ATOMIC MASSES AND NEUTRON SEPARATION ENERGIES FOR SOME ISOTOPES OF CADMIUM
Atomic Masses and Neutron Separation Energies for Some Isotopes of Cadmium

By

Roy Lovitt Bishop, B.Sc.

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AUTHOR: Roy Lovitt Bishop, B.Sc. (Acadia University)

SUPERVISOR: Professor H.E. Duckworth

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SCOPE AND CONTENTS:

The large double focusing mass spectrometer operating at its theoretical resolving power of more than 100,000 at the base of the peaks has been used to measure five mass spectral doublets.

The resulting single and double neutron separation energies for some cadmium nuclides are much more precise than those from previous work. It is noted that striking regularities occur amongst these energies.
ACKNOWLEDGEMENTS

It has been a privilege to have worked under the supervision of Professor H.E. Duckworth. To him, I wish to express my sincere appreciation for his patience and guidance during the course of this work.

A considerable contribution to the work described herein was made by Dr. R.C. Barber, Mr. W. McLatchie and Mr. P. Van Rookhuyzen.

My wife and Miss Joyce Wellwood assisted greatly in the preparation of this thesis.

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CHAPTER 1
INTRODUCTION

1. Importance of Atomic Mass Determinations

The mass of an atom is the most important single piece of information that one can have concerning this unit of matter. An atom's mass is less than that of its separate constituents by an amount equivalent to the so-called binding energy of the atom. A small fraction of this energy is associated with the orbital electrons, while the remainder determines the stability of the nucleus and its behavior in nuclear reactions. The large-scale variations of the binding energy with nucleon number give insights into the general nature of nuclear forces. Finer variations are related to nuclear shell structure, collective nucleon behavior, et cetera.

At this point it seems appropriate to recall that a mass spectrograph was involved in the first experimental verification of the ubiquitous Einstein relation for mass-energy equivalence. (Bainbridge, 1933).

An often unmentioned feature of an experimental datum such as an atomic mass determination is its intrinsic value. I feel that an appreciation of this value is one of the traits of a physicist.
2. Mass Standards

The unit of atomic or nuclidic mass is defined as one-twelfth of the mass of $^{12}\text{C}$ (Mattauch, 1960). The acceptance of this standard by the International Unions of Physics and Chemistry in 1960 and 1961 respectively, put an end to the unsatisfactory state of affairs in which different physical and chemical scales of atomic mass had existed side by side for over thirty years. (Wichers, 1962).

It should be mentioned that we still do not have a single standard of mass. The other standard is, of course, the platinum-iridium kilogram of the Bureau International des Poids et Mesures at Sèvres, France. This arbitrary standard will no doubt exist for some time due to its convenience and to the relative uncertainty in the Avogadro number ($\sim 27$ppm).

3. Methods of Atomic Mass Determinations

Alpha decay data provide the bulk of atomic mass information for nuclei heavier than bismuth. A knowledge of the alpha particle energy allows one to calculate the mass difference between the parent and daughter nuclides. Since the magnetic or electrostatic analysers used to
measure this energy are usually calibrated with the Po$_{210}$ alpha ray whose energy has an uncertainty of about 2 keV, the resulting mass differences can only approach this accuracy.

Another source of mass data is beta-ray spectroscopy. The information required to link the isobars involved is contained in the beta-ray end points and often in the energies of correlated gamma rays. The probable errors in such measurements vary from about 0.1 keV to the order of 0.1 MeV.

A third method of determining atomic mass differences is experimental work in which the energy released in induced nuclear reactions is measured. Many such reactions involving charged particles, neutrons and photons have been studied. Accuracies of a few kilovolts have been attained for (n,γ), (p,n) and some charged particle reactions. However, the calculation of masses from reaction data alone is unsatisfactory for the heavier elements as usually one can proceed in steps of only a few mass units at a time from the C$^{12}$ standard.

An independent method of checking atomic masses is afforded by the techniques of microwave spectroscopy and the dependence of the rotational energies of molecules on the masses of the constituent nuclides. The agreement of such
measurements with mass spectroscopic and nuclear reaction data is generally good; however, the associated precision is limited and the method can only be applied to particular types of molecules (Geschwind, 1957).

A fifth technique for ascertaining atomic masses is that of deflecting charged atoms in magnetic and electric fields. This is the well known mass spectroscopic method which has been in use for half a century. By employing the so-called doublet method, in which ions having nearly the same specific charge are observed, comparisons can be made between nuclides both closely and widely separated in the periodic table. Precisions of one part in $10^8$ or better have been attained in some laboratories, so that the resulting values compete favorably with those obtained by other means.
CHAPTER 2
MASS SPECTROSCOPES

1. Time of Flight and Deflection Instruments

Two basic types of mass spectroscopes have evolved during the last few decades. The older of these, the deflection-type instrument, is the more common and has been applied to a wide variety of tasks. It is based on the deflection of ions in electric and magnetic fields. This topic will be discussed in more detail below.

The time of flight idea was first proposed by Smythe (1926). Such instruments involve a measurement of either the time for ions in a monoenergetic beam to traverse a known distance, or the cyclotron frequency of an ion circulating in a uniform magnetic field. Both of these variables are related to the mass of the ion. Time of flight instruments have made a significant contribution to mass spectroscopy in general, and to mass determinations in particular. The latter contribution has resulted from the refinement of the cyclotron resonance spectrometer since the last war.

2. Analyzing Properties of Electric and Magnetic Fields

In this brief description of some of the properties of electric and magnetic fields, I shall only consider
homogeneous magnetic and radial electric fields. Such fields are commonly used in mass spectroscopes.

An ion with charge q moving in electric and/or magnetic fields has two parameters, its mass (m) and velocity (v), which determine its trajectory. If such an ion is travelling in a uniform magnetic field, the radius of curvature of its path \(a_m\) is related to these parameters by

\[ mv = Bqa_m \]  

(2-1)

where B is the magnetic flux density. Hence a magnetic field is a momentum analyser, or if the ion's velocity is determined, a mass analyser.

In single focusing mass spectroscopes the relative velocity spread, \(\frac{\Delta v}{v} = \beta\), is kept small by using both an ion source possessing a small energy spread and a large accelerating potential.

In double focusing instruments the ions are first passed through a radial electric field which is established between the plates of a cylindrical capacitor. Such plates have singly curved surfaces; however, spherical electrodes have also been employed. If the radii of curvature of the surfaces of the electrodes are \(a_e + k\) and \(a_e - k\) respectively, the path of an ion with charge q travelling
normally to the electric field at a radius $a_e$ is given by

$$mv^2 = \frac{qV}{2k} a_e \quad (a_e \gg k) \quad (2-2)$$

where $V$ is the voltage applied across the electrodes. Hence an electrostatic analyser can be used to define the energy of an ion. If the ion then passes into a magnetic analyser, its mass is uniquely specified by $a_m$.

3. **Focusing Properties of Electric and Magnetic Fields**

If a beam of ions having a direction spread of $2\alpha$ radians is injected normally into a homogeneous magnetic field, the ions will return to the starting point after traversing circular paths. This is an example of perfect direction and velocity focusing, that is, ions of mass $m$ possessing both a direction spread and a velocity spread are focused at a point. Unfortunately however, there is no momentum dispersion. Hence such a $2\pi$ deflection is of limited practical interest. An approximate direction focus is achieved in such an arrangement after a deflection of $\pi$ radians and in this case there is momentum discrimination. This property of a $180^\circ$ magnetic field was first exploited in the study of positive ions by Dempster in 1918.

The direction focusing property of sector magnetic
fields was first pointed out by Aston in 1919; however, no rigorous theory was presented until Herzog (1934) derived the general focusing equations for both homogeneous magnetic and radial electrostatic fields. As these equations have been recently given by several authors they will not be repeated here (Duckworth, 1958; Isenor, 1959; Barber, 1962).

The Herzog theory shows quantitatively that it is possible to use an electrostatic analyser together with a magnetic analyser in such a way that the velocity dispersions cancel, while at the same time direction focusing is achieved by the combination. Such an arrangement is termed double focusing. However, Herzog's equations describe only first-order focusing; that is, in the expression for the image width (which involves terms in $\alpha, \beta, \alpha \beta, \alpha^2, \beta^2$ and higher powers) only the coefficients of $\alpha$ and $\beta$ are made to vanish. Hence instruments based on this theory are designed so that $\alpha$ and $\beta$ are kept as small as possible.

König and Hintenberger (1957) have developed the corresponding second-order relations and show that it is possible to obtain a first-order double focus for all masses plus a second-order double focus for one mass in certain field arrangements. No instruments of this type have yet been constructed although some do possess partial second-
order focusing in that the coefficient of $\alpha^2$ is zero.

With certain precautions the fringing field at the boundaries of both magnetic and electric analysers can be utilized to achieve direction focusing in the $z$-direction, that is, normal to the deflection plane. However, this feature is often omitted, care being taken only to eliminate $z$ defocusing.

4. Resolution and Dispersion

The resolution or resolving "power" of a mass spectroscope is defined as the ratio $\frac{m}{w}$, where $w$ represents the mass width of the collector trace corresponding to ions of mass $m$. Thus two ion groups will be resolved if their relative separation $\frac{m}{\Delta m}$ is equal to or less than the resolution of the instrument. For double focusing arrangements the resolution depends solely on the parameters of the electrostatic analyser. This follows readily from Herzog's theory.

The dispersion of a mass spectroscope is given by the separation of the images formed by ion groups of masses $m_1$ and $m_2$. It is usually quoted as so many centimeters for a relative mass difference of one percent. The dispersion is a function of the parameters of the magnetic analyser.
In mass determination work where a high resolution is desirable, the images are made as sharp as possible by reducing the appropriate slit widths to their workable limits. These limits are usually determined by the minimum acceptable ion intensity, or in the case of photographic detection, by the graininess of the plate. The resolution can be further improved only by increasing the dispersion, that is, by constructing larger instruments.

5. Development of the Mass Spectroscope

The first mass spectroscope was the positive-ray parabola apparatus used by J.J. Thomson in 1912. This instrument originally had a resolution of about 20. With it Thomson established the identity of the positive-ray particles and found strong evidence for the existence of isotopes.

F.W. Aston continued Thomson's investigations by constructing in 1919, an instrument which possessed velocity focusing and a resolving power of about 130. His first experiments verified the existence of isotopes and during the next decade and a half he carried out an intensive, systematic investigation of isotopes and their masses.

As mentioned earlier, A.J. Dempster was the first
to make use of the direction focusing properties of a semi-circular magnetic field. With such an instrument he made a study of the isotopes of some of the more common metals during the early 1920's.

A modified version of the Dempster instrument was used by K.T. Bainbridge in 1933 to make a number of valuable mass determinations.

With Herzog's presentation of the general focusing equations in 1934 the number and variety of mass spectroscopes began to increase. Double focusing instruments also began to appear in this period, the first few being constructed by Dempster at Chicago, Bainbridge and Jordan at Harvard, and Mattauch and Herzog in Vienna. In the intervening years instruments of this type have supplied most of our information concerning atomic masses.

Until the last decade most mass spectroscopes designed for precision mass determinations used photographic detection. That is, in Aston's terminology, they were mass spectrographs. This method of detection has several disadvantages: instrument alignment is slow and difficult; proper plate exposure and development is necessary to insure the location of the centre of gravity of asymmetrical spectral lines; an energy difference between doublet members is difficult to detect;
and the dispersion of the spectrograph must be accurately known. In large instruments the dispersion law may never be actually known owing to the difficulty of obtaining a uniform and reproducible magnetic field. All in all, under typical conditions, a spectral line can be located to only about \(1/50\)th of its width.

Recently electrical detection has become common in precision mass determinations. In this technique a fixed collector slit is used, so the various ions must follow the same path through the spectrometer in order to be detected. Thus, except for the requirement of a double focus, inhomogeneities in the magnetic field are of no concern. According to a theorem given by Bleakney (1936), if the magnetic field is fixed, ions of mass \(m'\) will follow the path taken by ions of mass \(m\) when the electric fields encountered by these ions are in the ratio

\[
\frac{E}{E'} = \frac{m'}{m} \tag{2-3}
\]

In double focusing instruments this means that the potentials applied to the electrostatic analyser and to the source must be altered to bring one member of a doublet and then the other to the collector slit. However, the latter voltage change need not be accurately determined because of the velocity
focusing property.

In spectrometers using electrical detection some variation of the peak-matching technique introduced by Smith (Smith and Damm, 1953, 1956) is usually employed. In the case of deflection instruments the ion beams are swept across the collector slit by modulating either the magnetic field or the field of the electrostatic analyser. The resulting collector signal is displayed on an oscilloscope whose sweep is of the same form and frequency as that of the modulation, so that the two ion groups are represented as "peaks" on the oscilloscope screen. On alternate sweeps a voltage $\Delta V$ is applied to the plates of the electrostatic analyser. This increment shifts one oscilloscope trace with respect to the other in accordance with expression (2-3). The magnitude of $\Delta V$ is adjusted until the peaks corresponding to the two ion groups appear to coincide. The mass difference may then be calculated by use of Bleakney's equation.

In addition to the ease of reproducing electric fields, the other advantages associated with electrical detection are roughly the opposites of the disadvantages encountered in photographic detection. Also the precision in locating a mass spectral line or peak is about $1/1000^{th}$
of its width or better, representing an improvement of a factor of 20 over the photographic method.

Recently three spectrometers have been used in mass determinations. Nier's instrument at Minnesota has a resolution of about 40,000 and, as electrical detection and peak matching are used, achieves a precision of approximately one part in $3 \times 10^7$ (Quisenberry et al., 1956). Demirkhanov's spectroscope in Russia uses photographic detection and with a resolution of about 50,000 provides a precision of one part in $3 \times 10^6$ (Demirkhanov et al., 1956). Both of these instruments are of relatively small physical size. The third spectrometer is the one used in this work. It will be described in detail below.

Five large instruments are currently under construction or have been recently completed. Of these, that of Ogata (1960) uses photographic detection while those of Stevens (1960), Smith (1960), Bainbridge (1960), and Mattauch and Hintenberger (1960) will use electrical detection and some variation of the peak-matching technique. All of these spectrometers are of the deflection type except that of Smith. His instrument is an improved version of the "mass synchro-meter", a cyclotron-resonance spectrometer. With resolutions of $10^5$ to over $10^6$, the precisions predicted for these
instruments range from less than one part in $10^8$ to better than one part in $10^9$. The higher figures must be regarded as hypothetical, at least for the time being.
CHAPTER 3
McMASTER INSTRUMENT

1. Geometry

The basic features of the mass spectrometer used in this investigation are illustrated in Figure 1. It is a modified Dempster-type instrument, the modifications being that the object and image distances, \( l^1_o \) and \( l^1_i \), of the electrostatic analyser are equal, and electrical detection is used. Since the first analyser forms a direction focus at the entrance to the magnet and \( \Phi_m = 180^\circ \), a first order direction focus occurs at the collector slit \( S_5 \). Herzog's equations show that the electrostatic analyser produces a velocity dispersion of magnitude \( 2\beta a_e \) at \( S_4 \), and that the magnetic analyser produces a similar dispersion \( 2\beta a_m \) in the opposite sense. Thus, with \( a_e = a_m \), the instrument possesses first order double focusing for one value of \( a_m \), i.e. for one mass at a time.

Since the analysers are employed symmetrically, the overall magnification is unity. The resolving power as given by the Herzog theory is then \( \frac{a_e}{S_o + S_c} \) where \( S_o \) is the width of the object slit \( S_1 \) and \( S_c \) is the collector slit width. Using the appropriate values given in the caption to Figure 1, the theoretical resolving power is \( \sim 107,000 \).
**FIGURE 1**

SCHEMATIC DIAGRAM OF INSTRUMENT

Dimensions: \( a_e = a_m = 107.5" \)
\[ 1' = 1'' = 37.67" \]
\[ 1' = 1'' = 0 \]
\[ 2k = 1.000" \]
\[ \phi_e = \pi/2 \]
\[ \phi_m = \pi \]

Slits:

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<tr>
<td>( S_1 )</td>
<td>0.0005&quot;</td>
<td>Principal or object slit. (Preceded by a 0.010&quot; slit so ( S_1 ) is in a field free region)</td>
</tr>
<tr>
<td>( S_2 )</td>
<td>0.060&quot;, variable</td>
<td>Determines ( \alpha )</td>
</tr>
<tr>
<td>( S_3 )</td>
<td>0.020&quot;, variable</td>
<td>Limits height of ion beam</td>
</tr>
<tr>
<td>( S_4 )</td>
<td>0.080&quot;, variable</td>
<td>Determines possible range of ion energies admitted to magnetic analyser</td>
</tr>
<tr>
<td>( S_5 )</td>
<td>0.0005&quot;, variable</td>
<td>Collector slit</td>
</tr>
</tbody>
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As mentioned above, the expression for the image width in a double focusing arrangement involves terms in $\alpha$, $\beta$, $\alpha \beta$, $\alpha^2$, $\beta^2$, et cetera, with the first order coefficients being zero for a first order double focus. The second order coefficients for the McMaster instrument have been found to be small compared with those of several other spectrometers currently being used for mass determinations. (Barber, 1962).

2. Ion Source

The ion source used in the McMaster instrument is the conventional electron bombardment type (Inghram and Hayden, 1954). Its chief feature is the small energy spread ($\sim 1 \text{ ev}$) of the ions produced.

Figure 2 is an oblique view of the source with its outer casing and supports omitted. The rhenium filament, which is maintained at a negative potential with respect to the source, emits electrons which are constrained by the magnetic field to travel in a narrow beam through the ionization region. The sample to be ionized is introduced as a vapor at a low pressure ($\sim 10^{-3} \text{ mm Hg}$). The resulting ions are pushed through the source slit by the electric field produced by the repeller plate.

In this investigation the ion sample was a solid with
FIGURE 2

ION SOURCE

π - Iron pole piece
μ - Alnico magnet
φ - Rhenium filament (0.050" x 0.002")
ρ - Repeller plate
σ - Location of source slit
β - Inconel baffle
e - Gas inlet
ι - Ionization region

FIGURE 3

SOURCE ASSEMBLY

The ion source is insulated from ground by glass. The two micrometers provide for adjustment of slit S1. Lathe cross-slides are used to adjust the source position. The gate valve allows the source region to be isolated from the electrostatic analyser.
a relatively high boiling point (\( \sim 900^\circ C \)). It was placed in a small (\( \sim \frac{1}{2}'' \times 1'' \)) nichrome cylinder and heated by electron bombardment. This, combined with the heating due to the electron emission filament, was sufficient to ensure an adequate vapor pressure in the ionization chamber.

The source circuitry is shown in Figure 4. As indicated, most of the apparatus at high voltage is enclosed within a grounded aluminum cabinet. Perspex is used as insulation. The high voltage supply (Beta Electric Corp., N.Y., Model 2069) is capable of supplying 100kv at 2 ma with a regulation of about one part in 30,000. The details of its circuit have been presented elsewhere. (Dewdney, 1955; Isenor, 1959; Barber, 1962).

Figure 3 shows an external view of the source and the mechanical adjustments which determine its position. These adjustments allow for movement along the ion beam and in two perpendicular directions in a plane normal to the ion beam. In addition, the source can be rotated slightly about the principal slit.

3. Electrostatic Analyser

The electrodes of the 90\(^\circ\) electrostatic analyser are both composed of eleven gold-plated iron blocks (3'' thick
FIGURE 4

SOURCE CIRCUITRY
x 6.5" high x 15" long) which have been accurately machined to form a smooth, continuous arc. Each block rests on three alumina insulators which are precisely 0.625" thick. These insulators in turn rest on a heavy steel base plate the inner edge of which is used as the fiducial surface for positioning the electrodes.

The effective field boundaries of the analyser are established by means of grounded diaphragms which are positioned in accordance with Herzog's theory (Herzog, 1935). These diaphragms have a gap of 0.250" and are located 0.255" from the ends of the electrodes.

The analyser plates are enclosed in a housing constructed of 0.50" welded aluminum. This cover is clamped onto the steel base plate with a neoprene gasket being used as a vacuum seal.

The source is fastened to the analyser base plate by means of a channel iron frame. A vacuum connection between the source and electrostatic analyser is maintained by a 3" copper pipe and bellows, the latter to allow for source adjustments. A similar arrangement is used to join the electrostatic and magnetic analysers. In this case the connecting frame is attached to a pivot located vertically below the desired point of entry of the ions into the
magnetic field.

The entire electrostatic analyser is supported by three 2" ball bearings. Each of these sits on a platform which rests on a cluster of 1" ball bearings. With this arrangement the analyser and source assembly, which weigh about three tons, can be easily swung as a unit about the entrance to the magnet. This adjustment is one of the variables used to achieve a double focus.

A d.c. voltage is applied to the plates of the electrostatic analyser in such a manner that the central ion path is virtually at ground potential. This voltage is supplied by twelve 45 volt batteries which are kept in a temperature controlled brass box. In addition, this voltage is modulated in a fashion that will be described below.

Figure 5 shows a view of the electrostatic analyser. The source is located below the lower-right corner of the photograph.

4. Magnetic Analyser

The magnetic analyser is shown in Figure 6. The 180° field is produced by 28 equal angle sectors, each one of which is a "C" electromagnet. Each coil consists
FIGURE 5

ELECTROSTATIC ANALYSER

The aluminum housing, steel base plate and two oil diffusion pumps are conspicuous. The steel bar and support in the center foreground determine the angle of entry of the ion beam into the magnetic analyser. The tube connecting the two analysers is visible at the upper left edge of the photograph.

FIGURE 6

MAGNETIC ANALYSER

Approximately four-fifths of the magnetic analyser is shown in this photograph. The electron multiplier detector is visible at the far end of the analyser.
of approximately 20,000 turns of #26 wire. These units are connected as four banks in series, each bank consisting of seven coils in parallel. The pole pieces are 7" wide and have a gap of 0.810". The fringing of the field at the end of the analyser is reduced with the aid of soft-iron diaphragms. The ions travel in a copper tube of rectangular cross-section which is located between the pole faces of the magnet. The entire analyser, which weighs about fourteen tons, is supported by a "dexion" frame.

Azimuthal variations in the magnetic field can be largely corrected by means of a trimming rheostat in series with the coil of each sector. In addition, each upper pole piece can be tilted slightly by means of three screws in order to adjust radial variations in the field. The existence of a double focus is very sensitive to such radial variations (Barber, 1962).

The magnet current is supplied by the circuit described by Dewdney (1955). The current is regulated by a transistorized circuit due to Garwin et al. (1959) and described by Barber (1962). This regulator invariably has a stability of one part in 100,000 over several minutes. Short term stability is better than one part in 10^6.
5. Vacuum System

A vacuum is maintained in the source region by a conventional rotary pump combined with a 90 liter/second oil diffusion pump and a glass liquid air trap. Part of this apparatus is visible in Figure 3. The pressure is about $5 \times 10^{-6}$ mm Hg before the sample vapor is introduced and is an order of magnitude higher under operating conditions.

The electrostatic and magnetic analysers are evacuated by five identical pumping units, two on the former and the other three on the magnetic analyser. These consist of a rotary pump, a stainless steel 400 liter/second oil diffusion pump, a water cooled baffle, metal cold trap, and a pneumatically operated gate valve. The gate valves shut in the event of electrical power failure, water failure or deterioration of the vacuum. The pressure in the electrostatic analyser is usually below $4 \times 10^{-6}$ mm Hg, while that in the magnetic analyser is an order of magnitude lower.

6. Ion Detection

The ions which pass through the collector slit are detected by an Allen type, 14 stage electron multiplier (Allen, 1947). The gain of this multiplier is about $10^6$
with an interstage voltage of 400 volts. Provision is made for mechanical adjustments in a plane normal to the ion beam in order to obtain maximum intensity.

In addition to the final collector, the ion beam can be monitored at three intermediate points. The first monitor electrode is the outer plate of the electrostatic analyser. This is employed as a detector only when the source is badly out of adjustment. Under typical conditions an ion current of about $5 \times 10^{-8}$ amperes is collected here.

Besides limiting the height of the ion beam, slit $S_3$ serves as a monitor for the ions leaving the electrostatic analyser.

The third monitor is a Faraday cup which may be positioned just behind slit $S_4$ to measure the total ion current entering the magnetic analyser. A typical value for this current is $5 \times 10^{-10}$ amperes.

During typical operation of the instrument the ions reaching the final collector correspond to a steady current of $\sim 10^{-13}$ amperes.

7. Measuring Technique

A general description of the peak matching technique is given above in Chapter 2. In the McMaster instrument the
ions of the mass doublet under study are swept across the collector slit by a small 60 cps sawtooth potential which is applied to the plates of the electrostatic analyser. Superimposed on and synchronized with this modulation is a 30 cps square wave voltage of amplitude \( \Delta V \). The circuit for applying these voltages to the electrostatic analyser is given by Barber (1962).

The accelerating voltage on the source is also varied in a square wave fashion in order that the ion groups being matched follow the same path through the instrument. The amplitude of this modulation is related to \( \Delta V \) by the geometry of the electrostatic analyser.

The output of the electron multiplier is amplified by an a.c. amplifier and is viewed on the oscilloscope which provides the sawtooth voltage for sweeping the ion beams. In order to facilitate matching, alternate traces are displaced vertically on the oscilloscope screen, and also the amplitude of each trace can be independently controlled. The matching of two peaks is shown schematically in Figure 7. A photograph of a matched doublet as it appears on the oscilloscope is shown in Figure 8.

It is possible to match a doublet in two ways: the lighter member to the heavier one and the latter to the former.
**FIGURE 7**

BLOCK DIAGRAM OF ION DETECTION

AND PEAK DISPLAY

---

**FIGURE 8**

MATCHED DOUBLET

$\text{Cd}^{114}\text{Cl}^{35}, \text{Cd}^{112}\text{Cl}^{37}$
\[ \tau = \frac{1}{60} \text{s.} \]

Ions → Electron Multiplier → Amplifier → Displacement & Attenuation → C.R.O.

Time interval \( \tau \) is shown at intervals of 5 seconds for three cycles.
The mass difference for these two cases is given by

\[ \Delta m = m_h \frac{\Delta V}{V_h + \Delta V} \]  \hspace{1cm} (3-1) 

and

\[ \Delta m = m_l \frac{\Delta V}{V_1 - \Delta V} \]  \hspace{1cm} (3-2) 

respectively. \( m_h \) and \( m_l \) represent the masses of the heavy and light ions, and \( V_h \) and \( V_1 \) the corresponding voltages applied to the electrostatic analyser.

In this investigation, the error in the measurement of \( V \) and the statistical error due to the instrument were sufficiently large that either of the two above equations could be written.

\[ \Delta m = m \frac{\Delta V}{V} \]  \hspace{1cm} (3-3) 

where \( m_h \) or \( m_l \) is replaced by \( m \), and \( V_h \) or \( V_1 \) by \( V \).

Before a measurement of a doublet spacing can be performed, a double focus has to be achieved. A direction focus is characterized by a distinct sharpening of the peaks as the angle of entry (\( \epsilon' \)) of the ion beam into the magnetic field is varied. The existence of a velocity focus is checked by applying a 30 cps square wave modulation to the accelerating voltage. As indicated in Figure 4, a 15 volt energy
difference may be applied. If the instrument is not velocity focused a peak will appear displaced with respect to its position on the previous trace. A velocity focus can usually be achieved by slightly varying $e'$. 

Once the two foci have been located, the direction focus may be brought to the velocity focus by varying the distance $l_e'$. However, since the characteristics of the magnetic field depend on its history, it is sometimes necessary to demagnetize the magnet before a double focus can be attained. Small adjustments of the ion beam in the vertical direction are usually needed to obtain maximum intensity.

As mentioned above, one may match the heavier member to the lighter or vice versa. Also, the sawtooth sweep may be reversed, thus reversing the relative position of the two peaks on the oscilloscope screen. In addition, the two traces may be vertically transposed. The several combinations of these three variations result in eight different oscilloscope patterns. In order to avoid errors arising from the operator's judgement of the matching condition, all eight patterns were employed, with the average representing the value of one "run". The average of 25 to 30 runs was accepted as the final value of a doublet spacing. In an
attempt to eliminate any systematic errors, these runs were distributed among three or more operators, and were performed over a minimum period of two days. In addition, the spectrometer was readjusted before each run.

In this work the values of the runs on a particular doublet had a spread of approximately $38\mu u$. The statistical error ($\epsilon$) was calculated from

$$
\epsilon = 0.6745 \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n(n-1)}}
$$

(3-4)

where $x_i$ is the value for a particular run and $\bar{x}$ is the mean of $n$ runs. This expression is known as the probable error of the mean; that is, the chance is 50% that the true value lies within $\bar{x} \pm \epsilon$. However, this interpretation is valid only for data having a gaussian distribution about the mean. The distributions obtained in this work were gaussian to a good approximation.

The electrostatic analyser voltage ($V$) was measured in two steps with a differential voltmeter. The limit of error was 0.03% on each measurement. A high precision potentiometer was used to measure $\Delta V$. In this case the limit of error was 0.015%.
The final error on a doublet measurement was taken as the root-mean-square value of these four errors.
CHAPTER 4
EXPERIMENTAL RESULTS

1. Doublets Studied

The mass width of a peak (or line) at mass $m$ is
\[ \frac{m}{R} \]
where $R$ is the resolving power. The position of a peak (or line) can be located to some fraction $f$ of its width, where $f$ is determined by the characteristics of the mass spectrometer. Hence the precision of a measurement is

\[ \delta m = f \frac{m}{R} \]  \hspace{1cm} (4-1)

The statistical relative error representing the performance of the instrument in the determination of a doublet spacing is

\[ \frac{\delta m}{\Delta m} = \frac{fm}{R \Delta m} = \frac{fV}{R \Delta V} \]  \hspace{1cm} (4-2)

Thus the fractional error intrinsic in the spectrometer is largest for close doublets (small $\Delta m$).

The measurements of $V$ and $\Delta V$ introduce a fixed error (0.045% in this instance). Since it is desirable for this error to, at worst, double the error on a measurement, one is restricted to doublets having a maximum relative spacing of
\[ \frac{\Delta m}{m} = \frac{f}{R} \times \frac{\sqrt{3}}{4.5 \times 10^{-4}} \approx \frac{1}{107,000} \times \frac{\sqrt{3}}{4.5 \times 10^{-4}} \sim \frac{1}{30,000} \]

The factor of \( \sqrt{3} \) is due to the root-mean-square method of combining errors. Thus with the present system of measuring the variables, the McMaster spectrometer is limited to doublets having \( R > \frac{m}{\Delta m} > 30,000 \). A high precision resistor network due to Nier (1957) is currently under construction. It is hoped that this circuit will make practicable the measurement of much wider mass doublets, possibly including doublets with \( \Delta m = 1u \).

The doublets chosen for this study of the cadmium isotopes were of the type \( \text{Cd}^{A+2}\text{Cl}^{35} - \text{Cd}^{A}\text{Cl}^{37} \). In addition to satisfying the restriction discussed above, the members of such doublets are chemically identical. This feature ensures that the two ion groups will have the same angular spread and energy when they enter the electrostatic analyser. Also, the two chlorine isotopes are not badly mismatched in abundance and their mass difference is known to reasonably good precision (1.8 ppm).

The \( \text{CdCl} \) ions were obtained by electron bombardment of \( \text{CdCl}_2 \) vapor which, in turn, was obtained by heating a small quantity (\( \sim 0.1g \)) of \( \text{CdCl}_2 \cdot 2\text{H}_2\text{O} \) crystals in an electron
bombardment oven to several hundred degrees Centigrade.

With the eight stable isotopes of cadmium there are six doublets involving CdCl ions. Of these only four were found to be measurable when the elements involved are present in their normal abundances. The low abundance of one or both members of the other two doublets combined with \( \frac{m}{\Delta m} \sim R \) excluded these measurements. However, the wider of these, which corresponds to the Cd\(^{110}\) - Cd\(^{108}\) mass difference, was measured with the aid of a 13.7 mg sample of CdO enriched to 69\% in Cd\(^{108}\) and to 10\% in Cd\(^{110}\). This compound was obtained from the Union Carbide Nuclear Company at Oak Ridge. It was treated with one drop of 20\% HCl to convert it to CdCl\(_2\). Only six runs were obtained on this doublet before the sample was exhausted.

2. New Mass Differences

The mass differences obtained for the five cadmium doublets are given in Table 1. The probable error given represents the reproducibility of matching conditions and the corresponding voltage measurements. Using Equation (4-1) the precision inherent in the matching alone

\[
\frac{\delta m}{m} = \frac{f}{R}
\]  

(4-3)
TABLE 1 — NEW MASS DIFFERENCES

<table>
<thead>
<tr>
<th>Doublet</th>
<th>Mass Difference in ( \mu u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cd}^{110}\text{Cl}^{35} - \text{Cd}^{108}\text{Cl}^{37} )</td>
<td>1 764 ( \pm 5 )</td>
</tr>
<tr>
<td>( \text{Cd}^{112}\text{Cl}^{35} - \text{Cd}^{110}\text{Cl}^{37} )</td>
<td>2 701 ( \pm 2 )</td>
</tr>
<tr>
<td>( \text{Cd}^{113}\text{Cl}^{35} - \text{Cd}^{111}\text{Cl}^{37} )</td>
<td>3 174 ( \pm 2 )</td>
</tr>
<tr>
<td>( \text{Cd}^{114}\text{Cl}^{35} - \text{Cd}^{112}\text{Cl}^{37} )</td>
<td>3 547 ( \pm 2 )</td>
</tr>
<tr>
<td>( \text{Cd}^{116}\text{Cl}^{35} - \text{Cd}^{114}\text{Cl}^{37} )</td>
<td>4 353 ( \pm 2 )</td>
</tr>
</tbody>
</table>

is found to range from one part in \( 1.2 \times 10^8 \) to one part in \( 1.5 \times 10^8 \) for these doublets, excluding the case where only six runs were obtainable. At the designed resolving power of 107,000, this corresponds to matching to approximately \( 1/1300 \) of a peak width.

When the data given in Table 1 are combined with the mass difference \( \text{Cl}^{37} - \text{Cl}^{35} = 1.997 \ 041 \ 4 \ \pm 36 \ u \) (Konig et al., 1962), mass differences of the type \( \text{Cd}^{A+2} - \text{Cd}^A \) are obtained. These are shown in Table 2.

3. Double Neutron Separation Energies

When the data in Table 2 are combined with the mass of two neutrons, \( 2n = 2.017 \ 330 \ 88 \ \pm 86 \ u \) (Konig et al., 1962), and the conversion factor \( 1u = 931.441 \ \pm 10 \ MeV \) (Everling
TABLE 2 — ATOMIC MASS DIFFERENCES (in u)

<table>
<thead>
<tr>
<th>Nuclide Differences</th>
<th>Mass Difference (in u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(^{110}) - Cd(^{108})</td>
<td>1.998 805 ±6</td>
</tr>
<tr>
<td>Cd(^{112}) - Cd(^{110})</td>
<td>1.999 742 ±4</td>
</tr>
<tr>
<td>Cd(^{113}) - Cd(^{111})</td>
<td>2.000 216 ±4</td>
</tr>
<tr>
<td>Cd(^{114}) - Cd(^{112})</td>
<td>2.000 588 ±4</td>
</tr>
<tr>
<td>Cd(^{116}) - Cd(^{114})</td>
<td>2.001 394 ±4</td>
</tr>
</tbody>
</table>

et al., 1960), the energy necessary to remove two neutrons from the heavier nuclide can be calculated. These double neutron separation energies (S\(_{2n}\)) are given in Table 3. In six instances our values differ from the others listed. These differences range from about 30keV to 170keV.

The values of S\(_{2n}\) obtained in this investigation are plotted against neutron number in Figure 9. The points at N = 60 and N = 67 are taken from the Nuclear Data Sheets. The value at N = 61 is the sum of the single neutron separation energy (S\(_n\)) for Cd\(^{108}\) given in the Nuclear Data Sheets, and S\(_n\) for Cd\(^{109}\) calculated by the method described in the next section. These two S\(_n\) values are given in Table 4. The value at N = 63 is obtained in a similar fashion.

A remarkably smooth curve results when points of even N are joined. The negative slope is due chiefly to
FIGURE 9

DOUBLE NEUTRON SEPARATION ENERGIES

FOR CADMIUM
$S_{2n}$ (MeV)

$N$

$Z = 48$
<table>
<thead>
<tr>
<th>Element</th>
<th>This Work</th>
<th>1960 Nuclear Data Tables (Konig et al., 1961)</th>
<th>Nuclear Data Sheets (1960)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(^{108})</td>
<td>17.256 ± 6</td>
<td>17.100 ± 60</td>
<td>17.090 ± 60</td>
</tr>
<tr>
<td>Cd(^{109})</td>
<td>17.676 ± 27</td>
<td>17.560 ± 70</td>
<td></td>
</tr>
<tr>
<td>Cd(^{110})</td>
<td>16.383 ± 4</td>
<td>16.730 ± 170</td>
<td></td>
</tr>
<tr>
<td>Cd(^{111})</td>
<td>15.942 ± 4</td>
<td>15.710 ± 200</td>
<td>15.860 ± 110</td>
</tr>
<tr>
<td>Cd(^{112})</td>
<td>15.595 ± 4</td>
<td>15.460 ± 70</td>
<td>15.426 ± 70</td>
</tr>
<tr>
<td>Cd(^{113})</td>
<td>15.201 ± 36</td>
<td>15.206 ± 41</td>
<td></td>
</tr>
<tr>
<td>Cd(^{114})</td>
<td>14.844 ± 4</td>
<td>14.800 ± 310</td>
<td>~ 14.6</td>
</tr>
</tbody>
</table>

the increasing neutron excess, an effect which forms the basis of a symmetry term in the semi-empirical mass formula.

Recently, similar curves have been found to exist among the stable isotopes of zirconium, molybdenum, tin and tellurium; however, in the cases of zirconium and molybdenum, a change of slope is found at \(N = 56\). This is presumably due to the completion of the \(d_{5/2}\) subshell (Bishop et al., 1963). A similar break due to the \(g_{7/2}\) subshell at \(N = 64\) is not evident for cadmium.
On the basis of the independent particle model one would not expect a subshell effect at \( N = 60 \) or 62. For this reason the curve of Figure 9 has been projected back to \( N = 60 \). The difference of 180 keV between the Nuclear Data Sheet value and the "expected value" is not out of line with the discrepancies existing in Table 3.

4. Single Neutron Separation Energies

The energies required to remove one neutron from each of ten of the cadmium isotopes are given in Table 4. Of the results listed in the first column, those for \( \text{Cd}^{109} \) and \( \text{Cd}^{116} \) are calculated from the appropriate \( S_{2n} \) values (Table 3) and the Nuclear Data Sheet values of \( S_n \) for \( \text{Cd}^{110} \) and \( \text{Cd}^{115} \) respectively. The other three results are calculated from \( S_{2n} \) values and Groshev's precise \( S_n \) for \( \text{Cd}^{114} \). It is worth noting that Groshev's value is in good agreement with the previously accepted value of 9.046 ±8 MeV (Kinsey and Bartholomew, 1953).

In seven instances the calculated single neutron separation energies differ from the others given in Table 4. These differences range from 6 keV to 99 keV. For \( \text{Cd}^{113} \) the value obtained in this work is in excellent agreement with that reported by Jackson and Bollinger (1961). These authors
TABLE 4 — SINGLE NEUTRON SEPARATION ENERGIES (MeV)

<table>
<thead>
<tr>
<th></th>
<th>This Work</th>
<th>1960 Nuclear Data Tables (Konig, 1961)</th>
<th>Nuclear Data Sheets (1960)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$^{107}$</td>
<td></td>
<td>7.540 ± 360</td>
<td>7.600 ± 100</td>
<td></td>
</tr>
<tr>
<td>Cd$^{108}$</td>
<td></td>
<td>10.420 ± 60</td>
<td>10.310 ± 40</td>
<td></td>
</tr>
<tr>
<td>Cd$^{109}$</td>
<td>7.416 ± 12</td>
<td>7.260 ± 60</td>
<td>7.250 ± 60</td>
<td></td>
</tr>
<tr>
<td>Cd$^{110}$</td>
<td></td>
<td>9.847 ± 16</td>
<td>9.840 ± 10</td>
<td></td>
</tr>
<tr>
<td>Cd$^{111}$</td>
<td>6.995 ± 8</td>
<td>6.970 ± 190</td>
<td>7.250 ± 150</td>
<td>6.980 ± 100$^a$</td>
</tr>
<tr>
<td>Cd$^{112}$</td>
<td>9.388 ± 6</td>
<td>9.300 ± 200</td>
<td>9.480 ± 80</td>
<td>9.460 ± 50$^a$</td>
</tr>
<tr>
<td>Cd$^{113}$</td>
<td>6.554 ± 5</td>
<td>6.420 ± 70</td>
<td>6.380 ± 70</td>
<td>6.550 ± 100$^a$</td>
</tr>
<tr>
<td>Cd$^{114}$</td>
<td>9.046 ± 8</td>
<td>9.046 ± 8</td>
<td>9.041 ± 3$^b$</td>
<td></td>
</tr>
<tr>
<td>Cd$^{115}$</td>
<td>6.154 ± 35</td>
<td>6.160 ± 40</td>
<td>6.160 ± 100</td>
<td></td>
</tr>
<tr>
<td>Cd$^{116}$</td>
<td>8.684 ± 40</td>
<td>8.640 ± 310</td>
<td>~8.400</td>
<td></td>
</tr>
</tbody>
</table>

(a) Neutron capture gamma-rays observed by Jackson and Bollinger (1961).

(b) Neutron capture gamma-ray observed by Groshev et al. (1962)

take particular note of the low separation energy given in the Nuclear Data Sheets for this nuclide, since their result should represent a minimum value for $S_n$. This discrepancy and the corresponding one with the Nuclear Data Tables are both due to a $(d,p)$ reaction Q-value (Wall, 1954) which is included in the input data of these compilations. In the
corresponding input data for Cd$^{115}$, precise ($\gamma$,n) values are favored to the exclusion of another (d,p) result by Wall. In this case his result is appreciably smaller than the adopted value for $S_n$. There appears to be a systematic error of approximately 300 keV in Wall's two Q-value measurements. This also accounts for the low $S_{2n}$ values for Cd$^{113}$ and Cd$^{114}$ listed in the second and third columns of Table 3.

The single neutron separation energies calculated in this work are plotted as a function of neutron number in Figure 10. The points at N = 59, 60, 62 and 67 are taken from the Nuclear Data Sheets. Groshev's value is plotted at N = 66, although on the scale used its position does not differ from that of the older energy.

A straight line is drawn through points of odd N and is projected back to N = 59 for the same reason as in Figure 9. The difference of 140 keV between the Nuclear Data Sheet value and the "expected value" is not unreasonable in view of the discrepancies mentioned above.

The curve for even N values appears to break at N = 64; however, in the opposite direction to that corresponding to a subshell closure. The reason for this behavior is not known; it may simply arise from an error in some of the data that we have used in order to compute single neutron
FIGURE 10

SINGLE NEUTRON SEPARATION ENERGIES
FOR CADMIUM
separation energies from our own results.
CONCLUSIONS

The large double focusing mass spectrometer at McMaster has been used to measure five cadmium doublets to a precision of better than one part in one hundred million. This figure represents the reproducibility in the results.

The final values quoted carry somewhat larger errors because of limitations in the voltage measuring apparatus.

The neutron separation energies derived from this work are much more accurate than any previous work. This accuracy has revealed the existence of remarkable regularities amongst these energies. The variation of the double neutron separation energies with neutron number indicates that there is no subshell effect at N = 64 for cadmium; however, the corresponding evidence presented by the single neutron separation energies is inconclusive.
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