant to the charge of the electron h/e has been discussed for several years.¹⁻⁶ Some light should be thrown on the discrepancy by considering properly *other* directly measured combinations of constants in addition to the three accurately known constants, namely the ruled grating e , e/m_0 from both free electron and spectroscopic measurements and h/e from the limit of the continuous x-ray spectrum. In recent years, these other combinations have either been omitted from the discussion because of their lesser accuracy, or have been reduced to the form of e/m_0 (by assumption of h/e); or to the form of h/e (by assumption of e/m_0).⁷ This reduction tends to confuse the problem and to conceal evidence which may exist as to the source of the discrepancy. Eight additional types of experiments, which possess sufficient accuracy to be significant, have been recalculated. These, together with the experiments giving the three most accurately known constants, have been analyzed as to the basic laws or equations involved.

To compare the various experiments, the results have first been plotted on a Birge-Bond diagram.⁸ In general, an experiment gives $e=f(m_0, h)$, but the electron mass m_0 can be eliminated through use of the Rydberg formula

$$R_\infty = \frac{2\pi^2 e^4 m_0}{ch^3}.$$

Hence the results of any experiment can be reduced to the form $e=Ah^n$, where A is an experimentally determined constant and n the

power to which h occurs. If a value of h which is approximately correct is assumed (call it h_0) and a value of e computed (call it e_n) by use of this h_0 and the observed constant A , then it can be shown that a substantially linear relationship exists between this e_n and the exponent n . A Birge-Bond diagram merely consists of a plot of the computed e_n values as a function of n . The slope of any line determines the value of h (zero slope means $h=h_0$; positive slope $h<h_0$). The value of e is given by the $n=0$ intercept.

Considerable time was spent in obtaining the auxiliary constants used in this paper (see Table I). A detailed study was made of the electrical conversion units from both of the international systems (standard cell system designated by (v) , and silver voltameter system by (a)) to absolute units. A *least-squares solution* was made of all significant data. In the light of the work that has been done since the earlier study by Birge,^{8a} it is felt that distinction should be made between the two systems, though fortunately the difference is small. All measurements involving a standard cell are in the (v) system. The standard of resistance is common to both systems.

A reevaluation of the faraday was also made. The best value of the chemical atomic weight of silver gives for the faraday 96493.7 ± 0.9 int. (a) coulombs, while the work of Vinal and Bates⁹ with the iodine voltameter gives 96510.3 ± 6.8 int. (a) coulombs. The weighted mean of these was used.

The ratio of the mass spectrograph to chemical atomic weights was calculated from the abundances of the oxygen isotopes as given in the

TABLE I. Auxiliary constants used in this work. B indicates value by Birge. D indicates value as recomputed by author. References listed in the table are found at the end of this paper.

SYMBOL	DESCRIPTION	VALUE USED
F	Faraday in international coulombs (D)	$96494.0 \pm 1.5^{(14a)}$
c	Velocity of light in cm/sec. ($B^{12}-D$)	$(2.99776 \pm 0.00015) \times 10^{10}$
p	Conversion factor from N.B.S. int. to absolute ohms (D)	1.000485 ± 0.000007
q	Conversion factor from N.B.S. int. (a) to absolute amperes (D)	0.999970 ± 0.000020
r/p	Conversion factor from N.B.S. int. (v) to absolute amperes (D)	0.999926 ± 0.000020
r	Conversion factor from N.B.S. int. (v) to absolute volts (D)	1.000411 ± 0.000022
R_H^1	Rydberg constant for H^1 in cm^{-1} (B^{13})	109677.76 ± 0.05
R_0	Gas constant in ergs/deg/mole (B^{13})	$(8.3136 \pm 0.0010) \times 10^7$
k_A	Ratio of mass spectrograph to chemical atomic wt. (D)	1.000275 ± 0.000020
k_λ	Ratio of ruled grating to Siegbahn wave-lengths (Bearden ¹⁴)	1.00203 ± 0.00002
R_∞	Rydberg constant for infinite mass in cm^{-1} (B^{13})	109737.42 ± 0.06
h_0	Arbitrarily adopted value of Planck's constant in erg·sec.	6.610×10^{-27}

Report of the Committee on Atoms of the International Union of Chemistry.¹⁰ The sources of the other constants are indicated in the table. It is to be emphasized that all experimental work discussed in this paper has been recalculated with these auxiliary constants. In the case of work done in other countries allowance has been made for the difference in the units of the country in question.¹¹

All uncertainties given are least-square probable errors, and the value given is always the larger of the two kinds of error (internal and external).¹⁵

MORE ACCURATELY KNOWN COMBINATIONS OF CONSTANTS

A. Ruled grating e

This value is obtained in principle as follows: the wave-length of a characteristic x-ray radiation is measured through the use of a ruled grating. The glancing angle of this same radiation from a calcite crystal is then determined and from this the grating space of the calcite is calculated with the Bragg equation (corrected for refraction in the calcite). Finally, the electron charge is calculated from the constants of crystalline calcite (the grating space, the density, the unit crystal volume factor, and the molecular weight) and from the faraday and the velocity of light. This calculation involves the important assumption that the calcite is geometrically perfect.^{16a}

On the basis of a re-evaluation of all these factors, the author obtains¹⁶

$$e_0 = (4.8025 \pm 0.0004) \times 10^{-10} \text{ e.s.u.}$$

This is plotted in the Birge-Bond diagram as point (1) at $n=0$ in Fig. 1. The arrows indicate the probable error.

B. Specific electron charge e/m_0

A summary of the various significant observations has been given by the author in an earlier paper,¹⁷ in which it was shown that there was a disagreement between the free electron and the spectroscopic values. Three new determinations¹⁸⁻²⁰ have been made, and the final results of a fourth published.²¹ The net result, as has already been pointed out by Birge,²² is to

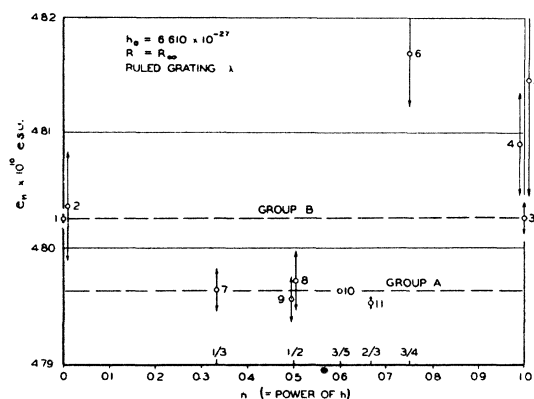


FIG. 1. Birge-Bond plot (i.e., of $e_n = Ah_0^n$) of all known significant experimental data. Based on $h_0 = 6.610 \times 10^{-27}$ erg-sec. and the assumption that the ruled grating wave-lengths are correct. Probable error is indicated by the diameter of the circle around point (10), and in other cases by the arrows. A description of the points and their values are given in Table VI.

effectively remove the discrepancy between the free electron and spectroscopic values. Thus, Houston's²⁰ more objective Fourier analysis method of fine structure analysis has given a higher value of e/m_0 and indicated that the previous methods used are probably in error. Also, the interesting determination by Bearden¹⁹ based on a measurement of the index of refraction of x-rays in a diamond prism has given a high value in good agreement with the other free electron work.

These newer determinations are given along with the earlier ones in Table II. The published values have all been recalculated with the auxiliary constants of Table I. Williams¹⁸ result replaces that of Gibbs and Williams since it represents a continuation of the same work. Shane and Spedding's result²³ has been corrected for reduction of wave-length to vacuum.²⁴ Shaw's value²¹ has been corrected for the change from international to absolute electrical units.

The weighted average of all ten e/m_0 determinations is

$$e/m_0 = (1.7591 \pm 0.0002) \times 10^7 \text{ e.m.u.}$$

In this, the external probable error is given. The fact that R_e/R_i (the ratio of external to internal probable errors¹⁵) = 1.39 shows that the mutual consistency is now fairly good.²⁵

On substituting the free electron value of e/m_0 in the Rydberg equation, and with $h_0 = 6.610$

TABLE II. Summary of e/m_0 determinations. The first five are bound electron ("spectroscopic") values, the last five are free electron values. No important discrepancy is to be noted now between the two groups.

EXPERIMENTERS	DATE	METHOD	e/m_0 $\times 10^{-7}$ e.m.u.	PROB- ABLE ERROR $r \times 10^4$	WEIGHT $= \frac{169}{r^2}$
Houston ²⁶	1927	Fine structure H ¹ -He ⁴	1.7607	10	1.69
Kinsler and Houston ²⁷	1934	Zeeman effect	1.7571	7	3.45
Shane and Spedding ²³	1935	Fine structure H ¹ -H ²	1.7582	4	10.57
Williams ¹⁸	1938	Fine structure H ¹ -H ²	1.7580	4	10.57
Houston ²⁶	1938	Fine structure H ¹ -H ²	1.7593	5	6.76
Perry and Chaffee ²⁸	1930	Linear acceleration	1.7610	10	1.69
Kirchner ²⁹	1932	Linear acceleration	1.7590	9	2.09
Dunnington ¹⁷	1937	Magnetic deflection	1.7597	4	10.57
Shaw ²¹	1938	Crossed fields	1.7581	13	1.00
Bearden ¹⁹	1938	X-ray refraction	1.7600	3	18.79

Weighted Average: 1.7591 ± 0.0002

$\times 10^{-27}$ erg·sec., there results:

$$e_{3/5} = (4.7963 \pm 0.0002) \times 10^{-10} \text{ e.s.u.}$$

This is plotted as point (10) at $n = \frac{3}{5}$ in Fig. 1. The size of the circle indicates the probable error.

C. h/e from the limit of the continuous x-ray spectrum

The experiment consists of the determination of the minimum voltage at which electrons are able to produce x-rays which can pass through a spectrometer. The spectrometer is left fixed at a position for transmission of an x-ray line, the wave-length of which has been found with a ruled grating. Since the voltage V and the wave-length λ are measured, the ratio h/e can be found from the energy equation $hc/\lambda = Ve$.

The most recent and probably the most accurate work in the field is that of DuMond and Bollman.³⁰ In the isochromats representing their results (i.e., plot of x-ray intensity passed by spectrometer *versus* electron voltage) they detected a hitherto unknown knee located only a few volts (they estimate 18) above the quantum limit. The existence of another knee about 100 volts above the quantum limit had been known for some time. For the present discussion, the importance of the existence of a knee is its possible effect on the accuracy of location of the quantum limit. Ross and Kirkpatrick³¹ have shown that if the resolving power of the spectrometer used is not sufficiently high, the isochromat will be smeared to a straight line and

the apparent value of the quantum limit will be lower than the true value. Thus, the resolving power of the spectrometer used is an important factor in evaluating any determination.

The three results which will be considered here are listed in Table III. One puzzling point is this: Schaitberger³² used a single-crystal spectrometer with a resolving power an order of magnitude smaller than that in the other two determinations. On the above argument one would then expect his result to be lower. On the contrary, it is higher.

The need is apparent for further work, both experimental and theoretical,³³ before high precision of the results can be established; but certainly no large changes are likely. The probable error of the weighted average given in Table III will therefore be increased slightly, and the continuous x-ray result be taken as^{33a}

$$h/e = (1.3763 \pm 0.0004) \times 10^{-17} \text{ e.s.u.}$$

Combination of this with h_0 gives:

$$e_1 = (4.8026 \pm 0.0014) \times 10^{-10} \text{ e.s.u.}$$

This is plotted as point (3) at $n = 1$ in Fig. 1.

OTHER COMBINATIONS OF CONSTANTS

In the eight types of experiments that follow, the first four involve the electron mass m_0 , the remaining four do not.

A. $(h/e)(e/m_0)^{1/2}$ from electron diffraction measurements of von Friesen³⁴

Electrons of known voltage were diffracted at the surface of an etched galena crystal and the angular deviations measured for several orders of diffraction. The experiment therefore gives the de Broglie wave-length of the electrons in terms of the grating constant of galena. The latter was

TABLE III. Determinations of h/e from the limit of the continuous x-ray spectrum.

EXPERIMENTERS	DATE	$h/e \times 10^{17}$ e.s.u.	EXPERI- MENTERS ESTIMATE OF P.E.	P.E. USED IN AVER- AGING
Ross and Kirkpatrick ³¹	1934	1.3754	0.0001	0.0005
Schaitberger ³²	1935	1.3773	0.0004	0.0007
DuMond and Bollman ³⁰	1937	1.3765	0.0003	0.0003

Weighted average: $(1.3763 \pm 0.0003) \times 10^{-17}$ e.s.u.

determined by von Zeipel in the same laboratory on a sample of the same crystal by the usual x-ray method.

In expressing the results of this important experiment, von Friesen assumed a value of e/m_0 and combined his results with the Rydberg formula to give e and h . His experiment, without any such assumptions, yields upon recalculation:

$$(h/e)(e/m_0)^{\frac{1}{3}} = (1.00084 \pm 0.00058) \times 10^{-8} \text{ e.s.u.}$$

The probable error was completely recomputed with von Friesen's estimates of his experimental uncertainties and with the uncertainties in the auxiliary constants as given in Table I. Most of the uncertainty in the result originates in the measurement of the angle of diffraction.

With the Rydberg equation and the assumed h_0 , von Friesen's experiment gives:

$$e_{1/3} = (4.7964 \pm 0.0019) \times 10^{-10} \text{ e.s.u.}$$

This is plotted as point (7) at $n = \frac{1}{3}$ in Fig. 1.

For purposes of comparison of this experiment with other experiments there is an essential difference between the above treatment and one which involves the assumption of some combination of constants (for example e/m_0 as was assumed by von Friesen). The above treatment gives a point on the diagram which uniquely represents the results. This is the case since *the relative position of the point with respect to the others is not dependent upon the assumed value of any combination of constants.*³⁵ The Rydberg formula is of course involved in either treatment. The following graphical picture will perhaps clarify the situation: in Fig. 1 a straight line through the point (7) representing von Friesen's work and the point (10) representing e/m_0 will give values of e and of h/e at its intersections with the left and right sides of the figure, respectively, (i.e., at $n=0$, and $n=1$). Except for corrections introduced by the author, these values will be the same as those given by von Friesen. Their dependence on e/m_0 is evident.

B. h/m_0 from electron diffraction measurements of Gnan³⁶ and of Meibon and Rupp³⁷

These are also measurements of the de Broglie wave-length of electrons but differ in two respects from von Friesen's work. First, instead of measuring the electron voltages they measured

the electron velocities in terms of a distance and an electrical frequency (Kirchner's method²⁹). Second, they used films instead of crystals.

Gnan determined the grating space of his bismuth film by direct comparison with NaCl, the grating space of which is known from x-ray work. Meibon and Rupp did not determine the grating space of their gold films. They assumed³⁸ that it was the same as that of gold in sheets, in which form the grating space has been found by x-ray measurements.

Their experiments gave the following values: Gnan: $h/m_0 = 7.258 \pm 0.022 \text{ erg} \cdot \text{sec./g.}$

Meibon and Rupp:

$$h/m_0 = 7.289 \pm 0.022 \text{ erg} \cdot \text{sec./g.}$$

The mean of these is

$$h/m = 7.274 \pm 0.016 \text{ erg} \cdot \text{sec./g.}$$

When it is combined with the Rydberg formula and h_0 one obtains

$$e_{\frac{1}{2}} = (4.7972 \pm 0.0026) \times 10^{-10} \text{ e.s.u.}$$

This is plotted as point (8) at $n = \frac{1}{2}$ in Fig. 1. The above internal probable error is 50 percent larger than the external probable error which probably indicates that the authors have been conservative in their estimation of experimental uncertainties.

C. h/m_0 from the Compton effect

Compton effect experiments involve the measurement of the change in wave-length $\Delta\lambda$ of an x-ray radiation when scattered at an angle θ by atomic electrons of a gas or a solid. If the binding of the electron to its nucleus is taken into account, the ordinary Compton equation $\Delta\lambda = (h/m_0c)(1 - \cos\theta)$ must be modified by the addition of a negative correction term proportional to λ^2 . This was shown theoretically by Ross and Kirkpatrick³⁹ and Bloch⁴⁰ and demonstrated experimentally by Ross and Kirkpatrick.⁴¹ The latter have made the only set of measurements complete enough to be of use here. A series of measurements of $\Delta\lambda$ at three wave-lengths was made with carbon as the scatterer, and also with beryllium. An extrapolation of these to zero wave-length, at which point the correction is zero, gave:

$$h/m_0 = 7.264 \pm 0.012 \text{ erg} \cdot \text{sec./g.}$$

This value has been converted to the ruled grating wave-length scale.

Combining this value with the Rydberg equation and h_0 , one obtains:

$$e_1 = (4.7956 \pm 0.0020) \times 10^{-10} \text{ e.s.u.},$$

which is plotted as point (9) at $n = \frac{1}{3}$ in Fig. 1.

D. $(e/m_0)(e/h)$ from x-ray photoelectrons

Electrons are ejected from a thin film or target by x-rays of known wave-length. The $(H\rho)$ values (magnetic field times radius of curvature) are measured for each of several groups of ejected electrons. Then the energy of an ejected electron should equal the energy of the incident photon minus the energy to eject it. The latter energy is obtained from the absorption limit wave-length of the level from which the electrons originated.

In writing an energy equation as indicated above, there is a small but appreciable error due to the fact that the energy to eject the photoelectron is not correctly obtained from the absorption limit wave number. The latter is proportional to the energy to move the electron from its initial inner level to the first possible unoccupied level.⁴² Hence, approximately the ionization energy of the next element in the periodic table should be added to the energy corresponding to the series limit wave number.

The work of Robinson and his co-workers⁴³⁻⁴⁶ is outstanding in this field of x-ray photoelectrons and has extended over a period of more than 15 years. To avoid the rather large uncertainties in the absorption limit wave-lengths and the corrections necessary to them, Robinson has taken measurements with three different x-ray radiations and then used energy differences. That is, the difference in energy of photoelectrons ejected by a hard radiation and by a soft radiation should be equal to the difference in energy of the photons in the two radiations. Three pairs of differences obtained from Mo $K\alpha$ -Cu $K\alpha_1$, Mo $K\alpha$ -Cr $K\alpha_1$, and Cu $K\alpha_1$ -Cr $K\alpha_1$ were used for each initial level in each element. Measurements of $H\rho$ were made on electrons from several levels in each of the three elements Au, Pt and Ag.

The computations from the large amount of data, when averaged yield:

$$(e/m_0)(e/h) = (3.8220 \pm 0.0029) \times 10^{34} \text{ e.s.u.}$$

In this, as previously, the ratio of the ruled grating to the Siegbahn scale wave-lengths has been taken as 1.00203 ± 0.00002 . No correction has been necessary for the geometry of the magnetic spectrograph⁴⁷ because the diameter measurements were made from the head of a line to the inner edge of the slit.

The above probable error has been conservatively taken as the *limit* of error given by Robinson. (His observational probable error was of the order of one-tenth of this.) This has been done to allow for any possible error that might have been made in estimating the position of the head of a line (the high energy edge). Measurements are made to the head of a line because the head is produced by electrons which have suffered no energy loss in getting out of film.

The combination of the above value with the Rydberg equation and h_0 gives:

$$e_{2/3} = (4.7953 \pm 0.0006) \times 10^{-10} \text{ e.s.u.}$$

This has been plotted as point (11) at $n = \frac{2}{3}$ in Fig. 1.

Kretschmar⁴⁸ has also made measurements of photoelectron energies. He did not measure the radius of curvature of the most energetic electrons but rather measured that of the most probable energy (corresponding to the peak of a line). Hence an energy correction is needed for his measurements. Alvarez⁴⁹ has suggested an approximate correction of +0.23 to +0.47 percent based on thickness measurements of one of Kretschmar's films.⁵⁰ A geometrical correction for slit width of +0.09 percent in the radius, or +0.18 percent in the energy,⁵¹ is also needed.

Thus a total correction (reduction) of the order of $0.35 + 0.18 = +0.53$ percent is required. The $(e/m_0)(e/h)$ value obtained from his work is lowered by this same fraction to $(e/m_0)(e/h) = 3.8067 \times 10^{34}$ e.s.u. on the ruled grating scale. The corresponding e_n is $e_{2/3} = 4.7922 \times 10^{-10}$ e.s.u.

It is to be noted that this value of $e_{2/3}$ is one part in 1500 lower than that from Robinson's work. It should also be mentioned that if only the slit correction is made to Kretschmar's results, then there results a value of $e_{2/3}$ quite close to Robinson's (about one part in 4400 higher). Since the energy correction to Kretschmar's work is so uncertain, his results have not been plotted in Fig. 1.

TABLE IV. *Recent viscosity of air measurements. For comparison, Harrington's value was $(1822.6 \pm 1.3) \times 10^{-7}$ c.g.s.*

EXPERIMENTER	METHOD	YEAR	$\eta_{25^\circ} \times 10^7$	PUBL. PROB. ERROR	WEIGHT GIVEN
Kellstrom ⁵²	Rotating Cylinder	1937	1834.9	2.7	2
Houston ⁵³	Rotating Cylinder	1937	1829.2	4.5	1
Bond and Rigden ⁵⁴	New Capillary	1938	1830.3	0.7	1
Banerjee and Pattanaik ⁵⁵	Capillary	1938	1833.3	2.1	1
Weighted mean:		1832.5 \pm 1.5 c.g.s.			

E. Oil drop e

As is well known, this value of the electron charge is based on measurements of the velocity of oil drops in a gravitational field, and in a combined gravitational and electrical field. The density of the drop is assumed to be the same as that of the oil in bulk. Stokes law is assumed to be exactly true in the limit as the product of the pressure and drop radius approaches infinity.

Most of the probable error in the oil-drop value arises in the uncertainty in the value of the viscosity of air. The four recent viscosity determinations given in Table IV^{51a} indicate a value slightly over half a percent higher than that of Harrington,⁵⁶ which was used by Millikan.⁵⁷ The calculated probable error of the weighted mean was ± 0.9 . This was increased to ± 1.5 to allow for fundamental uncertainties.

It is difficult to understand the large increase in the value given by recent measurements, for none of the older measurements listed by Millikan approached the new high value. However, the recent "high" value given in Table IV will be adopted somewhat arbitrarily, although modern equipment and technique provide partial justification.

For the actual oil-drop experiments, there is the classical work of Millikan⁵⁸ which, with the "high" viscosity value, and the auxiliary constants of Table I, gives:

$$e_0 = (4.8059 \pm 0.0052) \times 10^{-10} \text{ e.s.u.}$$

More recently Backlin and Flemberg⁵⁹ have given a preliminary report on a redetermination. Work at atmospheric pressure, 260 velocity observations on 9 drops gave:

$$e_0 = (4.7941 \pm 0.0089) \times 10^{-10} \text{ e.s.u.,}$$

when the calculations are made with the "high"

viscosity value and the above auxiliary constants. Ishida, Fukushima and Suetsugu⁶⁰ have reported a determination in which over 1000 velocity observations at atmospheric pressure were made on 31 drops. This work, with the "high" viscosity value, gives:

$$e_0 = (4.8453 \pm 0.0043) \times 10^{-10} \text{ e.s.u.}$$

Which is about 0.9 percent higher than the preceding two values and also the ruled grating value. The work seems to have been carefully executed and valuable supplementary work⁶¹ has been done on nonspherical drops. However, in personal correspondence, Ishida has indicated that there may be some uncertainty in the voltage calibration and that this will soon be checked. Their uncertainty should therefore be considered much larger than that quoted.

Pending further work on this last determination, we shall take a least-square mean of the results of Millikan and of Backlin and Flemberg, thus:⁶²

$$e_0 = (4.8036 \pm 0.0048) \times 10^{-10} \text{ e.s.u.}$$

This value is plotted as point (2) at $n=0$ in Fig. 1.

F. h/e from ionization and excitation potentials

Lawrence⁶³ measured the ionization potential of mercury by directing electrons into an ionization chamber and determining the minimum electron voltage at which ionization occurred. A magnetic velocity filter limited the electrons to a narrow band of energies and a potential difference method of obtaining the electron voltage eliminated error due to contact potentials, at least to a first approximation. The ionization potential found was 10.40 ± 0.02 int. volts. Insertion of this in the photoelectric equation, together with the spectroscopic term value $84,178.5 \text{ cm}^{-1}$ of the series limit of mercury and the conversion factor r from international to absolute volts gives:

$$h/e = (1.3753 \pm 0.0027) \times 10^{-17} \text{ erg} \cdot \text{sec.} / \text{e.s.u.}$$

Van Atta⁶⁴ measured the excitation potentials of several lines in helium, neon and argon. Electrons scattered in a forward direction in a collision chamber were analyzed by an electrostatic velocity selector. In most of the

work the energy of the electrons entering the collision chamber was fixed at a value several times that required for ionization. The energy loss was then found in terms of the difference in deflecting potential required for electrons which had excited a given line.

Each measured excitation potential (converted to absolute volts) together with the corresponding wave number of the transition can be used to obtain a value of h/e . The weighted mean calculated from the five identified transitions is:

$$h/e = (1.3753 \pm 0.0025) \times 10^{-17} \text{ erg} \cdot \text{sec.}/\text{e.s.u.}$$

Van Atta's voltage uncertainties⁶⁵ were used in the computation. The internal probable error of ± 0.0017 was chosen since it was larger than the external probable error. The probable error has been increased to ± 0.0025 because of systematic errors, such as errors due to surface charges on the deflecting plates⁶⁶ and the fact that the central path of the electrons was not at ground potential, but at a negative potential of 2.25 percent of the total deflecting potential.

Over a period of years, Whiddington and his co-workers have measured excitation potentials of the same gases as those used by Van Atta. The apparatus⁶⁷ differs essentially from Van Atta's only in the use of a 180° magnetic velocity selector. The electron spectrum was recorded on an oil-sensitized photographic plate, on which the full energy electrons and the groups of electrons which have lost various discrete amounts of energy appear as lines. An ingenious procedure was used to avoid the necessity of calibration of the magnetic field and of measurement of the radii of curvature; without gas in the collision chamber the electrons were retarded by known voltages in such a manner as to give a series of calibration lines on the plate. The voltage difference between the full energy electrons and a group of lower energy was measured by interpolation between adjacent calibration lines.

The most recent results are those of Whiddington and Woodroffe.⁶⁸ From their results, six lines,⁶⁹ the precision of which was fairly good and the spectroscopic classification reasonably certain, give a weighted mean of

$$h/e = (1.3737 \pm 0.0018) \times 10^{-17} \text{ erg} \cdot \text{sec.}/\text{e.s.u.}$$

Here again the internal probable error, ± 0.0010 ,

was about twice the external. This probable error has been increased to ± 0.0018 because of possible errors from surface charges on the oiled photographic plate. Whiddington and Woodroffe state that there was no evidence of charging-up of the film, but do not mention what tests were made. Probably the building up of the equilibrium charge occurs quickly so that little change with time of exposure would be expected. But a sufficiently long exposure with one-tenth the current would offer one critical test as to the existence of errors from surface charges.⁷⁰

The weighted mean of the three values from Lawrence, Van Atta, and Whiddington and Woodroffe's work is:

$$h/e = (1.3745 \pm 0.0013) \times 10^{-17} \text{ erg} \cdot \text{sec.}/\text{e.s.u.}$$

Here again the internal probable error given is twice the external, which probably means the estimates of uncertainty have been conservative. By combining with h_0 , there results:

$$e_1 = (4.8090 \pm 0.0045) \times 10^{-10} \text{ e.s.u.},$$

which is plotted as point (4) at $n = 1$ in Fig. 1.

G. Stefan-Boltzmann constant σ

This constant comes from the measurement of the net radiation per square centimeter of surface from a heat source at a known temperature to a receiver at a known temperature. There are numerous experimental difficulties, so that really accurate results are impossible. A large number of determinations by different experimenters with a variety of methods serves to partially offset the inaccuracy of any one result.

Ladenberg⁷¹ has given a summary and a value based on a selection of seven results (out of

TABLE V. *Stefan-Boltzmann constant σ determinations.*

EXPERIMENTER	YEAR	σ	STATED ACCURACY	WEIGHT GIVEN
Gerlach	1916	5.80	± 1 percent	1
Coblentz	1917	5.73	± 1 percent	1
Hoffman	1923	5.764	± 1 percent	1
Kussmann	1924	5.795	± 1 percent	1
Mendenhall	1929	5.79	± 1 percent	1
Muller	1933	5.774	$\pm \frac{1}{2}$ percent	2

$$\text{Weighted Average: } (5.775 \pm 0.022) \times 10^{-5} \text{ erg} \cdot \text{cm}^{-2} \cdot \text{sec.}^{-1} \cdot \text{deg.}^{-4}$$

TABLE VI. Summary of the eleven types of measurements and the experimental results obtained. There is also shown (third from the last column) the dependence of these experimental values on the values of the first ten auxiliary constants listed in Table I. A' represents the remainder of A after factoring out the constants indicated. The next to the last column gives the formulas for e_n (e_n is the value of e which represents the given experiment on the Birge-Bond diagram). The last column gives the values of e_n .

POINT	DESCRIPTION	COMBINATION OF CONSTANTS MEASURED	EXPERIMENTAL VALUE A	DEPENDENCE OF A ON CERTAIN CONSTANTS. FORMULA FOR A	FORMULA FOR e_n	e_n FOR BIRGE-BOND DIAGRAM E.S.U. $\times 10^{10}$
1	Ruled grating	e	$(4.8025 \pm 0.0004) \times 10^{-10}$ e.s.u.	$(F q c k \lambda^2) A'$	e	4.8025 ± 0.0004
2	Oil drop	e	$(4.8036 \pm 0.0048) \times 10^{-10}$ e.s.u.	$(c/r) A'$	e	4.8036 ± 0.0048
3	Limit of cont. x-rays	h/e	$(1.3763 \pm 0.0004) \times 10^{-17}$ e.s.u.	$(k \lambda r / c^2) A'^{77}$	$(1/A) h_0$	4.8026 ± 0.0014
4	Ionization and excitation	h/e	$(1.3745 \pm 0.0013) \times 10^{-17}$ e.s.u.	$(r/c^2) A'$	$(1/A) h_0$	4.8090 ± 0.0045
5	Radiation constant c_2	h/e	$(1.3730 \pm 0.0029) \times 10^{-17}$ e.s.u.	$(R_0/c^2 F q) A'$	$(1/A) h_0$	4.8145 ± 0.0101
6	Stefan-Boltzmann constant	$e/h^{3/4}$	$(2.0778 \pm 0.0020) \times 10^{10}$ e.s.u.	$(F q c^{3/2} / R_0) A'$	$(A) h_0^{3/4}$	4.8168 ± 0.0046
7	Electron diffraction (V)	$(h/e)(e/m_0)^{1/2}$	$(1.00084 \pm 0.00058) \times 10^{-8}$ e.s.u.	$[(r/c)^{1/2} k \lambda] A'^{78}$	$(c R_{\infty} A^2 / 2 \pi^2)^{1/3} h_0^{1/3}$	4.7964 ± 0.0019
8	Electron diffraction (v)	h/m_0	7.274 ± 0.016 erg · sec./g	$(k \lambda) A'$	$(c R_{\infty} A / 2 \pi^2)^{1/4} h_0^{1/2}$	4.7972 ± 0.0026
9	Compton effect	h/m_0	7.264 ± 0.012 erg · sec./g	$(k \lambda c) A'$	$(c R_{\infty} A / 2 \pi^2)^{1/4} h_0^{1/2}$	4.7956 ± 0.0020
10	Specific charge	e/m_0	$(1.7591 \pm 0.0002) \times 10^7$ e.m.u.	Depends on method	$(c^2 R_{\infty} A / 2 \pi^2)^{1/5} h_0^{2/5}$	4.7963 ± 0.0002
11	X-ray photoelectrons	$(e/m_0)(e/h)$	$(3.8220 \pm 0.0029) \times 10^{24}$ e.s.u.	$(c^2 p^2 / k \lambda^2) A'^{79}$	$(c R_{\infty} A / 2 \pi^2)^{1/6} h_0^{2/3}$	4.7953 ± 0.0006

twenty-four which have been made). The basis of selection was: (1) use of sufficiently perfect blackbody radiators and receivers and (2) correction for absorption of radiation in the water vapor and CO₂ in the air. Muller⁷² later made a redetermination with increased care. Also, the results of Hoare,⁷³ which Ladenberg included, were apparently not corrected for absorption.⁷⁴ A new summary has therefore been made as shown in Table V. When combined with Planck's radiation formula, the average value is:

$$e/h^{3/4} = (2.0778 \pm 0.0020) \times 10^{-10} \text{ e.s.u.}$$

This, with the usual h_0 , gives:

$$e_{3/4} = (4.8168 \pm 0.0046) \times 10^{-10} \text{ e.s.u.}$$

and is plotted as point (6) at $n = \frac{3}{4}$ in Fig. 1.

H. Radiation constant c_2

This constant occurs in the Wien displacement law. No new work seems to have been done for over fifteen years so that the value given by Birge,⁷⁵ namely:

$$c_2 = 1.432 \pm 0.003 \text{ cm deg.}$$

is still the best value. Again by using the related part of Planck's radiation law, there results

$$h/e = (1.3730 \pm 0.0029) \times 10^{-17} \text{ e.s.u.}$$

With h_0 , this gives:

$$e_1 = (4.8145 \pm 0.0101) \times 10^{-10} \text{ e.s.u.}$$

and is plotted as point (5) at $n = 1$ in Fig. 1.⁷⁶

SUMMARY OF EXPERIMENTAL DATA

The eleven types of measurements which have been described are summarized in Table VI. The experimental values A depend on one or more of the ten constants listed in the first section of Table I. They have been computed with the assumption of the correctness of the ruled grating wave-lengths. The values of e_n , which represent the points in the Birge-Bond diagram on Fig. 1, are collected in the last column of Table VI. They are obtained from the A values by the formulas in the next to the last column. The two additional constants necessary for this are given in the second section of Table I.

ANALYSIS AND DISCUSSION

The analysis will be made in two ways: first from Birge-Bond diagrams, and second by least-squares solutions.

A. Analysis from Birge-Bond diagrams

(1) *Analysis as to cause of the discrepancy when ruled grating wave-lengths are assumed correct.*— Inspection of Fig. 1 reveals not only the well-known discrepancy between e , h/e and e/m_0 (points 1, 3 and 10), but also a peculiar and perhaps significant grouping of half of the points (points 7 through 11). These points lying in the center of the diagram (Group A) are uniformly lower than points to the right and left on the diagram (Group B).⁸⁰ This lower group indicates a value of e of the order of 4.796×10^{-10} ,

while the upper group indicates a value of the order 4.803×10^{-10} e. s. u.

The discrepancy between these two groups seems to be well beyond experimental uncertainties. If this is accepted, then the trouble must of necessity be in one of the laws or equations used. Further, if there is only one such erroneous theory, it should be possible to find a theory which satisfies these criteria: (1) all the points which involve it are mutually consistent; (2) all the points which do not involve it are mutually consistent; (3) these two groups are mutually inconsistent.

An analysis of the dependence of the eleven types of measurements on seven of the more important laws or equations is given in Table VII. The consistency as to the first two criteria is qualitatively indicated in the lower two lines of the table. As to the third criterion, the two groups are inconsistent in every case. It is seen that the two groups as determined by Rydberg's constant formula are the only groups which satisfy the above criteria. Further, these two groups are the same as those mentioned above. *The existing experimental data thus strongly indicate that the Rydberg formula is the cause of the discrepancy in the fundamental atomic constants.*

The only other possibility is the photoelectric equation, but the indication is relatively weak because the two radiation points are inconsistent with the "other measurements" (i.e., other than the photoelectric). If, however, these relatively

uncertain radiation points are rejected until better data are available,⁷⁶ or if they are included with the photoelectric points, an analysis as in Table VII indicates that *the photoelectric equation is also a possible source of the discrepancy.*

Most of the remainder of this paper will be concerned with the question of which of these two possibilities is the more likely seat of trouble.

(2) *Effect of an arbitrary change in the Rydberg formula.*—Over two years ago, Birge¹ suggested as one of three possible explanations of the discrepancy between e , e/m_0 , and h that the Rydberg formula was in error, but more recently³ came to the opinion that the trouble was in the value of h/e . Still more recently DuMond⁵ suggested that the Rydberg formula might require revision and pointed out that if a constant multiplier $(1-\alpha)$ is added to the present Rydberg formula the discrepancy vanishes. (α = fine structure constant.) The discussion in DuMond's letter is based on the change in the h/e computed from e/m_0 and e with the Rydberg formula. As is evident from the last column of Table VII, changing the Rydberg formula affects not only e/m_0 but four other determinations as well. It is of considerable importance to determine the effect of such a change on these other measurements.

The change which will be tried in the Rydberg formula is:

$$R_\infty (= 109,737.42) = \frac{2\pi^2 e^4 m_0}{ch^3} \cdot \frac{1}{1+\alpha}$$

TABLE VII. Analysis of the eleven types of measurement as to the more important fundamental laws or equations involved. The laws or equations involved in any type of measurement are indicated by (X). How well a straight line can be drawn through the points marked (X) in any column is indicated qualitatively in next to the last line. This test is a measure of their consistency. A similar test for the points in any column which are not marked by (X) is indicated in the last line.

POINT	DESCRIPTION	RULED GRATING WITH X-RAYS $n\lambda = d[\cos\theta - \cos(\theta + \alpha)]$	CRYSTAL GRATING BRAGG LAW $n\lambda = 2d \sin \theta$	DE BROGLIE EQUATION $\lambda = h/mv$	PHOTO- ELECTRIC EQUATION $hc/\lambda = \frac{1}{2}mv^2 = Ve$	PLANCK'S RADIATION EQUATION	CALCITE CRYSTAL PERFECT GEOMETRY FORMULA $d = [Me/2\rho Fc\phi(\beta)]^{\frac{1}{3}}$	RYDBERG CONSTANT FORMULA $R = 2\pi^2 e^4 m_0 / ch^3$
1	Ruled grating e	X	X(x-rays)				X	
2	Oil drop e							
3	Limit of continuous x-rays	X			X (inverse)			
4	Ionization and excitation				X (inverse) ^{84a}			
5	Radiation constant c_2 ⁸⁵					X		
6	Stefan-Boltzmann constant ⁸³					X		
7	Electron diffraction (V)	X	X (electrons) ⁸¹	X				X
8	Electron diffraction (e)	X	X (electrons)	X				X
9	Compton effect ⁸⁴	X	X(x-rays)					X
10	Specific charge e/m_0							X
11	X-ray photoelectrons	X			X (direct)			X
	Mutual Consistency of Measurements Marked by (X)	Extremely poor	Good	Only 2 pts.	Good	Only 2 pts.	Only 1 pt.	Very good
	Mutual Consistency of Other Measurements	Poor	Very poor	Extr. poor	Fair	Extr. poor	Very poor	Fairly good

This is equivalent to saying that the combination of constants ($2\pi^2 e^4 m_0 / ch^3$) must be increased in value by the fractional amount α .^{84b}

The fine structure constant α was not given with the eleven measurements of Table VI because of its large experimental uncertainty. The three best measurements of $1/\alpha$ gave: 139.9,⁸⁵ 137.4 ± 0.2 ,⁸⁶ 139.3.⁸⁷ The mean of these is 138.9 ± 0.6 . If this value is used, then the R_∞ in the next to the last column of Table VI is increased by $1/138.9 = 7.20 \times 10^{-3}$ parts. If the values of e_n in the last column are recomputed with this increased R_∞ , the results are those shown in Fig. 2. The points are fairly consistent and in particular e/m_0 (point 10) is in good agreement with e (point 1) and h/e (point 3).⁸⁸

Because of the varying power to which R_∞ occurs,⁸⁹ the central group of points (7 through 11) has not only been raised but also tilted^{89a} clockwise so that points (7) and (11) are two or three times their probable error from the dotted line. (This line is the same as that labeled Group B in Fig. 1.) This can be taken as an argument against the Rydberg formula change as a solution to the problem, or it can be taken as an indication that the experimental values are in error. Certainly the desirability of further experimental work on these two points is strongly indicated. If a functional change is found necessary in the Rydberg formula, rather than mere multiplication by a constant, then the resulting picture might be quite different.

The only other discrepancy indicated in both Fig. 1 and Fig. 2 is that of point (6), the Stefan-Boltzmann constant. A peculiar feature of this point is that the elimination in recent years of the error from absorption in the moisture and CO_2 of the air has raised the point from a position of good consistency with the other points. Whether there is another appreciable source of error as yet unknown or whether there is need of revision of Planck's radiation theory, remains to be determined.

(3) *Effect of a functional change in the Rydberg formula.*—The possibility of a functional rather than a linear change in the Rydberg formula has been mentioned. It should be *emphasized* that a functional change can in no way alter the value of h/e found from any one of the measurements represented by the point (7), (8), (9) or (11)

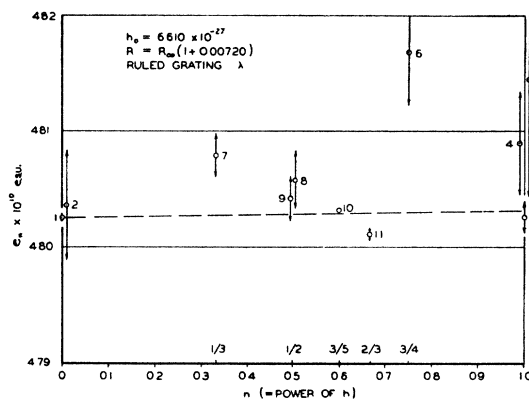


FIG. 2. Same as Fig. 1 except with the combination of constants occurring in the Rydberg equation increased by $\alpha (= 7.20 \times 10^{-3}$ parts). Under this assumption, the discrepancy of Fig. 1 is largely, though not entirely, removed.

when combined with the value of e/m_0 .⁹⁰ Graphically this means that the two points must always determine a line which passes through the value of h/e at $n=1$. Hence no functional change in the Rydberg formula can cause the points (7) through (11) in Fig. 2 to all fall on or near the dotted line.⁹¹

(4) *Analysis as to cause of the discrepancy when perfect calcite geometry is assumed.*—In all that precedes, the correctness of the ruled grating wave-lengths has been assumed. An alternative to this is the assumption of a perfect calcite crystal geometry. This, together with the Bragg law, enables wave-lengths λ to be expressed in terms of constants of the calcite crystal, of the Bragg angle for the radiation in question, and of the electron charge. Briefly: $\lambda = Ce^{\frac{1}{2}}$. A Birge-Bond diagram made on this basis, without any change in the Rydberg constant, is given in Fig. 3. Comparison with Fig. 1 shows that the points in Group A have been compressed towards point (10) representing e/m_0 ; the latter remains fixed. In Group B, point (3) has moved⁹² from $n=1$ to $n=0.75$. The division into the two groups has therefore not changed.

An analysis of the points Fig. 3, made in the same way as Table VII, gives exactly the same indications as before, so that the perfect calcite geometry concept is in complete accord with that of wave-lengths obtained from ruled gratings.

(5) *Possibility of the discrepancy being experimental.*—The preceding analysis and discussions

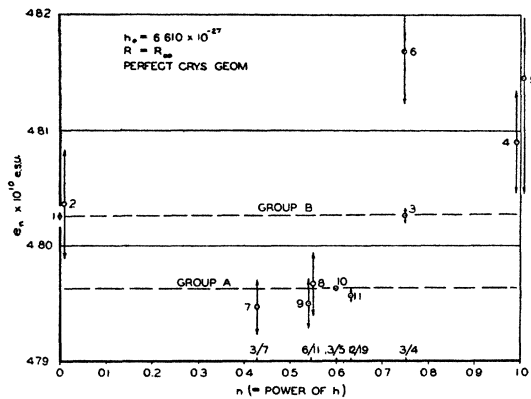


FIG. 3. Birge-Bond diagram similar to Fig. 1 but with the assumption of perfect calcite crystal geometry to obtain the x-ray wave-lengths, instead of the use of ruled grating wave-lengths. Exception: point (1) which involves both the perfect calcite geometry assumption and the use of ruled grating wave-lengths. The discrepancy seen in Fig. 1 has not appreciably changed in this figure.

of the discrepancy in Figs. 1 and 3 has been based on the view that this discrepancy between Groups A and B is beyond experimental uncertainties. If this view is not accepted, the situation can be summarized as follows: the upper group of points, Group B in Figs. 1 and 3, is structurally weak because it is scattered to the left and right sides of the figures with no points in between. On the other hand the lower group of points, Group A, is structurally strong, and there is also a surprisingly good consistency among the points in spite of the wide range of theory involved. Consequently, one is lead to put much more confidence in the correctness of the lower group than in the upper. If one then considers the lower group to provide a fulcrum, located approximately in the center of the figure, about which the line representing the solution must pivot, either points (1) and (2), or the points (3) through (6), must be lowered.

In considering the first alternative, it is to be noted that the present rather unsatisfactory state of the oil-drop work makes it possible that later work may lower point (2). But it seems most improbable that the new experimental work will appreciably change point (1), for this point involves no experimental results which are not also involved in several other points.⁹³ Further, in the reevaluation of the many constants used in computing this point no indication was seen of any uncertainty great enough to produce

the necessary lowering of the point. The first alternative therefore seems most improbable.

The second alternative requires the lowering of points (3) through (6). The experimental correctness of point (3) is reasonably well established by several determinations. The experimental and perhaps theoretical uncertainty of the two radiation constants (points 5 and 6) makes their consideration secondary for the time being.⁹⁴ Point (4), however, is not so well established, and further work⁹⁵ is most desirable.

If the improbable should happen and later work on points (3) and (4) indicates a "high" value of h/e for both points (i.e., so that they fall on a line through (1) and (10)), then of course, the major discrepancy will have vanished. There will remain only the problem of bringing the relatively inaccurate radiation points into agreement.

On the other hand, if later work on points (3) and (4) confirms their present "low" value of h/e , there seem to be three interpretations all of which involve changes in theory: (a) the results confirm the view that the Rydberg formula is in error; (b) the photoelectric equation is in error in such a way as to indicate low values of h/e ; (c) the application of the photoelectric equation to the *inverse* photoelectric effect is in error in such a way as to indicate low values of h/e . (b) involves a change in theory which would not only lower the inverse photoelectric points (3) and (4) but also would *lower* the direct photoelectric point (11) by an amount one-sixth as great. This would put point (11) below the assumed solution line (1-10) but not so far as to create another major discrepancy. In contrast, interpretation (c) would not affect point (11). However, it implies a basic difference between the direct and inverse photoelectric effects. The reason for this suggestion, rather than (b), is that the *direct* effect point (11) is in excellent agreement with all experimental points other than the *inverse* points (3) and (4), and the relatively uncertain radiation points (5) and (6). But the difficulty of both interpretations (b) and (c) is that in offering any change in theory that will raise the h/e results of the inverse photoelectric effect, conservation of energy is violated. In brief: the photon leaves with *too much* energy.^{95a}

B. Analysis of the discrepancy by least-squares solutions⁹⁶

(1) *The method.*—The Birge-Bond diagram has been used in the preceding analysis because it has been the only way available of portraying the complete situation graphically. But since the validity of the Rydberg formula on which it is based is in question, it is highly desirable that the discrepancy be examined by other means. The application⁹⁷ of least-squares methods to the set of equations representing the experimental data has been found to yield some additional information as to the source of the discrepancy.

The least-squares method here used is in outline as follows. The existing body of experimental information has been summarized in the eleven equations (in three unknowns, e , m_0 and h) given in the third and fourth columns of Table VI. There is in addition the equation

$$e^4 m_0 / h^3 = (1.666564 \pm 0.000083) \times 10^{14}, \quad (12)$$

which comes from the Rydberg formula together with values of R_∞ and c in Table I. These twelve observational equations can be reduced in number to eight by using weighted mean values of e , h/e and h/m_0 . There results the observational equations given in Table VIII. These equations were reduced to linear form by the usual Taylor series expansions and then selected groups solved simultaneously by standard least-squares methods.^{97a} The essential feature of the present application is the *choice* of these groups so as to obtain information as to the source of the discrepancy. For this, a key solution was first made, based on all the classes of observations

not in question. Then additional solutions were found in each of which one doubtful class of observation was added to those of the key solution. Information is obtainable both by comparison of changes caused by the addition of classes in doubt and also by comparison of the results of the key solution with the directly observed values.

It is perhaps well to point out the similarity and difference between such a least-squares procedure and those that have been employed previously. The procedure conceived by Bond⁹⁸ and improved by Birge⁸ consists in the reduction of the three variables e , m_0 , and h to two, namely e and h , by the use of the Rydberg formula. The resulting observational equations are then reduced to linear form by expansion in a Taylor's series and retention of the first term. Birge introduced a new parameter $e_n \equiv a_n h_0^n$, where a_n is a numerical constant calculable from the A_n value of the experimental results (see next to last column of Table VI), h_0 is the assumed value of h , and n , the power to which it occurs. This made possible the expression of the results in a form used in the Birge-Bond diagram, namely as points approximately fitting the straight line

$$e_n = e + bn,$$

where e is the value of the electron charge and b is the slope of the line representing the least-squares solution, and from which the value of h can be found. The most important feature of this method is that it makes possible a graphical presentation of the experimental results⁹⁹ and of their least-squares solution (i.e., the straight line best fitting the points). Birge also derived a

TABLE VIII. *The eight observational equations and the types of experiments on which they are based. The weight given each equation is computed by the usual least-squares formula: $W = c/r^2$.*

SYMBOL	OBSERVATIONAL EQUATION (ALL E.S.U.)	WEIGHT	TYPE OF EXPERIMENTS INVOLVED	POINT NO. (AS IN TABLE VI AND ALL FIGS.)
A	$e = (4.8025 \pm 0.0004) \times 10^{-10}$	252.8	{ Ruled grating	1
B	$h/e = (1.3761 \pm 0.0006) \times 10^{-17}$	9.3	{ Oil drop	2
C	$e/h^2 = (2.0778 \pm 0.0020) \times 10^{10}$	1.9	{ Inverse photoelectric	3 and 4
D	$(h/e)(e/m_0)^{1/2} = (1.00084 \pm 0.00058) \times 10^{-8}$	5.2	{ Radiation constant, c_2	5
E	$h/m_0 = 7.268 \pm 0.010$	1.0	{ Stefan-Boltzmann constant	6
F	$e/m_0 = (5.2734 \pm 0.0007) \times 10^{17}$	96.0	{ Electron diffraction (voltage)	7
G	$(e/m_0)(e/h) = (3.8220 \pm 0.0029) \times 10^{34}$	3.1	{ Electron diffraction (velocity)	8
H	$e^4 m_0 / h^3 = (1.666564 \pm 0.000083) \times 10^{14}$	698.0	{ Compton effect	9
			{ Specific charge	10
			{ X-ray photoelectrons	11
			{ Rydberg formula	(12)

method for the computation of the probable error in any function except m_0 and R_∞ (as calculated from e , m_0 , and h).

Shiba,¹⁰⁰ independently, made a least-squares solution which resembled the preceding in that the unknown (in this case, h) was eliminated by use of the Rydberg formula. The resulting simultaneous equations in two unknowns e and e/m_0 were solved by the usual least-squares methods, and hence were not graphically presentable. Probable errors were not computed from the observational equations. They were merely estimated.

Recently Beth⁹⁷ has made a least-squares solution in three unknowns. He has emphasized particularly the calculation of least-square errors from the normal equations and the value of the errors so computed in the light they might shed on the discrepancy situation.

(2) *Solution with photoelectric equation and Rydberg formula assumed in doubt.*—The Rydberg formula (Eq. *H*) and the photoelectric equation (involved in Eqs. *B* and *G*) are the two possible sources of the discrepancy indicated by the analysis of the Birge-Bond diagram. There is also indicated the relatively less important discrepancy of the radiation points (Eq. *C* and a minor part of Eq. *B*). Because they seem in fair agreement, the radiation parts have been grouped with the photoelectric points. Perhaps the argument that follows would be clearer if the radiation points had been omitted entirely, but

their exclusion would have made a negligible difference in the results of the solutions.

The results of the least-squares solutions are tabulated in Table IX. Solution I is the key solution since it contains no classes of experiments that are in doubt. Solution II contains in addition the Rydberg formula. Solution III has all photoelectric and radiation points added. Differences¹⁰¹ in the solutions (see last two columns) are negligible for e , m_0 , and e/m_0 , and are about equally large and of opposite sign for h , h/e and R_∞ . This indicates an equal discrepancy between both the photoelectric equation and the Rydberg formula with the rest of the classes of measurements.

Although it is not possible to fully present graphically a least-squares solution, it is possible to partially illustrate it graphically by use of the familiar Birge-Bond diagram. The necessary condition is that the value of R_∞ used be that found by calculation from the least-squares solution, for then the least-squares values of all combinations of constants lie in a straight line. If further, as a convenience, the least-squares value of h is used for h_0 , the straight line representing the solution will be horizontal. This has been done in Fig. 4 for Solution III. The agreement of any experimental point with the solution is of course a function of the distance of the corresponding circle from the dotted line, and the discrepancy can be judged by the ratio of this distance to the length of the arrow (i.e., the

TABLE IX. Results of least-squares solutions¹⁰² when the possible sources of the discrepancy are assumed to be the Rydberg formula and the photoelectric equation. The key or base solution, I, does not contain any experimental work in doubt. The effect of adding the Rydberg equation is seen in II; the effect of adding all photoelectric work (plus radiation constants) is seen in III. The uncertainties are probable errors computed from the observational equations.^{102a} See Table VIII for a list of the observational equations A, B, C, etc.

QUANTITIES	DIRECTLY OBSERVED VALUES (MEAN)	RESULTS OF LEAST-SQUARE SOLUTIONS			DIFFERENCES ¹⁰¹	
		SOLUTION I Eq. USED: (A, D, E, F)	SOLUTION II (A, D, E, F) + (H)	SOLUTION III (A, D, E, F) + (B, C, G)	(II - I) × 10 ⁴ (EXCEPT R _∞)	(III - I) × 10 ⁴ (EXCEPT R _∞)
e	4.8025 ±4	4.8025 ±4	4.8025 ±4	4.8025 ±7	0 ± 4	00 ± 7
m_0		9.1070 ±14	9.1070 ±16	9.1073 ±24	0 ± 16	+3 ± 24
h		6.6189 ±36	6.6242 ±10	6.6133 ±34	+53 ± 36	-56 ± 36
e/m_0	1.7591 ±2	1.7591 ±4	1.7591 ±3	1.7590 ±4	0 ± 4	-1 ± 4
h/e	1.3761 ±6	1.3782 ±7	1.3793 ±1	1.3771 ±7	+11 ± 7	-11 ± 7
R_∞	109,737.42 ±.06	110,007. ±177.	109,739. ±8.	110,291. ±167.	-268 ± 177	+284 ± 177

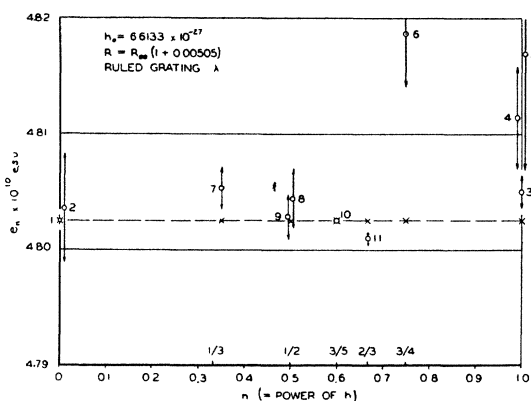


FIG. 4. Birge-Bond diagram adjusted to represent, insofar as it is possible, the least-squares solution of all the experimental data, except the Rydberg formula.¹⁰³ This is Solution III of Table IX, and III' of Table X. The dotted line indicates the least-squares solution. The circles represent the experimental results and the crosses the least-square results for various values of the exponent n . The value of R_∞ is that calculated from the least-squares solution.

probable error). Points (7) and (11) are observed to lie much nearer to the line than in Fig. 2.

(3) *Solution with the inverse photoelectric equation and the Rydberg formula assumed in doubt.*—The objection to the analysis on the basis of the preceding section is, as has already been pointed out in Section A(5) of Analysis and Discussion that the photoelectric experiments are of two types: direct and indirect, and it is only the latter that are in disagreement with the other work.

Hence in the second set of solutions, the possible sources of error have been assumed to be the inverse photoelectric equation (Eq. B) and the Rydberg equation (Eq. H). Here again the radiation points have been included with the inverse photoelectric work, but their entire omission would not appreciably alter the results. The difference, then, between the solutions of this section and those of the preceding is simply the shift of the *direct* photoelectric work from the uncertain to the certain classification.

The results are given in Table X, and the numbering of the solutions is the same as that in Table IX, with primes added. Again differences in the solutions are negligible for e , m_0 and e/m_0 . But for h , h/e and R_∞ the differences are almost three times as great when the inverse photoelectric points are added (Solution III) than when the Rydberg formula is added (Solution II). Hence the indication is that the *inverse photoelectric effect is the seat of the discrepancy*, rather than the Rydberg equation.

This view is considerably strengthened by the comparison in Table XI of the results of the two key solutions with the directly observed values. In neither solution is the calculated value of R_∞ greater than the spectroscopic value by much more than the uncertainty. But in both key solutions the indicated value of h/e is greater than the directly observed value by about three times the uncertainty.

TABLE X. Results of least-squares solutions¹⁰² when the possible sources of the discrepancy are assumed to be the Rydberg formula and the inverse photoelectric effect. The key or base solution, I', does not contain any experimental work in doubt. The effect of adding the Rydberg equation is seen in II'; the effect of adding the inverse photoelectric work (plus radiation constants) is seen in III'. As in Table IX, the uncertainties are probable errors computed from the observational equations.^{102a} See Table VIII for a list of the observational equations A, B, C, etc.

QUANTITIES	DIRECTLY OBSERVED VALUES (MEAN)	RESULTS OF LEAST-SQUARE SOLUTIONS			DIFFERENCES ¹⁰¹	
		SOLUTION I' EQ. USED: (A, D, E, F, G)	SOLUTION II' (A, D, E, F, G) +(H)	SOLUTION III' (=IIJ) (A, D, E, F, G) (B, C)	(II' - I') × 10 ⁴ (EXCEPT R _∞)	(III' - I') × 10 ⁴ (EXCEPT R _∞)
e	4.8025 ±4	4.8025 ±4	4.8024 ±1	4.8025 ±7	-1 ±4	0 ±7
m_0		9.1073 ±14	9.1071 ±14	9.1073 ±24	0 ±14	0 ±24
h		6.6214 ±29	6.6242 ±10	6.6133 ±34	+28 ±29	-81 ±34
e/m_0	1.7591 ±2	1.7591 ±4	1.7591 ±2	1.7590 ±4	0 ±4	-1 ±4
h/e	1.3761 ±6	1.3787 ±7	1.3793 ±1	1.3771 ±7	+6 ±7	-16 ±7
R_∞	109,737.42 ±.06	109,888. ±142.	109,741. ±8.	110,291. ±167.	-147 ±142	+403 ±142

TABLE XI. Comparison of the least-squares key solutions, I and I', which are based on results not in question, with the directly observed values Q. Solution I' involves the direct photoelectric results which are omitted from I.

QUANTITIES	DIFFERENCES	
	I-Q	I'-Q
e	0 ± 4	0 ± 4
e/m_0	0 ± 4	0 ± 4
h/e	+21 ± 7	+26 ± 7
R_∞	+270 ± 177	+151 ± 142

Hence there seems to be good evidence for holding the inverse photoelectric effect as the probable source of the discrepancy. And since the experimental uncertainty of this work (in particular that of point (3)) is far too high to expect newer work to remove the discrepancy, the situation seems to require either a new interpretation of the experimental results, or a change in the theory of the inverse photoelectric effect. The former seems more likely.

SUMMARY

This paper has presented the results of all known significant measurements of the atomic constants e , m_0 and h , made either separately or in combination. For this the experimental results of the various authors have been recomputed with two changes: (1) all assumptions as to values of combinations of constants have been eliminated, so that the results given represent what the experiments actually yield; (2) auxiliary constants (such as the faraday, the electrical conversion factors from international to absolute units, etc.) have been revaluated and used in the recomputation. These experimental results are summarized in Table VI and presented graphically in Figs. 1 and 2.

The experimental results of all types have been analyzed as to the fundamental laws or equations involved (see Table VII). Comparisons of the mutual consistency of experiments involving any given law with the mutual consistency of those which do not involve it indicate strongly that the Rydberg formula is the source of the discrepancy in the atomic constants. However, if the relatively inaccurate radiation measurements which involve Planck's equation are either rejected, or are included with the photo-

electric results, there is an equally strong indication that the photoelectric equation is the source of the discrepancy.

The introduction into the Rydberg formula of an arbitrary factor $1/(1+\alpha)$ greatly reduces the discrepancy but does not entirely remove it.

A least-squares analysis of the experimental results, made on the assumption that the possible sources of error are the Rydberg equation and the photoelectric equation, does not offer evidence to decide between them. Rather, it seems to indicate both are in error, for results involving them disagree (with *opposite* tendencies) with all the remaining experiments.

However, a least-squares solution made on the assumption that the Rydberg equation and the theory, or interpretation, of the *inverse* photoelectric effect are the possible sources of error gives fairly strong evidence that the inverse photoelectric effect is the source of the discrepancy. The justification of this distinction between direct and inverse effects is that the results of the former are in good agreement with the remaining experimental points while the latter are not. Further support of the view that the inverse photoelectric is the source of the discrepancy is found in the fact that a least-squares solution based on all experimental results *not* in question gives a value of R_∞ (calculated) in fair agreement with the spectroscopic value, but gives a value of h/e differing from the observed value by about three times the uncertainty.⁷⁶

This study has shown the need for further experimental work along several lines: (1) h/e by any method, but in particular by methods other than from the limit of the continuous x-ray spectrum since the precision of measurements of that method is already fairly high; (2) $(e/m)(e/h)$ by x-ray photoelectrons; (3) $(h/e)(e/m)^{1/2}$ by electron diffraction with voltage measurement; (4) e/h^2 through determination of the Stefan-Boltzmann constant.

The author wishes to express his thanks to Professor R. T. Birge of the University of California, Professors W. V. Houston and J. W. M. DuMond of the California Institute of Technology, Professor R. A. Beth of the Worcester Polytechnic Institute, and to his colleagues in the Department of Physics at

Rutgers University, all of whom read and criticized the manuscript. Of the latter, the cooperation of Mr. Franklin Miller has been particularly appreciated. Through the courtesy

of the editors of *The Physical Review* and the author I have been privileged to see the manuscript of DuMond on physical constants which will be published shortly in *The Physical Review*.

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- 14a. This probable error does *not* include an allowance for uncertainty as to inclusion in the voltameter for this uncertainty (± 0.002 percent) was included in the factor q . The two always occur together in this work. Thus in absolute units on the chemical scale, the faraday is $(F \cdot q) \times 10^{-1} = 9649.11 \pm 0.24$ e.m.u., and on the physical scale is $(F \cdot q \cdot k_A) \times 10^{-1} = 9651.76 \pm 0.30$ e.m.u.
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77. In every case, values have been used which were correct for the country in which the experiment was done.
78. Since it was not known whether von Friesen used English or German electrical standards, a mean value of r for these two countries was used, namely $r = 1.000396 \pm 0.000060$. The probable error was increased to that given to allow for this uncertainty in standards.
79. Robinson made no statement that a $(p/r)^2$ correction was made. Hence such a correction, appropriate to England, was made. The value used: $r/p = 0.999941 \pm 0.000020$.
80. The two dotted lines *A* and *B* in Fig. 1 have drawn quite arbitrarily as there seemed to be no particular point in computing least-square solutions.
81. Actually the crystal was used as a transmission grating, but the fundamental phenomena are the same as in the more usual Bragg case.
82. The radiation constant c_2 occurs in the Wien displacement law as obtained from Planck's radiation formula.
83. The formula for the Stefan-Boltzmann constant is obtained from Planck's radiation formula.
84. Involves the Compton equation with a correction term for the nuclear binding.
- 84a. These experiments are inverse photoelectric in the sense that they assume conservation in the conversion of electron kinetic energy to photon energy $h\nu$. The process, however, occurs in two steps: (1) excitation or ionization; (2) radiation.
- 84b. The simplicity of this statement constitutes the entire reason for the choice of the form $1/(1+\alpha)$ instead of $(1-\alpha)$.
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88. If $1/\alpha = 137$, the points are all raised a bit more but the consistency is still good.

89. See the next to the last column in Table VI.
- 89a. For any change in the value of R_∞ , the motion of the points involving R_∞ can be easily visualized if these points are conceived to be plotted on a separate and elastic sheet which then is subjected to vertical shear with the right edge remaining fixed. Change in h_0 causes a similar shear of *all* points about the left edge.
90. An illustration: the h/e found by von Friesen from data represented by point (7) and an e/m_0 value slightly below point (10) lies at the intersection of a line through (7) and (10) and the ordinate $n=1$. This intersection point remains fixed no matter what is done to the Rydberg formula. See 89a.
91. The exception to this statement is the improbable case that the functional change will shift all of these points to within a very small range of n (the power of h).
92. The movement here illustrates clearly what happens in all cases: point (3) in Fig. 3 is on a line determined by points (1) and (3) of Fig. 1. The reason that the motion is always on a line through point (1) is that this point involves the assumption of *both* ruled grating wave-lengths and perfect crystal geometry. Hence any point involving wave-length in Fig. 1 and the same point in Fig. 3 have to be mutually consistent with point (1) (i.e., lie on the same straight line.)
93. In Fig. 1, points (3), (7), (8), (9) and (11) also involve ruled grating wave-lengths, and points (7), (8) and (9) also involve the Bragg law. In Fig. 3, points (3), (7), (8), (9) and (11) also involve the Bragg law and the perfect calcite geometry assumption.
94. It seems probable that a second discrepancy (that of points (5) and (6) which involve Planck's radiation formula) will remain after the other points have been brought into agreement. Previously, Shiba (see second paper in reference 100) has expressed doubt as to the correctness of the Planck radiation formula. However, see new work mentioned in reference 76.
95. The author has started such a redetermination.
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96. In the writing of the least-squares sections, the suggestion has been followed of Dr. J. W. M. DuMond that any hint be avoided of the finality that is usually associated with least-squares solutions and "best" values.
97. A conversation with Dr. R. A. Beth in February, 1937 indicated that both Beth and the author had come to the conclusion that a solution made without involving the Rydberg formula was needed. Such a solution, using provisional values of the experimental results, has been made by Beth (see *Phys. Rev.* **54**, 865 (1938)).
- 97a. See for example A. F. Palmer, *Theory of Measurement* (1912), Chapters VII and IX. The probable errors of functions of e , m_0 and h were obtained following W. Chauvenet, *Treatise on the Method of Least Squares* (1868), pp. 541-3. Actually, the bracket term () of his Eq. (83) is the square of the reciprocal of the weight of the desired function. Hence multiplication of the square root of this bracket by the probable error of an observation of unit weight gives the internal probable error of the function, while multiplication of the same quantity by the probable error of an unknown of unit weight gives the external probable error of the function. See R. T. Birge, *Phys. Rev.* **40**, 217-8 (1932), Eqs. (17) and (18).
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101. The uncertainty given is the larger of the two probable errors involved. The probable error in any quantity in Solution II or III contains all of the uncertainty in the same quantity in Solution I. Hence, the probable errors should *not* be added, as is done with independent errors.
102. It should be pointed out that the e of Solution I (also of Solution I' in Table X) is not a "least-squares" value. By this it is meant that the value of e is not influenced by the values of any experiments other than those in Eq. A. The author's understanding of this has been greatly clarified by an ingenious diagram given by Dr. J. W. M. DuMond in personal correspondence. The value of e is only influenced by Eqs. C and H and hence in the other solutions the resulting e is a least-squares value if one, or both, of these equations are used.
- 102a. It is to be emphasized that the probable error of a function of e , m_0 and h can *not* be found from the probable errors in e , m_0 and h because the latter are not independent. It is necessary to go back to quantities occurring in the least-squares solution (see W. Chauvenet, reference 97a. The ratio of the external to internal probable error in the three solutions in Table IX is respectively: 0.004, 0.73 and 1.66; and in Table X: 0.62, 0.61 and 1.66. The larger error is always given.
103. It should be kept in mind that in a Birge-Bond diagram so modified, a change in the experimental value of any point will change to some extent the position of every other point, except those at $n=0$. The reason for this is the changes that result in R_∞ and h_0 .